

How fluids unmix

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How fluids unmix

Discoveries by the School of Van der Waals and Kamerlingh Onnes

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NIST, USA

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Writing a book could have been a solitary endeavor. Long lonely hours, days and weeks are spent at the keyboard in the study, or surrounded by dusty books in the library. Strangely, my experience has been the opposite of a retreat into isolation. Since I began the book, I have had the privilege of interacting with dozens of interesting people, both old friends and new acquaintances. They provided many new insights and interesting facts, and were generous and helpful when asked for input, advice or review. At times I consider this book a collective enterprise, as was the work of the Dutch School a century ago.

Note on conventions

Both in quotations and in references, square brackets enclose material added by the author of this book, such as a translation into English, or words that make a terse quote more understandable. Years in italics, following the name of an individual in parentheses, indicate the life span. In the text, the year of publication, in parentheses, follows the name(s) of the author(s). It directs the reader to the list of references in the back of the book, which is arranged alphabetically by the last name of the first author. If the first author has published more than one paper in a given year, these are distinguished by letters a, b, etc. For details on the conventions used in references, please consult the notes preceding the list of references.

Regarding the units of physical quantities, the following policy has been followed. Presently, by global agreement, the units of physical quantities are those of the *Système International* (SI), which did not exist in the time period covered in this book. Here, therefore, these units are used only if reference is made to modern work. For the historical accounts, the units are those reported in the original papers.

Frequently used abbreviations

GTP	The paper by Korteweg (1891b) on the General Theory of Plaits
HMW	Koninklijke Hollandse Maatschappij van Wetenschappen [Royal Holland Society of Sciences and Humanities]
KNAW	Koninklijke Nederlandse Akademie van Wetenschappen [The Royal Netherlands Academy of Arts and Sciences]. In the text, it is referred to as ‘the Academy’ when the context is clear.
K&S	The paper by Van Konynenburg and Scott (1980)
PP	The paper by Korteweg (1891a) on Plait Points

1. Introduction

1.1 *Historical setting: time period and place*

This book narrates the story of pioneering scientists in the Netherlands who reached a profound and comprehensive understanding of fluid mixture phase separation within a brief time span around the turn of the 19th century. This achievement was the consequence of the felicitous collaboration of two Dutch physicists, Johannes Diderik van der Waals (1837-1923) at the University of Amsterdam, and Heike Kamerlingh Onnes (1853-1926) of the University of Leiden. Both were to win Nobel prizes along with several other of their countrymen of that period, including Hendrik Antoon Lorentz, Jacobus Henricus van 't Hoff, and Pieter Zeeman.

This period of flourishing science in the Netherlands was coined 'the Second Golden Age' by Willink (1998). He named it in reference to the glorious 17th century Golden Age of the Dutch republic, when Holland became a dominant power at sea, and could boast not only of its unsurpassed school of painters, but also of scientists such as Anthony van Leeuwenhoek and Christiaan Huygens.

This second Golden Age of science in the Netherlands did not arise by accident. As is carefully documented in the biography of Van der Waals by Kipnis *et al.* (1996), the way to a scientific revival was paved by the restructuring of Dutch secondary education in the 1860s. Before that time, only gymnasia, or Latin schools, reserved for sons of the privileged, gave access to university education. When a solid middle class of business owners and industrialists began to form due to the upturn of the economy, a need was felt for a more practically oriented type of school, with emphasis on mathematics and science instead of the classical languages. In 1862, a non-sectarian, free-market-oriented government under prime minister Johan Rudolph Thorbecke came to power. Thorbecke had democratized elementary education during an earlier period of governing. During his new tenure, he opened secondary education to the middle class. In 1862, a new type of school, the 'Hoogere Burgerschool' (HBS), or high school for (male) burghers, was signed into law.

The 5-year HBS taught a solid curriculum of mathematics and the sciences, in addition to Dutch, three modern foreign languages, history and geography. Curiously, it did not give direct access to university education until more than half a century after its founding. After completing the HBS, students aspiring to a university education had to pass a 'state' (nation-wide) exam in Latin and Greek, which usually took another year of preparation. The new HBS required an influx of well prepared science and mathematics teachers. Improved economic conditions in the country provided the opportunities for the necessary expansion of science education at the universities.

Although it was possible to obtain teacher qualification by other paths, many of the new HBS teachers were university-trained, which enabled them, in turn, to inspire their students and open the prospect of a university education for them. On finishing a mathematics or science doctorate, many would find secure, well paid and respected jobs as HBS teachers, from which they might later graduate to an academic position. As a consequence, a strong interaction resulted between HBS and university science education. As stated by Kipnis *et al.*, 'Almost all Dutch scientists passed through the HBS, either as students or as teachers, or both.' For instance, Van der Waals, who himself never had the privilege of an HBS education, let alone a gymnasium, taught HBS for a dozen years before he became a university professor in 1877.

In the Netherlands, the HBS, as founded by Thorbecke, functioned largely unchanged until well into the 1960s. Then, as had happened in the United States early in the 20th century, the demand for mass access to high schools led to reforms of the high school teacher education system that ruptured the tie between university education and teacher training. Some ascribe the current decline of interest in mathematics, the natural sciences and engineering in the Netherlands to the fact that teachers with specialized university degrees no longer electrify the high school classroom.

It is within this context that science flourished in the Netherlands around the turn of the 20th century. In this time period, Dutch scientists achieved primacy in the field of fluid criticality and fluid phase behavior, the topic of this book

1.2 *Understanding fluid phase behavior – the challenge*

For millennia past, humanity has built up practical knowledge about the behavior of fluids and fluid mixtures and their changes of state: freezing, evaporation, and boiling; mixing and separation; dissolution and precipitation. Experience about dissolving solids, boiling and distilling liquids, melting and purifying metals, has accumulated since fire was tamed long before

recorded history. Several of these processes are basic to survival even in primitive societies.

The modern industrialized world produces and transports chemicals on an unprecedented scale. Key raw materials are natural gas and oil, from which are derived the gaseous and liquid fuels that energize the factories and electric power plants, as well as most modes of transportation. Gas and oil also form the basis for the production of an immense array of chemicals and plastics, without which modern living is unthinkable. Underlying almost all production methods in this gigantic industrial enterprise are the processes of evaporation and condensation, and the mixing and separation of fluids and solids. Mixing processes precede and separation processes follow the chemical reactions that create new compounds out of a mixture of reactants.

Processes of mixing and phase separation involving liquids and gases can be surprisingly complex, especially when these processes occur at elevated pressures. Even in the middle of the 19th century, while the industrial revolution was in full swing, the basic process of phase separation of a pressurized fluid mixture was not understood.

The leap in understanding of the phase behavior of fluids achieved by the school of Van der Waals and Kamerlingh Onnes did not arise without precedent. There were many precursors and essential elements upon which the Dutch scientists would build. To begin with, there was the concept of fluid criticality, discovered by Cagniard de la Tour (1822). Only below the critical temperature can a vapor be condensed to a liquid, or a liquid evaporated. This was a very important insight. Two coexisting fluid phases, such as a vapor and a liquid, may become *identical* at a critical point. In contrast, coexisting fluid and solid phases always remain distinct. It took a fair amount of time before scientists became comfortable with this idea.

Once it was realized that a gas needs to be cooled below its critical temperature before it can be liquefied, the process was set in motion to sequentially liquefy gases of ever-lower critical temperatures. Throughout Europe, scientists were engaged in this challenge throughout the 19th century. Michael Faraday, for instance, had determined the critical temperatures of many fluids by the middle of that century.

Thanks principally to the experimental work of Thomas Andrews (1869) the behavior of a pure fluid around its critical point was discovered.

The involvement of Dutch scientists began when Johannes Diderik Van der Waals (1873), see also Rowlinson (1988), showed in his doctoral thesis how a simple model of molecular repulsion and attraction leads to an equation of state of the form experimentally found by Andrews. By 1880, he derived from his equation the famous principle of corresponding states.

Quite a few experiments on the phase separation of pressurized fluid mixtures were carried out by the 1880s, mainly in France, but also by Van der Waals and by Andrews. Before 1890, however, the results were quite mysterious to the experimenters, because a proper framework for interpretation was lacking.

It was the American Josiah Willard Gibbs (1873-1878) who laid the theoretical foundation for an understanding of the phase separation of fluid mixtures. Among European scientists, only James Clerk Maxwell and Van der Waals quickly grasped the importance of this work. Van der Waals, who in 1877 was appointed a professor of physics at the newly founded University of Amsterdam, soon made himself quite familiar with Gibbs's work. Gibbs's papers on phase separation of mixtures formed the basis, still firmly in place today, upon which Van der Waals built his own theory of mixtures, which was published in 1890.

The unique contribution of Van der Waals was to bring Gibbs's theory to life by generalizing the Van der Waals equation to fluid mixtures. Van der Waals's former graduate student, the Amsterdam professor of mathematics Diederik J. Korteweg, played a little known but essential role in developing the theory of mixtures. The first exciting result was the possibility of coexistence of *three* fluid phases (two liquids and one vapor) in binary mixtures. This phenomenon was known experimentally, but it was quite an achievement to actually derive it from the Van der Waals equation of state. The road was opened towards an understanding of the phase behavior of pressurized fluid mixtures on the basis of the molecular dimensions and interactions of the constituents.

At the venerable University of Leiden, in the meantime, Kamerlingh Onnes was appointed a professor of physics in 1880. He decided to establish a cryogenics laboratory. His primary goal was to liquefy on a large scale the so-called permanent gases – air constituents, hydrogen, and later, the ultimate challenge indeed, the noble gas helium, isolated by William Ramsay in 1895. Kamerlingh Onnes soon realized how Van der Waals's principle of corresponding states could be used for estimating unknown critical temperatures of 'permanent gases.' By the mid-1880s, Van der Waals and Kamerlingh Onnes began a collaboration that lasted till the end of Van der Waals's life in 1923.

The rapid progress in understanding fluid mixtures was a result of the collaboration of Van der Waals, the provider of the theoretical framework, and the experimental group in Leiden. Kamerlingh Onnes's graduate student Johannes Petrus Kuenen, in 1891, was the first in the world to discover how to make reliable measurements of the properties of compressed fluid mixtures. In a brief time span, Kuenen discovered several phenomena that are now integral parts of fluid mixture phase separation technology, such as

retrograde condensation, critical azeotropy, and various types of binary fluid phase behavior. Other Leiden researchers, the Belgian visitor Jules Émile Verschaffelt, as well as Kamerlingh Onnes's successor-to-be, Willem Hendrik Keesom, then helped fill in the picture, which reached completion around 1906. The Amsterdam 'mathematical chemist', Johannes Jacobus van Laar, played a not always appreciated but certainly constructive and colorful role in reaching an understanding of binary fluid phase equilibrium.

Thus, between 1890 and 1906, scientists in Amsterdam and Leiden obtained a full and deep understanding of the intricacies of phase separation and criticality in fluids and fluid mixtures. This period and process form the focus of this book.

Throughout this entire period of work on fluid mixtures, which developed in parallel with the major buildup of large-scale facilities for gas liquefaction, a feud simmered between Kamerlingh Onnes's group and experimenters throughout Europe. The topic was fluid criticality. A number of experimentalists in England, France, Italy, and Germany claimed that the Andrews-Van der Waals picture of fluid criticality was incorrect. For more than 15 years, while he was building his cryogenic facility and preparing for the liquefaction of helium, Kamerlingh Onnes and his group took the offensive, repeated the experiments, and pointed out the sources of error in experiment and reasoning. This epic is narrated in this book, including its sequel in the 20th century.

The work of Van der Waals has aroused new interest recently, thanks largely to the efforts of John Shipley Rowlinson, who translated Van der Waals's doctoral thesis and his paper on fluid mixtures into English (1988). Rowlinson's book contains an extensive description of the connections between Van der Waals's work and modern molecular science. Earlier, Rowlinson translated Van der Waals's paper on capillarity (1979). Kipnis, Yavelov and Rowlinson (1996) recently published a biography of Van der Waals, with an exhaustive bibliography and much biographical detail.

Because of this recent work, the present book does not need to be focused primarily on Van der Waals. Rather, it will expose the synergy of Amsterdam and Leiden scientists in those heady days of Dutch science. It will focus on a number of basic ideas and concepts, and show how they developed from the vital interactions of theorists and experimentalists, with input from mathematics, physics and chemistry. More than once, the Dutch scientists were far ahead of their time, with several of their discoveries and insights reinvented throughout the 20th century.

The book is arranged by topic, in roughly chronological sequence. After introductory chapters on Van der Waals's equation of state and the theorem of corresponding states, fluid mixtures become the principal topic. Van der Waals's

theory of mixtures is summarized, and Korteweg's mathematical work on plaits (folds) in surfaces is described. Then follow the experimental discoveries of the various types of phase behavior in binary fluid mixtures by Kamerlingh Onnes, Kuenen and Keesom. These were complemented by the theoretical understanding reached by Van Laar amidst spirited disputes about matters of priority.

Fluid criticality received much attention from Dutch scientists. The book describes how Van der Waals invented and calculated critical exponents, and discovered, to his dismay, that experiment did not confirm his theory. Verschaffelt pinpointed the problem, and reached insights that then lay dormant for half a century. Kamerlingh Onnes, Kuenen and Keesom waged a lengthy campaign against persistent literature reports contradicting the Andrews-Van der Waals's picture of continuity of states and fluid criticality.

Finally, at one time or another, almost all members of the Dutch School directed their attention to dilute mixtures near critical points. This is the only instance where the influence was felt of another famous Nobel prize winner, Van 't Hoff, who was not a member of the school of Van der Waals and Kamerlingh Onnes. Van 't Hoff's work set the tone for describing the general behavior of dilute solutions. Near a critical point, however, dilute mixtures show unusual behavior, which was elucidated by Korteweg, Keesom, Verschaffelt and Van Laar.

An effort has been made to link the issues discussed to modern developments and practical applications. The last chapter sketches some of the paths along which the work of the Dutch School permeated science and technology throughout the world. This chapter also takes note of some profound early insights that were lost and rediscovered much later.

The book is intended for those interested in the history of science, as well as for teachers and students of thermodynamics who want to know more about the origins of their discipline. It should be accessible to beginning graduate students of physics, chemistry, or engineering with some background in thermodynamics and physical chemistry. A basic knowledge of calculus is assumed. A few chapters will require more effort than the others. A summary of the various chapters is given in the second part of the introduction, including some guidance regarding the presence of advanced material and passages that may be skipped in a first reading.

1.3 *A description of the individual chapters*

Chapter 2 presents the background material and terminology that will be used in the chapters that follow. It is limited to the phase behavior of one-component fluids. Van der Waals's equation of state, and the corresponding

Helmholtz energy are treated, along with the underlying mean-field assumption and its limitations. Criticality is discussed in some depth, and criticality conditions are given. The Van der Waals picture of phase separation is described, including the double-tangent construction of coexisting phases. Concepts such as plaits, tie lines, plait point, connodal (or binodal) and spinodal, frequently used by the Dutch School, are introduced. The chapter closes with some remarks about cubic equations, of which the Van der Waals equation is the prototype. This chapter includes biographical information about Van der Waals's life prior to his doctorate.

Chapter 3 discusses the powerful theorem of corresponding states, which Van der Waals derived from his equation of state, and Kamerlingh Onnes's generalization beyond the confines of the Van der Waals equation, based on the concept of 'mechanical similarity.' Kamerlingh Onnes also understood that the principle hinges on the existence of two substance-specific scale factors. The chapter describes the usefulness of this principle in predicting unknown critical temperatures for the 'permanent gases.' A crucial application was the prediction of the critical temperatures of hydrogen and helium well before these gases were liquefied. Biographical information on Kamerlingh Onnes is included.

This chapter includes an overview of more than a century of applications of the principle of corresponding states in gas liquefaction, in science, and in chemical engineering. Generalizations of the principle to include an additional scale factor occurred throughout the 20th century. Some of these, such as the Pitzer 'acentric factor,' and the quantum parameter of De Boer are discussed in this chapter.

The book then turns to the topic of fluid mixtures. Chapters 4 and 5 give the theoretical foundation by Van der Waals and Korteweg. A comprehensive understanding of binary fluid phase separation was reached by a combination of theory and experiment, due mainly to work of Kuenen, Korteweg and Van Laar, as described in Chapters 6 and 7. Chapters 8 and 11 discuss specific applications to gas-gas equilibria and to dilute mixtures near the solvent critical point.

Chapter 4 is devoted to Van der Waals's theory of mixtures, formulated in 1890. It is basic to the chapters that follow. First, a separate section summarizes the underlying concepts, due to Gibbs (1873-1878), which are needed in order to follow all chapters on fluid mixtures in this book. Concepts such as limits of stability, chemical potentials, double-tangent planes, tie-lines, and the phase rule are introduced. It is then shown how Van der Waals used his equation of state and the principle of corresponding states to construct an equation of state and Helmholtz energy for binary fluid mixtures. Attention is given to the criticality conditions for a binary mixture, which derive from stability considerations for the Helmholtz energy.

Van der Waals showed that at sufficiently low temperature, the isothermal Helmholtz energy surface has at least one ‘plait’ or fold, separating a vapor and a liquid phase. He called this plait the *transverse plait*. Van der Waals discovered that under certain conditions a second plait might arise, the *longitudinal plait*, which separates two liquid phases of different compositions and gives rise to three-phase equilibrium. Pictures are reproduced of demonstration models built by Van der Waals for isothermal Helmholtz energy surface with two and three coexisting phases.

Chapter 5 discusses the theory of plaits and plait points by the mathematician Korteweg, about whom biographical information is included. It is based on two papers by Korteweg, published alongside Van der Waals’s theory of mixtures in the French-language Archives néerlandaises in 1891. Because the papers are mathematical in origin and have never been translated into English, they are not widely known. In fact, Korteweg prepared for Van der Waals the mathematical tools needed to derive practical results from his equation of state. A plait, in Korteweg’s definition, is a smooth fold (without sharp edges or creases) arising on a two-dimensional mathematical surface free of singularities. Such a fold may terminate in a plait point, presently called a critical point. In the first paper, Korteweg characterized a plait point by the special form of a Taylor expansion at such a point, and analyzed the various ways in which a plait point can originate or disappear as a parameter varies in the analytic representation. In a second paper, Korteweg studied the way tangent planes to the analytic surface touch in more than one point when a plait is present, and, when rolled across the surface, trace out connodals or loci of double-tangent points. He classified a variety of plait points, and worked out how new plaits are born, grow, and interact with existing plaits as the surface is gradually deformed. Many of the original pen drawings by Korteweg have been reproduced in Chapter 5. Underlying this work is a little-known set of three mathematical theorems published by Korteweg in Dutch. They are introduced in Chapter 5 along with part of Korteweg’s second paper.

The latter half of Korteweg’s second paper on the theory of plaits is an application to the Van der Waals Helmholtz energy for a binary mixture, and it is incorporated into Chapter 7 of this book. Although it is impossible to do full justice to these two major treatises, the papers are described in some detail, in the hope that this may entice others to study a very interesting but forgotten chapter in mathematical physics.

Chapter 5 gradually increases in difficulty as it progresses through Korteweg’s first paper, but an effort has been made to present the material pictorially, by making use of many of Korteweg’s own pen drawings. It is sensible to return to parts of Chapter 5 as needed when reading further chapters of the

book, especially Chapter 7. Better yet, the reader may wish to consult the systematically and clearly written original papers.

Chapter 6 is devoted to early experiments in fluid mixtures by the Leiden School. This chapter begins by describing how Kamerlingh Onnes founded a premier research laboratory by establishing the experimental methods for accurate measurement and control of temperature and pressure, including calibration standards. His graduate student Kuenen was able to obtain the first reliable data on pressurized fluid mixtures. Shortly after, Kuenen discovered and interpreted the phenomenon of retrograde condensation. Next, Kuenen discovered the phenomenon of critical azeotropy in a mixture with a minimum in the critical temperature. This chapter contains some biographical information on Kuenen.

Kamerlingh Onnes, fascinated by the power of Van der Waals's equation for mixtures, began to build plaster models representing isothermal Helmholtz energy and pressure surfaces as functions of volume and composition. He represented the Van der Waals surface, as well as experimental data fitted with an empirical equation. These surfaces allowed him to actually perform the double-tangent construction and locate the connodals. Many of these models still exist, and a photograph of one of them is reproduced in this chapter.

Chapter 7 is the most substantial chapter in the book. The topic of this chapter, binary fluid phase diagrams, is fairly complex, and no longer automatically included in thermodynamics texts and courses. It is introduced from a modern perspective: the classification of all possible types of binary fluid phase diagrams that derive from Van der Waals's equation of state for equal-size molecules. Scott and Van Konynenburg accomplished this classification when digital computers became available in the 1960s. There are two parameters in the problem: the relative strength of attraction of the two components, and the relative strength of the interaction between unlike components. The introductory part of Chapter 7 is based on the 1980 paper by Van Konynenburg and Scott, and will be frequently referred to in this chapter as well as those following it.

The early calculations for a special case of the Van der Waals equation for mixtures are those by Korteweg. In 1891, he derived all possible phase behaviors of Van der Waals's equation of state for mixtures of two components that are *identical*. The only parameter in this symmetric model is the interaction between the first and second components, which is allowed to vary. The symmetry of this model leads to surprisingly complex phase behavior. Many of Korteweg's marvelously detailed drawings of isothermal phase equilibria, critical points and tie lines for the symmetric model in the volume-composition plane are reproduced. Several of Korteweg's algebraic results were later rediscovered by the use of digital computers. The relationship is shown between

Korteweg's work and 20th-century studies of phase separation in ternary mixtures, as well as the so-called three-state Potts model.

The next topic of the chapter covers the next phase of experimental work by Kuenen, which he carried out as a physics professor at the University of Dundee in Scotland. With his genius for choosing interesting systems, he found the predicted three-phase behavior liquid-liquid-vapor at elevated pressure. He discovered that criticality of one of the liquid phases with respect to the vapor could be achieved in systems of greatly differing volatility. Around 1900, he found types of phase diagrams hitherto unknown. His systems were mixtures containing associating components, such as a variety of alcohols, which he called *anomalous* systems, expecting that they could not be described by Van der Waals's equation.

Kuenen's findings were an inspiration to the Amsterdam mathematical chemist Van Laar, about whom some biographical information is included. Around 1905, Van Laar was able to calculate several possible phase behaviors for a Van der Waals mixture of equal-size components, which differ in strength of attraction, but in which the attraction between different components is fixed by those between like components. Van Laar found several types of systems with three-phase equilibria and more than one critical line, such as had been found experimentally by Kuenen. He thus showed that the phase behavior of Kuenen's anomalous systems could be derived from the Van der Waals equation.

Van Laar also studied how the different types of phase behavior transform into each other as a parameter characterizing the molecular attractions varies. He found what is now called the Van Laar point, where three different types of phase diagrams meet.

Due to the work of Korteweg, Kuenen, and Van Laar, all types of binary-fluid phase diagrams derivable from the Van der Waals equation were recognized by 1906, in part from experiment, in part from analytic or approximate numerical calculations, or both.

Chapter 8 describes an interesting new phenomenon that Kamerlingh Onnes and Keesom discovered in 1906. When trying to dissolve gaseous helium into liquid hydrogen, they found they could not make the gaseous phase disappear by applying pressure. Using Van der Waals's original paper on mixtures, they were able to explain how this phenomenon was due to the presence of a longitudinal plait on the Helmholtz energy surface. They termed this equilibrium gas-gas equilibrium. At high enough pressure, the density of the helium-rich gas phase became high enough for the gas and liquid phase to exchange their positions in the tube, the so-called barotropic effect.

A clash erupted with Van Laar, who claimed priority for the discovery of the longitudinal plait. The chapter describes the nature of the dispute, and

how it was resolved. This will require familiarity with the work of Van Laar described in Ch. 7. Ch. 8 includes biographical information about Keesom.

Fluid criticality is the subject of Ch. 9 and 10. Ch. 9 covers fundamental problems discovered in the 1890s with Van der Waals's predictions of fluid property behavior near a critical point. Ch. 10 covers a lengthy period, from 1889 through 1906, of disputes about experiments near critical points, with flare-ups until the middle of the 20th century. Each of these two chapters is more or less self-contained and light on mathematical formulae.

Chapter 9 describes the discovery by Verschaffelt that the Van der Waals equation is fundamentally flawed at the critical point. The starting point was Van der Waals's theory of capillarity of 1894, which predicted the way the surface tension must approach zero at a critical point. In an appendix to the German version of his paper, Van der Waals introduced the modern concept of a critical exponent sixty years ahead of the time; he noted that experiment and theory did not agree. Verschaffelt discovered over the course of several years that the discrepancy was fundamental. His work was not appreciated, and only at the very end of his life, in 1955, did scientists begin to regain interest in this subject. This chapter contains biographical information about Verschaffelt.

Chapter 10 addresses disputes and confusions that arose when a multitude of experimenters reported findings of failure of the Andrews-Van der Waals concept of fluid criticality. The chapter begins by discussing the sources of experimental error, and why their effects are disproportionally large near fluid critical points, preparing the reader for the most common pitfalls in the multitude of experiments discussed. Such claims began in 1880. Kuenen first pinpointed the principal sources of error in 1892, but reports disproving the Andrews-Van der Waals view continued to be published in many countries. Kamerlingh Onnes took these reports personally, and, with Keesom, spent an enormous amount of effort redoing and invalidating several of these experiments during the first decade of the 20th century. The chapter then describes how the same theme of 'a new experiment disclaiming the Andrews-Van der Waals view' recurred during the 20th century.

Chapter 11 connects the topics of criticality and fluid mixtures, and reintroduces many of the characters described in this book. This closing chapter resumes and unites earlier themes, and illustrates once more the synergy of the Dutch School.

The topic of dilute mixtures near critical points is introduced from a wider context: that of dilute solutions in general, a topic of great interest among chemists at the end of the 19th century. This approach permits the introduction of the Amsterdam professor Van 't Hoff, who won the first Nobel prize in chemistry for his contributions to the thermodynamics of dilute solutions.

Biographical information on Van 't Hoff is included in the chapter. It was natural for the Dutch School to enquire if and how dilute-solution laws would be modified near the critical point of the major component.

Apart from this fundamental interest, there was the question of the effect of impurities on experiments near the critical point of a one-component fluid. Most members of the Dutch School worked on aspects of this question at some time in their lives. Van der Waals was the first to present some fundamental thermodynamic identities, while Korteweg, Verschaffelt, Keesom, and Van Laar developed models, each of them according to his own special expertise. This chapter epitomizes the synergy of the Dutch School.

Since the properties of dilute mixtures near critical points are relevant to modern-day interest in supercritical solvents, the chapter has been written with this application in mind. The chapter introduces a limited number of mathematical equations, and it does require a modicum of familiarity with the previous chapters, particularly Ch. 4-7 and 10.

Chapter 12 focuses on the impact of the Dutch school of Van der Waals and Kamerlingh Onnes. In addition to laying the groundwork for the well known prowess of Netherlands scientists in the areas of statistical mechanics and molecular science, the experimental heritage was retained at several of the Netherlands universities. Early in the 20th century, the work of the Dutch School was embraced by Russian physical chemistry, and reached from there to mineralogy, metallurgy and the geosciences. The practical importance of the work of the Dutch School was gradually rediscovered, triggered by the growth of 20th-century exploration and processing of petroleum and natural gas.

2. The equation of state of Van der Waals

The Van der Waals equation of state is essential to the work of the Dutch School described in this book. It was the first mathematical model incorporating the gas-liquid transition and fluid criticality. Even its shortcomings have raised profound questions, resulting in deeper insights. Its foundation on molecular concepts, although not rigorous, affirmed the reality of molecules at a crucial time in history. One of its consequences, the law of corresponding states, would give powerful guidance to experiment. The generalization to fluid mixtures would open up a new field of scientific research of immense practical importance. This chapter begins with a sketch of the historical setting, within which Van der Waals developed his equation of state. The Van der Waals equation and the corresponding Helmholtz energy are discussed, and the terminology of the Dutch School encountered throughout this book is introduced.

2.1 *Gas non-ideality in the 19th century*

The ideal-gas law, $PV = RT$, named after Boyle and Gay-Lussac, describes the relationship between the pressure P , the molar volume V (which is the inverse of the molar density), and absolute temperature T of a mole of gas. R represents the molar gas constant, which is the same for all gases. The P - V *isotherm*, the relation between P and V at fixed temperature, has the form of a hyperbola. Robert Boyle proposed this hyperbolic form of the P - V isotherms in 1662 on the basis of his experiments on the elasticity of air. In 1801/02, Joseph Louis Gay-Lussac demonstrated experimentally that, on heating at constant pressure, all gases expand at the same rate, the volume increasing linearly in temperature.

As knowledge about the behavior of gases and liquids increased in the 19th century, it became very obvious that the law of Boyle and Gay-Lussac is a limiting case, valid only for low pressures and high temperatures, far away from the region where gases liquefy. Thus, accurate measurements performed by Henry Victor Regnault in the period from 1840 to 1870 showed

departures from the ideal-gas law for gases even at modest pressures. More seriously, the law of Boyle and Gay-Lussac could not describe the P - V - T behavior of liquids, nor the transition from vapor to liquid.

With the development of steam engines during the 18th century, interest increased in the vapor-liquid phase transition at temperatures above the boiling point. The French engineer and nobleman Charles Cagniard de la Tour (1777-1859), foreseeing that the pressure might increase rapidly, heated a liquid that filled about one third of a pressure vessel constructed out of the plugged barrel of a cannon, to far above the boiling point. A silica sphere, rolling back and forth in the rocking barrel, made a splashing sound as it crashed through the liquid-vapor interface. Cagniard de la Tour (1822) noted that the splashing stopped above a certain temperature, which we presently call the critical temperature, and concluded that the distinction between vapor and liquid disappears at this temperature.

Cagniard de la Tour also heated glass capsules, which were filled partially with liquid and sealed. He measured the critical temperature, at which the meniscus disappeared in the center of the cell. By this same method Michael Faraday in England and Dmitry Ivanovich Mendeleev in Russia determined the critical temperatures of quite a few fluids by the middle of the 19th century. By that time it was also appreciated that gases such as ammonia and carbon dioxide could be liquefied by compression at ambient temperature, while others such as air, nitrogen and oxygen resisted liquefaction under ambient temperature conditions, no matter how high the pressure. These gases were called *permanent*.

2.2 Andrews and the P - V relation near the critical point

The Irishman Thomas Andrews (1813-1885) (1869) was the first to make a detailed study of the P - V relation of carbon dioxide along isotherms near the critical point. The work, carried out in his laboratory in Belfast, made it clear how the vapor-liquid phase transition takes place, and why there is a critical point (Fig. 2.1). The pressure-volume diagram from Andrews's publication shows that as the temperature increases the liquid phase expands, while the coexisting gas phase becomes denser due to the increased pressure. Finally, a temperature is reached at which these two phases become identical. Above this temperature, which is about 31°C for carbon dioxide, there is no longer a distinction between liquid and vapor. Andrews called the state point at which vapor and liquid become identical the *critical point*. At temperatures above the critical, the fluid density increases continuously on compression, without the occurrence of a phase transition. For this phenomenon, Andrews coined the phrase *continuity of states*. Van der Waals (1873, 1881) used Andrews's

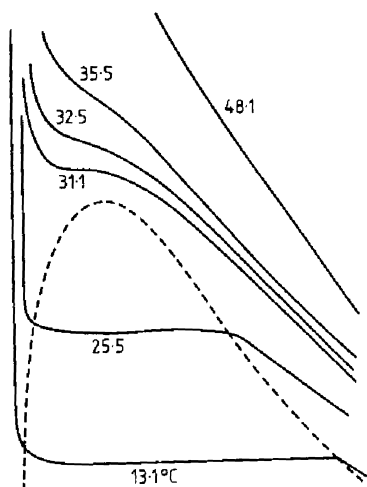


Figure 2.1 Andrews's P - V isotherms of carbon dioxide. These were graphed by Maxwell (1871) and reproduced in Fig. 8 of the German version of Van der Waals's thesis. The isotherms are labeled by their respective temperatures. The horizontal sections represent coexistent liquid and vapor phases. The dashed curve, the connodal or coexistence curve, is the border of the region of two-phase coexistence.

terminology, and even adopted the title of Andrews's (1869) Bakerian lecture, without reference, almost verbatim as the title of his doctoral thesis of 1873. Van der Waals developed his equation of state independently, but he did compare it with Andrews's results.

2.3 *Van der Waals's background*

Kipnis *et al.* (1996) published an extensive biography of Van der Waals, from which the following facts are taken. Johannes Diderik Van der Waals (1837-1923) was born in Leiden, the oldest of the ten children of a carpenter. As a child from the working class, he finished his public schooling at the age of fifteen, after completion of three years of advanced primary education. He became a teacher's apprentice in an elementary school. At the age of nineteen, while teaching, he began to take courses and examinations that would improve his qualifications as a teacher. In 1862, he began to attend lectures at the University of Leiden. For those not qualified to be enrolled as regular students for lack of the proper college-preparatory schooling, the University had a provision to take up to four courses a year. Van der Waals studied first mathematics, then astronomy, and finally physics with Professor Rijke, who would be thesis advisor to both Van der Waals and Lorentz. When the new HBS was founded and teacher qualifications were specified in 1864, Van der Waals, while a director of an elementary school, spent two strenuous years to study for the required examinations in mathematics and physics. In 1865, he was appointed a physics teacher at the HBS in Deventer in the east of the Netherlands, and in 1866, he received such a position in the Hague. Around

1870, while living in the Hague, he resumed his coursework at the University of Leiden, where he must have been a classmate of Lorentz and Van 't Hoff. After receiving a dispensation from the study of classical languages, he brilliantly passed the exams in physics and mathematics qualifying for doctoral studies. At Leiden University, on June 14, 1873, he defended his doctoral thesis on the continuity of the gaseous and liquid state.

2.4 *The Van der Waals equation*

It is easy to overlook that the origin of the chemical bond and of the (weaker) intermolecular forces was not elucidated until well after the advent of quantum mechanics in the 20th century. By the late 1800s, however, much empirical quantitative knowledge had been acquired about chemical reactions, for instance, the fixed ratio of the volumes of reacting gases in the formation of a compound. The much weaker intermolecular forces, however, which manifest themselves in phenomena such as the condensation of vapors, surface tension, and adsorption, had remained elusive. Spearheaded by Mach and Ostwald, a strong philosophical current that denied the existence of molecules arose towards the end of the 19th century. Van der Waals's work affirmed the reality of molecules and allowed an assessment of their size and attractive strength.

As is well known, Van der Waals modified the law of Boyle and Gay-Lussac by taking into account the facts that molecules occupy space, and that they exert an attraction on each other. Van der Waals's (1873) equation of state for a mole of gas is given by

$$(P + a/V^2)(V - b) = RT, \quad (2.1)$$

where P and V are the externally measured pressure and volume. The molecules are assumed to have a core in the form of an impenetrable sphere. The volume they exclude by their mutual repulsions is called the *excluded volume* b , while the attraction is incorporated by the coefficient a . By comparing the equation of state with experimental data, Van der Waals was able to obtain estimates for the actual size of molecules and the strength of their mutual attraction.

The effect of the excluded volume is that the pressure increases more rapidly with density than given by Boyle's law. To the surprise of luminaries such as Maxwell, Van der Waals posits that the excluded volume b equals *four* times the volume occupied by the hard spheres. This is indeed the exact result in the low-density limit, for which there are only binary collisions between the hard spheres. Each sphere excludes the centers of others from eight times its volume, while counting doubly must be corrected for. At higher densities,

however, these exclusion spheres begin to overlap, and the excluded volume shrinks. This density dependence of the excluded volume is a problem Van der Waals wrestled with all his life. In his thesis, however, b is assumed to be constant, so that the volume available to the molecules equals $V - b$.

Van der Waals then introduces a second characteristic of the molecules, namely their mutual attraction incorporated by the parameter a . This effect is called *cohesion*. The result is a reduction of the pressure on the walls to values lower than those given by Boyle's law. These forces are universally known as *Van der Waals forces*, but the origin of these forces was unknown at the time. It would not be until the 1930s that the origin and range-dependence of the Van der Waals forces would begin to be understood.

In the first half of his thesis, Van der Waals starts out with the mathematical expressions Laplace had derived for the phenomenon of capillarity at the beginning of the 19th century, under the assumption that the attraction was short-ranged (see Rowlinson 2002). Van der Waals, however, is not able to connect Laplace's expressions with the pressure exerted by the fluid on the wall of the vessel. Then he makes a bold move (Thesis §36) and calculates the molecular pressure approximately, assuming that the attractive interactions on a molecule in the interior of the fluid cancel each other. The only interactions that do not cancel are those exerted by molecules in the bulk fluid on those in the boundary layer, since the latter have neighbors only on one side. Van der Waals argues that there is a limited volume within the bulk liquid *near* the boundary layer from which molecules exert attraction on those *in* the boundary layer. On average, the force per unit area of the surface from these molecules must be proportional to the density. On the other hand, the number of molecules in unit surface of the boundary layer must be proportional to the density as well. This leads to the expression a/V^2 for the molecular pressure, a being a constant characterizing the strength of attraction. This expression had been derived earlier, but had never been incorporated into an equation of state (See Rowlinson 1988).

The assumption that the molecular pressure is proportional to the square of the bulk density was coined a *mean-field* assumption by later scientists such as Weiss (1907), who made a similar assumption for the internal field of a magnet. The mean-field assumption ignores spatial density variations that may arise as a consequence of the intermolecular forces.

Kamerlingh Onnes (1881, Second Part p. 2) expressed the opinion that the Van der Waals equation could be valid only if many molecules are present in the sphere of attraction. Boltzmann (1896-1898) stated explicitly that the Van der Waals cohesive force decreases slowly over a much longer range than the average separation of the molecules. As recounted by Kipnis *et al.* (1996, p. 224), Van der Waals learned about Boltzmann's statements in 1898, and

reacted immediately, pointing out that he never made the assumption that the range of attraction was long, and thought this improbable. Boltzmann, however, replied, that he could find no foundation for the Van der Waals equation unless he assumed that the attractive forces were long-ranged. Finally, it was shown by Kac *et al.* (1961) that the Van der Waals equation can be rigorously derived (in one dimension) if each molecule interacts with all others by means of a weak long-range potential.

If anything was imbedded firmly in Van der Waals's mind, however, it was Laplace's assumption that molecules had to have a short range of interaction. He had proof for the short range by taking the ratio of surface tension to the bulk cohesion a/V in liquids for which the values of a and b were known (see his thesis, §9, §66-69, and Rowlinson 1988, 2002). The resulting length, an estimate for the range of the attractive forces, was found to be roughly the same as the molecular diameter derived from b . This conflict between the condition of long-range forces underlying the mean-field assumption and the actual short range of attraction is a profound issue, to be discussed further in Ch. 9.

Above the critical temperature, the P - V isotherms for the Van der Waals equation behave like those of Andrews shown in Fig. 2.1. Supercritical isotherms develop a region where they are flatter than Boyle's hyperbolas. At the critical point the isotherm has a horizontal inflection point. The *isothermal compressibility* K_T , which measures the decrease in volume due to an increase in pressure at constant temperature, is defined as

$$K_T = - (1/V) (\partial V / \partial P)_T \quad (2.2)$$

Because the P - V isotherm is horizontal at the critical point, the compressibility becomes infinite at this point. The criticality conditions are:

$$(\partial P / \partial V)_T = 0; \quad (\partial^2 P / \partial V^2)_T = 0 \quad (2.3)$$

The first criticality condition represents the zero slope of the P - V isotherm at the critical point. The second one states that the critical isotherm has an inflection point. If this second condition were not imposed, the critical isotherm would pass through an extremum so that on one side of the critical point the pressure would *increase* when the gas expands. This is strictly forbidden by the requirements of thermodynamic stability.

Below the critical point, the Van der Waals isotherm develops a loop with a section of negative compressibility (Fig 2.2). Curiously, even before 1873, James Thomson (1871) had suggested that Andrews's subcritical experimental isotherms be drawn as loops without the discontinuities in slope so that metastable states, known to exist, could be included (see Maxwell 1875a Ch. VI). The region of negative compressibility being forbidden by the

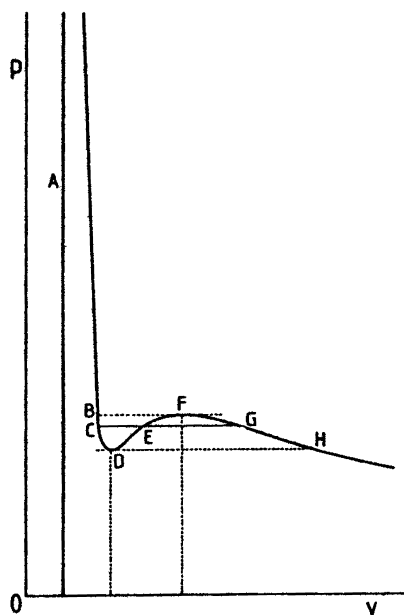


Figure 2.2 A P - V isotherm according to the Van der Waals equation. After Fig. 6 of the German version of Van der Waals's thesis. Below the critical point, the isotherm develops a loop CDEFG, which is cut off by means of the Maxwell equal-area rule CG.

stability requirements of thermodynamics, Maxwell (1875a,b) corrected this feature by the equal-area rule named after him. The horizontal portion of the isotherm in Fig. 2.2 cuts off the loop in such a way that the areas between the two sections of the loop and the horizontal line are equal. This equal-area rule in the P - V plane guarantees that no net work is gained or lost when the system moves through a closed isothermal cycle, one way along the loop, the other along the horizontal part of the isotherm. Van der Waals included this feature in the 1881 German version of his thesis (See Rowlinson 1988).

That the two-parameter equation explained fluid criticality and continuity of states and was able to qualitatively describe the experiments of Andrews was a major achievement. Andrews, however, kept his distance from 'empirical formulae' and only sporadically referred to the Van der Waals equation. Recognition came to Van der Waals gradually, after Maxwell wrote a laudatory but also critical review in *Nature* in 1874, and after abstracts of his work began to appear in German in the *Beiblätter* of the *Annalen der Physik*, beginning in 1877 (See Kipnis *et al.* 1996, pp. 52-55, 60-63).

In his 1873 doctoral thesis Van der Waals made an effort to test the predictions of his equation of state with what was experimentally known at that time about fluids such as hydrogen, carbon dioxide, sulfur dioxide, alcohol, ether and water. He tried to estimate values of a and b for these fluids. Given the limited accuracy of the experiments at that time, and the inconsistencies between data of different origins, trends observed in the values of a and b for

a given substance at different pressures and temperatures could generally be ignored. The large body of carbon dioxide data by Andrews, however, forced him to conclude that the excluded volume b decreased substantially with increase of the density. It did not escape his attention either that there was no set of values for a and b that was simultaneously consistent with the observed critical volume, temperature and pressure of the gas.

2.5 *The Helmholtz energy according to Van der Waals*

The Van der Waals equation is an equation of state, which gives only a partial description of the thermal properties of a system. Thus, by differentiation, it gives the inverse compressibility, but not the heat capacity. The Dutch School prefers to describe fluid properties by means of Gibbs's ψ -function, now called the *Helmholtz energy*, one of several free energies or thermodynamic potentials that give a complete description of the thermal properties of a system. Each free energy has its own set of independent macroscopic variables. When the system attains equilibrium all free energies reach an extremum at given values of their respective independent variables.

The Helmholtz energy $A(V, T)$ for a one-component system has volume and temperature as independent variables. Other thermodynamic potentials we will encounter are the energy $U(S, V)$, the entropy $S(U, V)$ and the Gibbs energy $G(P, T)$. Definitions of these potentials, their derivatives, and their interrelations, can be found in textbooks on thermodynamics. The chemical potential plays a major role in the thermodynamics of mixtures. Limiting ourselves in this chapter to a one-component system, the chemical potential measures the increase in the total Gibbs energy of the system as a mole of substance is added at constant pressure and temperature. Therefore, the chemical potential $\mu(P, T)$ in a one-component system equals the molar Gibbs energy.

In equilibrium, for given temperature and volume, the Helmholtz energy is a minimum, so that internal rearrangements of the system (for instance, by a movable piston) will lead to an increase of the Helmholtz energy. In the context of the present book, another face of this minimum principle will play a crucial role. There are cases that the homogeneous state of the system is not a true equilibrium state for the given temperature and volume. Then the Helmholtz energy can be lowered by the system splitting into two phases. This is why this free energy occupies such a central role in the work on fluid phase separation by the Dutch School.

The isothermal derivative of the Helmholtz energy with respect to volume is the negative of the pressure, which is a force per unit area. The Helmholtz energy is thus analogous to the potential energy of mechanical systems, for

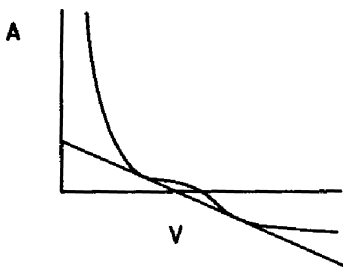


Figure 2.3 The isothermal Helmholtz energy A as a function of volume. The Helmholtz energy develops a loop with two inflection points below the critical point. The double-tangent construction cuts off the metastable and unstable parts. The tangent points represent coexisting vapor and liquid phases. After Van der Waals (1890), Fig. 2.

which the first derivative with respect to distance yields the negative of a force. The second volume derivative yields the inverse compressibility.

$$(\partial A / \partial V)_T = -P; \quad (\partial^2 A / \partial V^2)_T = (V K_T)^{-1} \quad (2.4)$$

Since the pressure is commonly not negative, the Helmholtz energy has a negative slope if plotted with respect to volume. Since the compressibility must be positive for thermodynamic stability to prevail, the Helmholtz energy of stable states must curve upwards as a function of volume.

Van der Waals integrated his equation with respect to volume, to yield a closed expression for the Helmholtz energy of a one-component system. Save for a temperature-dependent integration constant, this expression is:

$$A(V, T) = -RT \ln (V - b) - a/V \quad (2.5)$$

The criticality conditions in terms of the Helmholtz energy are

$$(\partial^2 A / \partial V^2)_T = 0; \quad (\partial^3 A / \partial V^3)_T = 0 \quad (2.6)$$

In the vicinity of a point for which these two derivatives are zero, a curve becomes very flat but retains its convex shape. At the critical point the $A(V)$ curve has a finite slope, but its curvature is zero. It does not have an inflection point, but remains convex, because the third derivative is zero as well. Below the critical temperature the isothermal $A(V)$ curve develops two inflection points (see Fig. 2.3). Between these points it is no longer convex. Therefore, the compressibility is negative between the inflection points, which is a thermodynamically unstable situation. The isothermal Helmholtz energy can now be lowered by the system splitting into two phases of different molar volume. A system composed of these two phases in different proportions follows the double tangent to the curve instead of the loop. The existence of a double tangent for the isothermal Helmholtz energy implies that the pressure and chemical potential are the same in coexisting phases. The construction is the exact equivalent of the Maxwell construction for the isothermal pressure $P(V)$ in Fig. 2.2.

2.6 Double tangent, tie line, connodal and spinodal

The double tangent points in Fig. 2.2 were called the *connodes* by the Dutch School. Their locus was called the *connodal* or the *binodal*. The modern term is *coexistence curve*. The three terms will be used interchangeably in this book. The *tie line* refers to the line segment connecting the double-tangent points. It may happen that the length of the tie line shrinks to zero. Then a *plait point* is reached, which soon was renamed a critical point.

The locus of the extrema in the pressure-volume isotherms, which is equivalent with the locus of the inflection points in the Helmholtz energy, is called the *spinodal*. This word is derived from the Latin word *spina*, for thorn. (This word is also the root of the English words *spine* and *spinach*. The former is self-explanatory, the latter derives from the thorny seeds of the old-fashioned European spinach, which seeds prevented Dutch children from enjoying this healthy but treacherous green.) Although the isothermal Helmholtz energy is a perfectly smooth function of volume at the spinodal points, the isothermal Gibbs energy $G(P, T)$, or chemical potential μ , is not a smooth function of pressure. It has a cusp as the pressure passes through an extremum at each of the spinodal points (Fig. 2.4), hence the name of this locus.

The parts of the isotherm between the connodal and the spinodal still obey *local* thermodynamic stability in that the pressure rises when the volume is decreased. They are not stable in the *global* sense, because a state of lower total Helmholtz energy can be reached by the system splitting into two phases. Such locally but not globally stable states are called *metastable*. The states inside the spinodal (between the two extrema in the isothermal pressure, or between the two inflection points in the isothermal Helmholtz energy) violate thermodynamic stability locally, and are called *unstable*.

It may well be well worth stressing that the spinodal is a characteristic of analytic equations of state such as the Van der Waals equation. Any exact statistical mechanical treatment, such as the Kac model mentioned above, *must* yield the horizontal section in the P - V diagram of Fig. 2.2 instead of the loop, and the double-tangent instead of the concave section of the A - V diagram in

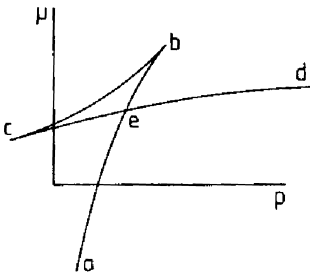


Figure 2.4 On a below-critical isotherm the chemical potential μ shows two cusps, b and c, as a function of pressure p . The cusps are located at the pressure extrema of the Van der Waals loop in Fig. 2.2. After Van der Waals (1890), Fig. 1.

Fig. 2.3. Thus the spinodal is a mathematical construct typical of a certain class of equations of state, and may not have any meaning in real fluids. Nevertheless, during the 20th century, the spinodal has assumed a pseudo-reality of its own in engineering science, especially in application to phase separation in polymeric liquids. Only by the latter third of the 20th century scientists began to come to grips with phenomena such as metastability and instability that arise so naturally from the Van der Waals model but are at odds with requirements of thermodynamic stability.

2.7 *Van der Waals's career at the University of Amsterdam.*

After Maxwell's qualified endorsement of his thesis in *Nature* in 1874, (Kipnis *et al.*, p. 52-54), Van der Waals's reputation was established. He was elected to the Royal Netherlands Academy of Arts and Sciences (KNAW) in 1875, and to the Holland Society of Arts and Humanities in 1878. In 1877, the University of Amsterdam was founded. Van der Waals, the forty-years-old high-school teacher, was appointed as the first and only professor of physics. With utter dedication, Van der Waals served the University until his retirement in 1908. Notwithstanding a crushing teaching load, he produced an enormous œuvre, including his major papers on corresponding states, fluid mixtures, and capillarity. He served as the General Secretary of KNAW from 1896 to 1912. In 1910, he received the Nobel prize in physics for his studies of the physical state of liquids and gases. (Kipnis *et al.*, 1988)

2.8 *Cubic equations*

The Van der Waals equation is an example of a cubic equation. It can be written as a third-degree polynomial in the volume, with coefficients depending on temperature and pressure. Notwithstanding the shortcomings of the Van der Waals equation, its cubic form has the advantage that there are at most three real roots for the volume at given temperature. In the numerical calculation of phase equilibrium, one simply discards the middle root, for which the compressibility is negative. Increasing the accuracy of an equation of state by including higher powers of the volume comes at the expense of the appearance of multiple roots, which complicates numerical calculations. This is why cubic equations still enjoy great popularity in the data representations used by the chemical process industry. Within the framework of the cubic equation, it is not too difficult to obtain more accuracy than offered by the Van der Waals equation. Kamerlingh Onnes and coworkers preferred the equation of state proposed by Clausius in 1881, in which an additional parameter, a constant, was added to the volume in the attractive term. Including more than two adjustable parameters is an obvious way of increasing the accuracy. Having the

attractive parameter depend on the temperature is a much-used device that conserves the cubic character. Designing better cubic equations has occupied scientists and engineers for well over a century. Workhorses in the natural-gas industry are the Redlich-Kwong and Peng-Robinson cubic equations. Hardly a year passes without the publication of another improved cubic equation (For a recent review and many references, see Anderko 2000).

2.9 *Relation to coming chapters*

Concepts and terminology introduced in this chapter will be frequently encountered. For instance, Chapter 4 generalizes the Van der Waals equation to binary fluid mixtures. Chapters 4 through 7 use the terminology and build upon the concepts of thermodynamic stability introduced here. Problems with the mean-field approximation in relation to the short range of molecular interactions are discussed in Chapters 9 and 11.

3. The law of corresponding states – Van der Waals and Kamerlingh Onnes

3.1 *The principle of corresponding states from the Van der Waals equation*

Van der Waals (1880a,b) formulated the principle of corresponding states on the basis of his equation of state. It has proven to be of immense importance for practical applications and, in various guises, has been in use until the present day.

The simple form of Van der Waals's equation, the prototype of the many cubic equations to follow in the century to come, made it possible for him to calculate explicitly the coordinates of the critical point. The conditions of criticality, Eq. (2.3), applied to the Van der Waals equation yield for these coordinates:

$$P_c = a/(27b^2), \quad V_c = 3b, \quad RT_c = 8a/(27b) \quad (3.1)$$

The *critical ratio*, defined as $P_c V_c / RT_c$, equals 3/8 for the Van der Waals equation.

Van der Waals then proposes to use the critical parameters themselves as units of measurement, thus replacing the constants a , b and R . The resulting equation of state, in what is called a *reduced form*, now reads:

$$(P^* + 3/V^{*2})(3V^* - 1) = 8T^*,$$

with $P^* = P/P_c$, $V^* = V/V_c$, and $T^* = T/T_c$ (3.2)

This is a truly remarkable result. Equation (3.2) is *universal*: all characteristics of individual fluids have disappeared from it or, rather, have been hidden in the reduction factors. The reduced pressures of two fluids are the same if the fluids are in *corresponding states*, that is, at the same reduced volume and temperature.

In his presentations to the Academy, Van der Waals (1880a,b) deduces straightforwardly that in reduced coordinates, the vapor pressure curve and the coexistence curve must be the same ('fall on top of each other') for all fluids. He also points out that this principle can be used to predict the vapor pressure of a substance in a temperature range in which it is not known, by

comparing the vapor pressure curve in a known range with that of a well-characterized reference substance. As an example, Van der Waals obtains crude estimates for then unknown critical pressure and temperature of water by scaling the water vapor pressure curve in the range of 128 to 201°C to that of ether. For ether the vapor pressure curve is known all the way up to the critical point. For water he predicts $T_c = 390^\circ\text{C}$, while the presently accepted value is 373.9°C – not a bad estimate for an extrapolation of over 150°C .

3.2 *Van der Waals tests the principle of corresponding states*

With his characteristic thoroughness, Van der Waals then tries to find out whether saturated vapor volumes of different fluids as functions of temperature indeed fall on top of each other. He consults data from six European laboratories for a dozen fluids with known covolumes b . For ether, ethanol, acetone, and chloroform he expresses the volumes in units of b and compares them at two different pressures, which are fixed fractions of the respective critical pressures. He finds that these reduced volumes agree within 2%. Carbon tetrachloride and carbon disulfide, however, are found not to comply.

This particular presentation by Van der Waals (1880a,b) is of interest for two other reasons. First of all, it contains the first indications of his interest in applications to fluid mixtures (see Ch. 3.6), a topic that would take another ten years to ripen (Ch. 4). Secondly, it contains several experiments Van der Waals himself carried out on phase separation of a mixture of carbon dioxide and air at pressures up to 100 bar. These experiments are discussed in Ch. 4.

Like Van der Waals himself, scientists were quick to realize the power of the principle of corresponding states. As early as the 1880s the limited accuracy of the Van der Waals equation was well known. For example, the critical ratio of common fluids ranges from 0.23 (water) to 0.29 (noble gases), while the prediction of $3/8 = 0.375$ grossly overestimates this value. The principle of corresponding states, however, frees the scientist from the particular constraints of the Van der Waals equation. The properties of a fluid can now be predicted if only its critical parameters are known, simply from correspondence with the properties of a well characterized reference fluid. Alternatively, unknown critical properties of a fluid can be predicted if its properties are known in a region not necessarily close to criticality, based on the behavior of the reference fluid.

Van der Waals's tests of the principle of corresponding states for properties such as the coefficient of expansion gave less than convincing results,

but, as Van der Waals (1880a,b) points out, the reliability of the existing experimental results left much to be desired. In his 1913 Nobel lecture, in hindsight, he recalled his disappointment when he found out that the principle of corresponding states had only approximate validity and was thus not a law of nature.

3.3 *Importance of the principle of corresponding states for gas liquefaction*

S. Wroblewski made use of the principle in estimating the correct critical temperature of hydrogen ten years before this gas was liquefied by James Dewar in 1898. In the early 1900s Kamerlingh Onnes did not know a priori whether helium could be liquefied at all, so it was essential for him to have an estimate of its critical temperature. But not until a year before the actual liquefaction of helium was Kamerlingh Onnes (1907e) in a position to obtain an accurate estimate. Measuring and comparing P - V isotherms of hydrogen and helium in regions around the critical point of hydrogen permitted him, on the basis of corresponding states, to estimate the helium critical temperature as 5.3 K. This is only just over 0.1 K above the presently known value of 5.189 K. He then calculated the dimensions for his liquefier and estimated how much liquid air and liquid hydrogen he would need in order to produce liquid helium. He barely made it. Only towards the end of a long, arduous and nerve-wracking day, July 9, 1908, was a liquid-vapor interface finally spotted inside the liquefier. This is how Kamerlingh Onnes (1908) described the achievement in a letter to Van der Waals, at the occasion of the latter's retirement on July 11, 1908:

At the time that the last bottle of liquid hydrogen was coupled [to the liquefier], no [liquid] helium was visible. [Apparently, however], the apparatus had filled up with liquid helium during one of the expansions. A little bit later, the interface appeared. [Translated from the Dutch]

And this is how Kamerlingh Onnes credited Van der Waals:

In what I described to you, your theory has been my guide. To calculate the critical temperature of a permanent gas from the $[P$ - $V]$ isotherms brings your dissertation to memory in a new way. The calculations were performed entirely on the basis of the law of corresponding states. Guided by that law, I estimated – even though I did not put that on paper – to need 20 liters [of hydrogen]. Had I estimated a few liters fewer, the experiment would not have succeeded – had I estimated much more, then I would have judged it unwise to proceed, in view of the available resources. [Translated from the Dutch]

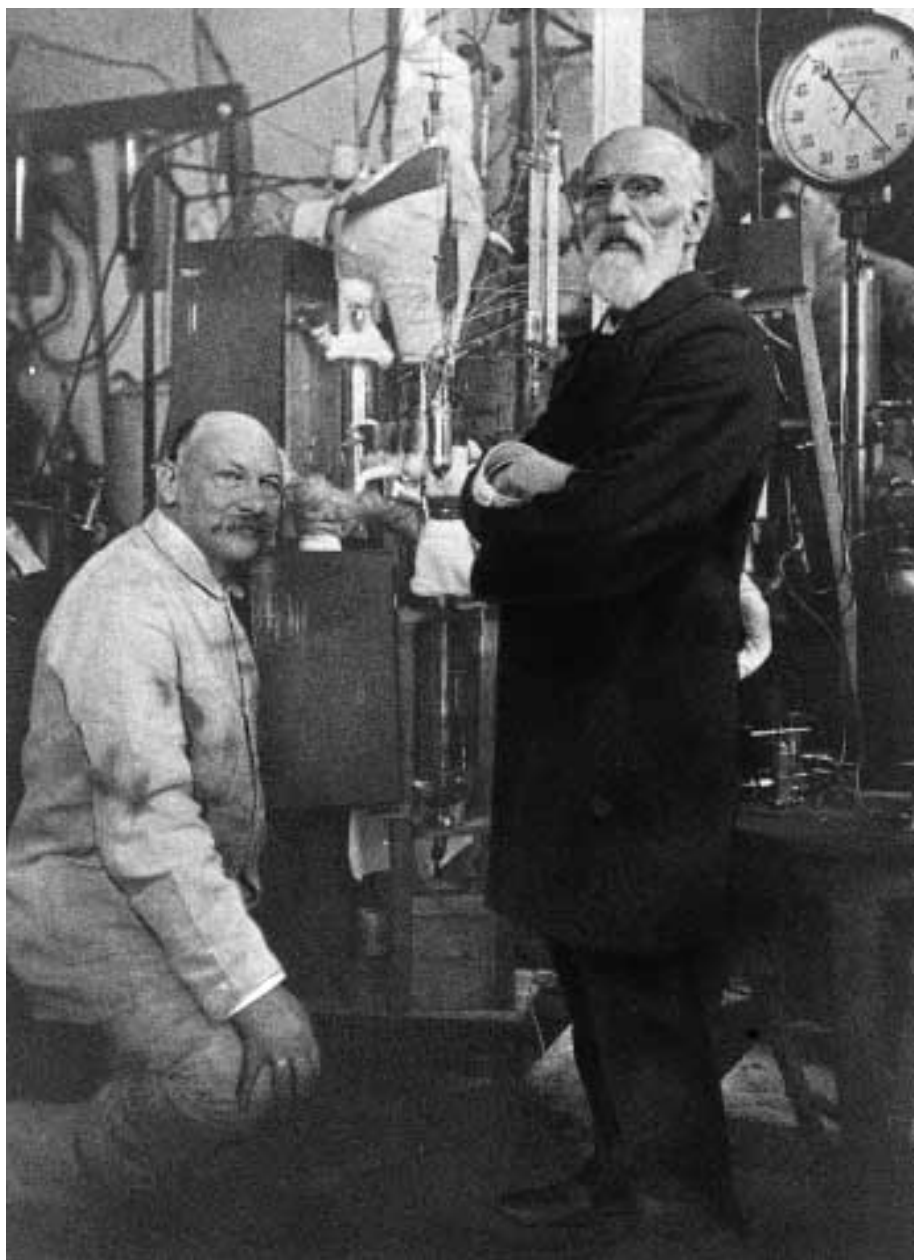


Figure 3.1 Kamerlingh Onnes (l) and Van der Waals posing by the helium liquefaction apparatus. Copied with permission of the Boerhaave Museum, Leiden.

3.4 *Kamerlingh Onnes and the principle of mechanical similarity*

3.4.1 *Biographical notes.* Heike Kamerlingh Onnes (1853-1926), was the son of a well-to-do industrialist from whom he inherited his mechanical propensity. He completed his undergraduate studies in physics and mathematics in his hometown, at the University of Groningen. Before he started his graduate work in that city in 1873, he spent three semesters with Bunsen and Kirchhoff in Heidelberg, Germany. By that time he had already won several competitive prizes. In 1879, he obtained his doctorate in physics *magna cum laude* with Prof. R.A. Mees in Groningen. In 1878, he was appointed an assistant to Johannes Bosscha, Professor of Physics at the Delft Polytechnic School. Kamerlingh Onnes was appointed to a professorship at the University of Leiden in 1882.

His 42-year tenure at the University would be filled with remarkable discoveries. He established a world-class laboratory, uniquely equipped for cryogenic work related to the liquefaction of gases. Details on his work in the period of 1880 to 1908 will be encountered in many of the chapters to follow. His crowning achievement was the liquefaction of helium in 1908, which opened the new field of low-temperature physics.

Kamerlingh Onnes was elected to the Royal Netherlands Academy of Arts and Sciences as early as 1883, before his 30th birthday. He was elected to the Dutch Society of Sciences in 1886. He received the Nobel prize in physics in 1913.

3.4.2 *Mechanical similarity.* Even before Van der Waals's (1880) presentation on corresponding states appeared in print, Kamerlingh Onnes had grasped the idea, and sought a molecular justification (see Kipnis et al. 1996, p. 105). While still an assistant to Bosscha, he wrote a paper on the foundation of the principle of corresponding states. In December 1880, Van der Waals presented Kamerlingh Onnes's (1881) paper to the Academy. This was the beginning of one of the most fruitful and long-lasting relationships ever between two scientists.

Kamerlingh Onnes's (1881) purpose is to demonstrate that the principle of corresponding states can be derived on the basis of what he calls the principle of similarity of motion, which he ascribes to Newton. He assumes, with Van der Waals, that the molecules are elastic bodies of constant size, which are subjected to attractive forces only when in the boundary layer near a wall, since the attractive forces in the interior of the volume are assumed to balance each other (Ch. 2.4). He realizes that this can be valid only if there is a large number of molecules within the range of attraction (see the second part of the 1881 paper), an issue that would come up time and again, as mentioned in

Ch.2.4. Kamerlingh Onnes ascribes the following characteristic parameters to the molecules of a fluid: the molar mass M , the molecular volume m , and the 'absolute molecular attraction' A . He considered a state in which N molecules occupy a volume v , and all have the same speed u (no Maxwellian distribution!). The problem is to express the external pressure p , required to keep the system of moving particles in balance, as a function of the five parameters. He solves this problem by deriving a set of scaling relations for M , A , v , u and p , which pertain if the units of length, mass, and time are changed. Two fluids are in corresponding states if, by proper scaling of length, time and mass for each fluid, they can be brought into the same 'state of motion.' It is not clearly stated what he means by this, but he must have had in mind an exact mapping of the molecular motion in one system onto that of another system if the systems are in corresponding states. A much later interpretation of Kamerlingh Onnes's intention, in a book by his former student Kuenen (1907, pp. 144-147) supports this. In modern terms: suppose a movie is made of the molecular motions in one fluid. Then, after setting the initial positions and speed of the molecules, choosing the temperature and volume of a second fluid appropriately, and adjusting the film speed, a movie of the molecular motion in a second fluid can be made to be an exact replica of that in the first fluid.

Certainly this argument, which uses none of the insights of statistical mechanics, imposes far more stringent conditions on molecular motion than are necessary for the validity of a law of corresponding states. Moreover, although Kamerlingh Onnes claims that this derivation follows from mechanics with no input from the Van der Waals equation, this does not appear to be quite true. First of all, the assumption of a molecular volume ascribed to molecules considered as elastic hard spheres is one also made in the derivation of the Van der Waals equation. Kamerlingh Onnes's argument, however, does allow for density dependence of the excluded volume. The trickiest part, however, is the scaling of the 'absolute molecular attraction' A . From the way Kamerlingh Onnes does this, it is clear that he assumes that A/V^2 has the dimension of a pressure. Thus, implicitly, he adopts the attractive term used by Van der Waals.

None of this criticism diminishes the merit of Kamerlingh Onnes's attempt at founding the law of corresponding states on attributes of the molecular interaction and on molecular mass and motion, instead of on a particular form of an equation of state. In the last part of his paper, moreover, Kamerlingh Onnes makes an extremely useful extension of the principle of mechanical similarity to include viscosity. Kamerlingh Onnes's quest would be resumed in the middle of the 20th century, after a deeper understanding of intermolecular forces was obtained.

3.5 Empirical scale factors

Originally, the principle of corresponding states was tested by making fluid properties dimensionless through the use of either the critical parameters, or the molar gas constant R and the parameters a and b . The first method requires commitment to an unavoidably inaccurate equation of state based on two molecular parameters. Either method suffers from a loss of accuracy due to the fact that the reduction parameters are generally far less well known than the fluid properties to be compared. Kamerlingh Onnes circumvents this problem by making graphs of measured fluid properties coincide through the use of two empirical scale factors, a method to be extensively used by him in subsequent years for pure fluids as well as for fluid mixtures. A set of P - V isotherms is plotted on a double logarithmic scale for each of two fluids. By superimposing and shifting the plots so as to make them interlace, empirical scale factors are obtained for pressure and volume. Around 1900, Kamerlingh Onnes and his collaborators used different variants of this method, generalizing it to fluid mixtures, see Chapter II. As narrated by Kipnis *et al.* (1996, p. 236), in 1896 the French high-pressure expert Émile Amagat, whom we will encounter in several chapters of this book, devised an ingenious optical projection method for superimposing grids of P - V isotherms for pairs of fluids. Amagat noted that the principle did not apply universally, but was valid in classes of related substances.

An interesting application, again by Kamerlingh Onnes, was the wedding of the principle of corresponding states to polynomial representations of P - V isotherms. In the 1880s the deficiencies of the Van der Waals equation were quite well known. Kamerlingh Onnes was beginning to produce accurate P - V data for several fluids in his laboratory, and he did not like the idea of representing those good data by an inadequate equation of state. Instead, he experimented with describing the data along isotherms by series expansion of the PV product in terms of the density. He called the coefficients in the expansion *virial coefficients*. The word virial (from the Latin *vis*, genitive *viris*, which means force) is taken from Clausius's exact virial theorem, which relates the average kinetic energy of a system of moving molecules to the average of the inner product of intermolecular force and intermolecular distance.

The *virial expansion*, as it is presently used, is given by

$$PV = RT [1 + B(T)/V + C(T)/V^2 + \dots] \quad (3.3)$$

with the virial coefficients B , C ...still functions of temperature. Kamerlingh Onnes (1901b) used an expression akin to Eq. (3.3). He expanded the product PV , retaining only as many terms as he needed for practical purposes,

and omitting some of the intermediate powers. Thus, in the 1901 paper, he used the powers 1, 2, 4, 6 and 8. Allowing five adjustable parameters per isotherm, instead of two molecular parameters for the entire data set, obviously must lead to a much more accurate representation of the data. This accuracy, however, comes at a high price: the loss of an underlying molecular model and its predictive power, and the need for additional numerical interpolation between the representations of the individual experimental isotherms.

Kamerlingh Onnes (1901b) dealt with these difficulties in the following way. He used the accurate P - V - T data published by Amagat for the gases carbon dioxide, nitrogen, oxygen and hydrogen in a range up to a maximum of 3000 atmospheres. The data were brought into reduced form by using the known critical pressure and temperature for each of the fluids. Kamerlingh Onnes represented each of the reduced virial coefficients as a function of reduced temperature, using four adjustable parameters for each of the five virials. The result is a 20-term function of reduced and temperature that represents the entire experimental data set for the four fluids and can be used for interpolation. For these reference fluids, the representation was shown to be accurate to a few tenths of a percent at low pressures, increasing to several percent at the highest pressures. There was a problem with representing states of carbon dioxide close to saturation. The systematic deviations are chiefly due to departures from the law of corresponding states, and partly to uncertainties of the critical parameters.

As reliable data for more diverse fluids became available, however, it became evident that the validity of the law of corresponding states was limited to fluids that were similar in molecular structure. A big divide, for instance, occurred between polar and non-polar fluids. Simple non-polar fluids, such as the noble gases and air constituents, followed the principle of corresponding states to the extent that departures did not greatly exceed the then-available experimental accuracy. Polar fluids such as water and the alcohols displayed what was known, in Van der Waals's time, as *association*. They have an anomalously dense vapor phase, which was ascribed to formation of double molecules. Such substances showed large departures from the law of corresponding states, if compared with non-polar fluids. The critical ratio $P_c V_c / RT_c$, for instance, is more than 20% lower for water than it is for argon. Van der Waals and his contemporaries labeled those fluids 'anomalous,' and accepted that the Van der Waals equation would not apply to such fluids.

3.6 *The principle of corresponding states as the foundation for a molecular theory of phase separation of fluid mixtures*

In the later part of his first Academy presentation on the law of corresponding states, Van der Waals (1880a) not only speculates about phase separation of fluid mixtures but also presents some experimental results of compression of carbon dioxide mixed with air (see Ch. 4.2). Although his theory of mixtures would still be a decade in the making, he makes some profound statements in 1880. Thus, he rejects the picture underlying Dalton's law that the components of a mixture behave as if the other components are not there. On the contrary, says Van der Waals, in the homogeneous phase the mixture behaves as if it is one fluid. He mentions the possibility of describing a mixture of constant composition by means of two constants a and b which are dependent on the composition. This correspondence between a mixture of constant composition and a pure fluid is the key idea that will lead him to his 1890 theory of mixtures. Ch. 4 describes Van der Waals's theory of mixtures and the role the law of corresponding states played in its formulation.

3.7 *The principle of corresponding states in the 20th century*

3.7.1 *Two-parameter corresponding states.* The principle of corresponding states, though of limited validity, has been of lasting importance throughout the 120 years since it was first invented. It makes it possible to estimate the thermodynamic properties and the viscosity of a fluid over the entire range of density and temperature on the basis of a few data points (plus the ideal-gas heat capacity, usually very well known from spectroscopy). Knowledge of the properties of a well characterized reference substance is a prerequisite.

Fundamentally, the principle is based on the assumption that, in addition to the universal gas constant, only two properly chosen parameters are needed to make fluid properties dimensionless. Obvious choices for these two parameters were two of the critical parameters, or two molecular constants a and b , an energy and a size parameter not necessarily tied to a particular equation of state. The Dutch School was well aware that the choice of parameters is arbitrary, and consequently introduced the idea of experimental scale factors around 1900. All these two-parameter applications are essentially equivalent, and conversions from empirical to critical or to molecular scale factors are straightforward. Which choice to make is a matter of expediency, depending on which scale factors are the best characterized, and on the particular application at hand.

An important new application of the principle of corresponding states originated from a deepening understanding of intermolecular forces, which

began in the 1920s. First proposed by Jones (1924) (who later changed his name to Lennard-Jones), the intermolecular potential $\varphi(r)$, with r the distance between the centers of two molecules, is assumed to be spherically symmetric. It is composed of a steep repulsion at short distance, and an attraction over a somewhat larger range. The empirical repulsive term varies as the inverse of a high power of the distance r between the centers of a pair of molecules, a repulsion somewhat softer than that between hard spheres. Values between 9 and 15 have been experimented with, but the value 12 is used most often for the sake of mathematical simplicity. The attraction varies as the inverse sixth power of r , as follows from theoretical considerations:

$$\varphi(r) = \varepsilon [(r/\sigma)^{12} - (r/\sigma)^6]. \quad (3.4)$$

This equation contains two parameters characteristic of individual substances, namely the distance σ at which the interaction potential changes sign, and the energy ε which represents the depth of the potential well.

As pointed out by De Boer and Michels (1938), Pitzer (1939), and Guggenheim (1945), such a description of molecular interaction in terms of a universal semi-empirical two-parameter intermolecular potential leads, under certain restrictions, to a principle of corresponding states in terms of the molecular force field. One such restriction is the additivity assumption: interactions between more than two molecules can be written as the sum of pair potentials. Another is that the interactions can be described in terms of classical mechanics, an assumption that is violated for light molecules and at low temperatures.

In the middle of the 20th century, thermodynamic and viscosity data were used extensively to determine two-parameter molecular force fields, very much in the spirit of Van der Waals and Kamerlingh Onnes. Alternatively, the Lennard-Jones potential was used to predict these properties. An example is the paper by Rowlinson and Townley (1952) representing to within a few percent the second virial, viscosity and diffusion coefficients of six pure gases and thirteen of their binary mixtures on the basis of the Lennard-Jones 6-12 potential.

This method was used until, predictably, it was found that intermolecular potentials require more than two parameters to be accurately described. Towards the end of the 20th century, for small molecules, intermolecular potentials are beginning to be developed from quantum mechanics. These *ab initio* potentials are not universal, and the principle of corresponding states played no role in their development.

3.7.2 Empirical scale factors. This book's author used the method of two empirical scale factors, introduced by Kamerlingh Onnes, when testing the

(limited) validity of the law of corresponding states for argon and xenon. See Levelt (1960). Beenakker and Van Eynsbergen (1968) modified the method by plotting iso- Z lines in the $\log P$, $\log T$ plane, where Z is the dimensionless quantity PV/RT . The graphs for two different substances can be brought into coincidence by linear shifts of the plots. They found that this could be done to within about 1% for the fluids argon, xenon, nitrogen and methane and suggested that the method could be used for viscosity as well.

In the spirit of Kamerlingh Onnes (1881), Kestin and collaborators (1972, 1977) showed that two-parameter scaling can be simultaneously applied to the second virial coefficient as well as to the viscosity and diffusion coefficients of dilute gases, in which interactions between more than two particles can be neglected. The gases they studied include the noble gases, non-polar diatomic gases and many of their mixtures. In the dilute gas, use of the two-scale-factor principle of corresponding states results in an accuracy approaching that of the best data (0.1%). It was found, however, that the scale factors calculated from critical parameters differ from those found for the dilute gas phase, indicating departures from the principle of corresponding states on the level of 1% in the Z -factor, consistent with conclusions by Levelt (1960) and by Beenakker and Van Eynsbergen (1968).

3.7.3 Generalized corresponding states – acentric factor. A fruitful idea with useful and sometimes profound ramifications has been the generalization of the law of corresponding states to more than two parameters. The basic idea is the following: if additional features are present in the molecular interactions, such as departures from sphericity, or a dipole moment, then systematic departures must be expected from corresponding states as defined by the noble gases. In certain cases, these departures can be represented in terms of a third parameter. One example has been the so-called *acentric factor* ω , introduced originally as an empirical parameter by Pitzer *et al.* (1955) to describe the departures from ‘noble-gas’ corresponding states that arise when the principle is applied to larger globular molecules. The Lennard-Jones potential is not centered on the molecular center, but is shifted outwards. Interactions between polar molecules involve more complicated non-central potentials.

The acentric factor of a fluid of multi-atomic molecules is seldom known *a priori*; in practice, it is estimated from easily accessible properties, such as the slope of the vapor pressure curve at a given distance from the critical point. Its value is now known for multitudes of industrial fluids, and correlations based upon this parameter abound in the chemical processing industry and in commercial data bases. *De facto*, it functions as a third parameter in cubic equations applied to fluids composed of multi-atomic, non-spherical or even polar molecules.

3.7.4 *Quantum-mechanical corresponding states.* At the other end of the spectrum from empirical to fundamental is the idea that *quantum effects* must cause departures from corresponding states. Kamerlingh Onnes and Keesom had detected appreciable departures from corresponding states in the gas phase for helium and hydrogen. In footnote 517 of their encyclopedia chapter on the equation of state, Kamerlingh Onnes and Keesom (1912) suggest that the Planck hypothesis, the quantization of phase space in volumes of size h , should have implications for the equation of state. Byk (1921) introduced the dimensionless Planck constant, $\Lambda = h / [(kT_c)^{1/2} M^{1/2} (V_c/N)^{1/3}]$, as a third parameter in the dimensionless free energy. Departures from corresponding states must be expected if the reduced Planck constant is not negligibly small. Molecules of low molar mass M and low critical temperature, such as the helium isotopes, hydrogen, deuterium and even neon, do have sizable Planck constants.

Jan de Boer and Antonius (Teun) Michels (1938), at the physics department of the University of Amsterdam, proposed making the Planck constant dimensionless by means of the molecular parameters ε , σ and the molecular mass m . The dimensionless quantum parameter Λ^* , known in the English literature as the De Boer parameter, is defined as $\Lambda^* = h / \sigma (m\varepsilon)^{1/2}$. The De Boer parameter is small for most gases, but it is greater than unity for helium-3, helium-4, hydrogen, deuterium and tritium, leading to considerable departures from corresponding states. De Boer (1948a), and De Boer and Lunbeck (1948c) ordered many reduced properties of the light gases as functions of Λ^* . In the tradition of Kamerlingh Onnes, De Boer and Lunbeck (1948b) predicted the critical parameters and the vapor pressure of helium-3 before these properties were measured. In the absence of quantum effects, the helium isotopes should have the same critical properties; in reality, the critical temperature of helium-4 equals 5.19 K, whereas that of helium-3 equals 3.32 K. Lunbeck (1951) also estimated the triple point and critical point values of the hydrogen isotopes HD, HT, DT, and T₂.

3.7.5 *Chain molecules.* A measure of the validity of the principle of corresponding states is the value of the critical compressibility factor $Z_c = P_c V_c / RT_c$. For the heavy noble gases, this factor is close to 0.29. For the helium isotopes, it is slightly over 0.30. For a series of normal alkanes, Z_c decreases from 0.288 (methane) to 0.262 (pentane). The chain length is an obvious candidate for a generalized principle of corresponding states. Engineering applications abound – see, for instance, Beret and Prausnitz (1975).

3.8 *Outlook*

The principle of corresponding states and its generalizations have provided a practical foundation for thermodynamic and transport property predictions in the chemical process industry throughout the 20th century. Over large ranges in temperature and density, it is accurate to about 1%, but only within a group of related substances, such as the heavy noble gases, or lower-weight diatomic molecules such as air constituents.

The principle plays a role in several of the following chapters. Foremost, in the next chapter, is Van der Waals's generalization of the principle in order to obtain a theory of fluid mixtures. The Leiden physicists preferred the principle to the use of the Van der Waals equation. Thus Verschaffelt neatly invoked corresponding states to estimate the effects of impurities on critical behavior, see Ch. 10.16.2 and 11.4.6.

4. The theory of mixtures – Van der Waals

4.1 *Early attempts at understanding mixture phase behavior*

Van der Waals's achievement, the formulation of the theory of mixtures, must be appreciated within the context of the state of knowledge in the 1880s. For gaseous phases, it was fairly obvious how to generalize Boyle's law to mixtures. As early as 1793, John Dalton (1766-1844) had postulated that the pressure in a volume V simply equals the sum of the *partial pressures*: the ideal-gas pressures P_i exerted by each of the components i in the absence of the others.

$$P = \sum P_i = \sum n_i RT/V \quad (4.1)$$

with n_i the moles of component i . This principle was generally accepted.

In the 19th century the interest in liquid phases was driven by the design of distillation processes for separation of fluid mixtures. If a liquid mixture of given mole fraction is brought to the boiling point, the more volatile components will be enriched in the vapor phase, and the less volatile ones will remain mostly in the liquid phase. The question was thus what 'partial pressure,' in the sense of Dalton's law, to ascribe to a component in the vapor phase when the mole fraction of the component in the liquid is given. Francois Marie Raoult (1830-1901) proposed the law that carries his name. If a non-volatile, non-ionic solute is added to a solvent, so that its mole fraction in the liquid is x , then the vapor pressure of the solvent is lowered by

$$(P_0 - P) / P_0 = x \quad (4.2)$$

with P_0 the vapor pressure and x the mole fraction of the solvent at the given temperature.

Thus, the vapor pressure of the solvent is lowered by a fractional amount equal to the mole fraction of the solute. This is one example of a *colligative property*, a dilute-mixture property that is independent of the nature of the solute. Raoult formulated this law in 1886 on the basis of careful experiments

by himself and by others, performed since the middle of the 19th century. Van 't Hoff, independently, gave a thermodynamic proof in the same year. Ch. 11.2 will give more detail about Van 't Hoff's contributions to the topic of colligative properties.

If Raoult's law is grossly extrapolated to solute mole fractions from 0 to 1, it can be applied to mixtures of two liquids – if the two partial vapor pressures are then added according to Dalton's law, a total vapor pressure results that interpolates linearly in liquid mole fraction from the vapor pressure of the first component to that of the second.

Towards the end of the 19th century, however, there was a sufficient amount of experimental information available to know that Raoult's law, although always valid at low mole fraction of any (nonionic) solute, was seldom valid at all mole fractions, or for all solutes. Departures from linearity of the partial and total vapor pressures were encountered often. Thus, for a fixed temperature, the system water-alcohol, with which humanity has had ample experience, was known to have a maximum in the vapor pressure at around 96% alcohol by volume. At this point, vapor and liquid have the same mole fraction, so that 96% alcohol can be purified no further by distillation alone. Such points are called *azeotropic* – this word is an early 20th century concoction from the Greek, and means 'not changing when boiling.'

The generalization of Raoult's law to all mole fractions must also fail when one component is above its critical point. In that case, that particular component, when pure, does not exist in two phases, and therefore *has* no vapor pressure.

Although not universally valid, Dalton's ideal-gas law for vapor mixtures, combined with Raoult's law for vapor pressures of liquid mixtures, formed a framework for many experimenters trying to understand how mixtures separate into two phases. Not knowing how to reconcile the separate treatment of vapors and liquids with the idea of continuity of states, however, left them baffled and confused when trying to explain experimental results.

4.2 Andrews, Cailletet, and Van der Waals – the liquefaction of gaseous mixtures

Andrews (1875) performed some early experiments with a mixture of carbon dioxide and 11% of air by volume. He noted that the presence of air brought down the critical temperature considerably. Five years later, both Van der Waals and Cailletet reported similar experiments in this and other mixtures.

In the first of his two Academy presentations on corresponding states, Van der Waals (1880a) was beginning to think about phase separation of mixtures (§21 – §25). Contrary to Dalton's view that each of the components acts in

the available space as if the other were not there, he strongly argued to consider the mixture as one substance. Thus, the P - V isotherms of air in the homogeneous region look just like those of a one-component fluid, 'so that one could almost forget that air is a mixture.' The values of a and b for the mixture must depend on the mole fraction. This insight is the seed from which Van der Waals's theory of mixtures will grow.

Van der Waals then expressed the opinion that for each value of the mole fraction, the critical conditions should depend on a and b in the same way as is the case for a one-component fluid. This is one place where his intuition did not serve him well, and a decade passed before he published the correct way to find the critical point of a mixture. Another statement towards the end of this paper 'all substances can mix if the pressure is high enough' suffered the same fate. In gas-gas equilibrium, for instance, the topic of Ch. 8, two dense gas phases refuse to mix, no matter how high the pressure.

Van der Waals (1880a) wrestled for several pages with the problem of phase separation of a mixture, recognizing that this process is quite different in a mixture than in a one-component fluid because the more volatile component will be enriched in the vapor phase. He based his comments on experiments he had performed in his own laboratory on mixtures of carbon dioxide with air. At room temperature in moderate climates, carbon dioxide is below its critical point of 31°C, and is readily liquefied when compressed, but the second component, air, is far above its critical point. For a mixture of nine parts carbon dioxide and one part air, Van der Waals found that the critical point is lowered by about 6°C below that of pure carbon dioxide, which is consistent with the drop in critical temperature noted earlier by Andrews. The mixture began to condense at a pressure close to the vapor pressure of pure CO₂, but it took a pressure of 95 atmospheres to fully liquefy the mixture at constant temperature. The lower the temperature, the higher was the required pressure. This is in contrast with the vapor-liquid state of a one-component fluid, for which the vapor pressure remains constant as long as two phases are present. Also, the vapor phase always disappears at a lower pressure, the lower the temperature. It is obvious that the condensation of the mixture takes place in a way quite different from that of a pure fluid.

Louis Paul Cailletet (1832-1913) pioneered the heavy-walled glass tubes that are named after him. They were filled with a gas, inverted, and dipped in liquid mercury. Applying external pressure to the mercury led to compression of the gas. The occurrence of a second phase could be directly observed. Cailletet had already made a name for himself in 1877 by liquefying the 'permanent gases' oxygen and nitrogen in such tubes. After cooling the tube and rapidly expanding the gas he saw the formation of a mist of droplets.

Cailletet (1880a,b) independently reported experiments on the condensation of mixtures of carbon dioxide and air. The more air was added, the more pressure was needed to liquefy the mixtures. For instance, Cailletet found that at ambient temperature a mixture of equal volumes of carbon dioxide and air resisted condensation at pressures of up to 400 atmospheres. A mixture of five parts carbon dioxide and one part air, on the other hand, produced a liquid phase under modest compression at temperatures below 20°C. On further compression of the two-phase system, however, Cailletet noted to his surprise that at pressures between 150 and 200 atmospheres the meniscus separating the two phases became hazy and disappeared. It did not reappear on further compression.

If Cailletet's homogenized high-pressure phase was now slowly expanded, a thick mist appeared in the tube and a meniscus was formed. Cailletet repeated these experiments at temperatures between 5 and 19°C, with essentially the same results. Only the value of the pressure at which the meniscus reappeared varied, from 132 atmospheres at 5.5°C to 110 atmospheres at 19°C.

One might argue, said Cailletet, that the meniscus had not really disappeared, but that it had become invisible because the refractive index of the compressed air had become equal to that of the condensed carbon dioxide. In that case, however, the meniscus should become visible again at higher pressures, beyond the point where the refractive indices of the two phases cross over, but definitely this did not occur.

Cailletet was of the opinion that the liquid and the gas 'had dissolved into one another' forming a homogeneous phase. This terminology is the same as used by other scientists of that time for describing a critical-point phase transition. According to the phase rule of Gibbs (Ch. 4.3), however, a binary mixture of given mole fraction has one critical point, not a series of critical points at different temperatures, so Cailletet's suggestion cannot be correct.

Van der Waals's (1880a) speculations have a lack of clarity similar to those of Cailletet. He described the isothermal condensation of his 9:1 CO₂ – air mixture as beginning with a liquid phase that is almost pure CO₂ and a vapor phase that contains a large fraction of air. As the volume is decreased 'the liquid accepts more air, while the vapor accepts more CO₂. The pressure increases, and finally the mole fractions of the two parts becomes equal again and the space is filled homogeneously.' (See §23). This wording appears to describe a critical-point phase transition, which cannot be the case except by unlikely accident. Van der Waals also struggled to find an equivalent of the Maxwell rule: 'The theoretical isotherm will in this case not be intersected by a straight line parallel to the volume axis, but by a curve.' However, he is clearly not yet able to find the form of this curve.

In addition, Cailletet and Van der Waals unknowingly experienced experimental problems. Neither scientist appreciated how long it would take for a fluid mixture to fully equilibrate in a tall tube of the kind they used. Only around 1890, the first reliable experiments in compressible fluid mixtures would become available in Kamerlingh Onnes's laboratory.

Furthermore, there were conceptual problems. Although Van der Waals's equation of state had given a molecular basis for understanding Andrews's experiments on pure carbon dioxide, it was not adequate to explain the condensation of fluid mixtures. Gibbs's theory, even if known to Cailletet, would not have helped him understand his experiments in condensing fluid mixtures. Although Gibbs's work was known to Van der Waals, it took him another ten years to fashion a practical understanding of the condensation of a mixture from Gibbs's principles.

Finally, the experimenters could not have known that their choice of a mixture of carbon dioxide and air was unfortunate: it displays a type of phase behavior that would not be properly understood until 1905 (Ch. 7, 8).

4.3 *Gibbs and the equilibrium of heterogeneous systems*

Shortly after Van der Waals (1873) defended his doctoral thesis, Gibbs (1876, 1878) produced his papers on the equilibrium of heterogeneous substances, including mixtures with both fluid and solid phases. He wrote these papers in splendid isolation at Yale College, at a time when the young United States had little or no interest in matters of lofty scientific theory. The more amazing and awesome is the perfection of Gibbs's work. It has required no corrections since it was published, and remains to this day the foundation for the study of phase separation. The underlying principles are few, and rigorous.

Gibbs's work is based on the concept of thermodynamic stability. In order to be stable against separation into two phases, the thermodynamic potentials of a homogeneous phase have to be convex functions of their natural variables. This implies conditions on the curvature of the surface, which Gibbs works out for the various thermodynamic potentials.

For a one-component fluid, Gibbs's own preference is for the $U(S, V)$ surface, with U the energy, V the volume, and S the entropy, and with the differential relation $dU = T dS - P dV$. The partial derivative of the $U(S, V)$ surface with respect to S equals the temperature T and that with respect to volume equals the negative of the pressure P . If a tangent plane is constructed at any point on an $U(S, V)$ surface, its intercept with the U -axis, $U - TS + PV$, defines the Gibbs energy G .

Stability at the tangent point requires that the surface must lie above the tangent plane everywhere. There are two ways this condition can be violated.

First, the surface may lie below the tangent plane everywhere around the tangent point, or only in certain directions. Then the tangent point is unstable. Second, the surface, while still *locally* stable around the tangent point, falls below the tangent plane somewhere else. The system is now *globally* unstable, and will split into two different phases. At a critical point a limit of local stability is reached.

Below the critical point, an analytic mathematical surface develops a fold, called a *plait* (akin to ‘pleat’, not to ‘braid’) by the Dutch School. On an analytic surface, this plait is entirely smooth, never sharply creased. The $U(S, V)$ surface has the interesting property that a tangent plane rolling along the surface touches in two points on opposite sides of the plait – these points the Dutch scientists call *connodes*. Connodes have the same pressure, temperature and Gibbs potential, because they share a common tangent plane. The line connecting these points is called a *tie line*, and the system can lower its energy U by following the tie line instead of the surface. The system splits into two coexisting phases of different density, a vapor and a liquid, represented by the two points where the plane touches.

We recall that the essential concept of equality of the molar Gibbs potential (which equals the chemical potential in a one-component system) in coexisting phases had been missing from Van der Waals’s 1873 thesis. In 1877, after Gibbs’s work had appeared in print, Maxwell introduced implicitly the equality of the chemical potential in the coexisting phases of a one-component fluid by his equal-area rule. This yielded a prescription for cutting off the unphysical Van der Waals isothermal P - V loop, as discussed in Ch. 2.4 (see Figs. 2.2 and 2.3).

The plait of an analytic mathematical surface is bounded by the locus of the connodes, which the Dutch scientist call the *connodal*, or *binodal*, but which is presently called the coexistence curve. A plait ends at a point where the tie line shrinks to zero. Such a point was coined a *plait point* by Korteweg (1891a), but was usually referred to as a critical point shortly after.

Plaits are properties of analytic mathematical surfaces. Since part of the surface inside the plait is thermodynamically unstable, a plait, strictly speaking, cannot exist in a real fluid, nor could it be the result of an exact theory. Therefore, the $U(S, V)$ surface of a real fluid will not have a plait, but below the critical temperature, it will follow the ruled surface formed by the tie lines connecting the coexisting phases, as traced out by the rolling tangent plane.

In fluid mixtures, the chemical potential μ_i of component i is defined as the derivative of the Gibbs energy of an open system with respect to the amount n_i of component i , while pressure, temperature, and amounts of the other components are kept constant. If the system consists of several phases,

these can be in equilibrium with each other only if, in addition to pressure and temperature, the chemical potentials μ_i of each of the components are equal in the two phases. Properties equal in coexistent phases are sometimes called *field variables*, following Griffiths and Wheeler (1970). A homogeneous phase exists over a range of field variables.

Gibbs introduced the concept of *degrees of freedom* f , with f the number of independent variables that can be varied within certain limits without the homogeneous phase becoming unstable.

Gibbs is the originator of the seemingly simple, but very powerful phase rule:

$$f = c - p + 2 \quad (4.3)$$

The rule follows straightforwardly from counting the number of components c , the number of phases p , the total number of independent variables, and the number of relations between them (equalities of chemical potentials, pressure and temperature in coexistent phases). This simple law makes it possible to grasp and classify the bewildering variety of phase behaviors occurring in mixtures. The following examples illustrate the power of the phase rule, and serve to introduce a number of concepts and terms encountered in the rest of the book.

For a one-component fluid, $c = 1$, a homogeneous phase, $p = 1$, has two degrees of freedom, $f = 2$, for instance pressure and temperature. In two phases, the fluid has only one degree of freedom: the system is monovariant, so that the choice of the vapor temperature fixes the vapor pressure. In three phases, there are no degrees of freedom left, so that the liquid-vapor-solid triple point is an invariant point. A special point is a critical point. Here, the bivariant homogeneous phase has to obey two criticality conditions (see Ch. 2.4), and thus two degrees of freedom are lost, resulting in the invariant critical point. Alternatively, on the monovariant coexistence curve, the densities of vapor and liquid must be equal to each other, yielding the invariant critical phase.

For a binary mixture, with $c = 2$, a homogeneous phase has three degrees of freedom, a two-phase system has two, and a three-phase system has one. In the bivariant two-phase system it may happen that the two coexisting phases have the same mole fractions. As mentioned in Ch. 4.1, this phenomenon goes by the name of *azeotropy*. This additional condition makes the azeotropic state of the two-phase binary mixture monovariant. Another new feature is the possibility that two different liquid phases coexist. These phases, in turn, can become identical along a *liquid-liquid* critical line. Liquid-vapor or liquid-liquid criticality imposes two constraints, the two criticality conditions, on the homogeneous phase; thus, one degree of freedom is left, and a monovariant critical line results. In a binary mixture, liquid-liquid-vapor, liquid-vapor-solid

and liquid-liquid-solid equilibria are monovariant. In field space, such three-phase equilibria take place along triple lines, usually called *three-phase curves*. For a binary mixture, it is possible for four fluid phases to coexist, resulting in an invariant quadruple point in field space.

In a ternary mixture, all the above dimensionalities are stepped up by one unit, so the homogeneous phase has four, two-phase regions have three, three-phase regions have two, and critical surfaces of various kinds, such as vapor-liquid(1), liquid(1)–liquid(2), have two degrees of freedom. Five-phase coexistence is possible at a non-variant quintuple point. In a ternary mixture, it is possible for three phases to become critical with respect to each other simultaneously if a vapor-liquid and a liquid-liquid critical point happen to coincide. Such a point is called a *tricritical point*. Since each critical point counts as a loss of two degrees of freedom starting from a homogeneous phase, a tricritical point in a ternary system is invariant.

A rich variety of possible phase behaviors in mixtures can be expected on the basis of the phase rule. Gibbs's edifice is fundamental, but abstract. In its grandeur and austerity, it is somewhat forbidding. Its validity is all-encompassing, but the path to specific applications is not transparent. Gibbs's work, however, was little known or appreciated in Europe (and even less in America) in the 19th century. The prevalent mode in Europe was that of experimentation, particularly in France, but also in England and Russia.

4.4 *The equation of Van der Waals for fluid mixtures*

4.4.1 *Historical setting.* Maxwell and Van der Waals were among the few who studied Gibbs's (1873–1878) papers immediately after they appeared. Nevertheless, after the formulation of the law of corresponding states in 1880 a decade passed before Van der Waals (1890) published another major piece of work, his theory of mixtures. The reason for the long delay was that Van der Waals's young wife, the mother of his four children, succumbed to tuberculosis in 1881. For Van der Waals, life had lost all taste, and it took him many years to overcome his deep depression. In the mid-1880s, however, Van der Waals began what would become a long relationship with his later Amsterdam colleague, the chemist Hendrik Willem Bakhuis Roozeboom (1854–1907), then still a graduate student in Leiden. Van der Waals was able to explain Bakhuis Roozeboom's observations of phase behavior and solid precipitation of gas hydrates on the basis of Gibbs's phase rule. See Kipnis et al. (1996), pp. 157–159, for a detailed account. In the late 1880s, Kamerlingh Onnes's plan to study fluid mixtures in his new laboratory helped Van der Waals recover his scientific interest.

We have already mentioned the mystifying experiments on phase behavior in fluid mixtures that were in great need of an explanation. Most scientists were not aware of the substance and power of Gibbs's thermodynamics, but Van der Waals was, and he had the essential tools: an equation of state incorporating molecular size and interaction, and the law of corresponding states. During the most difficult years of his life, he solved the problem of phase separation and criticality in fluid mixtures, which, in the words of Kipnis *et al.* (1996), p. III, had escaped even Maxwell.

4.4.2 *Molecular theory of a substance composed of two different species.* On this subject, a substantial paper by Van der Waals appeared in German (1890), and in French (1891). It was also part of the second German edition of his thesis, which appeared in two parts around 1900. Rowlinson (1988) included the paper in the English translation of Van der Waals's thesis.

Suppose two components, each one characterized by its own pair of Van der Waals parameters, a_1 , b_1 , and a_2 , b_2 , respectively, are mixed in a specific molar ratio x , where x is the mole fraction of the second component. Van der Waals makes the crucial assumption that the mixture obeys the Van der Waals equation with a new set of parameters, a_x and b_x , which depend on the mole fraction:

$$(P + a_x/V^2)(V - b_x) = RT \quad (4.4)$$

where V is the volume occupied by a mole of the mixture.

Thus the mixture at given mole fraction obeys the same two-parameter Van der Waals equation of state as the two pure components. The pure components as well as any mixture of fixed mole fraction obey a law of corresponding states. This simple assumption is presently called a *one-fluid model* for a mixture because it describes the mixture as a fictitious single substance. Obvious as this generalization may seem to us presently, it was a veritable breakthrough at the time. The Van der Waals mixture model made it possible to understand the phenomena accompanying the condensation of fluid mixtures. It inspired the Leiden experimentalists. It would prove itself fully equal to the task of producing the variety and complexity of fluid-mixture phase behavior, which would only be explored fully in the fifteen years to follow (Ch. 6-8, II).

In order to progress from Eq. (4.4), it is necessary to give a prescription for the calculation of a_x and b_x from the a and b values of the two components. In modern terminology, such relations go by the name of *mixing rules*. Since these parameters should assume the respective pure-fluid values at $x = 0$ and $x = 1$, quadratic interpolation formulae seem a sensible assumption:

$$\begin{aligned} a_x &= (1-x)^2 a_1 + 2x(1-x) a_{12} + x^2 a_2 \\ b_x &= (1-x)^2 b_1 + 2x(1-x) b_{12} + x^2 b_2 \end{aligned} \quad (4.5)$$

Van der Waals and his collaborators often replaced the quadratic expression for b by a simple linear one,

$$b_x = (1-x) b_1 + x b_2 \quad (4.6)$$

which is equivalent to assuming that $b_{12} = (b_1 + b_2)/2$; this is the rule of the *arithmetic average* for the mixing parameter in the excluded volume. Lorentz (1881) derived the quadratic equations, Eq. (4.5), from the virial theorem and found that the arithmetic average of the *radii* of the unlike molecules should be used to calculate b_{12} . The radii are proportional to $b^{1/3}$, but averaging $b^{1/3}$ complicates the calculations for mixtures. As long as the component molecules do not differ much in size, it is not overly important which form of combining rule for b is used. As long as the size difference is not extreme, the complexity of the phase behavior of compressible fluid mixtures arises principally from the differences in attraction of the two components and the mixture. Thus, in general, it is desirable to have flexibility in the choice of a value of the attractive parameter a_{12} , compared to those of the pure components. Van der Waals did not commit to a specific combining rule for a_{12} in his 1890 paper. Many calculations are simplified, however, if for this mixing parameter the *geometric-mean rule* is assumed:

$$a_{12} = (a_1 a_2)^{1/2} \quad (4.7)$$

Van der Waals noted that this relation yields an important condition for phase separation in the liquid phase (see Ch. 4.8.2), but found it unnecessarily restrictive. Van Laar, however, used it throughout in his calculations of binary phase diagrams (Ch. 7.5, 11.4.7). The geometric-mean assumption *is* restrictive. For instance, mixtures with unlike a_1 and a_2 that have an interaction parameter a_{12} stronger than the average of a_1 and a_2 are excluded by the geometric-mean assumption.

Having set up his equation of state for the binary mixture, Van der Waals's next task was to deduce the conditions for criticality and phase separation. The reader should not succumb to the temptation to calculate the critical constants of the mixture from Eq. (4.4) by means of the criticality conditions of the pure fluid, Eq. (2.3). This does not work, because the mixture has a means of lowering its free energy that is not available to a pure fluid: it can separate into two phases that differ not only in density, but also in mole fraction. As the temperature is lowered, the mixture will, in general, separate into two phases of different mole fraction well before it reaches the point at which its compressibility would be infinite had it remained homogeneous.

The next section will outline how Van der Waals went about the task of finding mixture phase coexistence. It roughly follows Van der Waals's paper in the translation and notation of Rowlinson (1988). Van der Waals obtained the mathematical principles from Gibbs and from the Amsterdam mathematician Korteweg, whose work is the topic of Ch. 5.

4.5 Helmholtz energy for a binary Van der Waals mixture

Van der Waals's task was to construct an appropriate thermodynamic potential for a binary mixture and find the conditions for phase coexistence, stability and criticality.

A binary mixture has an additional variable, the mole fraction x . The molar energy surface is now a function of three variables: $U(S, V, x)$, and the visually appealing construction of a tangent plane rolling over the $U(S, V)$ surface no longer applies. Van der Waals proposed to use instead the Helmholtz energy $A(V, x, T)$. Van der Waals cleverly reduces the problem to one in two independent variables by considering the Helmholtz function at fixed temperature, phase equilibrium conditions requiring equality of temperature in the first place. The isothermal Helmholtz energy is now a function of V and x alone and can be visualized as a two-dimensional surface in three-dimensional space, analogous to the $U(S, V)$ surface for a one-component fluid.

The form of the molar Helmholtz energy in analogy with Eq. 2.5, is readily obtained by integrating the Van der Waals mixture equation of state with respect to volume and by adding the Gibbs mixing term:

$$A(V, x, T) = -RT \ln (V - b_x) - a_x/V + RT [x \ln x + (1 - x) \ln (1 - x)] \quad (4.8)$$

Since $x < 1$, the mixing term is always negative, and has its lowest value, $-RT \ln 2$, at $x = 1/2$. Since it lowers the free energy, this term favors mixing, especially at high temperatures. Eq. (4.8), together with the combining rules and mixing rules for the mole-fraction dependence of a_x and b_x , Eq. (4.5), defines the Helmholtz energy surface of a binary fluid mixture, apart from some temperature-dependent contributions that do not affect the phase equilibrium.

What remains to be done is working out a method for finding coexistent phases and critical points on such a surface.

4.6 Double-tangent plane – coexisting phases

At fixed temperature, the equilibrium conditions for two coexisting phases are that pressure, as well as the chemical potentials of each of the components, must be the same in the two phases. These three properties can readily be

derived from the isothermal Helmholtz energy, through the thermodynamic relationships

$$\begin{aligned} (\partial A / \partial V)_x &= -P \\ (\partial A / \partial x)_V &= \mu_2 - \mu_1 \\ A - V(\partial A / \partial V)_x - x(\partial A / \partial x)_V &= \mu_1 \end{aligned} \quad (4.9)$$

Consider a point on the isothermal $A(V, x)$ surface. The first two equations define a tangent plane, with pressure and chemical potential difference defining the slope of the plane. The third condition defines the intercept of the tangent plane with the A axis, which equals the chemical potential of the first component.

If two points on the isothermal A surface have the same pressure and the same chemical potential difference, their tangent planes are parallel to each other. If these two planes have the same intercepts with the A axis, the tangent planes must coincide. Thus, equality of pressure, temperature and chemical potentials is equivalent with the existence of a common tangent plane, just as in the case of the one-component $U(S, V)$ surface. Likewise, as the double-tangent plane rolls over the surface, the length of the tie line may shrink to zero, and the plait ends in a plait point.

4.7 Stability of the mixture $A(V, x)$ surface – the spinodal and the plait point

4.7.1 *Taylor expansion.* How does one know whether, and if so where, plaits including regions of instability exist on a mathematical representation of a thermodynamic surface, such as Van der Waals's $A(V, x)$ at fixed temperature? For the one-component fluid, the (mechanical) stability condition is that the second derivative of the isothermal Helmholtz energy, $(\partial^2 A / \partial V^2)_T \equiv (V K_T)^{-1}$, must be larger than zero (Ch. 2.5). For $A(V, x)$ a generalization to two variables is required. For this purpose, a Taylor expansion is performed for the isothermal Helmholtz energy:

$$\begin{aligned} A(V, x) &= A(V_0, x_0) + (\partial A / \partial V)_x (\delta V) + (\partial A / \partial x)_V (\delta x) + \\ &+ (1/2)(\partial^2 A / \partial V^2)_x (\delta V)^2 + (\partial^2 A / \partial V \partial x) (\delta V) (\delta x) + (1/2)(\partial^2 A / \partial x^2)_V (\delta x)^2 + \\ &+ (\text{terms cubic in } \delta V, \delta x) + \dots \end{aligned} \quad (4.10)$$

The derivatives are taken at the point V_0, x_0 , and $\delta V = V - V_0$, $\delta x = x - x_0$. For the isothermal Helmholtz energy to be locally stable at V_0, x_0 , it may not locally intersect the tangent plane in any direction. The tangent plane is defined by the first three terms on the right side of Eq. (4.10). Thus stability requires that there may not be any real root if the sum of the next three terms in Eq. (4.10), those quadratic in δV and δx , is set equal to zero. This is guaranteed if the discriminant of the quadratic part is negative. The

negative of the discriminant is called the Hessian H . Thus the stability condition is

$$H \equiv (\partial^2 A / \partial x^2)_V (\partial^2 A / \partial V^2)_x - (\partial^2 A / \partial V \partial x)^2 > 0 \quad (4.11)$$

If the Hessian is positive at the tangent point, the surface curves the same way in all directions, and is said to have positive curvature. The surface, however, could still be either concave or convex. The isothermal Helmholtz energy surface, as required by thermodynamic stability, must be *convex*. This requires, in addition, that

$$(\partial^2 A / \partial V^2)_x > 0 \quad (4.12)$$

$$(\partial^2 A / \partial x^2)_V > 0 \quad (4.13)$$

The first expression, Eq. (4.14), is that of isothermal mechanical stability: the isothermal compressibility at constant mole fraction,

$$K_{Tx} = -(1/V) (\partial V / \partial P)_{Tx} = (1/V) [(\partial^2 A / \partial V^2)_{Tx}]^{-1} \quad (4.14)$$

must be larger than zero, just as in the one-component fluid. The second inequality, Eq. (4.13), demands that the isothermal mixture at constant volume must be *materially* stable, that is, the Helmholtz energy must be lower than for nearby states of different mole fraction. In general, neither of these two conditions is restrictive. The mixture might still fulfill these two conditions even in the case that Eq. (4.11) is not obeyed and the curvature is negative.

At a point where the Hessian happens to assume the value zero:

$$(\partial^2 A / \partial x^2)_V (\partial^2 A / \partial V^2)_x - (\partial^2 A / \partial V \partial x)^2 = 0 \quad (4.15)$$

the curvature of the surface changes from positive to negative, so that a limit of stability is reached. The locus of points on the surface for which the Hessian is zero is called the spinodal. On the spinodal, there are two equal roots of the quadratic part of the expansion Eq. (4.10). Van der Waals (1890) limits himself to the spinodal condition, Eq. (4.15), and does not discuss the plait point at all. In the next chapter, we will see that at the plait point of the binary mixture, a second condition must be obeyed, involving all third partial derivatives of the isothermal Helmholtz energy, just as in the case of the one-component fluid, Eq. (2.6).

As Gibbs has already shown, these two mixture criticality conditions assume a more familiar and much simpler, but essentially equivalent form if written in terms of the molar Gibbs energy $G(P, T, x)$, namely:

$$\begin{aligned} (\partial^2 G / \partial x^2)_{PT} &= 0 \\ (\partial^3 G / \partial x^3)_{PT} &= 0 \end{aligned} \quad (4.16)$$

Eqs. (4.16), however, were not useful to Van der Waals, because the pressure dependence of the Gibbs energy cannot be derived in closed form from the Van der Waals equation of state. Thus, the binary-mixture criticality conditions in the following chapter will be more complex ones based on the quadratic and cubic forms in the Taylor expansion of the Helmholtz energy.

4.7.2 *An exact expression for the spinodal.* The spinodal plays a major role in the work of the Dutch school. The reason is simple. The condition for the spinodal, $H = 0$, is a local condition that could be evaluated in specific cases with the mathematical means available at that time. The spinodal signals the presence of a plait just as well as does the connodal. The connodal, however, results from a global condition, and only exceptionally can it be calculated in closed form.

The Appendix, §19 of Van der Waals's (1890) paper, contains an important result for the spinodal on the isothermal Helmholtz energy surface. The expression is a relationship between volume and mole fraction, with the temperature a parameter. It is of the fifth degree in the inverse volume, and contains the first and second mole fraction derivatives of the mixture's parameters a_x and b_x . Evaluation of the expression requires a choice of combining rules for these parameters. The expression simplifies considerably if the second mole fraction derivative of either of the interaction parameters would equal zero, for instance, if b_x is assumed to be a linear function of the mole fraction.

Without doing exhaustive calculations, Van der Waals was able to draw gold from this exact result for the spinodal (see Ch. 4.8.2, 4.8.3).

4.8 *Plaits on the isothermal Helmholtz energy surface for binary mixtures*

4.8.1 *The transverse plait.* If both pure components are below their respective critical temperatures, the isothermal Helmholtz energy of each component, according to the equation of Van der Waals, has two inflection points, see Fig. 2.3. At sufficiently low temperatures, and when the unlike interaction is not particularly weak, the isothermal Helmholtz energy of the mixture develops a vapor-liquid plait beginning at the two sides and running all the way across the isothermal $A(V, x)$ surface from $x = 0$ to $x = 1$. Van der Waals calls this plait a *transverse plait* because it is his custom to consider the volume as the vertical, the mole fraction as the horizontal axis. By rolling a tangent plane across the $A(V, x)$ surface, the coexisting phases are found. If one of the components is above its critical temperature, however, the plait will not run all the way across the surface, and may end at a plait point somewhere in the middle of the mole fraction range.

4.8.2 *The longitudinal plait.* A most striking implication of the Van der Waals mixture equation of state is the possibility of an additional phase split in the liquid phase. Experimenters, who had long since given up hope that the Van der Waals equation could adequately represent experimental data regained interest in it because of this power of the mixture equation.

To find out whether this can happen, Van der Waals circumvents the complex calculations that would be needed in the general case. He limits himself to the state $V = b_x$, the close-packed liquid for which the pressure is infinite, which is the lowest-volume state possible for the mixture of mole fraction x . Since he has derived an exact expression for the spinodal (Ch. 4.7.2), he simply asks whether the spinodal has any points in common with the curve $V = b_x$. Interestingly, it turns out that this is only possible if $d^2b_x/dx^2 = 0$. This condition is fulfilled if b_x is a constant or a linear function of x . For the values of x at which the spinodal meets the curve $V = b_x$, an expression quadratic in x results

$$RT/[x(1-x)] = d^2(a_x/b_x)/dx^2 \quad (4.17)$$

Since b_x is at most linear in x , and a_x at most quadratic, the answer will depend on the value of the parameter a_{12} . Van der Waals now asks for the *coincidence* of the two points of intersection. That gives the x -value and the temperature at which the plait first enters the physical V - x space at the boundary $V = b_x$. Above this temperature, there will be no second plait on the surface. Van der Waals calls this temperature *the critical temperature of complete miscibility*. Complete miscibility of two liquids is possible only if a_{12} does not fall substantially below the average of a_1 and a_2 . It turns out that the geometric-mean condition for a_{12} is the smallest value for a_{12} , for which complete miscibility (no second plait) at all temperatures is still possible. This 'third critical temperature' of the binary mixture plays an important role in the work of Korteweg (Ch. 5) and of Van Laar (Ch. 7.5, 8.4 and 11.4.7).

4.8.3 *The isothermal Helmholtz energy surface at three-phase coexistence.* Van der Waals (1890) enters into another quite interesting part of the paper in §7. He discusses the case in which both a transverse and a longitudinal plait are present on the isothermal Helmholtz surface, and are interfering with each other. The longitudinal plait has to do with liquid-liquid (or high-density fluid) phase separation – the alliteration of *liquid* and *longitudinal* may help to keep the reader straight.

Inside each plait there are two branches of the spinodal curve, between which the surface is unstable. The connodal (also called binodal, or isothermal coexistence curve) of the first plait may now cut the two branches of the spinodal of the longitudinal plait, where the Hessian H equals 0, Eq. (4.15).

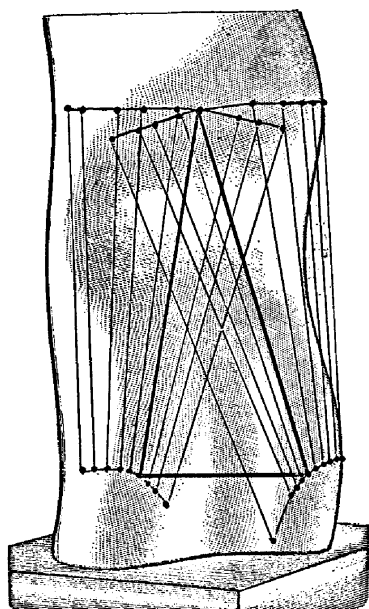


Figure 4.1 An etching of a Helmholtz energy model for a binary fluid mixture. The isothermal Helmholtz energy surface $A(V, x)$ is shown from below, the positive A axis pointing into the plane. The volume axis is vertical, the mole-fraction axis horizontal. The surface has a transverse vapor-liquid plait, and a longitudinal liquid-liquid plait at small volumes. The two plaits intersect, giving rise to three-phase coexistence. Strings spanning the plaits connect coexisting vapor-liquid and liquid-liquid phases. The triangle of three-phase coexistence is shown. (A few of the tie lines connect metastable phases that lie above the triple-tangent plane.) Copied from Van der Waals (1890), Fig. 3.

Between these two intersections, the liquid states of the first plait are unstable. Van der Waals's article contains an etching of a Helmholtz energy surface with three-phase coexistence (Fig. 4.1). The A axis is perpendicular to the page, pointing inwards, and thus the surface is shown from below. The vertical axis is the volume, with low-volume liquid states at the bottom and high-volume gaseous states near the top. The horizontal axis represents the mole fraction.

A transverse plait runs across the entire surface from left to right. It separates a low-volume liquid phase from a high-volume vapor phase at all mole fractions. On the part of the surface within the plait, the isothermal Helmholtz energy is higher than it would be in the tangent plane, and therefore these states are globally not stable.

A second, longitudinal plait runs more or less vertical, and separates two phases of different mole fraction in the low-volume liquid region. On the surface inside this plait the Helmholtz energy is again higher than it would be in the tangent plane.

A double-tangent plane can be rolled across the transverse plait, coming from the left, for instance. The strings shown on the surface connect points on the surface, at which the tangent plane touches as it rolls across the surface. As the tangent plane proceeds from the left, its progression is stopped when it touches a third point, to the right of the longitudinal plait. The tangent plane now touches one vapor and two liquid states; the heavy black

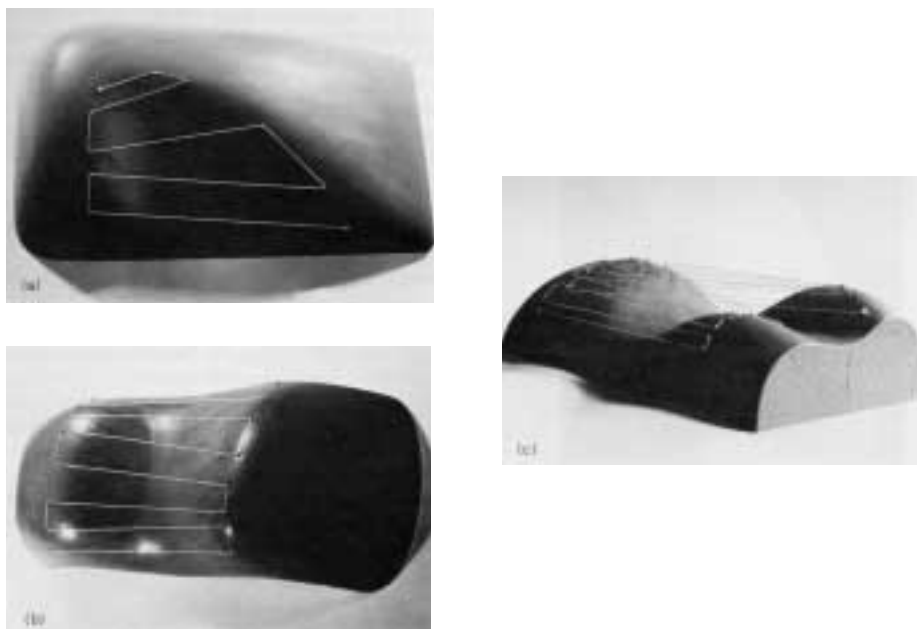


Fig. 4.2 A photograph of wooden models of isothermal Helmholtz energy surfaces for binary fluid mixtures, used by Van der Waals in his lectures. Model (a) shows a partial transverse plait terminating in a plait point. Model (b) shows a complete transverse plait. Model (c), represented in Fig. 4.1, shows both a transverse and a longitudinal plait, leading to three-phase equilibrium. Reprinted from De Boer (1974), with permission from Elsevier Science.

string indicates where this happens. Three fluid phases coexist at a triple point. From the three-phase triangle, the tangent plane may either continue its course along the transverse plait, or may follow the longitudinal plait. In either case, the tie lines undergo a discontinuous change of direction. This and two other models, which were made out of wood and used by Van der Waals in his lectures, were still in existence in 1974, and photographed by De Boer. See Fig. 4.2.

Van der Waals's discussion of the interaction of two plaits played a big role in Kamerlingh Onnes's decision to start work on fluid mixtures, and inspired his student Kuenen in the choice of systems he would study (Ch. 6).

4.9 Other significant results. In §6 of the 1890 paper, Van der Waals derives important exact differential relations for the properties of coexisting phases on the isothermal Helmholtz surface. By using the three conditions, equality

of pressure and of the chemical potentials of each of the components, Eq. (4.9), Van der Waals describes how, in principle, the pressure, volumes and mole fractions of the isothermal coexisting phases can all be expressed in terms of one variable, such as the mole fraction of one of the phases. As an example, Van der Waals derives a useful exact differential relation for the change of pressure as a function of the mole fraction x of one of the phases, for instance the gas phase (subscript G):

$$[\Delta V - \Delta x (\partial V_G / \partial x_G)_P] dP = \Delta x H^{-1} dx_G \quad (4.18)$$

Here Δ denotes the difference in the molar volume V or mole fraction x between coexisting phases, and H is the Hessian, Eq. (4.11). An analogous expression can be written for the change of mole fraction in the liquid phase. Van der Waals uses these expressions to deduce the form of the isothermal Helmholtz energy surface. He uses only qualitative information, such as, that the Hessian H is positive for stable phases, that the liquid volume is small with respect to the vapor volume, and that the vapor volume is only weakly dependent on the mole fraction. These are sufficient to prove that the vapor pressure is an extremum when the mole fractions in the two coexisting phases happen to be the same, the case of azeotropy. Note also that the isothermal P - x coexistence curve must go through an extremum at the plait point, where the Hessian is zero.

Van der Waals wisely refrains from actually trying to calculate properties of coexisting phases, and for good reason. He knew from hard experience that, even for one-component fluids, these properties cannot be derived explicitly in closed form from the Van der Waals equation.

Several other aspects of mixture phase separation are treated in this substantial paper. For instance, §15 is devoted to the alteration of binary-mixture phase equilibrium in the presence of external forces. Van der Waals gives explicit results for the density and composition gradients arising in binary mixtures due to gravitational forces.

4.10 *Concluding remarks*

Van der Waals's ideas about stability, the role of tangent planes in defining phase equilibria, and the use of models of thermodynamic surfaces were not new. They can be found in Gibbs's treatises (1873, 1876, 1878). Thomson (1871) built a P - V - T space model on the basis of Andrews's results, and Maxwell (1875) experimented with a space model of Gibbs's $U(S, V)$ surface of a one-component fluid. (For more detail, see Ch. 6.8). New, however, is the tool Van der Waals offered for quantitative evaluation of such surfaces and their plaits for binary fluid mixtures. Ch.5-8 will demonstrate how the

Dutch School made use of the Van der Waals equation for mixtures in order to discover the different types of phase equilibria that are to be found in binary fluid mixtures.

In Van der Waals's treatise, we see him stepping with confidence across the free energy landscape, its plaits and tangent planes. An obvious question is where Van der Waals's knowledge about plaits on surfaces originated; his paper gives only the slightest of hints. In Section 5, in parentheses, he refers to the end points of a plait as 'the tacnodal points of Cayley' and, in a footnote, as 'plait points' according to Korteweg; no reference to the literature is given. The German version of the paper has no references to any other scientists either, not even to Gibbs, whose methods and notation Van der Waals uses extensively. Incomplete referencing, however, is not an exception in the case of Van der Waals's publications. The presence of complete references throughout the English translation of the doctoral thesis and the paper on mixtures by Rowlinson is due to the diligence of the translator/editor, rather than to the original author.

The French translation of Van der Waals's theory of mixtures, published in *Archives néerlandaises* (1891), provides a clue as to where Van der Waals's knowledge of the theory of plaits may have come from. In the same issue of the *Archives*, there are two papers on the theory of plaits by the Dutch mathematician Korteweg. These papers form the topic of the next chapter.

5. The theory of plaits on surfaces – Korteweg

5.1 *Korteweg's origins*

Diederik Johannes Korteweg (1848–1941) was born and raised in 's Hertogenbosch, in the southern Dutch province of Brabant, one of five sons of a judge. He carried out his high school studies at a special school preparing for the military academy. Fascinated by mathematics, however, he chose to study at the Delft Polytechnic instead, but once there, he quickly became discouraged by the technical subjects. Instead, for several years, he took courses of mathematics and mechanics preparing him to become a high school teacher. Once he started teaching mathematics and mechanics at a high school in Brabant, he studied for the diploma that would give him access to university studies, in a fashion not uncommon among the great scientists of the 'Second Golden Age' in Holland.

During his years as a teacher, Korteweg began publishing scientific papers, and also established contact with Van der Waals. Once he passed the university admission exam in 1876, he studied mathematics for a year at the University of Utrecht, and then transferred to the newly founded University of Amsterdam. There his ascent was meteoric. He obtained the doctoraal (roughly a master's degree) in January 1878, and, only half a year later, defended his doctoral thesis with honors. His was the first doctorate granted by the young university and, for lack of a department of mathematics, physics professor Van der Waals acted as advisor and bestowed the degree. The topic of the thesis was the propagation of waves in elastic tubes. His inspiration came from physiological experiments on propagation of waves in arteries, caused by the beating heart.

In September 1881, at the age of 34, Korteweg was appointed a professor of mathematics at the University of Amsterdam. He was elected to the Royal Netherlands Academy of Arts and Sciences (KNAW) in 1881, and to the Holland Society of Sciences and Humanities (HMW) in 1886. He voluntarily ceded his chair to his brilliant pupil, Luitzen Egbertus Jan Brouwer, in 1913. See Van Dalen (1999).



Diederik Johannes Korteweg
Copy of a sketch by the Dutch artist Jan Veth, kindly provided by Bastiaan Willink, great-grandnephew of Diederik Korteweg.

The title of Korteweg's inaugural address was 'Mathematics as an Auxiliary Discipline,' and the address contained numerous examples of the role of applied mathematics in solving problems in science and statistics. Korteweg lived by his conviction that mathematics has an important role to play in science, as proved by his work in thermodynamics, kinetic theory and hydrodynamics. He is best known for the Korteweg-de Vries paper on the propagation of soliton waves in a channel, which has received strong recognition during the second half of the 20th century. Korteweg also studied the stress resulting from the density gradients at an interface between two fluids, which stress is named after him. A.J. Kox (2000) published a Dutch-language account of Korteweg's work at the University of Amsterdam, from which much of the historical information presented here originates.

This chapter will describe work by Korteweg that is less known: the mathematical foundation of the theory of plaits (folds) on analytic surfaces, and its application to Van der Waals's theory of mixtures.

Korteweg was associated with Van der Waals during the years that the latter was working on the phase separation of binary mixtures. From the beginning, and perhaps encouraged by Van der Waals, Korteweg took an interest in this topic. In two papers in *Archives néerlandaises* in 1891, following after the French translation of Van der Waals's (1890) paper on mixtures in the same volume, Korteweg (1891a,b) presented the mathematical tools for describing the formation of plaits and the coexistence of phases on the free energy surface.

In many papers by the Dutch School, reference to Korteweg's work is given, but often only in a perfunctory way. In Van der Waals's own paper, for instance, one has to struggle to find Korteweg's name somewhere in a footnote. Nevertheless, it appears that the Dutch contemporaries, such as Van der Waals and Van Laar, were thoroughly familiar with his work. The work of thermodynamicists of the next generation, Van der Waals's successor Kohnstamm (1875-1951), as well as Bakhuis Roozeboom's pupil Scheffer (1883-1954), who became a professor at the Delft Polytechnic, gives evidence of considerable familiarity with the work of Korteweg. So does the work of Schreinemakers (1864-1945), professor of physical chemistry in Leiden. Throughout the middle and latter parts of the 20th century, however, Korteweg's work on plaits appears to have been almost entirely forgotten. The Dutch native Paul Meijer (1994, 1999), a professor of physics at the Catholic University of America, deserves much credit for his recent rekindling of interest in Korteweg's work on the theory of plaits on surfaces.

In this chapter, we describe Korteweg's (1889, 1891a) paper on plait points. We then present the theoretical part of Korteweg's (1891b) paper on the general theory of plaits, interwoven with three mathematical theorems that Korteweg (1890) published in Dutch. The second half of the general theory of plaits is an application to the Van der Waals equation for mixtures, which is presented in Ch. 7.3.

5.2 *The shape of analytic surfaces*

5.2.1 *Korteweg's tools.* The discipline that describes the shapes of surfaces is called differential geometry. Some 19th-century mathematicians who were experts on this topic were Arthur Cayley (1821-1895), and George Salmon (1819-1904). The former is cited by Maxwell and Korteweg, while Korteweg also cites Salmon's book book, with Fiedler, on the analytic theory of space. In Maxwell (1871), Ch. XII, for instance, there is a clear, intuitive description

of the Gibbs $U(S, V)$ surface, the tangent plane touching in more than one point, and of the coalescing of the two tangent points in what he calls a tac-nodal point, citing Cayley.

Korteweg honed the tools of differential geometry for the investigation of plaits and plait points on two-dimensional smooth surfaces in three-dimensional space, by studying the way a tangent plane rolls over the surface. In addition, he studied the formation and evolution of plaits in the case that the representation of the surface contains a parameter that is allowed to vary. He applied the results to the isothermal Helmholtz energy for binary mixtures, which Van der Waals was developing at the same time (Ch. 4.5). In that case, the adjustable parameter is usually the temperature. Korteweg's mathematical surfaces are graphs $z_0(x, y)$ of bivariate functions having convergent Taylor expansions at every point. Such surfaces have no singularities and will be called *analytic* in this book.

A tangent plane rolling over an analytic surface may encounter regions where it touches in more than one point. As stated in Ch. 2.6, the points on the surface where a tangent plane touches simultaneously in different points are called *connodes*. The line segment that connects the connodes is called *tie line*. The locus of connodes traced out when the tangent plane rolls across the surface is called the *connodal* or *binodal*. The part of the surface spanned by the connodal is called a *plait*, an old-fashioned word for fold (pli in French, plooi in Dutch, Falte in German). The presence of a plait signals a change in the curvature of the surface. A plait may end in a *plait point*, presently called a critical point, where the length of a tie line shrinks to zero. The surface being analytic implies that the plait is entirely smooth, free of sharp edges or creases.

Whereas the theory of local stability on a surface was well developed in Korteweg's time, he was the one who developed the differential geometry of effects that occur non-locally.

5.2.2 Curvature of an analytic surface. To test the curvature of the surface, a tangent plane is constructed at the point of interest. Imagine this plane pressed ever so slightly, and parallel to itself, into the surface. Curvature is related to the shape of the *indicatrix*, the curve along which the displaced plane and the surface intersect. If the intersection forms a closed curve on the tangent plane, such as an ellipse, then the surface must lie above (or below) the tangent plane in all directions around the tangent point. Such points are called *elliptic* points. In elliptic points, the surface is said to have *positive curvature*, irrespective of whether the surface is concave or convex. As discussed in Ch. 4.7.1, surfaces representing a stable thermodynamic free energy must be convex. Korteweg, however, studies the wider class of general analytic surfaces,

which will, nevertheless, prove to be of great relevance to understanding the behavior of mathematical representations of thermodynamic free energies.

Surfaces may not have positive curvature at all points. An example is a pass in a mountain landscape, which has the shape of a saddle. The surface curves up towards the mountains on the sides, and down towards the valleys that are connected by the pass. At a saddle point, the tangent plane intersects the surface in two intersecting lines, and parts of the surface are below the tangent plane, while others are above it. If this tangent surface is shifted up or down lightly parallel to itself, the resulting indicatrix consists of the two branches of a hyperbola, and therefore points in regions that have saddle shape are called *hyperbolic*. At a hyperbolic point, it is said that the surface has *negative curvature*. (A thermodynamic free energy surface would be unstable at such points.)

The transition between an elliptic point and a hyperbolic point is a *parabolic* point, where the *curvature is zero*. At such a point, the indicatrix consists of two parallel lines: the ellipse on the surface of positive curvature has been flattened to two parallel line segments, or, alternatively, the angle of the intersecting lines of the tangent plane on the hyperbolic surface has gone to zero. A locus of parabolic points is called a *spinodal* (see Ch. 2.6 and Ch. 4.7.2). The spinodal forms the boundary between regions of opposite curvature.

5.3 On plait points – first part

5.3.1 *Overview.* Korteweg's (1889, 1891a) paper on plait points was first published in German, predating Van der Waals's (1890) paper on mixtures. Both Korteweg's and Van der Waals's paper were translated into French, appearing jointly in Archives néerlandaises of 1891, followed by Korteweg's (1891b) paper on the general theory of plaits. In this book, we follow the French editions of the two Korteweg papers. In his paper on plait points, to which we will refer as PP, Korteweg (1891a) characterizes the points where plaits begin or end on a two-dimensional surface in three-dimensional space.

In the first part of his paper, Korteweg develops a Taylor expansion of an analytic mathematical 2-dimensional surface in 3-dimensional space. He studies its special features at a plait point. He gives pictorial representations of three types of surfaces containing a plait ending in a plait point. He derives expressions for the connodal and spinodal, and for the flecnodal, defined in Ch. 5.3.4, to first and second order around the plait point. He develops the methods for finding a plait point on a surface. He shows that in general, depending on the geometry of the surface, there are two types of plait points, which he calls of the first and of the second kind. If certain conditions prevail between the coefficients of the Taylor expansion at the plait

point, a double plait point may arise, of which there are again two kinds, called homogeneous or heterogeneous.

5.3.2 *A look at analytic surfaces near plait points.* Korteweg's paper contains a folded-out figure with pictures of a plait and plait point on three different two-dimensional surfaces in three-dimensional space. A copy is shown in Fig. 5.1.

We begin with the two drawings on the left in Fig. 5.1. The left bottom figure might represent a region around the plait point of Gibbs's energy surface $U(S, V)$ for a one-component fluid, or Van der Waals's isothermal Helmholtz energy surface $A(V, x)$ for a binary fluid mixture, both looked at from the bottom up. In that application, the vertical axis represents the *negative* of $U(S, V)$ or $A(V, x)$. There is a plait ending in a plait point. The dashed curve through the plait point in the bottom figures helps to indicate the curvature of the surface. The full curve is the connodal. The spinodal is the dashed curve crosshatched on the side of the hyperbolic (thermodynamically unstable) region. The surface has positive curvature everywhere except in the region inside the spinodal. In each of its positions, the double tangent plane, not shown in the left bottom figure, touches in two connodes, marked K_1 and K_2 .

The figures at the top show projections of points and curves such as the connodal (heavy full curve) and the spinodal (heavy dashed curve) onto the double-tangent plane. A tie line in the double-tangent plane connects the connodes K_1 and K_2 . The plait ends in a *plait point* O where the length of the tie line shrinks to zero. The somewhat lighter, banana-shaped full curve in the top left drawing shows what happens if the tangent plane is pushed slightly into the surface. The resulting curve is not an ellipse, as in other points on the convex part of the surface, but a curve of higher order. Korteweg sometimes calls it an *indicatrix of the fourth order*. The dashed curves in the top drawings of Fig. 5.1 indicate the median of this special indicatrix.

An analytic surface that has negative curvature could also develop a plait. In that case, the region inside the spinodal has positive curvature. The center and right drawings in the bottom row of Fig. 5.1 represent such surfaces. In those cases, a plane tangent to the surface at the plait point must *intersect* the surface, indicating that the curvature is not positive. If the tangent plane is pulled up slightly, center, or pushed down slightly, right bottom drawing, fourth-order indicatrices result which are indicated in the corresponding top drawings in Fig. 5.1. Unlike the indicatrix at a hyperbolic point, which consists of two branches of a hyperbola, the indicatrix of fourth order consists of two branches of a higher-order curve.

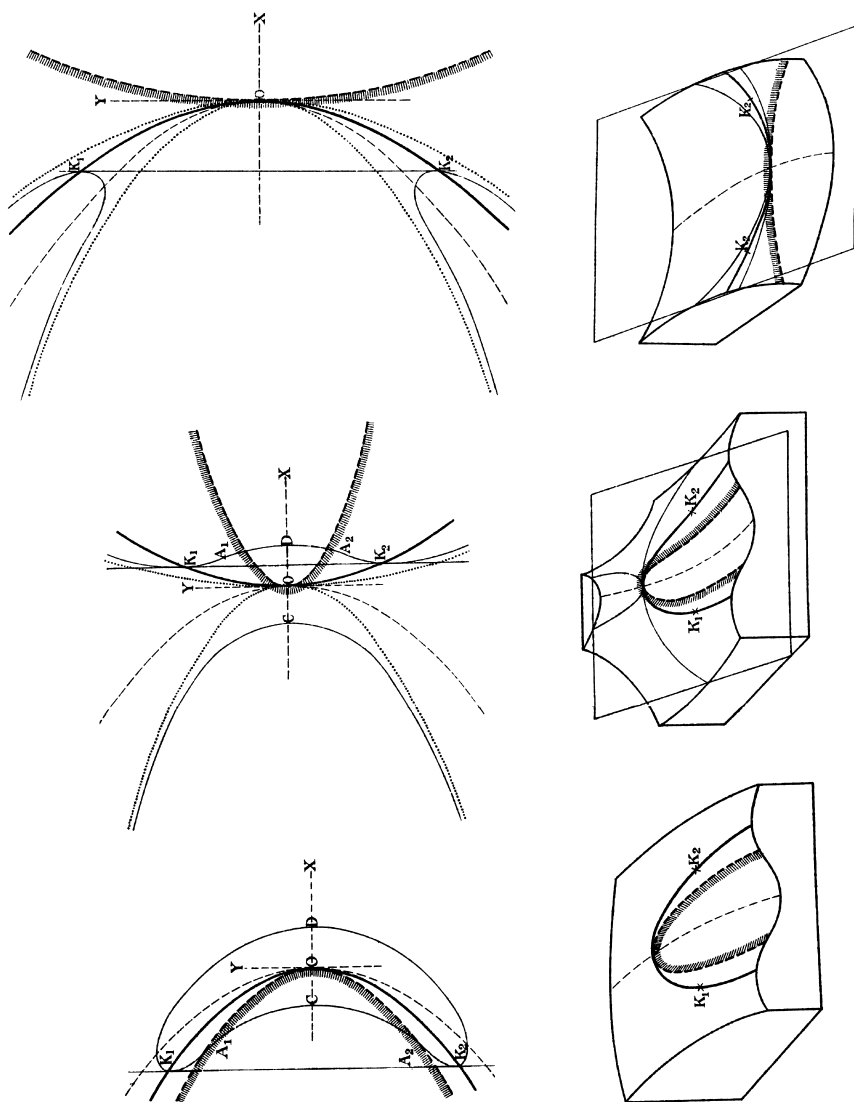


Figure 5.1 Three examples of plait points on analytic surfaces. From Korteweg (1891a), Fig. 1. The bottom figures show three different examples of analytic surfaces containing a plait ending in a plait point. The corresponding top figures show the projection of special curves on the tangent plane, such as the connodal (heavier full curve), the spinodal (dashed curve) and the fourth-order indicatrix (lighter full curve). K_1 and K_2 are two connodes. O is the plait point.

At first sight, the middle and right drawings in Fig. 5.1 seem to have nothing to do with free-energy surfaces, since they violate thermodynamic stability. For the mathematical representation of the $A(V, x)$ surface given by the Van de Waals equation for mixtures, however, these types do occur, albeit on unstable parts of the mathematical surface that are cut off by double- or triple-tangent-plane constructions. Korteweg's work will show that a new plait may originate deep inside an unstable region, and develop over quite a range of a variable parameter before it emerges on the stable part of the surface. Generalizing beyond the thermodynamic constraints permits him, as a mathematician, to reach a profound insight into the evolution of plaits on mathematical surfaces that, on their stable parts, represent the behavior of fluid mixtures.

5.3.3 *Taylor expansion of the surface – curvature and stability.* Korteweg, in the footsteps of 19th-century mathematicians interested in mechanical stability, approximates the surface $z_0(x, y)$ by expanding it, at any point chosen as the origin $x = 0, y = 0$, in a Taylor series in powers of x and y :

$$z_0 = a_1 + b_1 x + b_2 y + c_1 x^2 + c_2 xy + c_3 y^2 + \\ + d_1 x^3 + d_2 x^2 y + d_3 xy^2 + d_4 y^3 + \\ + e_1 x^4 + \dots \quad e_5 y^4 + \dots \quad (5.1)$$

Here the coefficients b_i equal first partial derivatives of the function z_0 calculated at the chosen point x, y , the coefficients c_i are proportional to second derivatives of this function, *etc.* In work to follow, Korteweg will allow for these coefficients to be functions of a variable parameter.

In the application to the thermodynamics of binary fluid mixtures, z_0 might represent the isothermal Helmholtz energy, while x and y represent the independent variables, composition x and volume y , or two linear combinations of these coordinates. An example is Eq. (4.10) in Ch. 4.7.1, giving the Taylor expansion of the isothermal Helmholtz energy $A(V, x)$. Although in that case the expansion is performed at fixed temperature, the coefficients are to be considered functions of temperature, the variable parameter.

If expanded at a general point, taken as the origin, the surface has positive curvature at this point if it lies on one side of its tangent plane in all directions. The tangent plane is represented by the constant and the linear terms in Eq. (5.1). The distance z between the surface and the tangent plane is then given to lowest order by

$$z = c_1 x^2 + c_2 xy + c_3 y^2 + \dots \quad (5.2)$$

Since the lowest-order terms in the expansion are of the second degree, lines through the tangent point in the tangent plane have at least two points

in common with the surface. It is a bit confusing that Korteweg calls this a first-order contact. In what follows, we will not use Korteweg's terminology, but rather state how many points a tangent line has in common with the surface.

For z to be larger than zero in all directions, the discriminant of Eq. (5.2), $c_2^2 - 4 c_1 c^3$, must be negative, so that there are no real roots of $z = 0$, except for the point $x = 0, y = 0$. The discriminant being negative is equivalent with the condition for the Hessian, $H > 0$, which was introduced and discussed in Ch. 4.7.1.

At a plait point, however, the surface reaches a limit of stability. As a consequence, a Taylor expansion at a plait point has a distinctly different mathematical form than that at other points.

5.3.4 Taylor expansion at the plait point – flecnodal. We have seen that at any point on the surface, a tangent plane can be constructed, and the distance to the tangent plane written in a polynomial expansion around the tangent point, starting with the quadratic terms, Eq. (5.2). It is obvious, however, that the plait point is not like other points on the surface. It lies on the spinodal, so the Hessian is zero. In addition, it is obtained as a limit where the length of the tie line in the tangent plane shrinks to zero. Now the tie line has two points in common with the surface at each of its tangent points (the connodes). In the tangent plane at the plait point, therefore, there must be a tangent line that has four points in common with the surface. Korteweg calls a point on the surface, in which a line can be drawn in the tangent plane that has four points in common with the surface, a *flecnodal point*. He calls the locus of flecnodal points the *flecnodal*. The plait point, therefore, must be located on the flecnodal.

If the common tangent at the plait point is chosen as the y -axis, and the tangent plane as the reference, then, to lowest order, an expansion of the surface at a plait point has the following form (PP §2, Eq. 4):

$$z = c_1 x^2 + d_3 xy^2 + e_5 y^4 \dots \quad (5.3)$$

Korteweg gives the following reasons for this special ordering of the terms. As usual, the constant and linear terms in Eq. (5.3) are missing because the surface is defined in reference to the tangent plane. Note that the variables x and y are special ones, generally different from those arbitrarily chosen in Eq. (5.2). Since the y -axis has four-point contact with the surface, the terms $c_3 y^2$ and $d_4 y^3$ are missing. That is, not only the constant and the linear terms are zero, but also the terms quadratic and cubic in y alone. Moreover $c_2 = 0$, since the Hessian $H = 4 c_1 c_3 - c_2^2$ equals zero while $c_3 = 0$.

Eq. (5.3) is a quadratic in x and y^2 . The three terms are of the same order of magnitude, Korteweg notes, without presenting a full argument why this is the case. If this is granted, it is easy to see that other terms omitted in Eq. (5.3) are ‘of higher order’ than the terms listed. Thus ‘ x is of order y^2 .’ This means that z increases much more slowly in the y direction than in the x direction. This is fundamentally different from other points on the surface, where x and y are equivalent, and where the lowest-order expansion of z with respect to the tangent plane yields a quadratic in both x and y , Eq. (5.2).

5.3.5 Landau expansion. In studies of critical phenomena in the second half of the 20th century, the analytic expansion of the Helmholtz energy surface at a critical point is referred to as the *Landau expansion*, in honor of the great Russian physicist Lev Davidovitch Landau (1938), who introduced such expansions both for an isolated critical point and for systems with crystalline symmetry at a critical line in 1937. In fact, Korteweg introduced the Taylor expansion for analytic surfaces at plait points as early as 1891, with applicability to the (less symmetric, more general) isothermal Helmholtz energy $A(V, x)$ of a binary mixture at any point on a critical line. Expansions of both the pressure and the Helmholtz energy of one- and two-component fluids were used expertly in the late 19th and early 20th century by members of the Dutch School, in particular by Korteweg, Van der Waals and Van Laar.

5.3.6 How to find a plait point on a surface. Suppose the surface is given explicitly, such as the Van der Waals equation for mixtures introduced in Ch. 4.4. The plait point conditions are that this point must be simultaneously located on the flecnodal and the spinodal. Korteweg gives the following procedure for finding a plait point (PP Sec. 7). The coordinate system is that used in Eq. (5.1), Ch. 5.3.3, not the special one used in Eq. (5.3), Ch. 5.3.4. At any given point x, y on the surface, a tangent plane is drawn, and the question is asked whether a straight line $x = my$ can be drawn in this plane in such a way that the line has four points in common with the surface. For this to be the case, the slope m of the line must fulfill two conditions simultaneously:

$$m^2 \partial^2 z / \partial x^2 + 2m \partial^2 z / (\partial x \partial y) + \partial^2 z / \partial y^2 = 0 \quad (5.4)$$

$$m^3 \partial^3 z / \partial x^3 + 3m^2 \partial^3 z / (\partial x^2 \partial y) + 3m \partial^3 z / (\partial x \partial y^2) + \partial^3 z / \partial y^3 = 0 \quad (5.5)$$

The values of the second and third partial derivatives in Eq. (5.4, 5.5) have to be calculated at the point under consideration. A point at which there is a common root m of these two equations lies on the flecnodal, and the common root m is the direction of the line that has four-point contact with the surface at the point in question. The reason is that in this special direction m both the quadratic and the cubic terms in the Taylor expansion of the surface

sum to zero, so that the expansion begins with terms of the fourth degree. For the flecnodal point to also be located on the spinodal, the quadratic equation, Eq. (5.4), has to have two *coinciding* roots, so that the discriminant of Eq. (5.2) equals zero. This condition can be rewritten in terms of two linear equations for m by a simple algebraic manipulation. In summary, the plait point conditions for a two-dimensional surface are:

$$\begin{aligned} m \partial^2 z / \partial x^2 + \partial^2 z / (\partial x \partial y) &= 0 \\ m \partial^2 z / (\partial x \partial y) + \partial^2 z / \partial y^2 &= 0 \\ m^3 \partial^3 z / \partial x^3 + 3 m^2 \partial^3 z / (\partial x^2 \partial y) + 3 m \partial^3 z / (\partial x \partial y^2) + \partial^3 z / \partial y^3 &= 0 \end{aligned} \quad (5.6)$$

At a point where the three equations have a common root, the value of the root determines the direction of the tangent to the binodal at the plait point in the V - x plane, and therefore also the limiting slope of the tie lines as the plait point is approached. To calculate the values of second and third derivatives in Eq. (5.6), the analytic equation defining the surface at the point in question is used.

Korteweg's equations still form the standard way of calculating critical points for a binary mixture if the Helmholtz energy is given. See, for instance, Rowlinson (1958), Van Konynenburg and Scott (1980), Rowlinson and Swinton (1982), and Heidemann (1994). Korteweg extensively uses this set of three simultaneous equations, Eq. (5.6), for calculating critical points in his subsequent work. They can be found in pp, Eqs. 34-36.

5.3.7 Two kinds of plait points. In pp Sec. 3, Korteweg analyzes the special expansion of the surface at a plait point, Eq. (5.3), a quadratic in x and y^2 . Under the assumption that $d_3 \neq 0$ en $4c_1e_5 - d_3^2 \neq 0$, it follows immediately that there are two kinds of plait points. If the discriminant of Eq. (5.3) is smaller than zero, then the tangent plane contains an isolated point with a real tangent, a plait point of the first kind. This is the type of plait point that is displayed in Fig. 5.1, left drawings, and which has been discussed in Ch. 5.3.2.

If the discriminant of Eq. (5.3) is larger than zero, as discussed in pp Sec. 4, then the tangent plane at the plait point intersects the surface, and the plait point is of the second kind. Thus, if this were a thermodynamic surface, it would not be stable at the plait point. Since the plait point is a parabolic point, the two curves along which the tangent plane intersects the surface must locally have the form of two coinciding parallel lines, and thus they must *touch* each other at the plait point. Examples are given in Fig. 5.1, center and right drawings. In the center drawing, these two curves are on opposite sides of the tangent in the plait point, and in the right drawings they are one the same side. The two cases differ in the sign of e_5/c_1 .

The drawings in the top row of Fig. 5.1 show the indicatrices of fourth order for the three surfaces in the bottom row. The banana-shaped curve in the top left drawing was already commented on. For the case in the center column of Fig. 5.1, if the tangent plane is pushed slightly into the surface, the intersection of the surface with the tangent plane assumes the shape of two branches, to the left and the right of the Y-axis, indicated by the light full curves passing through C and D in the drawing at top center. This surface is hyperbolic outside the spinodal, and elliptic inside it, being convex. In the case of the drawings in the right column of Fig. 5.1, if the tangent plane is pulled slightly out of the surface, the intersection has the form of two branches indicated by light full curves, one above and the other below the X-axis in the drawing at top right. The surface outside the spinodal is hyperbolic. Inside the spinodal the surface is elliptic, but concave, contrary to the case in the center column of Fig. 5.1. In all cases, the connodal points K_1 and K_2 have been indicated.

The essential difference between the plait points of the first and of the second kind is threefold. First of all, the fourth-order indicatrix has a different shape, a closed curve in the first case, but two branches in the second case. Secondly, the connodal is situated on a convex part of the surface in the first case, but on a hyperbolic part of the surface in the second case. Thirdly, the surface bounded by the spinodal is hyperbolic in the first case, elliptic in the second case.

Korteweg derives the algebraic expressions for the asymptotic shapes of the connodal, spinodal, and flecnodal to first and second order in y in pp Sec. 3, Sec. 7-9. Of these, the connodal has the smallest curvature, the spinodal follows, and the flecnodal has the strongest curvature. For all these curves, the first-order term is quadratic in y , the second-order term is proportional to y^3 .

5.3.8 Two kinds of double plait points. We described how Korteweg derived the conditions for a plait point on an analytic surface. Exceptional cases develop when the coefficients in Eq. (5.3) have special values. In pp Sec. 10, Korteweg first sketches the case that $d_3 = 0$, but the discriminant $d_3^2 - 4c_1e_5 \neq 0$. Korteweg calls this plait point a *homogenous double plait point*. In the second part of pp, he shows that it can be considered as the coincidence of two plait points of the same kind. If, on the other hand, the discriminant of Eq. (5.3), $d_3^2 - 4c_1e_5 = 0$ but $d_3 \neq 0$, another kind of double plait point arises, which Korteweg calls a *heterogeneous double plait point* (pp Sec. II). Korteweg shows that it can be considered as a coincidence of two plait points of different kinds.

To calculate the flecnodal, spinodal, and connodal, additional terms in the expansion come into play compared to the simple case, Eq. (5.3), discussed

before. The net results are that the spinodal and connodal have four points in common at the origin, whereas they only had two points in common for the ordinary plait point.

Both types of double plait points play an essential role in the formation and disappearance of plaits on the surface. They will be frequently encountered in what follows. The importance of these two types of double plait points will become apparent as Korteweg begins his study of how plaits originate on surfaces. An ordinary plait point cannot form by itself on a surface: plaits are born at double plait points.

5.4 *On plait points – second part*

5.4.1 *Korteweg's method of continuous transformation of surfaces.* In the second part of pp, Korteweg (1891a) studies what happens to plait under variation of a parameter defining the surface. When terms such as 'begins' 'moves', 'grows', 'develops' are used to describe features of the surface, these terms are short-hand substitutes for the phrase: how does a feature, such as a plait on the surface, get modified as a parameter changes continuously? Korteweg is the creator of the theory of deformations of analytic surfaces. Only some of the results of his highly technical mathematical treatment will be summarized here, namely those that are needed for an understanding of the work of the Dutch School on fluid mixtures presented in this book. In the application to the isothermal Helmholtz energy, the temperature is naturally used as the parameter that varies, but an interaction parameter in the model describing the Helmholtz energy will turn out to be another useful choice.

How does Korteweg's method of deformations of surfaces work? He assumes that the coefficients in the Taylor expansion of the surface, Eq. (5.1), are all functions of the parameter, linear to lowest order. Suppose a value of the variable parameter is chosen for which there is a special point present on the surface, for instance, a double plait point. If around such a point a Taylor expansion is made, with the tangent plane as a reference, it differs from a Taylor expansion at arbitrary points on the surface as was explained in Ch. 5.3.4. Now, the parameter is slightly changed, and with it, the shape of the surface. The question is: how? The way Korteweg answers this question is by re-expanding the surface at the original location of the special point, taking into account the dependence of z on the parameter. The special character of the point is spoiled, however, while terms that depend on the size of the parameter shift appear to all orders of x and y in the expansion, including terms linear and quadratic in x and y . In addition, the neat classification of terms by order of magnitude, as exemplified in Eq. (5.3), is

upended, and a very careful new grouping of terms is required. Using the expansion of this shifted surface and the techniques he already established, Korteweg can answer questions such as: what happens to a double plait point as a parameter representing the surface changes? He searches for the presence of a critical point in the Taylor expansion of the deformed surface, by means of Eq. (5.6). He finds that a homogeneous or heterogeneous double plait point splits into two plait points if the parameter is changed one way, but that it disappears if the parameter is changed the other way.

5.4.2 *The role of homogeneous double plait points in the evolution of plaits.* To make this process less mysterious, we move ahead of the story temporarily, and show two familiar cases of transition through a homogeneous double plait point, taken from GTP, Korteweg (1891b). The first case is that of a closed-loop coexistence curve, Fig. 5.2.

The case on the left, that of a coexistence curve with a lower and an upper critical point, is quite common in partially miscible binary mixtures of water and a polar organic. In several cases, the closed-loop coexistence curve has been shrunk to a double critical point and made to disappear by the application of pressure, or by varying the isotopic ratio of water. Closed-loop coexistence curves are discussed in Ch. 7.5.2.

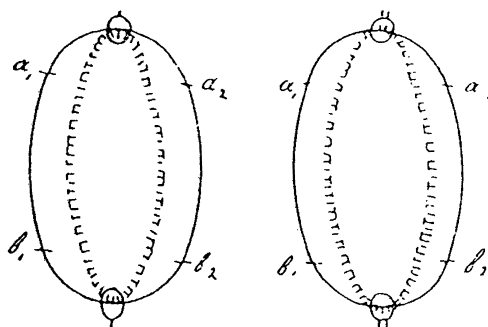


Figure 5.2 Two cases of a homogenous double plait point just having split into two plait points of the same kind. From Korteweg (1891b), Figs 7, 8. In the left drawing, the plait points are of the first kind (one mark on the circle), the region inside the spinodal is hyperbolic, and the region of positive curvature is outside. In the right drawing, the plait points are of the second kind (two marks on the circle), the region inside the spinodal has positive curvature, whereas the outside region is hyperbolic. The crosshatches on the spinodal indicate the location of the hyperbolic region. A double-tangent plane can roll over the surface from the lower to the upper critical point.

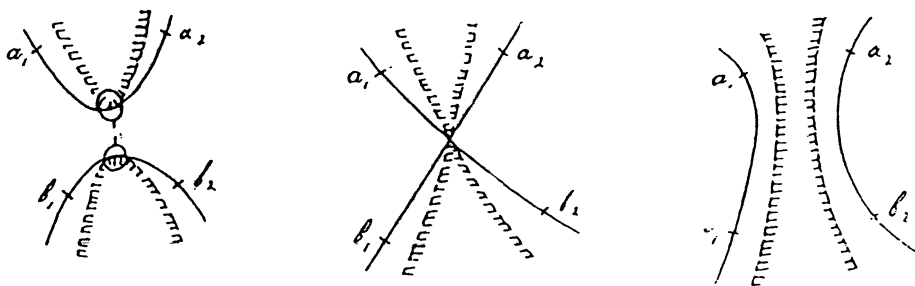


Figure 5.3 Two plait points of the first kind merging into a double plait point, and disappearing. From Korteweg (1891b), Figs. 9-11.

The second case Korteweg (1891b) considers is that of two plait points approaching each other and merging, forming an open plait. Fig. 5.3 shows how.

Two critical points of the first kind, each located on a different plait, approach each other (left), and then coincide (middle) in a homogeneous double plait point. After that, the connodals separate, exchanging branches in the process. No critical points remain after passage through the double plait point (right). The behavior displayed in Fig. 5.3 occurs in gas-gas equilibria, the topic of Ch. 8.

A plait point therefore cannot just appear or disappear on a surface as a parameter is varied. It originates when a double plait point splits. It must merge with another plait point to form a double plait point before it can disappear.

A discussion of the splitting of a heterogeneous double critical plait point requires some familiarity with Korteweg's theorems presented in Ch. 5.5, and is therefore postponed till Ch. 5.5.4.

The third kind of exceptional point on a surface studied by Korteweg is a point of osculation (pp Sec. 19). In the Taylor expansion of the surface with respect to the tangent plane at such a point, all quadratic terms are zero. The surface intersects the tangent plane in three directions, the roots of the cubic part of the expansion, one or three of which are real. Since these points play a minor role in this book, we will not delve deeply into their peculiarities. We just mention that at an osculation point, *three* plait points merge, either one or three of these being real, and the real ones being of the second kind. After passing through the merger, the three plait points reappear.

In this paper, Korteweg has assembled the tools necessary for the next task: the changes in the connodal, spinodal and flecnodal curves that accompany the formation and disappearance of plait points. This is the subject of his second major paper. Korteweg (1891b) based this paper on three facts about plait points on surfaces that he had published only in Dutch, in the form of three mathe-

mathematical exercises. These will be woven into the following sections, in which the first half of Korteweg's paper on the general theory of plaits will be discussed.

5.5 *The general theory of plaits (GTP)*

5.5.1 *Overview.* Korteweg (1890) published, in Dutch, three mathematical exercises, theorems to be proved regarding fundamental relationships between two branches of a connodal on an analytic surface. In his second major paper, on the general theory of plaits (referred to as GTP), Korteweg (1891b) makes ample use of these theorems. We have therefore inserted these theorems at the appropriate places in the following overview of the content of GTP.

In the first part of GTP, Korteweg (1891b) describes, by means of simple illustrations, what happens to plaits when one, or each, branch of the connodal intersects a spinodal. Next, it discusses the way plaits transform when double plait points, homogeneous or heterogeneous, appear or disappear, which is an elaboration of his paper on plait points. The paper then turns to the various ways tritangent planes, indicating coexistence of three phases, can arise, and follows up with a section on quadritangent planes.

Presenting the content of GTP in its entirety would heavily tax the reader's patience. The topics selected are of immediate relevance to the behavior of the Van der Waals equation for binary mixtures, a principal topic of this book. Interspersing GTP with the three mathematical theorems and linking it to applications has required some changes in the order in which Korteweg (1891b) presents the material.

The last part of GTP is an application to the Van der Waals equation for binary mixtures, but the discussion of these results has been deferred to Ch. 7.3.

5.5.2 *First theorem – directions of tie line and connodals.* Korteweg (1890) challenges his fellow mathematicians in the Netherlands to prove three mathematical theorems regarding the behavior of double-tangent planes rolling across surfaces containing plaits. He presents one algebraic solution to each of the exercises, along with a geometric solution provided by others. An English translation of the three theorems follows here.

The theorems posed in the exercises state that the local conditions of the surface at two connodes determine the direction of the connodal in each point through mediation by the tie line. Special conditions of the surface at the first connode affect the course of the branch of the connodal passing through the second connode.

In what follows, the concept of *conjugate directions* will play a role. This concept is valid for all types of conic sections (ellipse, hyperbola or parabola). For the ellipse, it is illustrated in Fig. 5.4. The directions d and e are conjugate to each other.

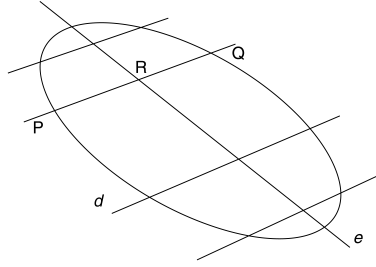


Figure 5.4 Conjugate directions d and e of a conic section. A set of parallel lines is drawn in the plane, defining a direction d . Consider those lines that intersect the conic section in two point P and Q . Let R be the middle point of the segment with endpoints P and Q . A geometry theorem states that the locus of points R is a straight line, which determines a direction e , called the conjugate direction of d . The relation between d and e is symmetric: d is the conjugate direction of e . (There is one exception, when d is the direction of the symmetry axis of a parabola. In that case the conjugate direction is perpendicular to d .)

Korteweg's (1890) first exercise (Problem CXXXVII) posits a conjugate relationship between the directions of the two branches of the connodal and that of the tie line. Suppose a plane touches a surface in two points (Fig. 5.5). Then:

The locus of the tangent points of the double-tangent planes of any surface is called 'the connodal line' of the surface. Prove that in each point of the connodal line the

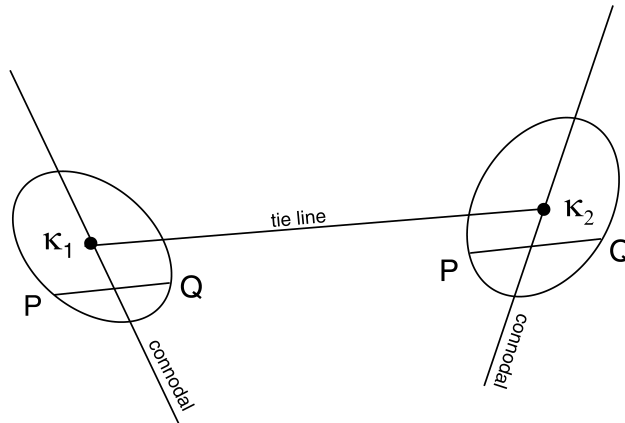


Figure 5.5 The relationship between the direction of the tie line and those of the two branches of the connodal. Around each of the two connodes K_1 , K_2 , the indicatrix of the surface is drawn. The directions of both branches of the connodal are conjugate to the direction of the tie line.

tangent to this line, and the tie line to the other tangent point of the same double tangent plane are conjugate directions of the indicatrix.

Thus, once the local indicatrices of the surface are known at each connode, the direction of the tie line determines the directions of the two branches of the connodal.

5.5.3 Second theorem – a connodal forms a cusp. The second exercise (Problem CXXXVIII) refers to the case that a branch of a connodal passes through a spinodal (Fig. 5.6).

If A_2 is a point of intersection of the connodal with the ‘spinodal’, that is, the locus of points with a parabolic indicatrix [two parallel lines], and if A_1 is the second tangent point of the double tangent plane that touches in A_2 , then A_1 is a cusp on the connodal.

Thus, a special event on the first branch of the connodal, the passing through a spinodal, evokes a spectacular response on the second branch, which reverses its direction.

5.5.4 Application to the evolution of a heterogeneous double plait point. Connodals passing through spinodals are associated with the plait that forms after a heterogeneous double plait point splits into two plait points of different kinds. This is illustrated in Fig. 5.7.

A double-tangent plane might begin at the plait point of the first kind. Rolling over the surface, it must revert its direction in the point marked α_2 , because the connode at α_1 lies on the spinodal. When the double-tangent plane reaches point b_2 , which lies on the spinodal, the tangent plane must reverse course at the connode b_1 . Finally, it stops being a double-tangent plane when it reaches the critical point of the second kind.

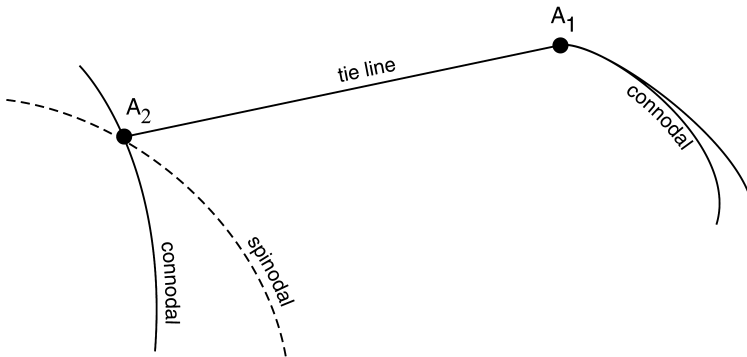


Figure 5.6 If a branch of the connodal passes through the spinodal at the one end of the tie line, then the other branch passes through a cusp at the other end.

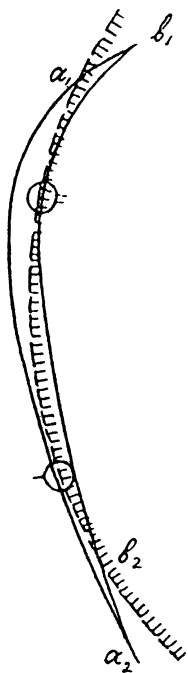


Figure 5.7 A plait formed after the splitting of a heterogeneous double plait point into two plait points of different kinds. From Korteweg (1891b), Fig. 12. A heterogeneous double plait point has split into two plait points of different kinds by variation of a parameter in one direction. (If the parameter would vary in the other direction, the plait points contract into a heterogeneous double plait point, which would then disappear). A long thin connodal is formed. The solid curve is the connodal, and the dashed curve the spinodal. The upper plait point is of the second kind, the corresponding part of the connodal lying on a part of the surface that has negative curvature as indicated by the crosshatches on the spinodal. The lower plait point is of the first kind, and its connodal lies on a part of the surface that has positive curvature. Notice that each cusp occurs at a point where its connode lies on the spinodal, which is an illustration of the second mathematical exercise.

Although these heterogeneous double plait points always arise on hyperbolic (unstable) parts of the surface, they betray their presence through the formation of accessory plaits such as the one shown in Fig. 5.7. The accessory plait may eventually protrude onto the elliptic (stable) part of the surface as it becomes large enough. This is the mechanism by which, starting with a single plait on a mathematical surface representing a thermodynamic free energy, an additional plait may appear, as a parameter such as the temperature varies.

5.5.5 Third theorem – exchange of connectivity of plaits. The third exercise (Problem CXXXIX) addresses the question of what happens if both connodes lie on the spinodal simultaneously (Fig. 5.8).

Prove that if the tangent points A and A' of the same double-tangent plane both lie on the spinodal, then the connodal in each of these points has two real or imaginary branches that are tangent to each other and have the same curvature.

Connodals with two intersecting branches on each side are hard to imagine. Their significance becomes clearer when Korteweg shows, in Fig. 5.9, what happens if a parameter changes slightly from the value that leads to Fig. 5.8.

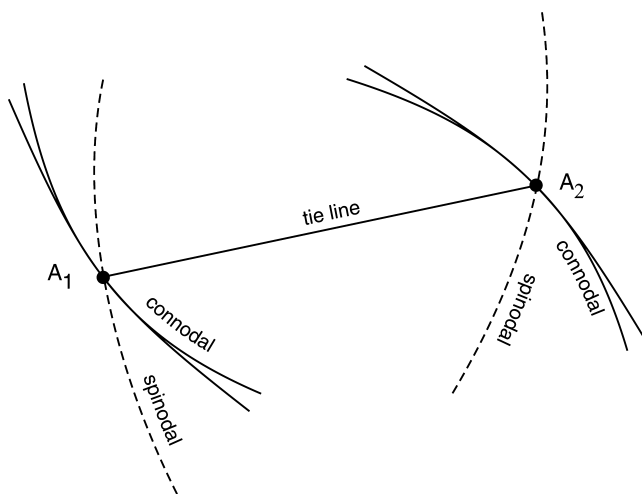


Figure 5.8 Two connodes A_1 , A_2 are simultaneously located on the spinodal. Then at each connode the connodal has two intersecting and touching branches.

An exceptional simultaneous passage of two branches of a connodal through a spinodal, as shown in Fig. 5.8 and in the middle drawing of Fig. 5.9, may be reached at a particular value of a parameter that continuously transforms the surface. The top and bottom drawings show what happens to the middle drawing when this parameter is changed slightly in one or another direction. The branches of the connodal pull away from each other in such a way that they become parallel on one side, and form two cusps on the other side. The cusps occur, according to the second mathematical exercise, for those points p and q whose connodes on the corresponding, now parallel branches lie on the spinodal. Depending on whether the parameter moves up or down, the cusps appear on one side or the other.

Note that something quite striking has happened. Two plaits have disengaged themselves from the single plait in the middle drawing. In the top drawing, the branches on which a and c lie form one plait terminating in plait points a_0 and c_0 (not shown). The branches on which b and d lie form the other, with plait points b_0 and d_0 . In the bottom drawing, on the other hand, the branches containing points labeled a and d form one plait, which ends in plait points a_0 and d_0 , while those labeled b and c form the other plait, which ends in plait points b_0 and c_0 . Thus, a mechanism exists for plaits to exchange branches, and for plait points to change connectivity, by a continuous transformation of the surface from the condition that both connodes are located on the spinodal.

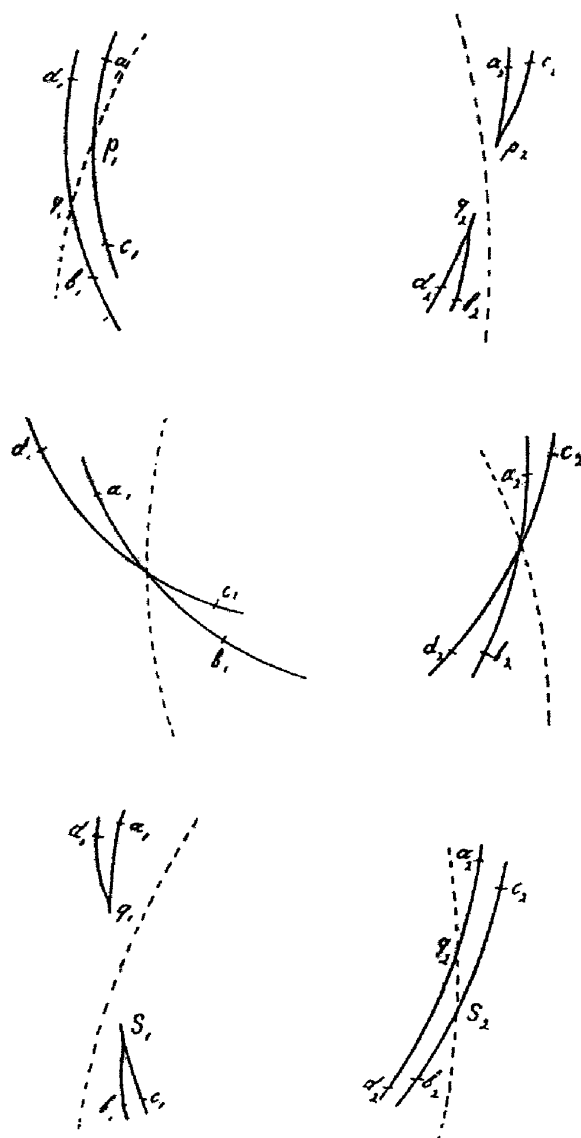


Figure 5.9 Two plaits merge and exchange branches by passing through a point where both connodes lie on the spinodal. From Korteweg (1891b), Figs 4-6. Full curves are connodals, dashed curves spinodals, and points indicated with the same letter are connodes connected by a tie line (not shown). The center drawing shows the two branches, left and right, of one plait, while each branch in turn consists of two branches. (It should be noted that Korteweg did not accurately draw the middle figure, which is the equivalent of Fig. 5.8. According to the third mathematical exercise, the curve $a_1 b_1$ should be *tangent* to the curve $d_1 c_1$ at the point where they intersect the spinodal, and likewise for the curves $a_2 b_2$ and $d_2 c_2$.)

In Ch. 7 we will see that such exchanges of connectivity of plaits are associated with the classification of types of binary fluid phase diagrams occurring in nature as well as in the mathematical representation of the free energy of the mixture. Korteweg elucidates the underlying mechanisms preceding such exchanges in a mathematical representation of the thermodynamic surface. The parameter deforming the surface might be the relative strength between the two components, a parameter that can be made to vary continuously in a mathematical representation.

5.5.6 *Triple-tangent planes.* Suppose it is possible to construct a tangent plane that touches the surface in three points. This case was discussed by Van der Waals, Ch. 4.8, and portrayed in Figs. 4.1 and 4.2c. Fig. 5.10 shows the arrangement of the connodals in that case.

How can a triple tangent plane disappear, or cease to have three real points of contact? Surely this happens if two points, say a_2 and a_3 , coincide. This means occurrence of a plait point on the corresponding plait, as shown in Fig. 5.11.

The bottom drawing in Fig. 5.11 represents the formation of the triple tangent plane displayed in the Van der Waals model of Figs 4.1 and 4.2c. Reading Fig. 5.11 from the bottom to the top, we find that the triple-tangent plane

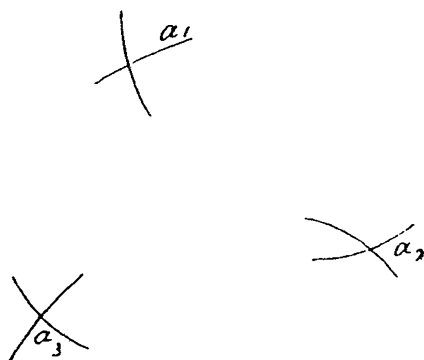


Figure 5.10 A tangent plane touches the surface in three points, a_1 , a_2 and a_3 . From Korteweg (1891b), Fig. 20. Points a_1 and a_2 are connodes of one plait. Likewise for the other two pairs. Thus, there are three plaits, and through each of the three points, connodals of two different plaits pass. If the three points are not on a straight line, and not on a spinodal, then these connodals of different plaits intersect at a non-zero angle. Considering the indicatrix at one of the points where the triple tangent plane touches, the tangents to the two connodals in this point are conjugate directions with respect to the tie lines to the other two tangent points (first mathematical exercise). From the condition of triple-tangency at a_1 , a_2 and a_3 , the tangent plane can roll in three different directions.

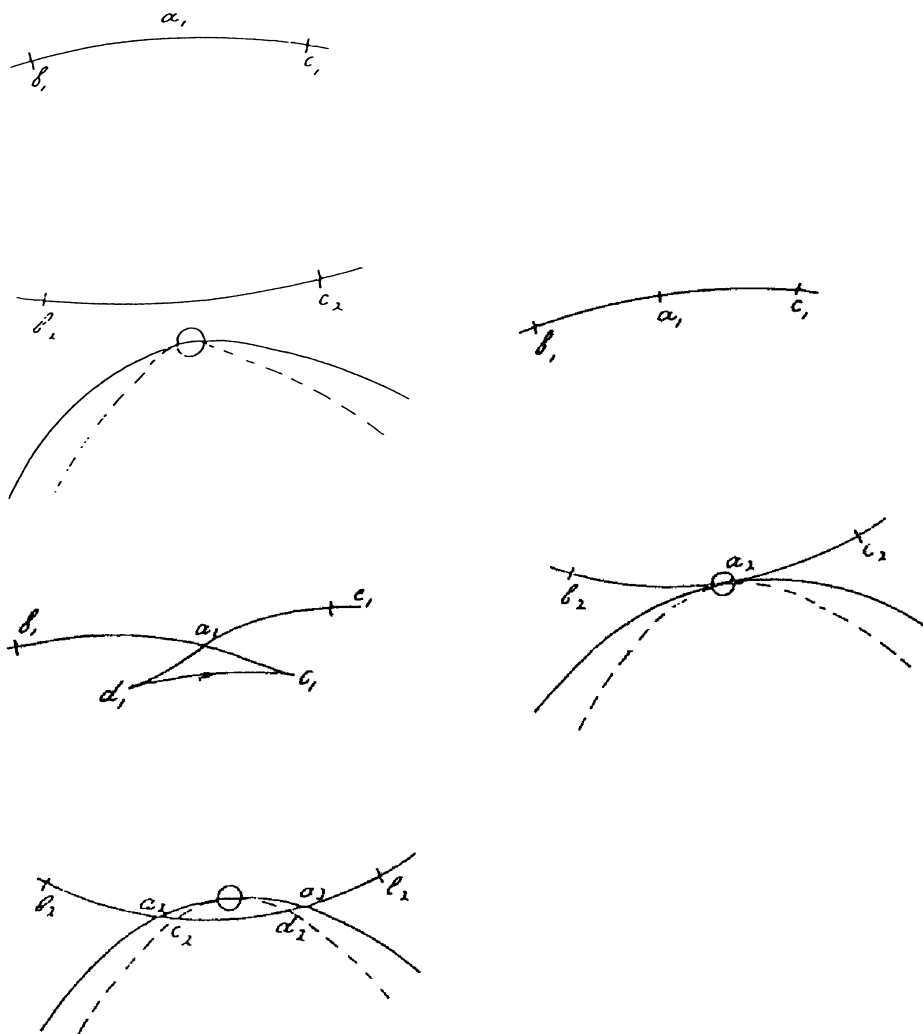


Figure 5.11 Formation or disappearance of a triple tangent plane. From Korteweg (1891b), Figs 21-23. In the top drawing, the surface has two plaits, the first running from left to right, the second approaching from below and ending in a plait point. As a parameter changes, the plait point of the second plait moves up and touches one branch of the connodal of the first plait (middle drawing, on the right). The connode a_1 corresponds with the plait point a_2 . As the second plait intersects the connodal of the first plait, (bottom drawing), a triple tangent plane develops, touching in a_1 , a_2 and a_3 . The lower branch of the first plait now intersects the spinodal of the second plait. According to the second mathematical exercise, the upper branch of the first plait must have cusps both at c_1 and d_1 , the connodes of the spinodal intersections c_2 and d_2 . The top branch of the connode of the first plait thus develops a double point and two cusps as a consequence of events on the bottom connode that send signals along the respective tie lines.

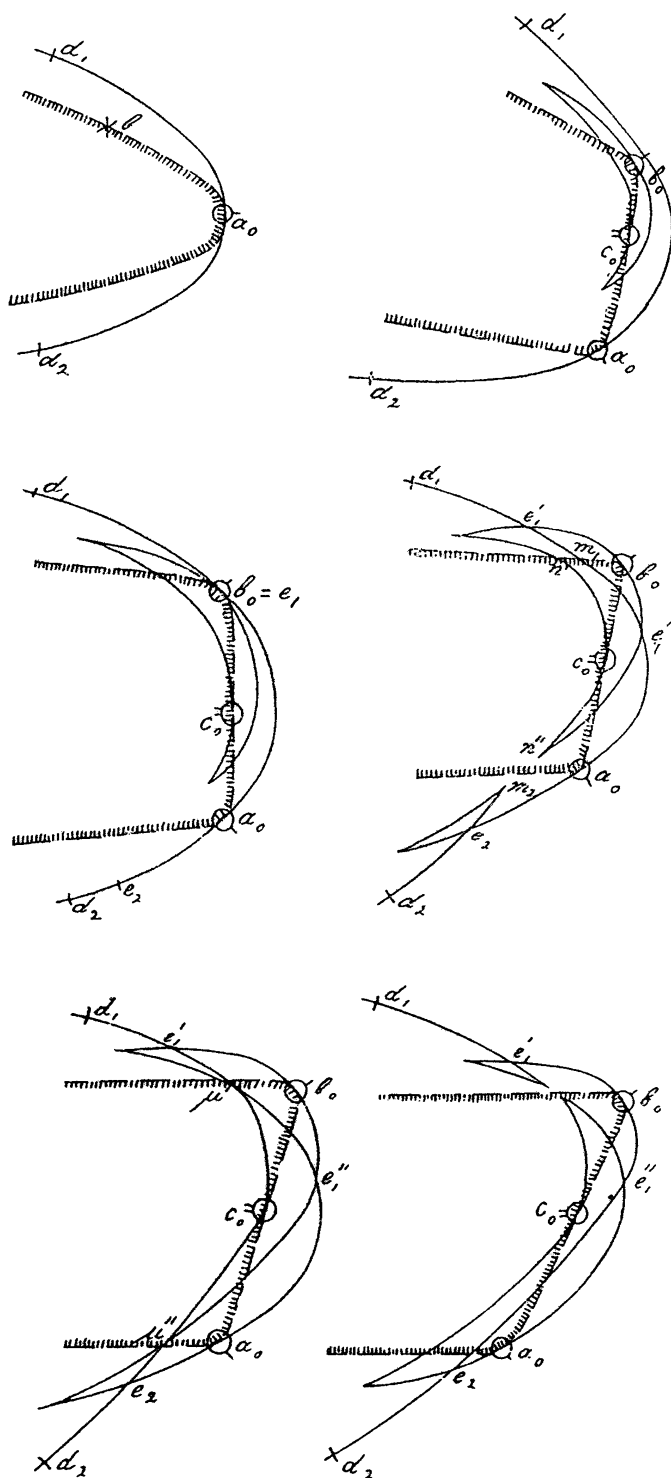


Figure 5.12 Formation of an accessory plait, and exchange of a principal and an accessory plait. From Korteweg (1891b), Figs 30-35. The top left figure shows the connodal (full curve) and spinodal (dashed curve with dashes indicating the region of negative curvature) of a plait ending in plait point a_0 . We call this plait the principal plait. Connodes a_1 and a_2 are indicated. There is one thing special about what otherwise appears to be an ordinary plait. On the spinodal, a heterogeneous double plait point has formed, indicated by the cross. In the top right drawing, as a parameter is varied, this inhomogeneous double plait point has split, and a thin elongated accessory plait has formed located in part on the region of negative curvature of the surface, in the same manner as shown before in Fig. 5.7. Each cusp on the accessory connodal corresponds to a passage through the spinodal by the other branch of its connodal, in accord with the second mathematical exercise. Two plait points, one of the first and one of the second kind, have appeared on the spinodal of the accessory plait. A double-tangent plane starting in a_1 and a_2 would still end up unencumbered in the plait point a_0 of the principal plait. A double-tangent plane on the accessory plate would likewise run independently on the closed loop from the first to the second plaitpoint. In the middle left drawing, however, the plait point of the first kind touches the connodal of the principal plait, then pierces it (middle right). Now the spinodal of the accessory plait intersects the connodal of the principal plait in two points, one of them marked m_1 . As a consequence, the connodal of the principal plait must develop two cusps according to the second mathematical exercise, and a triple tangent plane forms in the same manner as displayed in Fig. 5.10. The three connodes of the triple tangent plane are e_1' , e_1'' , and e_2 . A double-tangent plane that begins to roll on the connodal of the principal plait, starting in a_1 and a_2 , stops when it touches in the third point. From that position, it can roll further to the plait point of the principal plait, a_0 , after a change in direction, but it also has the option of rolling to the plait point of the accessory plait, b_0 , again after a change in direction. The connodal of the accessory plait is still a well-defined entity on which a tangent plane can roll independently, just as in the drawing above it.

On further change of the variable parameter, however, something extraordinary happens: one cusp of the accessory plait meets one cusp of the principal plait in the point μ' on the spinodal (bottom, left drawing). This yields the situation displayed in Fig. 5.9, center drawing. Therefore, the connode μ'' of μ' must also lie on a point of the spinodal where two branches of the connodal touch, according to the third mathematical exercise. On further change of the parameter, the touching branches in μ' develop into two parallel line segments, while those in μ'' pull apart, forming two cusps, precisely as shown in Fig. 5.9.

may disappear by two of the three tangent points coalescing at a critical point that then moves off the connodal of the first plait. There are two other ways in which a triple tangent plane can disappear, which Korteweg says are of less importance in the case of the Van der Waals equation for mixtures. We will therefore not describe these here. Those interested should consult Korteweg's (1891b) paper.

5.5.7 Accessory plaits. In Section 5.5, the formation of an accessory plait from a heterogeneous double plait point was described. An important incident happening in the mathematical representation of a thermodynamic surface is indeed the development of such an accessory plait from inside a principal plait – the accessory plait grows in size, it then pierces the connodal of the principal plait, which leads to the formation of a triple tangent plane – and finally, the accessory and principal plait exchange roles. This entire sequence of events is shown in Fig. 5.12. This figure is not for the faint-hearted, but it has been included because it illustrates almost all effects discussed in Ch. 5.5. It does homage to Korteweg's insight in the behavior of plaits on surfaces, and to his skill in representing them. Fig. 5.12 is relevant to the discussion of binary fluid phase equilibria in Ch. 7. It was familiar to practitioners of the work of the Dutch School, such as Schreinemakers and Scheffer.

A study of the right middle and bottom drawings in Fig. 5.12 reveals that the original principal and accessory plaits have managed to exchange roles through the formation of two mathematical double points on the unstable part of the surface. In the Van der Waals equation for binary mixtures, a passage through a mathematical double point (MDP) inside the unstable region is indeed the key to the process of transition from one kind of phase behavior to another as a model parameter varies. See Ch. 7.2.4, Fig. 7.6, and Ch. 7.5.5.

5.5.8 Quadritangent planes. Korteweg shows how, once a triple tangent plane exists, this plane may touch a surface in a fourth point if the surface is transformed due to the variation of a parameter. Coexistence of four fluid phases does indeed occur in the symmetric Van der Waals mixture that Korteweg investigates in the second and third part of GTP. We will return to this case in Ch. 7.3.5.

5.6 *Assessment and outlook*

Van der Waals must have worked on the theory of mixtures between 1881, when he first mentions some of his early ideas, and 1890, when his paper on mixtures was published. In his introduction to GTP, Korteweg (1891b) mentions as his purpose to study the passage from a state with only a transverse

plait, to states where two plaits are present on the surface and a tritangent plane exists. Korteweg refers to Cayley and to the Salmon-Fiedler book as sources of the discipline of differential geometry. These authors, however, were no experts in thermodynamics and, though they studied plait points, they may not have had interest in double tangent planes and connodals. Korteweg himself developed the tools he needed for application to Van der Waals's theory of mixtures. The sheer amount of formula manipulation alone must have taken a long time to complete. Perhaps he was so totally familiar with differential geometry that he did not even have to struggle with the tool he handled so deftly, and could just focus on the application.

Admirable craftsmanship went into the composition of the text and the illustrations, exposing the essence of this quite complex material. The presentation is clear, beginning with a brief summary of the results, followed by the mathematical treatment, while the detailed calculations and proofs are left for the last part of each of the papers. A discussion of the reliability of the work is postponed till Ch. 7.3.6.

Korteweg was the first mathematician to reach a clear understanding of deformations, the continuous transformations of analytical surfaces as function of a parameter that varies. The theory of deformations is part of the theory of singularities, under which modern catastrophe theory resides. It would be interesting to compare Korteweg's method of continuous transformation of surfaces with the methodology of catastrophe theory.

In selecting which of the Korteweg's results to present in this chapter, the main guideline has been to cover definitions, concepts, theorems and results that will be encountered in the chapters to follow. Korteweg's own application to the Van der Waals equation for mixtures is found in Ch. 7.3.

6. Mixture experiments and models – Kuenen and Kamerlingh Onnes

6.1 *The Physics Laboratory at Leiden University*

Kamerlingh Onnes received his appointment as a professor of physics at the University of Leiden in 1882. He chaired the Department of Experimental Physics until 1923. From the beginning, his goal was to advance scientific knowledge by careful experimentation. ‘Door meten tot weten’ [Through measurement to knowledge] was the motto stated in his inaugural speech, and chiseled in wall of the entrance hall to his laboratory. Kamerlingh Onnes’s principal goal was to establish a cryogenic laboratory devoted to the liquefaction of air and its constituents as preparation for the liquefaction of hydrogen, and later, after it was discovered, of helium. Kamerlingh Onnes was not one to think small. Large-scale gas liquefaction in a cascade of cycles, as was the custom in those days, required a gas compressor for each cycle, so Kamerlingh Onnes purchased massive high-pressure pumps from various providers in Europe. See Fig. 6.1, and Van Helden (1989).

Kamerlingh Onnes started out at a disadvantage. French scientists, most prominently Cailletet, had already made their mark in the field by liquefying air and oxygen, first by rapid expansion of the compressed and cooled gas in a transient mode in 1882, then by cascade-like cooling in substantial quantities by 1884. In 1884, there were even rumors, dispelled later, that Cailletet in France and Wroblewski in Poland had seen a transient liquid hydrogen mist when expanding the compressed fluid after it was cooled by liquid oxygen. That was long before James Dewar, a professor of chemistry at the Royal Institution, liquefied hydrogen by a non-transient method in 1898, winning the race against Kamerlingh Onnes.

Although it seemingly distracted from his main goal, Van der Waals’s theory of mixtures posed an irresistible challenge to Kamerlingh Onnes, so that, immediately after Van der Waals’s Academy presentation on the topic in 1889, he decided to test the new theory experimentally. To this effect, facilities would be required for synthesizing gaseous mixtures of well characterized composition, for observation and precise measurements of phase transitions

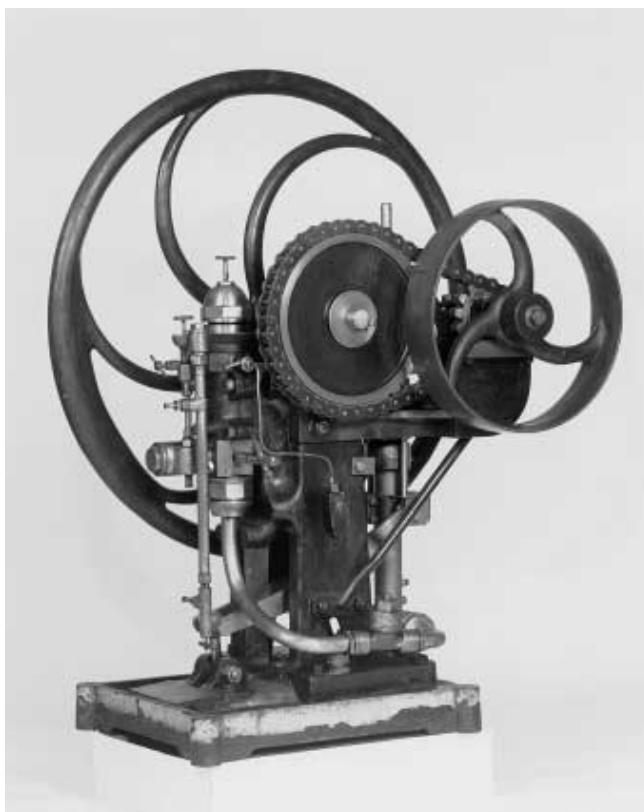
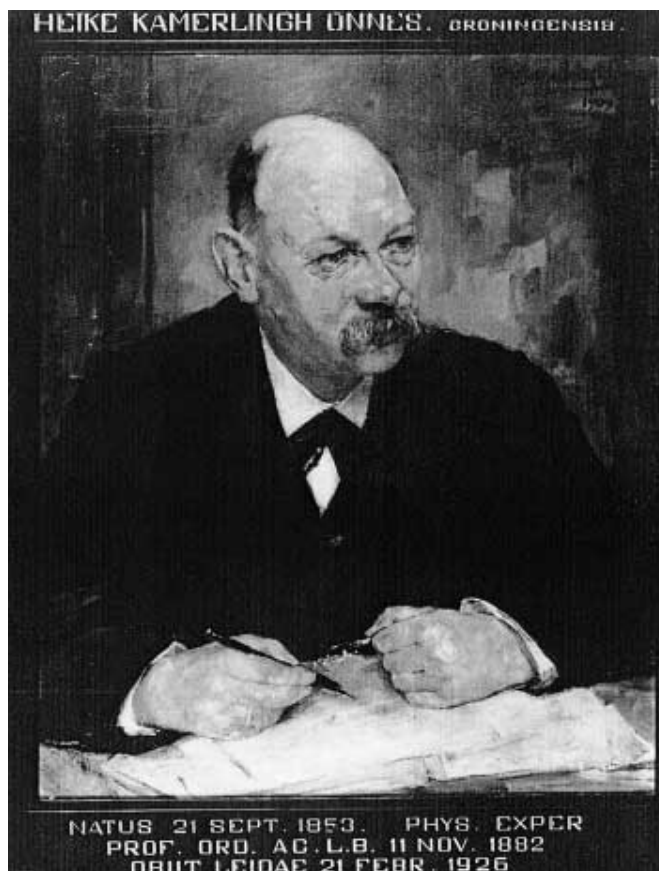


Figure 6.1 A Cailletet pump purchased by Kamerlingh Onnes in 1883. After extensive modification, it was used in the helium cycle of the refrigeration cascade. The pump is 1.41 m. tall. Copied with permission of the Museum Boerhaave, Leiden.

as functions of pressure and temperature, as well as for careful determination of the densities of coexisting phases. The measurement of the properties of cryogenic fluids, as well as the gaseous-mixture work, would require the establishment of standards of measurement of pressure, temperature and volume. It was going to be necessary to carry out experiments at elevated pressures, and over substantial temperature ranges. This called out for design and construction of specialized apparatus that would require the effort of skilled machinists and glass blowers working in a first-rate machine shop. Thus, Kamerlingh Onnes founded his famous school for instrument makers, which assured a steady supply of highly skilled craftsmen to his own laboratory and to other institutions in the Netherlands for many decades to come.



Heike Kamerlingh Onnes as a professor at the University of Leiden.
Senaatskamer. Collectie Academisch Historisch Museum, Universiteit Leiden.
Copied with permission.

6.2 *Measurement and calibration of pressure*

The established leaders in the field of pressure measurement were the French high-pressure experts Amagat and Cailletet. Although he was impressed and inspired by the boldness of design and experimentation of the French scientists, Kamerlingh Onnes had no tolerance for what he considered the unreliability of many of the reported results.

Kamerlingh Onnes devoted major effort to the establishment of standards of measurement. In particular, the standardization of pressure measurement took great effort. The commercial Bourdon-type pressure gages, in which a flattened metal tube, wound in a circle or spiral, unwinds under the influence

of internal pressure, needed calibration. For pressures up to a few atmospheres, comparison with a mercury manometer was feasible. Beyond that, every researcher had to devise his own pressure scale and calibration. Amagat was experimenting with dead-weight gages, pistons of well-defined diameter closely fitting into a matching cylinder filled with oil. The piston is loaded with a known mass of weights and the oil is pressurized. Once the piston floats, the pressure generated in the oil is proportional to the ratio of the mass of the piston plus its load to the area of the piston. The effective area of such gages cannot be calculated very accurately from their dimensions. Cailletet and Amagat had calibrated their laboratory pressure gages up to 400 atmospheres with respect to mercury manometers placed in church towers and mine shafts.

In principle, pressure could be measured by making use of the ideal-gas law, $PV = RT$. If an ideal gas is compressed at constant temperature, the volume decreases in inverse proportion to the pressure. Compression may be carried out in the Cailletet tube, an inverted glass U tube, dipped in mercury (Ch. 4.2 and Ch. 6.4). The pressure in a test system and that in the Cailletet tube serving as a reference are compared by means of a U-tube partially filled with mercury. The early work at the Leiden Physics Laboratory used a Cailletet tube filled with air for pressure calibrations above a few atmospheres.

A serious limitation of this method is that ideal gases do not exist. While for a gas such as air departures from ideality are small at lower pressures, deviations invariably get larger when the pressure rises, and exceed a percent at pressures above fifty atmospheres. One can correct for this non-ideality if the effect is known. In the early years of his laboratory, Kamerlingh Onnes used literature data on gas non-ideality at moderate pressures from Regnault, dating back to 1840-1870, and, more recently, from Amagat (1884), who measured P - V data up to 400 atmospheres in the mid-1880s.

This dependence on French pressure calibration and measurement methods was not satisfactory to Kamerlingh Onnes, and he proceeded to establish his own pressure calibration facilities. He designed and built a composite manometer, consisting of 15 glass tubes each about 3 m high, mounted side by side on the wall of the laboratory. The pressure generated at the bottom of each manometer was transferred to the top of the next one through a gas-filled capillary. By 1898, this apparatus was operational, see Kamerlingh Onnes (1898). Around 1890, however, when Leiden graduate student Kuenen started his measurements on mixtures described in this chapter, calibration of Bourdon gages at the Leiden Laboratory was still done by filling a Cailletet tube with a near-ideal gas such as air, measuring the change of volume starting at standard conditions, and correcting for gas non-ideality using data from the French experts.

The present-day unit of pressure is the newton per square meter (N m^{-2}), or pascal (Pa), a metric unit prescribed by the *Système International* (SI). In this book, this unit is used only if reference is made to modern work. European researchers mostly used the atmosphere, the pressure exerted by a column of mercury 76 cm tall at standard conditions of temperature and acceleration of gravity. One standard atmosphere equals 1.01325×10^5 Pa. For the historical accounts, we use the units reported in the original papers.

6.3 *Thermometry*

Thermodynamics provides the scientists with an absolute temperature scale. The pressure of an ideal gas confined to a constant volume can serve as a realization of the absolute temperature scale. The ratio of the pressure at the temperature of interest, to that at a reference temperature, presently the triple point of water defined as 273.16 K, equals the ratio of the temperature of interest to that at the reference point. Such a device is called a gas thermometer. It suffers from the same problem as the gas manometer: ideal gases do not exist. For the thermometer, the problem is somewhat easier to address than for the manometer, since gas thermometers can be used at low pressure where non-idealities are small. At the Leiden Physical Laboratory, a great deal of effort was invested in gas thermometry. It effectively served as the thermometry standards laboratory in the Netherlands for a good part of the 20th century.

Gas thermometers are difficult to operate. The first practical alternative instrument was the mercury thermometer, which was usually calibrated at the melting and boiling points of water, defined as 0°C and 100°C, respectively, on what was then called the Celsius scale. A ruler, mounted along the mercury capillary, was divided into 100 equal parts, each division equaling 1°C of temperature. A high-quality mercury thermometer allowed temperature resolution to 0.01°C.

The symbol °C used in those days is not precisely equivalent with the modern symbol used for corresponding SI unit. When the symbol is used in this book, it refers to the usage of the original work. We have mostly refrained from converting reported temperatures to the Kelvin scale.

Calibration of a mercury thermometer with respect to the absolute thermodynamic scale was, of course, quite another matter. Careful inter-comparison of high-quality, properly calibrated mercury thermometers by Chappuis (1888) revealed disagreements of the order of 0.1°C in the middle of the range from 0°C to 100°C.

Improvement of gas thermometry would remain an ongoing task at the Leiden Laboratory; better *P-V* data became available, reaching to low densities; nonideality corrections became more reliable; and the uncertainty

of realization of the absolute temperature scale decreased. Parallel to this effort, the design and construction of precise practical devices progressed, and this became a major task once the temperature range of the laboratory began to reach to lower and lower temperatures.

At the time that Kuenen started his experiments in Leiden, the mercury thermometers had been calibrated with respect to a gas thermometer, which was, again, a variant of the Cailletet tube.

6.4 *Measurement of density, and observation of phase separation*

The measurement of the density of gases as a function of pressure and the observation of phase separation took place in a Cailletet tube mentioned repeatedly. The Leiden Cailletet tubes were constructed of high-quality, constant-bore glass capillary. Ruled markings on the outside of the tube permitted accurate readings of the position of the mercury level. The volume between subsequent markings were carefully calibrated by weighing the amount of mercury flowing out of the tube as the level was made to drop from one marking to the next.

The gas in the tube was compressed by pressurizing the mercury in the reservoir, so that it mounted in the tube. The volume occupied by the gas was calculated from the level of the mercury in the tube. Starting at normal atmospheric pressure, the higher densities were calculated from the change in volume of the gas. The pressure of the gas equals that of the pressurizing medium in the mercury reservoir, corrected for the level difference of the mercury inside and outside the Cailletet tube.

In order to improve its accuracy, Kamerlingh Onnes made the following changes in the Cailletet tube arrangement (Fig. 6.2). He added a reservoir to the lower end of the tube, so that the gas was pre-compressed before entering the tube and would still occupy a volume large enough to be accurately measured even at the upper pressure limit. The glass reservoir resided in the pressurized part of the system, so that the wall did not have to sustain large pressure differences. The Cailletet tube proper was heavy-walled, so that it could withstand the pressure difference across the wall. It was surrounded by a glass cylinder, through which a temperature-controlled fluid was pumped. Typically, this fluid was a vapor generated by a liquid bath boiling at controlled pressure, and thus at a constant temperature. The vapor was re-circulated, and different liquids were used for reaching different temperature ranges.

The instrument was used for measuring the pressure-volume relation of the gas at constant temperature, and was also useful for visual observation of phase separation, and for determining the relative amounts of coexisting vapor and liquid phases.

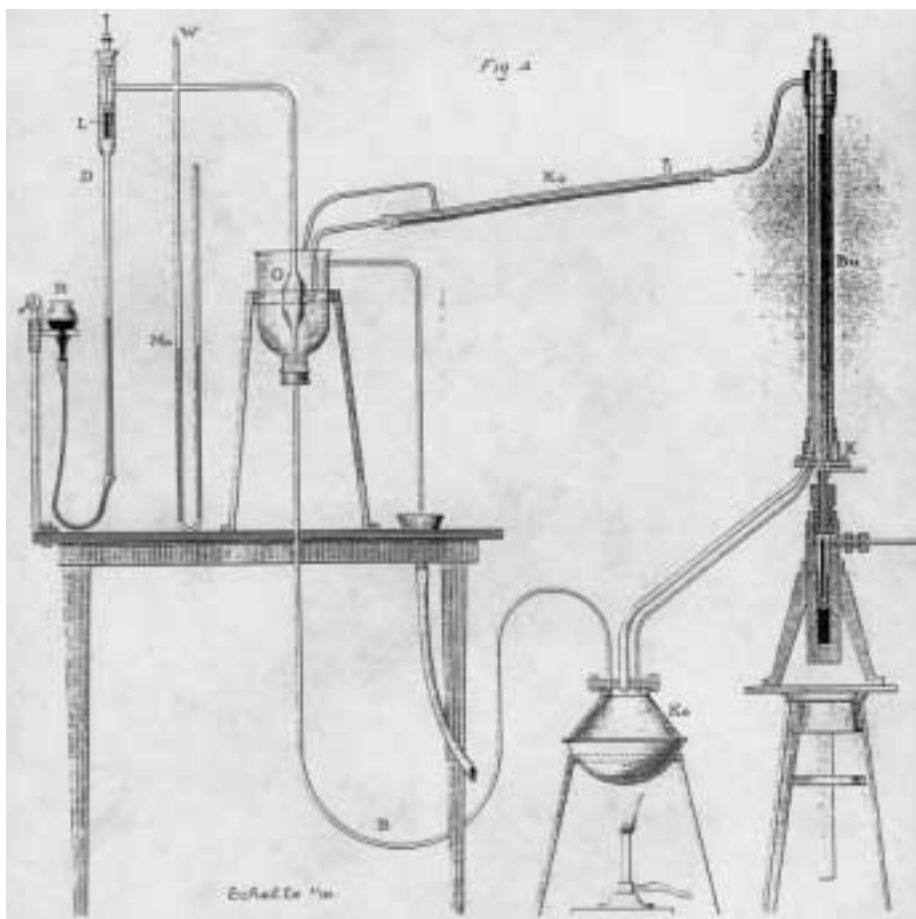
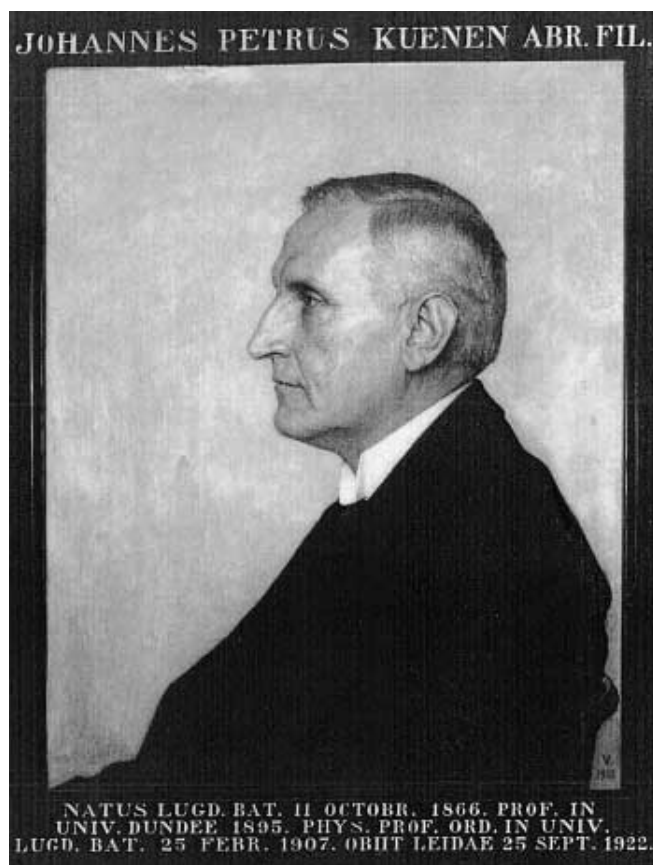


Figure 6.2 Kuenen's Cailletet-tube arrangement for P - V measurements and observation of phase separation at constant temperature. The Cailletet tube, dipping into a pressurized mercury reservoir, is shown on the right. The top part is heated by means of the vapor of a liquid, which boils in kettle Ke under controlled pressure, condenses in Ko , and returns to Ke through the O , and B . Copied from Kuenen (1893b), Plate VII.

6.5 *Kuenen performs the first measurements on gas mixtures*

6.5.1 *Kuenen's background.* It is hard to overestimate the impact on the Leiden experimenters of Van der Waals's theory of mixtures and his model of the interaction of a transverse and a longitudinal plait (Ch. 4.8.2). Immediately after the first Academy presentation was made by Van der Waals in 1889, Kamerlingh Onnes directed a promising graduate student to begin experimental tests of Van der Waals's theory. Johannes Petrus Kuenen (1866-1922) was born in Leiden, the son and grandson of theology professors. He began his physics studies in Leiden in 1884. He obtained his doctorate in 1892, earning a gold medal for his thesis. This gifted experimentalist was the first in the world to produce reliable data for a number of vapor-liquid binary mixtures. His laboratory results were sent to Van der Waals, and, in close consultation between the latter and the Leiden experimentalists, the results were interpreted. From 1892 onwards, Kuenen published a series of discoveries. He is known for his discovery of the phenomenon of retrograde condensation, but his contributions to the knowledge of binary fluid phase diagrams were equally fundamental and interesting. In this chapter, only his Leiden work concerning phase behavior of binary mixtures will be discussed. His later work on the various phase behaviors of fluid mixtures, performed after he moved to the United Kingdom, is described in Ch. 7.4. Kuenen's careful refutations of controversial studies of the critical point, concurrent with his early work on mixtures, are covered in Ch. 10.11 and 10.13.

6.5.2 *The first reliable experiments on fluid mixture phase separation.* The model surface in Van der Waals's paper (see Fig. 4.1, 4.2c), showing three coexisting phases, provoked the interest of the Leiden experimenters. Liquid-liquid phase separation was quite well known in the 19th century. As is clear from his 1893 publications, however, Kuenen's motivation was to find the liquid-liquid phase separation in the presence of a pressurized vapor, and to reach into the region of vapor-liquid criticality in such a system. Several investigators had already reported seeing an additional liquid phase in a binary vapor-liquid system with carbon dioxide as one of the components. Kuenen decided to study the system carbon dioxide-methyl chloride. The second component has a critical temperature of 141°C, much higher than that of carbon dioxide, 31°C, but methyl chloride has a lower critical pressure. The choice of carbon dioxide is obvious: it was one of the best characterized fluids with an easily accessible critical point. Kuenen does not mention what motivated him to choose methyl chloride as the second component, but the compound was available in the laboratory in large quantities. With its low boiling point of -90°C, it was used in the first of the refrigeration cycles in the air liquefaction cascade.



Johannes Petrus Kuenen as a professor at the University of Leiden.
 Senaatskamer. Collectie Academisch Historisch Museum, Universiteit Leiden.
 Copied with permission.

The publications on this system, see Kuenen (1892a,b, 1893a,c, 1894c: Leiden Communications 4, 7, and 13), form a veritable breakthrough in the understanding of fluid mixture behavior. It must have disappointed Kuenen (1892a,b) to report a negative result on the first mixture he studied: no three-phase region. What he did discover, however, more than made up for this disappointment.

That he did not find three-phase coexistence was related to his conclusion that all preceding work on vapor-liquid binary mixtures had been unreliable. None of the earlier experimenters had paid attention to the slowness of equilibration in a fluid mixture confined to a tall tube. Equilibration by diffusive

processes may take days, rather than hours. Kuenen's simple solution: putting a piece of iron in the Cailletet tube, and moving it up and down by means of an external magnet, revolutionized the study of vapor-liquid equilibrium in fluid mixtures. A mixture, appearing to be in equilibrium, might drop in pressure by several atmospheres after the stirrer was turned on. If Kuenen might occasionally observe an additional liquid phase in the mixture, stirring would make it disappear.

Kuenen also noted the flattening and disappearance of the meniscus, described by Cailletet and Van der Waals a decade earlier when they compressed two-phase mixtures of air and carbon dioxide to high pressure. Kuenen explained this right away as a transient effect, caused by the slow diffusion of material through the interface between two non-equilibrium phases on their way to a homogeneous state. Kuenen (1893b) discarded earlier reports by Wroblewski, Cailletet and Dewar on the existence of two liquid phases in several binary mixtures with carbon dioxide as one of the components. He repeated the experiments in his own stirred apparatus, with negative results.

Kuenen's (1893c) doctoral work consisted of measuring the pressure, volume, and phase split of pure methyl chloride, and of three mixtures of 25, 50 and 75% mole fraction, respectively. In his first publication, Kuenen (1892a) states as his original purpose to derive from the data the constants for the Van der Waals equation for the pure components, in order to construct from them the Van der Waals isothermal Helmholtz-energy surface for the mixtures. He quickly gave up that attempt after he found that the Van der Waals equation was not able to describe the pure-component data satisfactorily, thus reconfirming the insufficiency of that equation for an accurate description of fluid properties, by then well recognized by the Leiden group.

His inability to formulate a mixture Helmholtz energy set him free to select a different system of independent variables, more suited for representing his experimental observations than the volume and concentration used by Van der Waals. Since pressure and temperature at the phase boundaries for a mixture of constant composition are the prime observed data, Kuenen (1894c) introduced the pressure-temperature diagram, drew the critical line, and inserted loops of constant composition. Thus, for the first time, phase diagrams appeared which a modern chemical engineer recognizes immediately (Fig. 6.3). Also, by that time in Leiden, preference is given to the terms 'critical point' and 'critical line' over 'plait point' and 'plait point curve.'

The critical line connects the critical points of the two pure components. Along the critical line, each binary mixture of constant composition has a unique critical point, according to Gibbs's phase rule. A compression of a gaseous mixture at constant temperature occurs along a vertical path in this

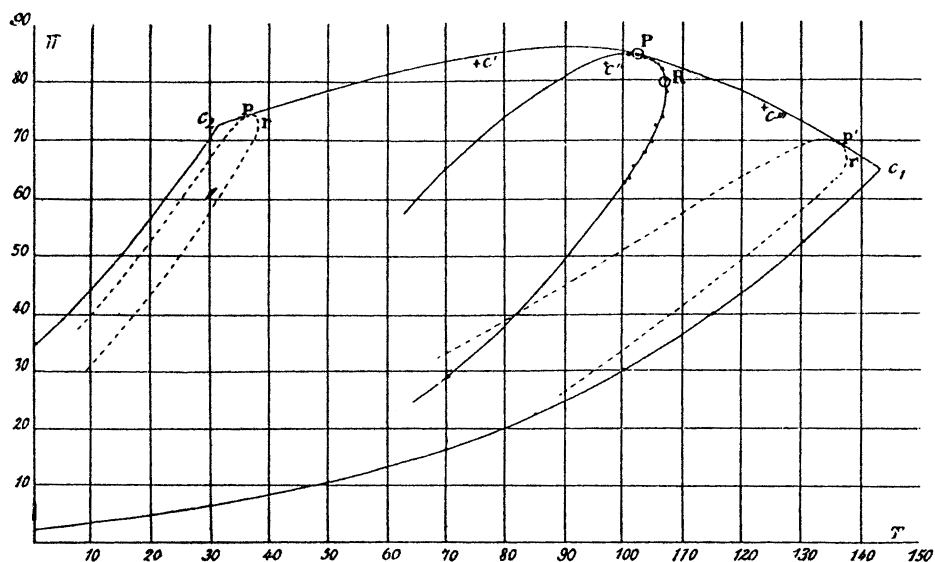


Figure 6.3 The phase behavior of a mixture of carbon dioxide, critical point C_2 , and methyl chloride, critical point C_1 , in a pressure-temperature diagram. The vapor pressures of the two pure components are shown; so are mixture critical points P on the critical line connecting C_1 and C_2 . The loops are curves of constant composition. The part of the loop to the right of P is the dew curve, along which the first drop of liquid forms on compression. The part to the left of P is the bubble curve, where the last drop of liquid disappears on compression. Between P and R on the dew curve, the phenomenon of retrograde condensation of the first kind takes place. Copied from Kuenen (1894c), Fig. 1.

diagram. Starting at low pressure, the gaseous mixture forms the first drop of a liquid phase, of different composition, at what is called its dew point. As it condenses, the liquid level rises and the pressure increases. This is different from the condensation of a pure component, which progresses at fixed pressure. Finally, the mixture is condensed completely at what is called its bubble point, the point where the last gas bubble disappears. On further compression, the mixture forms a homogeneous high-density phase, which may be called a liquid.

If the experiment is repeated at different temperatures, a dew curve and a bubble curve are traced out in the P - T diagram. These two curves do *not* represent branches of a coexistence curve. On the constant-composition dew-bubble curve no two points exist that have the same temperature and pressure. The properties of the liquid and vapor phases along the constant-composition dew-bubble curve become equal to each other at the critical point P ,

located on the critical line. At that point, the dew-bubble curve is tangent to the critical line, as proven by Kuenen (1894c). The highest temperature for which the mixture of fixed overall composition can exist in two phases is, in this case, *higher* than the critical point temperature of that mixture. This maximum temperature is marked by R on one of the loops in Fig. 6.3.

6.6 *Kuenen discovers retrograde condensation.*

6.6.1 *A liquid phase evaporates under pressure.* The first new effect that Kuenen (1892b) reported and explained qualitatively on the basis of Van der Waals's theory of mixtures, is that of retrograde condensation. Kuenen observed that when he compressed the mixture at a composition between that at the critical point P and that at the extremum R, a liquid phase would appear when the dew curve was crossed. On raising the pressure further, the liquid level would rise, reach a maximum, and then decrease again and disappear. This was simply unheard of in the condensation of a one-component fluid. On observing Fig. 6.3, it is clear why this happens. The path chosen is a vertical line running between P and R. All points on the dew-bubble curve that lie to the right of P are located on the dew curve. Thus, when entering the two-phase region from the low-pressure side, the mixture is in a dew-point state where the first drop of liquid forms, while on exiting, it is again in a dew-point state where the last drop of liquid disappears. Kuenen calls this *retrograde condensation of the first kind*.

As Kuenen (1894c) remarks at the end of Comm. 13, it is also possible for retrograde evaporation, or *retrograde condensation of the second kind*, to occur, in which, on expansion of the liquid, a vapor bubble forms, grows, and then declines and disappears. This happens when the point R is located on the bubble side of the dew-bubble curve. Kuenen (1894c) gives a possible scenario shown here in Fig. 6.4. The two components have almost the same critical temperature, but very different critical pressures. The top dew-bubble curve shows retrograde condensation of the first kind, but the bottom one shows retrograde condensation of the second kind. In practice, the latter happens far less frequently than retrograde condensation of the first kind.

6.6.2 *A controversy with Van der Waals.* Although Kuenen, in his publications, refers to Van der Waals's theory of mixtures at every occasion, the master was not always satisfied with the credit he received. A piqued letter by Van der Waals (1894a, Oct. 19) to Kamerlingh Onnes takes issue with the claim that Kuenen *discovered* the phenomenon of retrograde condensation. In Van der Waals's view, for the good reader his theory contained all there is to know about the behavior of the binodal, and Kuenen's work, valuable as it

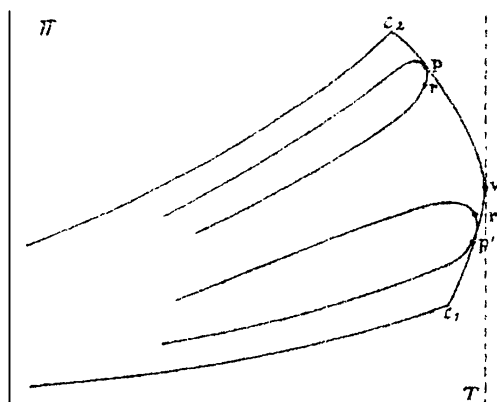


Figure 6.4 The condition for retrograde condensation of the second kind, in a pressure-temperature diagram. Retrograde evaporation should happen below the temperature extremum v in the plait point curve, in the region between r' and P' on the bubble curve. Copied from Kuenen (1894c), Fig. 2.

was, merely *confirmed* it. Although he concedes that he had not worked out many details in the published paper, he had decided to wait until the Leiden experiments were finished. He claims that he not only knew about what Kuenen felicitously calls retrograde condensation, but also had mentioned it in conversations. He feels Kuenen was not justified in claiming priority.

Kamerlingh Onnes (1894, Oct. 20) answered his friend the next day. Remarkably, he immediately places a protective shield around his pupil Kuenen. He takes full responsibility for any papers originating from his laboratory, because they all require his approval:

...so that justice is strictly maintained, and preferably somewhat less, but surely never more is claimed than what may be considered, in good faith, as original work. This simplifies matters, the question is not 'what does Kuenen think he may claim?' but 'what may Kuenen, according to my judgment, justly call his own work?' [Translated from the Dutch.]

A spirited defense of his pupil follows. Kamerlingh Onnes emphasizes that Kuenen has maintained in all his writings that Van der Waals's theory opened the way to the understanding of retrograde condensation. Even though this theory implies this phenomenon, however, Van der Waals had never stated this explicitly. Kuenen was the one who first said: 'something very special must happen in that region, something that is different from ordinary condensation.' Thus, Kamerlingh Onnes goes as far as claiming that Kuenen not only discovered, but *predicted* retrograde condensation.

The formulation of a theory and the application to a specific prediction are two incomparable entities, but there is room for the one next to the other. The prediction by Kuenen will be viewed as proof of the fertility of your theory. Many others are sure to follow, whose remarkable character and their deviation from common intuition, though perhaps obvious, have not been indicated by you, and may likewise be rightly called predictions. [Translated from the Dutch.]

Two more pages follow in the same vein, proof of how seriously Kamerlingh Onnes took this matter. Kamerlingh Onnes thus pointedly puts Van der Waals in his place, and finds Kuenen's claim fully justified. He even strengthens it from 'discovery' to 'prediction and discovery.'

An answer from Van der Waals (1894b, Oct. 21) was written the next day. In those days, Dutch mail was sorted in special postal car of the trains that ran frequently between cities in the West of Holland, facilitating these prompt responses. Van der Waals readily agrees that, driven by a desire to be brief, he has been wrong in limiting himself to the main points, but omitting what he considers issues of less importance. Furthermore, when he thinks something is clear, he wrongly assumes that just indicating the result is sufficient for others as well. He accepts that he will have to suffer the consequences of his own mistakes in this respect. Nevertheless, he feels somewhat pained because he had held back nothing in discussions of the behavior of mixtures with his Leiden friends, including discussions about the relation of tangent point and plait point. He would have appreciated it if trust had been answered with trust. Pages follow about the interpretation of the word 'predicting'. Ultimately, he states he is not convinced by Kamerlingh Onnes's arguments. The letter ends, however, in a conciliatory mode. Kamerlingh Onnes is invited for dinner at Van der Waals's home the coming Saturday. A moving apology ends the letter:

If this letter contain anything that might hurt you, please forgive me – I did not mean to do so. But when I am engaged in polemics, I feel the need to put matters sharply. But sharp, meaning correct, may easily deteriorate to sharp, meaning cutting. [Translated from the Dutch.]

6.6.3 *Retrograde condensation rediscovered.* Since the critical point and the temperature extremum of a dew-bubble curve in general do not coincide, there is always a region of retrograde condensation in a fluid mixture, but it may be so small that it is hard to find. In the natural gas industry, however, the retrograde region between the critical point and the temperature extremum R can be huge, because of the presence of admixtures of low volatility, such as long-chain alkanes. When deep-well gas drilling began in the 1930s in the United States, crews were often taken by surprise when the

gas would partially liquefy (or worse, solidify) as the pressure was released. The story goes that the Dutch native George Uhlenbeck, then a physics professor at the University of Michigan, reminded the puzzled engineers of the phenomenon of retrograde condensation, discovered in the Netherlands forty years earlier. History repeated itself once more, when gas drilling began off the coast of Great Britain in the 1960s. Engineers at the coastal pump station in Bacton, who found their lines blocked when they reduced the gas pressure, turned for help to John Rowlinson (2001), professor at Imperial College, who was able to enlighten them about retrograde condensation.

A phase diagram such as that found by Kuenen, with a simple connected critical line and no indication of an additional phase split in the liquid phase, is presently called a Type-I phase diagram, in the terminology of Van Konynenburg and Scott (1980) (*cf.* Ch. 7.2).

6.7 Kuenen discovers critical azeotropy

For the next system investigated, Kuenen (1895a) had the objective of finding retrograde condensation of the second kind. In that case (Fig. 6.4), the critical line in the P - T diagram must be almost vertical. Thus, two components of almost the same critical temperature but very different critical pressures must be mixed. Kuenen's choice was a mixture of ethane and nitrous oxide, N_2O . In contrast to the first mixture he studies, these two gases have almost the same critical temperature, but the critical pressure of nitrous oxide is over 70 atmospheres, while that of ethane is just below 50 atmospheres.

Again, Kuenen had a negative result for an unanticipated reason, which allowed him to make another discovery. It appeared that the critical line went through a *minimum* in temperature well below the critical temperatures of the two components (Fig. 6.5), the first time that such an observation was made.

In the case of a temperature minimum in the critical line, the mixture will display azeotropy (Ch. 4.9), which means that in the P - T diagram there is a locus of states for which the compositions of vapor and liquid phase are identical, although the other properties are different. At this locus, the vapor pressure is a maximum at the given temperature, and therefore the azeotropic line in the P - T plane lies above the vapor pressure curves of both pure components. In the mixture studied by Kuenen, the azeotropic locus is almost independent of temperature, and occurs near a mole fraction of 20% of ethane (Fig. 6.5). Negative azeotropy, in which the pressure goes through a minimum, is also thermodynamically possible, although less frequently encountered than the positive azeotropy found by Kuenen.

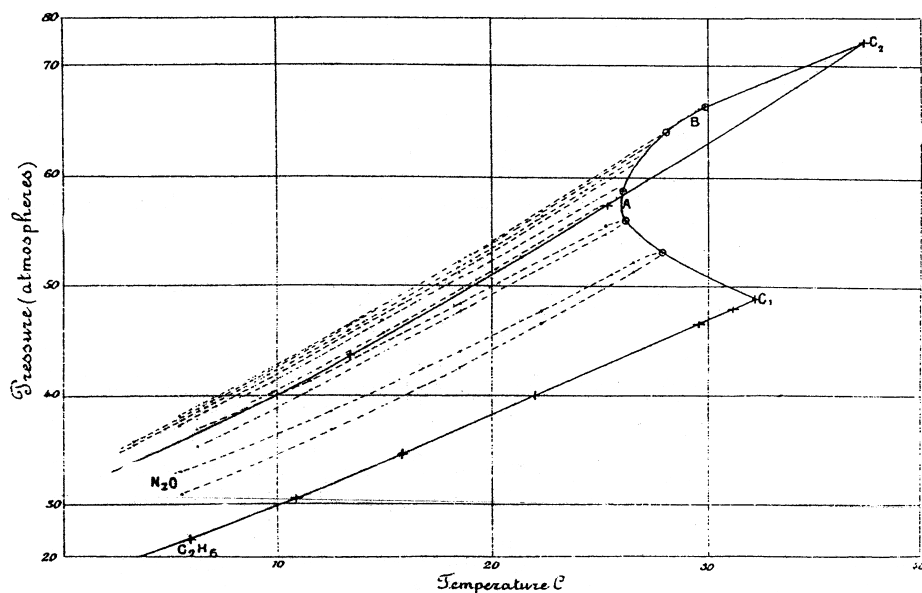


Figure 6.5 Critical azeotropy in the system ethane-nitrous oxide. The critical line passes through a temperature minimum in P - T space. The azeotrope ends tangentially to the critical line at B. All dew-bubble curves are quite narrow, compared to those in non-azeotropic mixtures, such as in Fig. 6.3. Copied from Kuenen (1895), Fig. 2.

Azeotropy was a known phenomenon at this time. The pressure maximum, for instance, had been reported by Guthrie and by Konowalow, and is the reason these mixtures cannot be separated by distillation. Usually, however, the azeotrope leaves the mixture phase space at one of the edges, $x = 0$ or $x = 1$, before it reaches the critical line. Kuenen's mixture, however, was the first in which azeotropy had been traced all the way up to the critical line. He found that the locus ended on the critical line at the azeotropic point B in Fig. 6.5. After receiving Kuenen's results, Van der Waals (1895a) proved that the azeotrope must be parallel to the critical line at this point, as a general consequence of the thermodynamics of phase coexistence. A few years later, Van der Waals's student Quint (1899), trying to find retrograde condensation of the second kind, studied the system ethane-hydrochloric acid in Amsterdam, again with negative results. This mixture turned out to be an azeotropic system very much like that studied by Kuenen.

If there is an azeotrope in the middle of a phase diagram, the difference in composition between dew and bubble curves remains small over the entire composition range, compared to composition differences between such curves

in non-azeotropic mixtures. Compare the widths of the dew-bubble curves in Figs. 6.3 and 6.5. Narrowness of dew-bubble curves implies that the points P and R are very close together, precluding detailed study of retrograde behavior. Although Kuenen describes in detail all retrograde phenomena to be expected theoretically in the case of a divided plait such as that in Fig. 6.5, the limited experimental resolution did not allow him to observe them.

Kuenen next describes the phenomena in the V - x plane, Fig. 6.6 following the example of Korteweg (Ch. 5, Ch. 7.3) and Van der Waals (Ch. 4). At temperatures below the minimum in the critical line, the plait is a transverse plait running roughly parallel to the x -axis over the full range of compositions. Compressing the mixture at a temperature between that minimum and the ethane critical point, however, the critical line in Fig. 6.5 is crossed twice. The starting point is a two-phase system. This ends in a critical point when the critical line is crossed for the first time. Then, a homogeneous region is

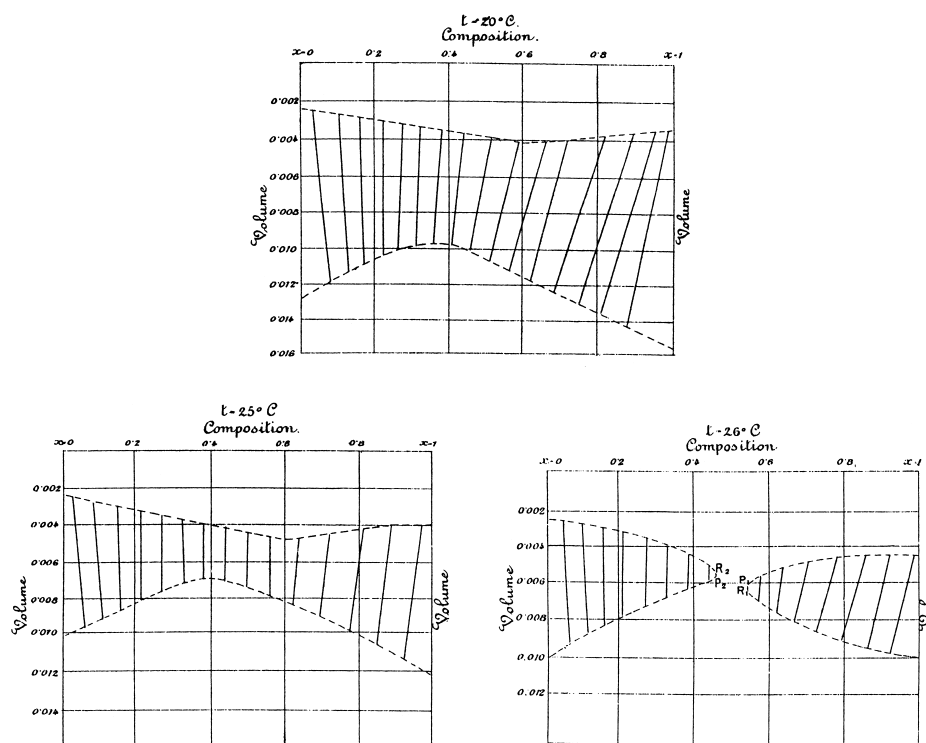


Figure 6.6 Phase separation in V - x space for a binary azeotropic mixture at increasing temperature. The transverse plait splits into two parts that recede towards the $x = 0$, 1 axes as the temperature rises. The compositions of vapor and liquid differ little. Copied from Kuenen (1895a) Figs 3, 4, 5.

traversed, after which the second part of the plait opens up at a second critical point. These two critical points approach each other when the temperature approaches that of the minimum, where they coalesce in a homogeneous double critical point, and disappear on further decrease of the temperature (Fig. 6.6). For lower temperatures, the plait runs across the entire surface uninterrupted. Kuenen gives reference to Korteweg (1891a,b) who indeed described this case, as discussed in Ch. 5.4.2, and shown in Fig. 5.3.

6.8 *Kamerlingh Onnes builds space models*

The thermodynamic free energy of a one-component fluid is a function of two independent variables; the number of independent variables increases as the number of components. A two-dimensional representation can have only one independent variable. So in order to obtain a visual representation of the thermodynamic surface, scientists are forced to keep one or more variables constant (sections) or to project invariant points and univariant curves onto a plane. This makes it difficult to get a good grasp on the spatial relations, and to figure out how the representation changes as a different set of independent variables is chosen. In addition, the need to roll tangent planes over such surfaces in order to trace out coexistence curves is quite a challenge to the insight.

Even before Gibbs (1873) published his paper on the geometric representation of thermodynamic surfaces, scientists felt the need for three-dimensional representations of surfaces, which we will call space models. Thus, James Thomson built a plaster P - V - T space model representing Andrews's data for carbon dioxide. As discussed in Ch. 4.3, Gibbs (1873) described the properties of what he called the 'primitive' (fundamental) $U(S, V)$ surface, based on Andrews's data. Maxwell's (1875, Ch. xii) graphic description of Gibbs's $U(S, V)$ surface suggests it existed physically. Maxwell himself built two plaster $U(S, V)$ models for water, including one solid and two fluid phases, and donated one to Gibbs. See Rowlinson (1988), p. 6.

The Dutch School pioneered the building of space models for thermodynamic surfaces of binary mixtures. Ch. 4.8 describes the space model that Van der Waals (1890) constructed to represent the isothermal Helmholtz energy of a binary mixture that shows a transverse and a longitudinal plait, and a triple-tangent plane (Fig. 4.1, 4.2c).

Kamerlingh Onnes began work on constructing such surfaces at the time that Kuenen wrote his thesis. At the end of his doctoral thesis, Kuenen wrestled with the problem of finding an equation that could represent his P - V - T - x data in the system carbon dioxide-methyl chloride. Finding the Van der Waals equation woefully inadequate, he modified it empirically, and made the parameters temperature-dependent. Instead of using mixing rules for the

parameters a_x and b_x , he calculated these values from the experimental data for mixtures at the experimental compositions of $x = 0, 1/4, 1/2, 3/4, 1$. Kamerlingh Onnes (1900a) integrated this modified equation, thus obtaining an expression for the Helmholtz energy, which he denotes by ψ , following Gibbs. He then used the equation to calculate the isothermal Helmholtz energy as a function of volume for a chosen temperature and for the chosen values of the composition. Carefully drafted charts accompany this paper, clearly revealing the plait in projections on various planes. Thus, for a chosen temperature between the temperatures of the two components, he had a space model $\psi(V, x)$ constructed in plaster, based on the $\psi(V)$ and $\psi(x)$ curves he had calculated and graphed. If a glass plate covered with ink is rolled over the surface, it will nicely trace out the connodal. A picture of the model is shown in Fig. 6.7.

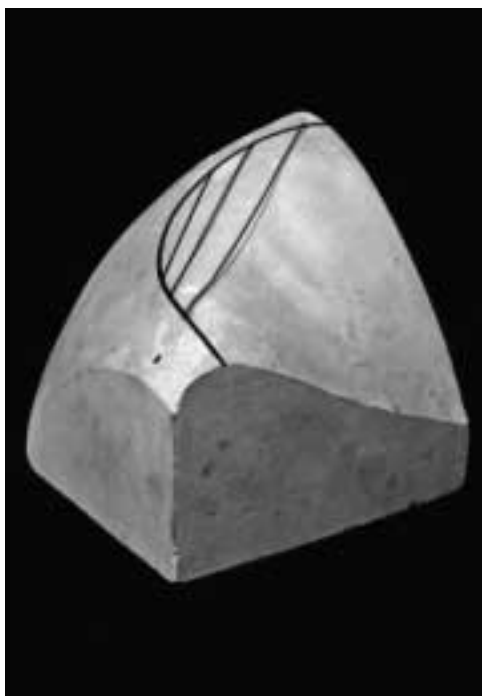


Figure 6.7 A plaster model of the Helmholtz energy surface for the system carbon dioxide – methyl chloride at 100°C, between the critical temperatures of the pure components, built by Kamerlingh Onnes and Reinganum (1900a). The negative of the isothermal Helmholtz energy ψ points upwards, the volume runs from front to back, and the mole fraction of carbon dioxide runs from right to left. A plait extends from the methyl chloride side, on the right, toward the center part of the surface. There it ends in a plait point. The connodal (coexistence curve) and several tie lines are indicated. Copied with the permission of Museum Boerhaave, Leiden.

Coexisting points are connected by wires. This model is an example of an actual isothermal Helmholtz energy representation of a real mixture.

As more mixture data became available, Kamerlingh Onnes and coworkers constructed several of such surfaces. For educational purposes, they constructed plaster Gibbs energy models and equation of state models for pure fluids as well, based on mathematical formulae for these properties. Some models include solid phases. The model shown in Fig. 6.7, as well as over a dozen other models, are part of the collection of the Boerhaave Museum in Leiden.

6.9 *Kuenen moves on*

Kuenen served as the conservator of the Leiden physics laboratory from 1893 to 1895. He then left the Netherlands. After a brief postdoctoral stay with Ramsay in London, he became a professor of physics at the University of Dundee in Scotland in 1896. In 1906, he returned to Leiden, to a chair in physics. While at Dundee, he successfully resumed the quest for liquid-vapor phase equilibrium in the presence of a second liquid phase. The discoveries he made at the University of Dundee are described in the next chapter.

7. Fluid phase diagrams – Korteweg, Kuenen, and Van Laar

7.1 Introduction

This chapter traces the history of the discovery of the different types of phase behavior that occur in binary fluid mixtures. Theoretical and experimental investigations took place in the Netherlands between 1890 and 1906, and all six different types of binary fluid phase diagrams presently recognized were found in that period. Amazingly, the Van der Waals equation for mixtures was proved capable of producing all but one of these six types.

A phase diagram displays the regions occupied by the different phases of a system, the boundaries that separate those regions, and the special points present in the system, as a function of two independent variables. A practical choice of variables is that of pressure P and temperature T , measured directly in the laboratory. The phase rule (Ch. 4.3) states that for a one-component system the coexistence curves, be it vapor-liquid, solid-vapor or liquid-vapor, are monovariant: they are represented by curves in the P - T phase diagram. These curves separate regions of phase space occupied by a vapor, liquid or solid. The critical point as well as triple point(s), are invariant, and are therefore points in the phase diagram. A simple P - T phase diagram is shown in Fig. 7.1. It reveals, at a glance, what state the system is in at given temperature and pressure.

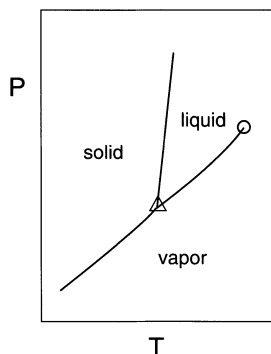


Figure 7.1 Phase diagram in P - T space for the simplest case of a one component system. The boundaries between the regions occupied by the solid, liquid and vapor phase are indicated in a pressure-temperature diagram. Special invariant points are the triple point Δ , where vapor, liquid and solid coexist, and the critical point O , where vapor and liquid become equal to each other.

As discussed in Ch. 4.3, in a binary mixture all dimensions step up by unity because of the extra degree of freedom. Therefore, in addition to the characteristic curves and points of the two pure components, monovariant critical curves, three-phase curves (triple lines) and azeotropes, as well as invariant quadruple points appear in the P - T phase diagram of a binary mixture.

Even in the absence of solid phases, binary-mixture phase diagrams are much more complicated than those for one component. Instead of one basic type, there are at least six, and several of these types have distinct subtypes and variants. This chapter describes how scientists learned about binary fluid phase diagrams.

Gibbs's principles of heterogeneous equilibrium enabled scientists to deduce the shape of a phase diagram on the basis of limited experimental information. The Dutch thermodynamicists excelled in this area, particularly Amsterdam chemist Hendrik Willem Bakhuis Roozeboom (1854-1907). In 1895/96, as a student in Leiden, he interacted intensively with Van der Waals, who showed him how Gibbs's phase rule could be used to interpret his experimental studies of solid precipitation from a number of hydrates, see Kipnis *et al.* (1996), pp. 157-159. Bakhuis Roozeboom became a chemistry professor in Amsterdam in 1896. He founded a school that specialized in fluid – solid phase equilibria up to high pressures. Well known chemists educated by Bakhuis Roozeboom, such as E.H. Büchner and F.E.C. Scheffer, as well as his successor A. Smits, followed in his steps in the early part of the 20th century. This work was very influential in geology and metallurgy; it falls mostly outside the scope of this book, but its history would well merit a separate study. The work on fluid phase equilibria described in this book is all based on, or inspired by Van der Waals's equation of state for binary mixtures.

Around 1900, experiments were carried out in Leiden specifically to investigate binary fluid phase diagrams that include fluid criticality. We have seen in Ch. 6 how Kamerlingh Onnes directed his student Kuenen, around 1890, to begin the investigation of fluid phase equilibria. This chapter will show how Professor Kuenen discovered two types of previously unknown phase diagrams in what were believed to be anomalous systems. These systems were not expected to obey the Van der Waals equation or the theorem of corresponding states because they have at least one associating component.

Van der Waals's (1890) theory of mixtures (Ch. 4) had already proved the possibility of predicting both liquid-liquid and liquid-vapor equilibrium. There was, however, a rather formidable problem when implementing Van der Waals's equation for mixtures. The increased number of parameters, two each for the pure components, and two more for the combining rules for the interactions between components, makes it difficult to sample the parameter space economically. Furthermore, because of the mole-fraction-dependence

of the Van der Waals a and b parameters, the calculation of any thermodynamic properties quickly becomes quite complicated. Finally, the properties of coexisting phases usually cannot be obtained analytically.

The Amsterdam mathematician Korteweg (1891b) was the first to attempt using the Van der Waals mixture equation for calculating phase diagrams. He designed the simplest mixture model he could think of, a mixture of two identical components, with the attractive interaction a_{12} between the two the only variable parameter. Korteweg derived expressions for the various types of critical points and for the spinodals of this mixture. This seemingly oversimplified and unrealistic model would turn out to be fiercely complex as well. Nevertheless, he worked out the various phase diagrams in great detail.

Van Laar, the ‘mathematical chemist,’ made the next attempt to extract exact results from the Van der Waals equation. Unlike Korteweg, he allowed the two components to be different, but adopted the geometric-mean rule, Eq. (4.7), for the interaction parameter a_{12} . This enabled him to obtain exact results for the spinodals and for the plait point line. He published close to a dozen papers on the topic between 1904 and 1906. Van Laar indeed obtained three principal types of phase diagrams presently known to be obtainable from the Van der Waals equation, two of which Kuenen discovered in his experiments. Then the subject rested for more than half a century.

In the 1960s, Robert L. Scott, professor of chemistry at the University of California in Los Angeles, proposed to his student Van Konynenburg that he use a new tool, the computer, to explore the phase behavior of the Van der Waals equation of state for binary mixtures. They exhaustively investigated the case of constant excluded volume b . The availability of this global study makes it possible to place the earlier work within a more comprehensive context. As a consequence, the content, significance and accuracy of the early work can be appreciated more fully.

The present chapter will therefore not be presented in chronological order. The experimental results, as well as the two specialized cases studied by Korteweg and by Van Laar, are easier to understand from the perspective of the work of Van Konynenburg and Scott. Thus, an overview of the K&S work will be presented first (Ch. 7.2), after which we will return to the period of 1890-1906, to discuss the work of Korteweg (Ch. 7.3), Kuenen (Ch. 7.4), and Van Laar (Ch. 7.5).

7.2 *Van Konynenburg and Scott (K&S) on the Van der Waals mixtures.*

7.2.1 *Scope of the work.* Van Konynenburg and Scott (1980) published the final results of over a dozen years of work in a comprehensive report containing references to their earlier publications on this topic. We will refer to

it as K&S. In addition, reference will be made to Scott's (1987) review, written at the occasion of his receiving the Hildebrand Award of the American Chemical Society.

The starting point for K&S is Van der Waals's equation of state for mixtures introduced in Ch. 4, Eq. (4.4): $(P + a_x/V^2)(V - b_x) = RT$, with P the pressure, V the molar volume, T the temperature, R the molar gas constant, a_x the attraction parameter characteristic of the mixture, and b_x the excluded volume parameter for the mixture at mole fraction x . The quadratic mixing rules for the mole fraction dependence of these two parameters are given by Eq. (4.5).

Most, though not all, of the K&S work, just as the early Dutch work, is done for components of equal excluded volume b , in which case $b_x = b$. A few caveats are in order. For the Van der Waals equation, this choice implies that the ratio of the critical pressures of the two components equals that of the critical temperatures. Thus, the less volatile component must have the higher critical pressure. Experimentally, there are many counter-examples, for instance, the mixture of carbon dioxide and methyl chloride Kuenen studied (Fig. 6.3), for which the second component has a much higher critical temperature than the first, while its critical pressure is lower than that of the first. Also, the equal- b case has some mathematical peculiarities. For instance, the critical azeotrope does not come in tangent to the critical line, such as happens in experiment (Fig. 6.5), and was proved for the general case by Van der Waals (1895a). Instead, the critical azeotrope intersects the critical line at a point where the latter develops a cusp.

For the case of equal b , K&S characterized the mixture by two parameters, one of which, ζ , describes the relative difference of the attraction parameters for the two pure components:

$$\zeta = (a_2 - a_1)/(a_2 + a_1) \quad (7.1)$$

By its definition, ζ ranges from -1 to +1. The sign of ζ depends on which component is chosen as the first. Customarily, this is the more volatile component, that with the lower critical temperature and the smaller value of a , so that ζ is positive

The other parameter, Λ , describes how strong, relatively speaking, the interaction between unlike components is compared to the average of the interaction parameters for each of the components:

$$\Lambda = (a_1 - 2 a_{12} + a_2)/(a_1 + a_2) \quad (7.2)$$

If the two components have a relatively strong affinity for each other, Λ is negative, and the fluids prefer to be mixed unless they are very different from each other (large ζ). If the interaction between the two components is relatively

weak, Λ turns positive, and the tendency for phase separations of several kinds, the real meat of this chapter, begins to show.

In the footsteps of Van der Waals, Eq. (4.8), K&S integrated the equation of state to obtain the Helmholtz energy, $A(V, x, T) = -RT \ln (V - b) - a_x/V + RT [x \ln x + (1 - x) \ln (1 - x)]$. Here $b_x = b$. They then set up the algorithms for calculating critical lines from Gibbs's criticality conditions, Eq. (4.16). This method is fully equivalent to that used by Korteweg, Eq. (5.6), discussed in Ch. 5.3.6. K&S were able to derive an exact expression for the relation between volume and mole fraction for critical points. This equation is of the seventh degree in both volume and mole fraction, and depends on Λ and ζ . It is listed in K&S Appendix A, along with companion expressions for the

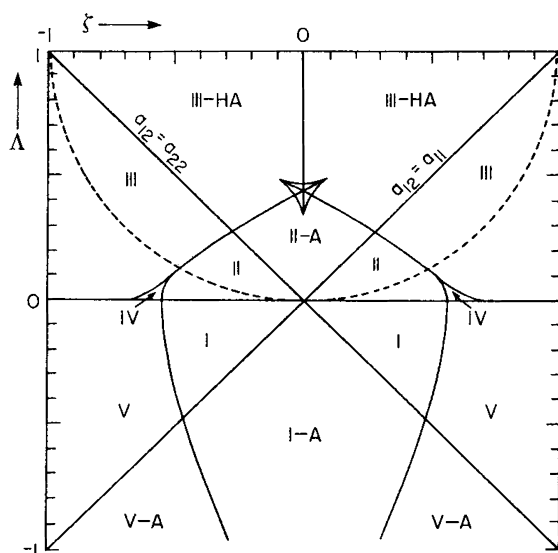


Figure 7.2 The global phase diagram for the Van der Waals binary mixture for equal excluded volumes of the components. Reprinted, with permission, from Scott (1987), Fig. 1. Copyright (1987) American Chemical Society. This figure shows the boundaries between the various types of phase behavior in the Λ, ζ plane. For the equal- b case, the diagram is symmetric around the $\zeta = 0$ axis. Different types of phase behavior are labeled by Roman numerals. The letter A denotes the presence of azeotropy. On the axis $\zeta = 0$, and near it, azeotropy must always occur. The two diagonals in Fig. 7.2 mark the boundaries of azeotropic regions. The other transitions between the various regions occur almost always by passage through a tricritical point, a point where three fluid phases become identical. The solid boundaries marked in Fig. 7.2 represent those choices of Λ and ζ that lead to the presence of a tricritical point. An exception is the boundary between Type IV and Type III, which is a line of double critical end points, points at which a critical line touches a three-phase line. The dashed curve represents the geometric-mean choice for the attractive parameter, Eq. (4.7).

corresponding critical temperatures and pressures. Meijer *et al.* (1990) and Levelt (1995) confirmed these expressions using computer algebra.

For chosen Λ and ζ , K&S numerically solved for the V - x - T - P values along the critical line(s). Phase boundaries were obtained from the Gibbs conditions for phase coexistence, equality of temperature, pressure and chemical potentials. All equations were solved numerically by means of a digital computer. The calculations were carried out on a grid of chosen ζ , Λ values.

7.2.2 The global phase diagram. Fig. 7.2 compactly summarizes the phase behaviors of the Van der Waals binary mixture equation with constant excluded volume. This picture is called a *global* phase diagram, because it represents and classifies the different phase behaviors that the mixture equation can display, depending on the values of the two adjustable parameters ζ and Λ .

7.2.3 The shield region. Near the $\zeta = 0$ axis, in the upper part of the diagram, a small region of very complex phase behavior appears, which is called the shield region. It is shown enlarged in Fig. 7.3, from K&S (1980).

At the time that the K&S work approached completion, Furman *et al.*, (1977), and Das and Griffiths (1979) were working on the phase diagram of the so-called three-state Potts model, investigated earlier by Straley and Fisher (1973), amongst others (Ch. 7.3.5). This lattice model can be made to represent either a three-component liquid mixture, or a two-component

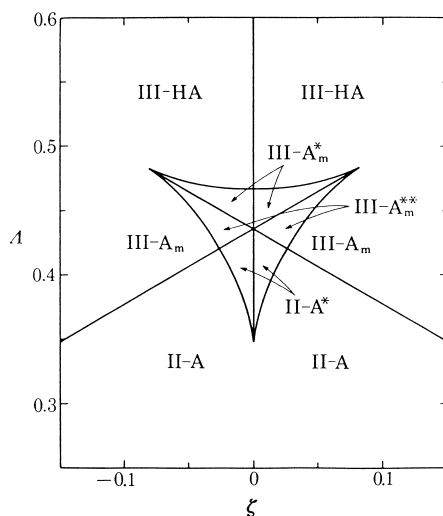


Figure 7.3 The shield region, magnified from Fig. 7.2. Copied, with permission, from Van Konynenburg and Scott (1980), Fig. 38. Copyright (1980) The Royal Society.

compressible fluid mixture. Furman *et al.* (1977) found a region of complex phase behavior, such as coexistence of *four* fluid phases, when the three components are not very different from each other. Furman and Griffiths (1978) then investigated the Van der Waals equation, and found a similar region of complex phase behavior, the shield region in Fig. 7.3, which occurs near $\zeta = 0$, about halfway up the positive Λ axis. K&S (1980) confirmed this, and presented detailed results for the 'symmetric mixture' of two identical components ($\zeta = 0$). It was Korteweg (1891b), however, who sampled the entire region along the $\zeta = 0$ axis almost a century earlier, as will be discussed in Ch. 7.3.

7.2.4 The six types of binary fluid phase diagrams. Representing the binary phase diagrams in the pressure – temperature plane (Fig. 7.4), also from Scott (1987), clarifies the meaning of the Roman numerals in Fig. 7.2.

The types of phase diagrams I–V can be derived from the Van der Waals equation, and have all been found experimentally. In addition, many fluid mixtures have been found to display Type-VI behavior, with a closed-loop region of liquid-liquid phase separation. Type-VI behavior cannot be derived from the Van der Waals equation. Van Laar was able to produce it by incor-

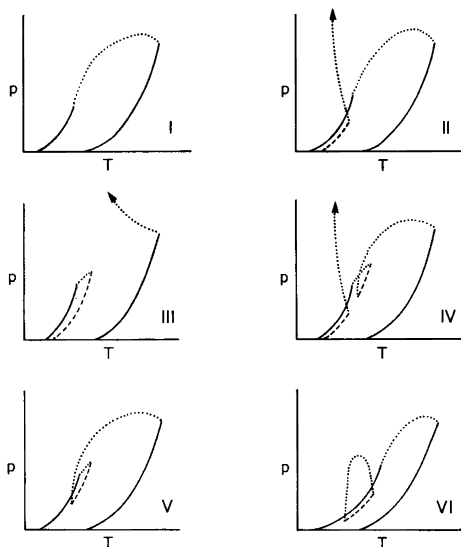


Figure 7.4 Six different types of phase behavior found in binary fluid mixtures. Reprinted, with permission, from Scott (1987), Fig. 2. Copyright (1987) American Chemical Society. Solid lines are the vapor pressure curves of each of the two components. The dashed curves are three-phase lines; they may end in upper (UCEP) or lower (LCEP) critical end points. The dotted curves are critical lines. The six types known to exist in binary fluid mixtures differ from each other in the number of critical lines and the presence or absence of three-phase lines. They are described in detail below.

porating an association reaction (Ch. 7.5.2). A close relative of Type VI, in which the liquid-liquid critical line has two branches running to infinite pressure, is not shown here. Schneider (1963) discovered it experimentally.

K&S introduced the nomenclature for the types shown in Fig. 7.4, and it is still in general use. Boltz *et al.* (1998) recently proposed a less arbitrary, more informative nomenclature, in which the salient features of the phase diagram are coded into its label. Here, we use the K&S nomenclature, allowing the reader to connect more easily with existing literature on the topic.

In engineering texts it is common to use the term ‘critical line’ in cases where a mathematician would use the word ‘curve.’ Thus, critical lines, as well as three-phase lines, are understood to be curves. Only tie lines are straight lines.

The phase diagrams for relatively strong attraction between the components are of Type I and Type V, and are located below the $\Lambda = 0$ axis. The simplest is Type I, for which the mixture critical line connects the critical points of the two components and no further phase separation occurs. A variant of this phase diagram, I-A, arises when the components of the mixture are rather alike (small ζ). See Fig. 7.5, from K&S (1980).

The negative azeotrope AZ lies *below* the vapor pressure curves of the pure components, because at given temperature the vapor pressure of the mixture is lower than that of the two relatively strongly interacting components. The critical line passes through a maximum at the azeotropic point. It is an artifact of the equal- b Van der Waals equation that the critical line develops a cusp where it meets the azeotrope. Van der Waals proved that in the general case the azeotrope is tangent to the critical line. Ch. 6.7 describes how Kuenen sought in vain to find this case experimentally. It is quite rare.

In the Type-V phase diagram, Fig.7.4V, the critical line is interrupted by a three-phase region limited by a UCEP and an LCEP. If an interaction

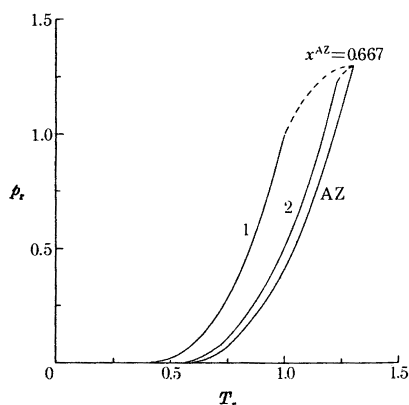


Figure 7.5 Negative azeotropy in a Type-I-A phase diagram in the reduced pressure-temperature plane. Copied, with permission, from Van Konynenburg and Scott (1980), Fig. 5. Copyright (1980) The Royal Society. The curves labeled 1,2 are the vapor pressures of the two pure components. The symbol AZ indicates the azeotrope

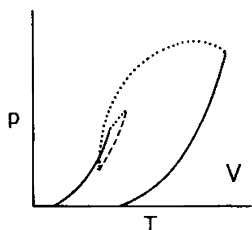


Figure 7.4 V. The Type-V phase diagram results when the difference between the two components is larger than in Type I. A critical line (....) starting at the first-component critical point ends in an upper critical end point (UCEP). If the fraction of second component is increased, it assembles in another liquid phase, and a region of three-phase coexistence (---) forms. As the temperature falls, the two liquid phases become identical at a lower critical end point (LCEP). A second vapor-liquid critical line begins at the critical point of the second component, and ends as a liquid-liquid critical line at the LCEP.

parameter is varied, the three-phase line can be made to shrink and disappear. Type I will return after that. The point of merger of the two critical points is an (unsymmetrical) tricritical point, at which three phases become identical, two liquid and one vapor phase. The phase rule forbids its occurrence in binary mixtures, except in the symmetric case, $\zeta = 0$. In a mathematical representation of binary mixtures in terms of a *continuously* variable parameter, however, tricriticality can occur even in the asymmetric binary. Efremova, a member of Krichevskii's group, was the first to experimentally discover an asymmetric tricritical point in a ternary system. See Krichevskii et al. (1963). Scott, Knobler and coworkers investigated the vicinity of tricritical points in quasi-binary systems in considerable detail. For a review, see Knobler and Scott (1984).

Korteweg's classification of special critical points, discussed in Ch. 5, does not include the tricritical point, but the possibility of tricriticality *is* mentioned in the text book by Van der Waals and Kohnstamm (1912). Also, Korteweg discovered and recognized what is now called a symmetric tricritical point in the symmetric Van der Waals model, see Ch. 7.3.5

For positive Λ , thus for relatively weak interaction between unlike molecules, there is always phase separation in the liquid phase, as well as a three-phase line where two liquid phases and one vapor phase coexist. All phase diagrams have a minimum of two critical lines, one of which runs to high pressures. Types II, III and IV fall in this category, and will be discussed sequentially, beginning with Type II in Fig. 7.4 II.

In the case of Type II, the vapor-liquid critical line connecting the two pure-component critical points is still present, but there is also liquid-liquid phase separation, and liquid-liquid-vapor coexistence. A variant II-A exists for small ζ (small difference between the two components.) Here positive azeotropy occurs: at given temperature, the vapor pressure of the mixture is above those of the pure components, because the attraction between the components is relatively weak.

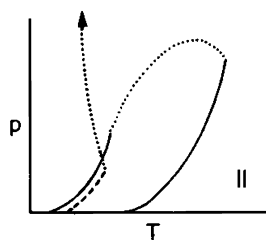


Figure 7.4 II Type II differs from Type I by the presence of a liquid-liquid-vapor three-phase line (----) that ends in an upper critical end point. From the UCEP, as the pressure is raised, a liquid-liquid critical line (....) develops, running to lower temperatures while the pressure increases steeply.

As the difference between the components increases, the critical points of the two components are no longer connected by a critical line, and Type III develops (Fig. 7.4 III). Characteristic of Type-III phase behavior is the critical line running to high pressure from the critical point of the least volatile component. Variants of Type III have been encountered experimentally. For instance, the critical line moving to high pressure may have a positive slope, or it may move through a temperature minimum. Alternatively, in Type III_m, this critical line moves to lower temperatures, through a maximum and a minimum in pressure, before moving to high pressure. In Type III-HA, azeotropy is again encountered, but in this case it involves a vapor phase and one of the two liquid phases. This is called *heteroazeotropy*. Positive heteroazeotropy manifests itself in the three-phase line lying *above* the vapor pressure curves of the two components.

The Type-IV phase behavior is the most complex (Fig. 7.4 IV). Type IV can be viewed as formed from Type III_m, when the minimum in the critical curve originating at the second component first touches in a double critical point, then cuts through the three-phase line, thus forming two critical end points. It can also be formed from Type II when on its vapor-liquid critical line a three-phase region with two critical end points opens after a passage through a tricritical point. Thus, we find Type IV bordered by Types II and III in the global phase diagram. The small size of the region allocated to it serves as a warning that it may be rather rare and

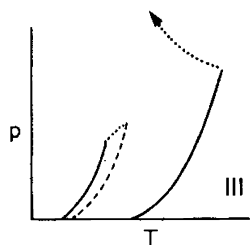


Fig. 7.4 III Type III occurs in regions of Figs. (7.2) and (7.3) where the attraction between the components is quite weak (large Λ). Starting at the critical point of the first component, we note that saturation of the vapor-liquid critical mixture occurs at a UCEP, just as in Type V. In this case, however, the three-phase line runs down to low temperatures and pressures. The liquid-vapor critical line, starting at the critical point of the second component, moves towards infinite pressure, as the liquid-liquid critical line does in Type II.

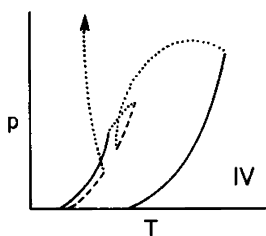


Figure 7.4 IV In Type IV, the three-phase line consists of two parts. The upper part terminates in an UCEP and an LCEP. A second UCEP terminates the lower part of the three-phase line. There are two critical lines connecting the components' critical points with the upper UCEP and the LCEP. A third critical line runs from an UCEP to infinite pressure

hard to find. A few examples have been found experimentally. A variant of Type IV, called Type IV*, occupying a region too thin to show in Fig. 7.2, must separate Types II and III elsewhere in the phase diagram. The regions II, III, IV and IV* meet at the special point, coined the Van Laar point by Meijer (1989). See Fig. 7.6. For clarity, the plot grossly exaggerates the size of the Type IV* region.

It is not always clear how to classify the observed phase behavior of a particular mixture. The reason is that the appearance of a solid phase may have cut off part of the fluid phase diagram. Thus, a Type-II diagram might appear to be of Type I, and a Type-IV diagram might be thought to be of Type V.

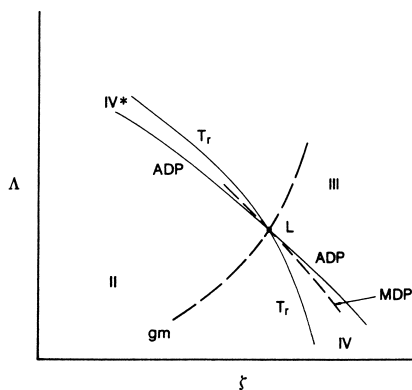


Figure 7.6 The way four regions of different phase behavior meet at the Van Laar point. Copied, with permission and minor modification, from Meijer (1989), Fig. 1. Copyright American Institute of Physics. A schematic view is given of the meeting of the Type II-IV phase diagrams at the Van Laar point (L) for the equal- b van der Waals equation. The following loci are shown. MDP: mathematical double point (primary and accessory plaits exchange roles); ADP: a critical line just touches a three-phase line in a double critical end point; Tr: a three-phase line with two critical end points shrinks to zero at a tricritical point; gm: locus of the geometric-mean rule $a_{12} = \sqrt{(a_1 a_2)}$, used by Van Laar (Ch. 7.5). This plot is not to scale. In reality, the regions of Type IV and IV* are extremely narrow in extent.

K&S (1980) also reported some calculations for the case of unlike excluded volume, $b_2 = 2b_1$, with linear mole fraction dependence of b_x , their Fig. 40. The phase diagram is no longer symmetric with respect to $\zeta = 0$. The general appearance of the global phase diagram has not changed much compared to the constant- b case. The geometric-mean locus, however, no longer passes through the point where Types II, III and IV meet. We will come back to this feature in Ch. 7.5.7. No novel phase behaviors were reported, except for the fact that in a small region of parameter space systems display both a positive and a negative azeotrope. Such systems have also been found experimentally.

7.2.5 *When were these phase diagrams discovered?* Having summarized the present-day knowledge of the global phase behavior of the Van der Waals equation for binary mixtures, we now turn to the historical question: how were these binary fluid phase diagrams first discovered from the Van der Waals equation and from experiment?

The first calculations for the case of $\zeta = 0$ were published by Korteweg in 1891 (Ch. 7.3), producing, in present-day language, Types I-A, II-A and III-A, and four-phase equilibrium. Kuenen and Robson then made an essential experimental contribution, discovering the Type-III and Type-V phase diagrams between 1899 and 1903 (Ch. 7.4). Van Laar (1905a) modified the Van der Waals equation in order to produce Type VI. In 1905 and 1906 he published a sequence of calculations for the unmodified Van der Waals equation for binary mixtures under the geometric-mean assumption (Ch. 7.5). He found Types II and III, and proved the existence of Type IV as an intermediary between Types II and III. By 1906, all major types of phase diagrams and several of their variants had been mapped, and most of them had been found by experiment.

7.3 *Korteweg and the Van der Waals symmetric mixture*

7.3.1 *The model.* After developing the general theory of plaits, GTP, see Ch. 5, the pioneer Korteweg applied his theory to the Van der Waals equation for mixtures of two identical components, which he calls the symmetric mixture. His work is thus confined to the axis $\zeta = 0$ in Figs. 7.2 and 7.3. The phase diagrams he obtains differ from the ones for the asymmetric case, Fig. 7.4, in that the vapor pressure curves of the two components fall on top of each other. This implies that all phase diagrams must have a positive or negative azeotrope, depending on whether the mixture vapor pressure is higher or lower than that of the two components.

The parameter a_x varies with mole fraction through the quadratic mixing rule, Eq. (4.5), with a_{12} a free parameter. Korteweg replaces it by the parameter κ , with

$$\kappa = a_{12}/a_1; \quad (\kappa \equiv 1 - \Lambda) \quad (7.3)$$

as a measure of the relative strength of the unlike interaction compared to that in the pure components.

Perhaps surprisingly, this highly artificial model of a binary mixture displays quite complex phase behavior, including a four-phase split. Korteweg (1891b) himself expresses optimism that such systems can be found experimentally. In a footnote, GTP p. 207, he lists quite a few pairs and even triplets of substances having roughly the same critical pressures and temperatures, such as nitrogen and carbon monoxide. Four-phase fluid equilibrium has, however, never been reported in such simple systems. According to Van Konynenburg and Scott (1980), optical enantiomers may be expected to obey this model, but up to the present day, no such systems have been studied. In Ch. 7.3.10, however, examples will be given of the relevance of Korteweg's model to phase separation in ternary mixtures.

For the case of $\kappa > 1$ (negative Λ in Fig. 7.2), the attraction between components is stronger than that characterizing each component, and the mixture behavior is not very different from that of a pure component. It shows liquid-vapor phase separation beginning at a temperature slightly above the critical temperature of the two components.

As soon, however, as the interaction between the two components is allowed to be *weaker* than that within each of the components separately, a richness of phase behavior blossoms. The entire arsenal of behaviors of plait points and plaits, catalogued by Korteweg (1881b) in the first part of GTP, is displayed by the symmetric model: homogeneous and heterogeneous double plait points, an osculation point, accessory plaits, a multiplicity of three-phase regions, and even four-phase coexistence. The symmetry of the model adds to the complexity. Events happen that Gibbs's phase rule would forbid in non-symmetric binary mixtures. Nevertheless, several features of phase separation are intuitively clear.

Here, we will work through some of Korteweg's pictorial examples of phase separation in the symmetric mixture, being very light on the mathematics.

7.3.2 Korteweg's graphical representations. Throughout the paper, and like Van der Waals, Korteweg uses molar volume V and mole fraction x as coordinates, but contrary to the usage of Van der Waals, he plots the volume axis horizontally, to the left, and the x axis vertically. The volume axis begins at the right, at $V = b$, where the pressure becomes infinite both for the pure components and for the mixture. In every drawing, Korteweg also indicates the line $V = 3b$, which represents the critical volume of the pure components. With Van der Waals, Korteweg calls plaits running more or less parallel to

the mole fraction axis transverse plait, and he calls those running more or less parallel to the volume axis longitudinal plait. In each region, Korteweg indicates the curvature of the transverse surface, and therefore its stability. In blank regions the surface has positive curvature and is convex, and therefore stable. If the surface is concave, and therefore not thermodynamically stable, the region is shaded in gray. In the regions indicated in black, the surface has negative curvature and is always unstable. Black regions are bounded by spinodals, or they may terminate at the $x = 0$, $x = 1$, or $V = b$ axes.

For each κ , or range of values of κ , Korteweg presents a sequence of V - x diagram at decreasing temperature. For instance, all pictures labeled A are for the range $0 < \kappa < 1/9$, but they are sequenced in order of descending temperature.

The plait point locations follow from an equation of the 8th degree in volume. Without solving it, Korteweg is able to deduce the number and nature of all plait points in each of the pictures he shows. Because of the model symmetry, he is also able to calculate the connodal for the longitudinal plait. Korteweg warns (GTP p. 323) that the pictures are not to scale, and that he did not calculate numerically the spinodals and connodals because that would take a lot of work of doubtful utility. Also, the scale would be very awkward once the gas volumes become very large.

7.3.3 Strong attraction between the two components. For the case $\kappa > 1$ (Λ negative), for which the attraction between the two components is stronger than that for each of the pure components, the mixture behavior is rather trivial, says Korteweg, who spends no more than half a page on this case (GTP Sec. 22). Because of the relatively strong attraction between the two components, the mixture will have no liquid-liquid phase separation, but as the temperature decreases, there will be vapor-liquid phase separation like the two pure components. Also, because of the stronger attraction, the mixture has a higher vapor-liquid critical temperature than the pure components. Beginning in the homogeneous region, as the temperature is lowered, the first sign of a phase split is the appearance of a homogeneous double plait point of the first kind (Ch. 5.4.2), at $x = 1/2$ and at a temperature T_2 given by

$$RT_2 = RT_1 (1 + \kappa) / 2, \quad (7.4)$$

with $T_1 = (8/27R) (a_1/b)$ the critical temperature of the pure components. Obviously, for κ larger than 1, the mixture critical temperature is higher than that of the components, and for κ smaller than 1 it is lower.

After the temperature falls below that of this homogeneous double plait point, the latter splits into two critical points and these two move away from

$x = 1/2$ towards smaller and larger x . Between them a vapor-liquid (transverse) plait opens, as in Fig. 5.2. On further lowering of the temperature, the two plait points reach the $x = 0$ and $x = 1$ axes at the critical points of the two components. The transverse plait now runs over the full range from $x = 0$ to $x = 1$. It spans a larger range of volumes as the temperature falls, the liquid phase getting denser, and the vapor phase expanding. At all temperatures below the critical point, the vapor and liquid phase have the same mole fraction at $x = 1/2$. This represents negative azeotropy: at fixed temperature the mixture has a lower vapor pressure than the two components because of the additional attraction between components. This is therefore a Type-I-A mixture phase diagram of a peculiar type, the pure-component vapor pressure curves falling on top of each other, and the critical line in P - T space folding back on itself at the negative azeotrope, $x = 1/2$ (see Fig. 7.5). The K&S diagram in Fig. 7.2 confirms Type I-A behavior at negative Λ near the $\zeta = 0$ axis.

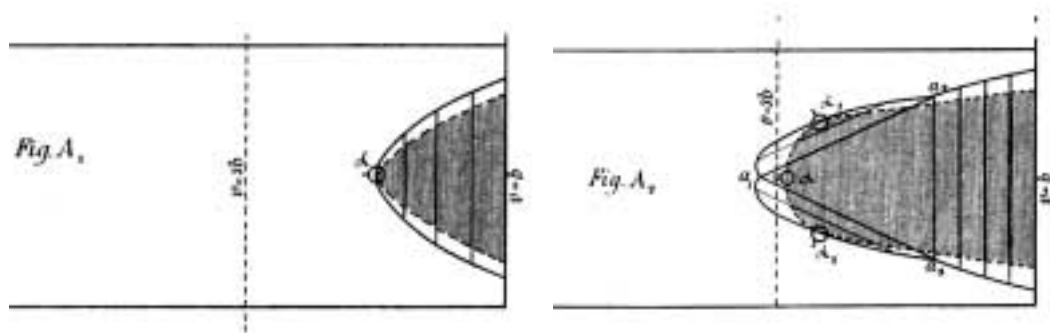
7.3.4 Weak attraction between the two components – three- and four-phase equilibria. As soon as the attraction between the components is weaker than that in each pure component, that is, $\kappa < 1$ and Λ positive, the model begins to become interesting. At sufficiently low temperature, there is *always* phase separation in the liquid phase, and the sooner, the weaker the mutual attraction of the components. There are three different cases. If a_{12} is only slightly less than a , the vapor-liquid plait will form at higher temperature than the longitudinal plait (Case E). If a_{12} is much smaller than a , the longitudinal plait forms first, at higher temperatures than the transverse plait (Case A). In both cases, the plaits will interact at low enough temperature, leading to the three-phase region shown in Fig. 4.1. The third and most interesting case, for an intermediate range of a_{12}/a , is when the two plaits form at roughly the same temperature and compete (Cases B, C, D). It is in this range that four-phase equilibrium is found (Case D).

The longitudinal plait begins at the line $V = b$, at infinite pressure (Fig. 7.7). The temperature at which it starts, T_1' , is given by

$$RT_1' = (a/b) (1 - \kappa) = (27/8) (1 - \kappa) RT_1 \quad (7.5)$$

If the attractive interaction between the two components is weak enough, κ small, the dense mixture separates into two phases of different composition at temperatures well above the critical temperature T_1 of the two components. Van der Waals (1890) proved the existence of such a plait for the general case (Ch. 4.8.2). His expression for the temperature at which the longitudinal plait first begins at $V = b_\kappa$, Eq. (4.17), reduces to that of Korteweg, Eq. (7.5), for this special case. From here on, we let Korteweg's pictures, Figs. 7.7-7.11, tell their own story.

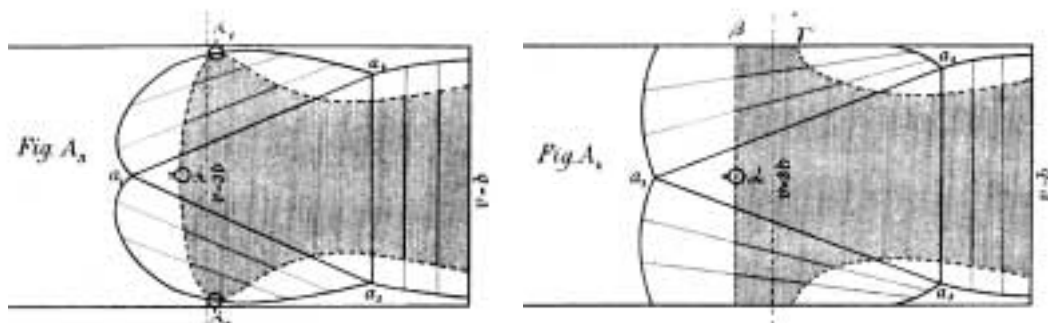
Figure 7.7 For weak attraction between unlike components, a longitudinal plait is always present, and gives rise to a three-phase region and a transverse plait as the temperature decreases. Copied from Korteweg (1891b), Plate XIII.



Korteweg labels the case of $\chi < 1/9$ with the letter A. For this case, near the top of the K&S diagram, Fig. 7.2, T_1' is much larger than T_1 , and thus the longitudinal plait already appears at temperatures too high for the transverse plait to exist. As the system cools, two accessory plaits form, and finally a full transverse plait develops.

The fate of the longitudinal plait, marked A_1 , is quite interesting. As the temperature falls, it grows to larger volumes. At a certain temperature, the plait point splits into three plait points, two of the first, and one of the second kind. Two accessory plaits form, and a three-phase region vapor-liquid-liquid appears, see A_2 .

The point at which the plait point of the longitudinal plait splits in three (presently called a symmetric tricritical point) is the last stable plait point of the longitudinal plait as the temperature falls. As the temperature decreases, the two stable plait points trace two new critical lines that end at the critical points of the two components. The tricritical point is therefore also an

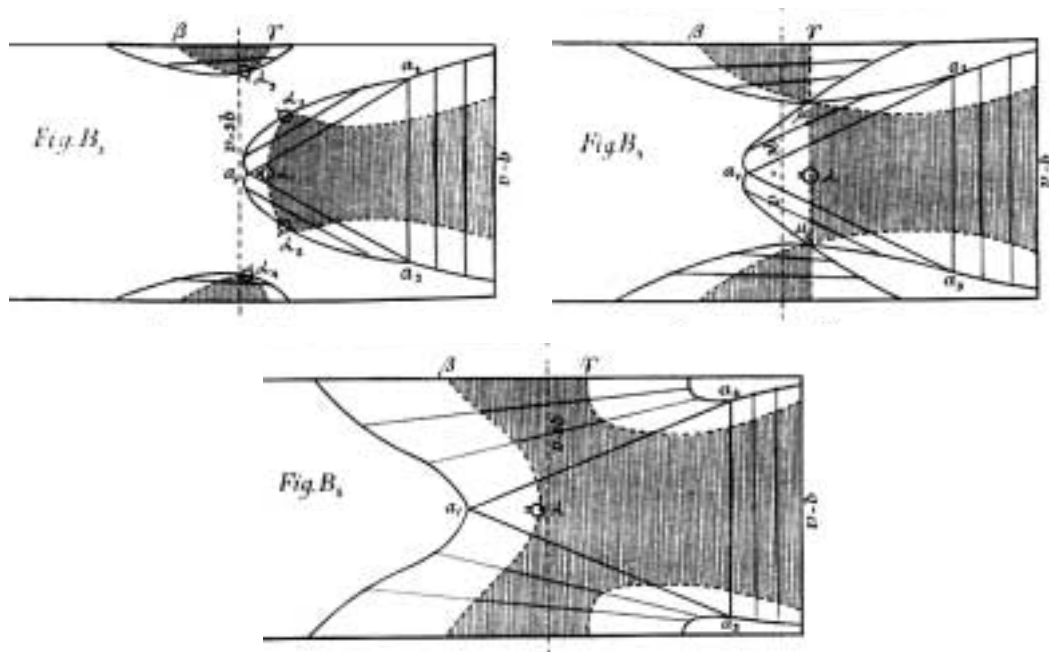


UCEP with respect to the critical lines starting from the two components. K&S classify this type of phase diagram in Fig. 7.2 and 7.3 as Type III-HA, but it is considerably more complex than vintage Type III.

Korteweg gives an exact expression for the temperature T_2' of the splitting-in-three of the plait point of the longitudinal plait as a function of x . It is important to emphasize that although Korteweg (1891b), in a footnote on p. 325, recognizes the splitting plait point as one where three critical points coincide, it is *not* listed among the special plait points identified and described by him.

In A₃, the accessory plait points move to the two sides $x = 0$, $x = 1$, which they reach at the critical temperature T_1 of the pure components, see A₃. At lower temperatures, the transverse plait, thus formed from the longitudinal plait, just widens, while the three-phase region persists, see A₄.

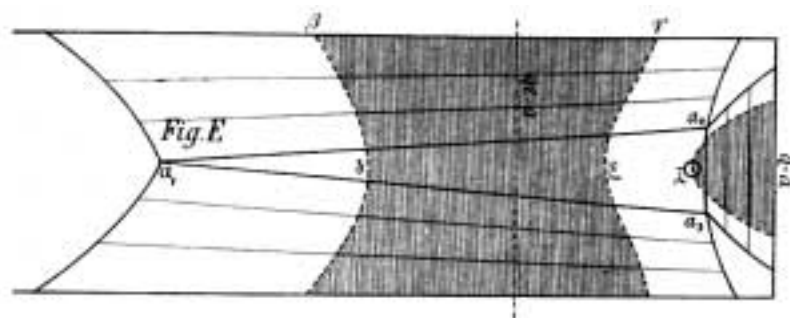
Figure 7.8 The attraction between the components is stronger than in Fig. 7.7, and the transverse plait forms from the sides $x = 0$ and $x = 1$, meeting the longitudinal plait midway. Copied from Korteweg (1891b), Plate XIV.



In the range of $1/9 < \kappa < 5/13$ ($0.889 > \Lambda > 0.616$, labeled B in the Korteweg drawings), still well above the shield region, accessory plaits have formed by the longitudinal plait point's splitting in three, giving rise to two regions of three-phase coexistence just as in the case of Fig. 7.7. Here, however, transverse plaits begin at the sides before the accessory plaits have reached that far, case B₃. The formation of an UCEP, which is the point at which the longitudinal critical line ends and two new critical lines begin as the temperature is lowered, is no different than before, and the phase diagram is again of Type III-HA.

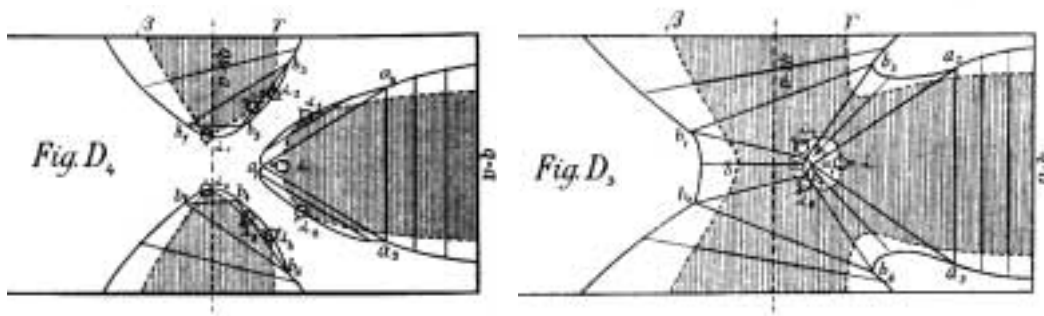
The budding transverse plaits meet the accessory plaits halfway, case B₄. The pairs of critical points α_1 and α_3 , α_2 and α_4 meet in homogeneous critical double points (Ch. 5.4.2) and disappear. At lower temperatures, the combined transverse-longitudinal plait just widens while the three-phase region remains, case B₅.

Figure 7.9 The attraction between the components is almost as large as that in each component. Copied from Korteweg (1891b), Plate XV.



For α almost unity, case E, the transverse plait forms fully while the longitudinal plait is still small. The transverse plait cuts the spinodal of the longitudinal plait in two points, and a three-phase region results, as discussed by Van der Waals (1890), see Ch. 4.8.3 and Figs. 4.1 and 4.2c, and by Korteweg, see Ch. 5.5.6 and Fig. 5.10. There still must be positive azeotropy. This represents Type-II-A phase behavior, just as indicated by K&S for the region of small positive Λ , and for ζ near 0, see Fig. 7.3.

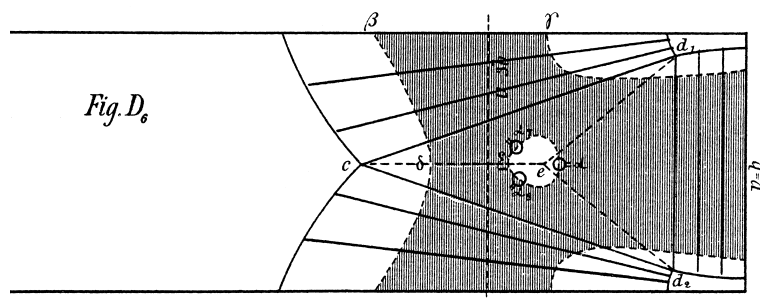
Figure 7.10 In the region of $0.534 < \kappa < 0.67$, the longitudinal and transverse plaits develop at roughly the same temperature, and meet in a complex fashion in the center of the phase diagram. Copied from Korteweg (1891b), Plate XIV.



In D_4 , the three plaits move towards the center, and each develops two accessory plaits, for a total of six plait points in the stable region. The accessory plait on the two parts of the transverse plait form from heterogeneous double plait points on their spinodals (Ch. 5.5.4 and 5.5.7, Figs. 5.7 and 5.12), while the one on the longitudinal plait is formed as before, by a splitting into three plait points. As the temperature continues to drop, the plait points merge in pairs, α_1 with α_3 , α_2 with α_4 , and α_5 with α_6 , forming homogeneous double plait points, and then disappear. Afterwards, a stable region of positive curvature is enclosed inside the unstable region.

In D_5 , three three-phase regions, alternating with three two-phase regions, radiate out from a tiny one-phase region in the center, which is part of the region of positive curvature that has been separated and pinched off from the original stable vapor phase. Three additional two-phase regions exist further from the central region. This figure can form from D_4 in different ways, depending on the value of κ . At a special point, $\kappa = 0.565$, the plait points α_1 and α_3 join, snapping the two transverse plaits together; simultaneously, the pairs α_5 and α_6 , α_2 and α_4 join, which snaps each transverse plait to the longitudinal plait. Above or below this value of κ , these two events are not simultaneous, the order depending on whether κ is above or below the special value.

Figure 7.11 Formation of a four-phase region. Copied from Korteweg (1891b), Plate XIV.



From case GTP D_5 , as the temperature drops, the central convex region of the surface shifts upwards, the small central stable one-phase region shrinks to a point, the two-phase regions collapse, and the three-phase regions all fall in the same tangent plane. Only one tangent plane is left, touching the surface in four points. Two liquid phases of small molar volume and of mole fractions close to $x = 0$ and $x = 1$, coexist with two phases at $x = 1/2$, one a vapor phase of large molar volume, the other a phase of intermediate molar volume.

After the system passes through this four-phase point to lower temperatures, the region of positive curvature enclosed inside the spinodal region pulls up from the tangent plane, and is not longer touched, so only one three-phase triangle is left, as in other cases such as A_4 in Fig. 7.7, B_5 in Fig. 7.8, and E in Fig. 7.9. Korteweg also mentions that as the temperature decreases, the region of positive curvature contracts to an osculation point, after which the region reappears as concave.

According to Korteweg's analysis, the characteristic distinguishing what is presently called the shield region is the occurrence of four-phase coexistence. Significantly, Korteweg (GTP p. 333) stresses that the occurrence of a quadruple tangent plane is *not* a consequence of the symmetry of the model, and should still happen even if the two components are not identical. For the Van der Waals equation, Wei and Scott (1988) have shown that indeed a skewed shield region occurs even in highly asymmetric binary mixtures. Das and Griffiths (1979) detected a shield region experimentally, in a five-component (!) liquid mixture.

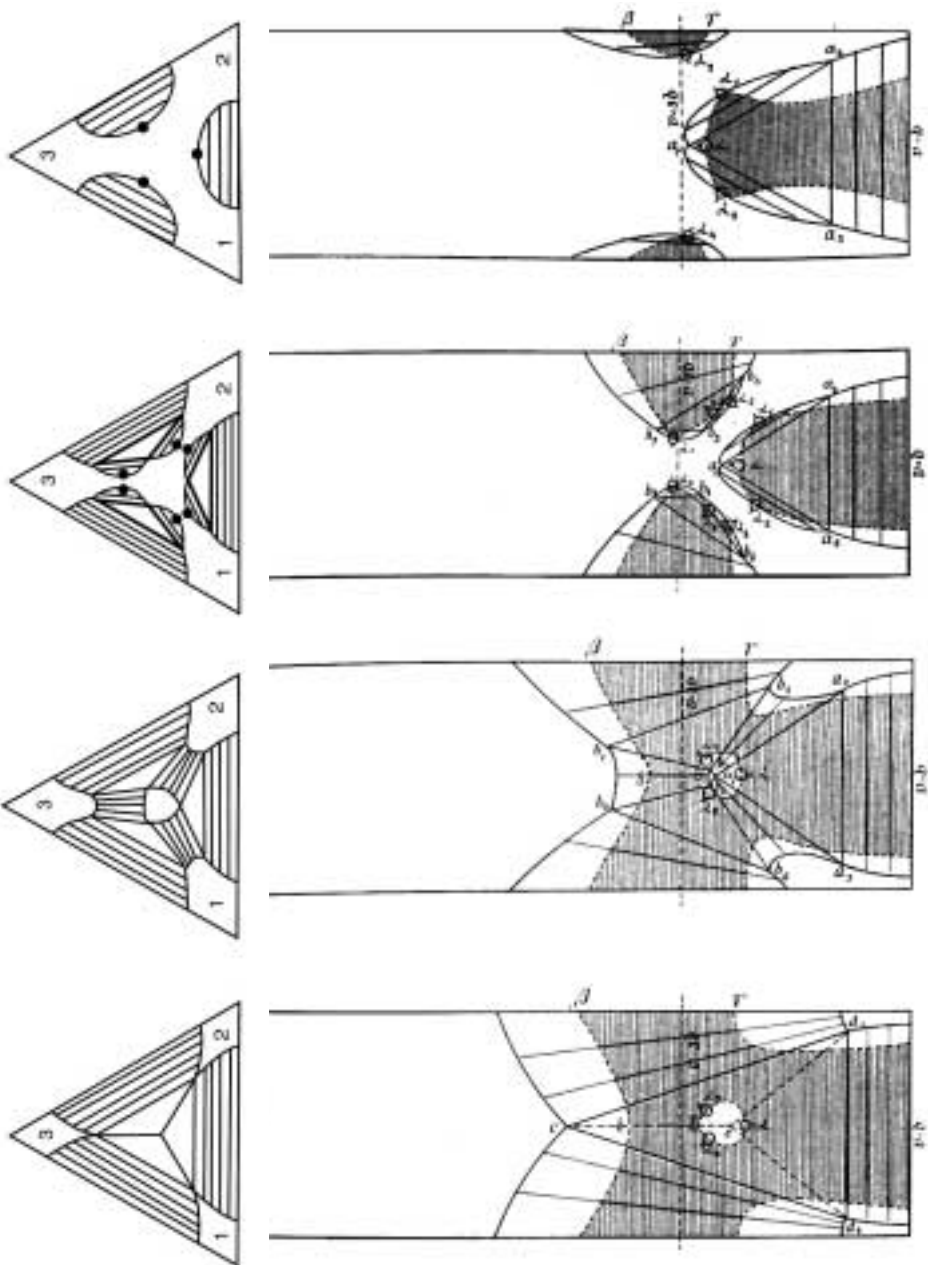
7.3.5 *Relevance of Korteweg's work – ternary mixtures and the three-state Potts model.* The phase separation of three-component mixtures containing both liquid and solid phases was studied extensively by Bakhuis Roozeboom and his school in the early years of the 20th century. This school did not base its work on mathematical models. They applied Gibbsian thermodynamics in an intuitive, phenomenological fashion. The third volume of the Bakhuis-Roozeboom series was published after his death by Schreinemakers (1913) and devoted entirely to ternary systems. Meijering (1951), at the Philips Physical Laboratory in the Netherlands, invoking Korteweg, modeled the Gibbs function of incompressible ternary solid solutions, and studied the phase behavior of a symmetric mixture of three identical components.

Shortly thereafter, statistical physics turned to the study of the three-dimensional Ising model, which, for the present purpose, may be seen as a model for phase separation of two components A and B, molecules of each singly occupying sites on a regular lattice. Only molecules placed on adjacent lattice sites attract each other. If the attraction between A and B molecules is weaker the average of the attraction between A-A and B-B pairs, the system will segregate itself at low temperatures, passing through a consolute critical point. There is a complete analogy with the criticality of a one-component compressible system. The lattice gas is an Ising model for which particles and holes, or empty spaces, are placed on the lattice.

The emphasis of the studies of the Ising model was the peculiar nature of criticality, departing from the classical picture of Van der Waals and Korteweg. This topic is discussed in Ch. 9. Once the criticality of the Ising model was elucidated, it became of interest to know the nature of criticality in a three-component mixture. A generalization of the Ising model had been introduced by Potts in 1951: a lattice point can be occupied by one of n different molecules. The three-state Potts model is a model for the phase behavior of a three-component liquid or solid mixture, and by replacing one of the components by 'holes,' it is a model for a binary compressible system such as the one studied by Korteweg.

The scientists who studied this model began quite naturally by studying the mean-field version of the three-state Potts model. Here, we limit ourselves to studies of a special case, the *symmetric* three-state Potts model. This

Figure 7.12 The correspondence between the passage through the shield region of the symmetric three-state Potts model, left column, and that of the symmetric Van der Waals binary fluid mixture. The figures in the right column are from Korteweg (1891b), Plate XIV. The figures on the left were copied, with permission, from Straley and Fisher (1973), Fig. 10. Copyright (1973) Institute of Physics.



is a model for three identical components, the mutual interaction between components described by one free parameter. Analytic results were obtained by Straley and Fisher (1973). Das and Griffiths (1979) established the phase behavior numerically, by means of a digital computer.

The symmetric three-state Potts model is of higher symmetry than the Korteweg symmetric Van der Waals model, in which only two components are identical. Nevertheless, the two models show a striking similarity. As was mentioned in Ch. 7.2.3, the three-state Potts model shows a region of four-phase coexistence, the shield region. In fact, in the region of values of the free parameter where such four-phase coexistence is found, the mixture passes through the same stages as the Korteweg model. This behavior is illustrated in Fig. 7.12.

The symmetric Van der Waals mixture studied by Korteweg thus was the prototype for ternary-mixture phase behavior. The historic sequence, from 1891 to 1979, is summarized in Fig. 7.13, which shows the analog of Korteweg's case of D_4 , compared to ternary mixtures studied throughout the 20th century. Note that in contrast to the later researchers, Korteweg includes the metastable and unstable regions.

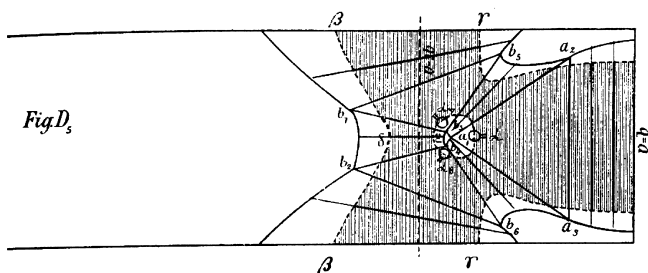
7.3.6 Was Korteweg right? Korteweg's GTP paper suffers from some errors in the equations. According to Levelt (2001), GTP Eqs. (17) and (19) are incorrect, while several other equations contain typos. There is evidence that these mistakes have not affected the conclusions about the $\zeta = 0$ case. The observed phase behaviors agree with those reported by Furman and Griffiths and by K&S, and numerical results that can be compared mostly agree.

Translated in terms of K&S variable $\Lambda (\equiv 1 - \kappa)$, Korteweg's region of four-phase coexistence region, for $\zeta = 0$, ranges for Λ from 0.33 to 0.466, and the special point is at $\Lambda = 0.435$. For the extent of the shield region in the symmetric system, K&S (1980, p. 528) cite $0.3478 < \Lambda < 0.4666$, and for the special point in the center, $\Lambda = 0.4364$. These numerical results were due to Furman and Griffiths (1978). The agreement is striking. Levelt (2002) found that the discrepancy in the lower bound is due to a sign error in the last term of Eq. 88 in Korteweg (1891b).

Figure 7.13 Korteweg's symmetric Van de Waals mixture: a prototype for 20th century studies of phase transitions in ternary mixtures. Copied from Korteweg (1891b), Plate XIV. The picture by Schreinemakers (1913) was copied from his Fig. 90. The picture by Meijering (1951b) was copied from his Fig. 26. The picture by Straley and Fisher (1973) was copied, with permission, from their Fig. 10. Copyright (1973) Institute of Physics. The picture by Das and Griffiths (1979) was copied, with permission, from their Fig. 1. Copyright American Institute of Physics.

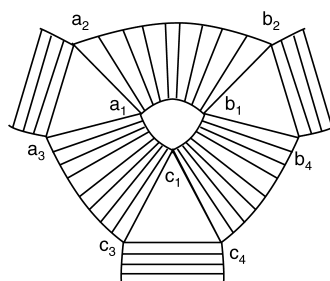
Korteweg (1891)

Binary fluid
Van der Waals
analytic



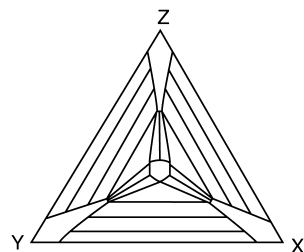
Schreinemakers (1913)

Ternary solution
phase theory



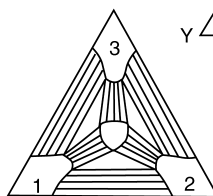
Meijering (1951)

Ternary solid solution
analytic



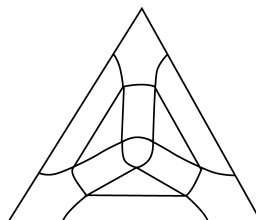
Straley and Fisher (1973)

Three-state Potts model
analytic



Das and Griffiths (1979)

Three-state Potts model
numerical



7.3.7 *Outlook.* By choosing to work on the symmetric Van der Waals mixture, Korteweg may not have anticipated how complex its behavior would turn out to be. The more respect does his work command. Much of the work was done analytically. The evolution and merging of plaits was studied exhaustively. The model exemplified the transformations of plaits that Korteweg (1891b) had catalogued. Azeotropic versions of three of the five types of binary fluid mixture phase diagrams, namely I, II and III, were found.

It is quite possible that physicists in Amsterdam and Leiden were intimidated by the model's complexity. After proving the existence of the longitudinal plait in 1890, Van der Waals turned to other aspects of mixture behavior, such as the variation of fluid properties along phase boundary curves. The Leiden scientists were reluctant to use the Van der Waals mixture equation anyway because of its lack of accuracy in representing experimental data. Almost fifteen years passed before Amsterdam chemist Van Laar took up the binary-mixture Van der Waals equation again and brought it to the point of applicability in real fluids, as will be described in Ch. 7.5. Van Laar knew Korteweg's theory of plaits, but his inspiration came from Kuenen's new experimental work.

7.4 *Kuenen, in Scotland, discovers new types of phase behavior*

7.4.1 *Kuenen's career.* After he received his doctorate in 1892, Kamerlingh Onnes's student Kuenen, featured in Ch. 6, served for another two years as the conservator of the Physics Laboratory, and then assumed a postdoctoral position at Ramsay's laboratory in London. He received a professorship at the physics department of University College, Dundee, Scotland and worked there from 1895 to 1906, returning to the University of Leiden as a professor of physics in 1907. Kuenen was elected to the Royal Netherlands Academy of Arts and Sciences (KNAW) in 1911, and to the Holland Society of Sciences and Humanities (HMW) in 1915.

7.4.2 *Aqueous three-phase mixtures.* By the time Kuenen brought his Scottish laboratory to the operational stage, quite a few researchers were experimenting with three-phase mixtures. Kuenen and Robson (1899) begin their report with an extensive review of experimental knowledge available at that time. The simplest way to study a three-phase system was to measure the vapor pressure of a system of two components only partly miscible in the liquid phase, so that one vapor phase and two liquid phases coexist from the outset. A mixture of ether and water was a favorite object of study. Because ether is so much more volatile than water, however, the vapor pressure of this mixture at ambient temperature is almost the same as that of pure ether.

Konowalow and Bakhuis Roozeboom had reported a few studies of the vapor pressure of other three-phase systems.

Quite a few reports on the mutual solubility of partially miscible liquids with water as a component had appeared as well. In many cases it had been found that on increasing the temperature the mutual solubility increased, until a so-called consolute critical point was reached where the liquids became fully miscible. In some cases, the solubility increased when the temperature was lowered, leading to a lower consolute critical point. In the 1890s, this disappearance of the difference between two coexistent liquid phases was already recognized as being analogous to vapor-liquid criticality. Scientists in those days generally left the vapor phase out of consideration, perhaps because they did not expect that the mole fractions of two incompressible liquid phases could depend much on the feeble vapor pressures in the glass vessels in their laboratories. Kuenen, raised on Gibbsian thermodynamics, knew well that at given temperature the equilibrium between two liquid phases is a function of pressure, and therefore not defined unless the pressure is fixed, or a vapor is present.

7.4.3 *Three-phase critical endpoint – heteroazeotropy.* Kuenen and Robson (1899) were looking for cases for which liquid-liquid phase equilibrium can interfere with gas-liquid criticality. They were the first to suggest that instead of the difference between two partially miscible liquids disappearing at a consolute point, one of the liquid phases might become critical with respect to a vapor phase.

Kuenen and Robson (1899) made use of a modified Cailletet apparatus provided with a stirrer. They used mercury-in-glass thermometers. Pressures up to 3 atmospheres were measured on an open mercury manometer. For higher pressures, they used air pressure manometers described in Ch. 6.1. Their first measurements concerned the then-popular system ether-water, which has two liquid layers. At all temperatures studied, they found that the mixture had a vapor pressure higher than that of the two components, an example of positive heteroazeotropy. The vapor composition is between that of the two liquid phases and becomes equal to that of one of the liquid phases at the azeotropic point. The authors pursued the three-phase region up to 201°C, at which temperature the vapor and one liquid phase became critical in the presence of the second liquid phase. This critical endpoint occurred close to the critical temperature of pure ether, but at slightly higher pressure. No liquid-liquid consolute point was found in this experiment. The vapor-liquid critical point of the aqueous phase was out of reach, both because of the pressure limitations of the apparatus, and because of the destructive action of the fluid on the glass tube at the higher temperatures.

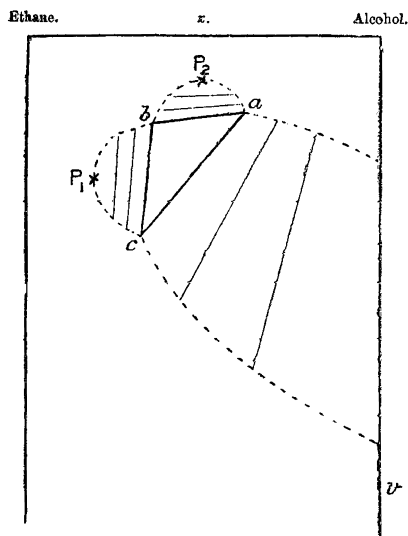


Figure 7.14 The phase behavior of the system ethane-ethanol in a V - x diagram at a chosen temperature. Copied from Kuenen and Robson (1899), Fig. 6. The triangle represents the three-phase region. In P_1 , two phases of different molar volume but almost the same mole fraction, mostly ethane, become critical at a vapor-liquid critical point. The connodal c - P_1 - b is part of a transverse plait, which runs from the vapor-liquid state of pure ethanol, interrupted by the three-phase region, to terminate at P_1 . In P_2 , two phases of almost the same small molar volume (high density) but different mole fraction become identical at a liquid-liquid critical point. The connodal b - P_2 - a is thus part of a longitudinal plait.

7.4.4 *Mixtures of ethane and alcohols – discovery of Type V.* Next, Kuenen and Robson (1899) initiated a systematic study of phase behavior of ethane mixed with members of the homologous series of alcohols: methanol, ethanol, isopropanol and butanol. Alcohols were known to associate in the vapor phase, and were therefore not expected to fit in with the Van der Waals equation. For the ethane-methanol system, the authors always found two liquid phases, not only above ambient temperature but even down to -78°C , the temperature of dry ice (solid carbon dioxide at atmospheric pressure). This system does not display azeotropy. Thus, the mole fraction in the vapor is always outside that in the two liquid phases, the vapor pressure at the three-phase line is between those of the pure components, and three-phase coexistence appears to reach down to very low temperatures.

In the ethane-ethanol system at fixed temperature, the authors again found a region of three-phase coexistence. At fixed temperature, the V - x diagram looks as shown in Fig. 7.14.

Contrary to the ethane-methanol system, the three-phase region in P - T space is bounded by *two* critical end points. The three-phase line begins at a liquid-liquid consolute point on the ethane-rich side at 31.9°C , a lower critical endpoint (LCEP). The three-phase line ends at a vapor-liquid critical point on the ethane-rich side at 40.7°C , an upper critical end point (UCEP). The latter lies well above the critical temperature of pure ethane, 32°C according to the authors.

In the next system, ethane and propanol, the miscibility of the two components in the liquid phase is improved even further, and the three-phase region spans only a few degrees in temperature, from 38.7 to 41.7°C. In this case, the authors measured a large stretch of the critical line beginning at the lower critical end point and moving to the critical point of the second component (Fig. 7.15).

This phase diagram, discovered experimentally by Kuenen and Robson, is currently called a Type-V phase diagram in the terminology of K&S. Note that one critical line begins at a liquid-liquid critical end point, C_3 , and ends at a vapor-liquid critical point, C_2 . This feature is a beautiful illustration of the principle of continuity of states. Liquid-liquid and liquid-vapor phase transitions in fluid mixtures are not sharply distinct. Along the right branch of the critical line in Fig. 7.15, the character of the phase transition changes continuously, from a difference mostly in density at the critical point of the less volatile component to a mostly compositional difference between the phases near the lower critical end point. Within the framework of the Van der Waals equation, however, there is an

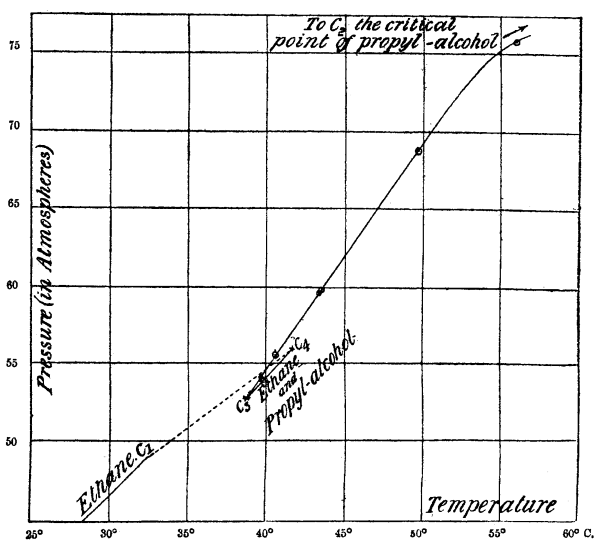


Figure 7.15 The phase behavior of a mixture of ethane and propyl alcohol (propanol) represented in the pressure-temperature plane. Copied from Kuenen and Robson (1899), Fig. 8. C_1 is the critical point of pure ethane, C_2 that of pure propanol. A critical line runs from C_1 to the upper critical end point C_4 . Another critical line runs from C_2 to the lower critical end point C_3 . A three-phase line begins in the liquid-liquid critical end point C_3 and ends in the vapor-liquid critical end point C_4 . From Kuenen and Robson (1899), Fig. 8, p. 199.

underlying competition between two plaits, which is played out on the metastable and unstable parts of the free energy surface in the temperature region where the three-phase line occurs. Near the top of the three-phase line in Fig. 7.15, the principal plait is a vapor-liquid plait, but a closed-loop accessory liquid-liquid plait has just protruded into the stable region. Near the bottom of the three-phase line, the situation is reversed. As the temperature is lowered, the plaits have exchanged roles at a mathematical double point, and the liquid-liquid plait is now the dominant one, exactly as portrayed by Korteweg, Fig. 5.12. See also Meijer (1999). This interpretation, however, was not given by Kuenen at that particular time, because his approach was entirely experimental. It is Van Laar who would make this connection (Ch. 7.5).

7.4.5 Ethane and methanol – Type III. Kuenen's next coup was the experimental discovery of yet another type of phase diagram, currently called Type III. Kuenen (1903) went back to the mixture of methanol and ethane, which apparently had only an upper, but no lower bound for the three-phase line. He posed the question of what would happen to the critical line emerging from the critical point of methanol, if it had nowhere to connect to on the three-phase line. In 1903, Kuenen's apparatus had been improved to the point that he could start his measurements at the methanol critical point of 240°C. Also, he could reach much higher pressures, well above 150 atmospheres. Kuenen thus measured a sizeable portion of the critical line starting at the methanol critical point (Fig. 7.16).

This is the Type-III_m phase diagram mentioned in Sec. 7.2, for which the critical line originating from the critical point of the less volatile component moves to lower temperatures, with a maximum and minimum in pressure.

In other variants of Type-III behavior, discovered later, the critical line moves to higher pressures immediately, with or without a minimum in temperature. It is therefore possible for this critical line to move to temperatures higher than the critical temperatures of the two components. Thus, certain fluid mixture with very weak attraction between unlike components can unmix at temperatures well above the critical temperatures of the individual components. As mentioned on several occasions, Van der Waals (1890) and Korteweg (1891b) noticed this possibility when they discovered the existence of the longitudinal plait even above the critical temperatures of the two components (Fig. 7.7, A₁). Nevertheless, forty years would pass until, for the first time, Krichevskii and Tsiklis (1941) measured binary mixture phase separation above the critical temperatures of both components in the system ammonia-nitrogen. This

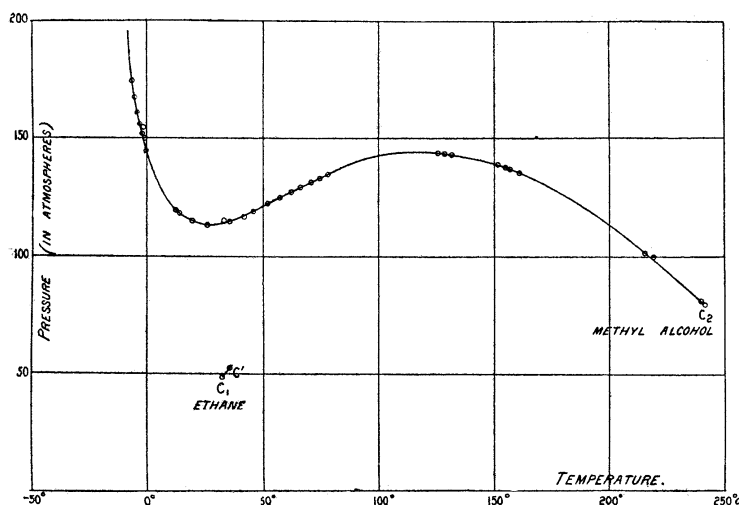


Figure 7.16 The critical line of the system ethane-methanol starting at the methanol critical point. Copied from Kuenen (1903), Fig. 1. This critical line has the following features. In anthropomorphic terms not due to Kuenen, it moves to lower temperatures. On the way, it passes through a high maximum in pressure, well above the critical pressures of either component. It then descends towards the critical point of ethane, but 'discovers' that the critical point is already connected to another critical line. It reconsiders, turns around, and departs for infinite pressure. Copied from Kuenen (1903), Fig. 1, p. 641.

phenomenon is called gas-gas phase separation, and is pursued further in Ch. 8.

Kuenen thus discovered experimentally two new types of phase behavior, Type V and Type III, both with three-phase coexistence.

From the beginning, Kuenen refrained from calculating the phase behavior from Van der Waals's theory of mixtures. His stated reason was that he found the Van der Waals equation too crude even to describe the behavior of the pure components, let alone the mixtures with associating components that he was studying.

It is obvious that the model of a phase diagram with three-phase coexistence, present in Van der Waals's (1890) paper on mixtures, had been very inspirational to the Leiden experimenters, leading them to the discovery of new types of three-phase coexistence. No equivalent, however, existed of Korteweg's treatment of the symmetric Van der Waals mixture that could generate from theory the phase diagrams found by Kuenen in real mixtures. Theoretical chemist Van Laar would accept this challenge.

7.5 *Van Laar calculates the global phase behavior of the Van der Waals mixture*

7.5.1 *Overview – biographical notes.* An English-language biography by Van Emmerik (1991) details the difficult life of Johannes Jacobus van Laar (1860–1938), who was orphaned at an early age. Before he had finished high school, where he had excelled in chemistry, Van Laar’s guardian uncle sent him to the Royal Naval Institute, where he received extensive training in mathematics. After a few years of life on board ship as a naval officer, Van Laar convinced his uncle that he should resign from the Navy, and he was honorably discharged in 1881. Encouraged by a personal encounter with Van ’t Hoff, he began taking classes at the University of Amsterdam. He studied physics, chemistry and mathematics in 1881–1882, but was not allowed to take examinations because of his insufficient high school preparation. He adored Van der Waals, considered himself as his pupil, and yearned to be part of the inner circle of the University faculty. Thanks to a recommendation by Van der Waals and his credentials in mathematics as a former naval officer, Van Laar obtained a teaching position at a HBS in Middelburg in 1883. There he taught mathematics until 1895 and fathered five children. Feeling very isolated on this island far south of Amsterdam, he taught briefly in Utrecht and then fell ill, leaving the family to subsist on a pension amounting to roughly 1/3 of his Middelburg salary. Despite these difficult circumstances, he published half a dozen textbooks on high school- and college-level mathematics, chemistry and thermodynamics between 1887 and 1904. He was repeatedly refused an academic teaching position in Utrecht because he lacked a doctorate. Finally, in 1898, he was admitted as an unsalaried lecturer of mathematical chemistry at the University of Amsterdam. By that time, his relation with Van der Waals began to deteriorate, and he was passed over for several paid positions in the next ten years, due to opposition by Van der Waals. Van Laar departed for Switzerland in 1911, where he spent the rest of his life. He was elected to the Holland Society of Sciences and Humanities, HMW, in 1910. He was granted his first doctorate – an honorary one – from the University of Groningen in 1914. In 1929, for his contributions to the theory of phase equilibria, Van Laar was honored by his native country with the prestigious Bakhuis Roozeboom medal. One year later, at the age of seventy, he was elected to the Royal Netherlands Academy of Arts and Sciences (KNAW).

Van Laar published profusely on the thermodynamics of fluids and solids. He made original contributions to the theory of electrolytes. Here, we will review several of about a dozen publications written between 1905 and 1906, in which he proved that the phase diagrams, which had been experimentally found for binary mixtures with at least one anomalous (associating) compo-



Johannes Jacobus van Laar in 1910.
Copied with permission of the Boerhaave Museum, Leiden.

nent, could be derived from the Van der Waals equation. This work was carried out in three steps.

First, Van Laar (1905a) considered the phase behavior of a binary partially miscible liquid, with water one of the components. He introduced association into an approximate Van der Waals equation, and was the first to produce closed-loop coexistence curves from an equation of state.

Next, using the magical intuition about phase diagrams then flourishing amongst the chemists in Amsterdam, Van Laar (1905b) sketched out the phase diagrams for the Type III- and Type V-cases studied by Kuenen, in a variety of coordinates. He speculated about the form of the transition between Type II and Type III, which we presently call Type IV.

Then, in a sequence of four communications to the Proceedings of the Royal Netherlands Academy, Van Laar (1905c, 1905d, 1905f, 1906a) systematically worked out the phase behavior of the Van der Waals equation for equal excluded volume of the components and the mixture, under the geometric-mean assumption for the attraction. He derived exact, relatively simple equations for the spinodal and the critical line. He showed that the critical line crosses over itself at a special point in the phase diagram, later coined the Van Laar point by Meijer (1989), and gave exact results for the coordinates of this point.

In a major paper in the Archives of the Teyler Museum, in French, Van Laar (1906a) summarized his results, added some proofs omitted earlier, and generalized to unequal excluded volume. Finally, he proved the existence of the Type IV phase diagram.

Many of Van Laar's papers, including some of the ones discussed here, have appeared in multiple languages. In those cases, given the availability of a full bibliography by Van Emmerik (1991), we cite only the English version, usually published in the Proceedings of the Royal Netherlands Academy of Arts and Sciences.

Van Laar was not allowed to make his own presentations at the Academy, as he was not a member. Van der Waals presented his earlier papers, until about 1903, when their relationship soured. Bakhuis Roozeboom sided with Van Laar and avoided contact with Van der Waals after that time, see Van Emmerik (1991), p. 32. Two professors at the University of Leiden, physicist Lorentz and chemist Schreinemakers, also volunteered to present Van Laar's papers.

7.5.2 *Partial miscibility in associating mixtures – 'especially water.'* Korteweg and Van der Waals derived liquid-liquid phase separation from a molecular model and found that separation always occurs if the attractive interaction of the unlike partners is weaker than the average of that in each of the components. This model, however, could not explain the *lower* critical consolute points observed in many aqueous mixtures, such as triethylamine and water. Van Laar (1905a) presents a modification of the Van der Waals equation that can give lower critical points, and even closed-loop coexistence curves (Type VI in Fig. 7.4). He begins with an approximation made earlier by Van der Waals to obtain an expression for the Gibbs energy suitable for liquid mixtures near close packing, where pressure effects on the volume are minimal. Van Laar now reasons on the basis of the observation that the molar volume of liquid water increases anomalously as the temperature drops below 4°C. He ascribes this phenomenon to association of water molecules, which he assumes are forming pairs that have a much larger excluded volume than twice that of a single molecule.

Van Laar interpolates for the degree of dissociation between full association at low temperatures and no association at high temperature, and calculates the effect on the Gibbs energy. The result is a rich set of binary phase diagrams, shown in Fig. 7.17, including one in which a plait is beginning at a homogeneous double critical point, and one that has a closed-loop coexistence curve.

Van Laar thus invoked the additional mechanism of association, to obtain closed-loop liquid-liquid phase separation from a Van der Waals-like equation

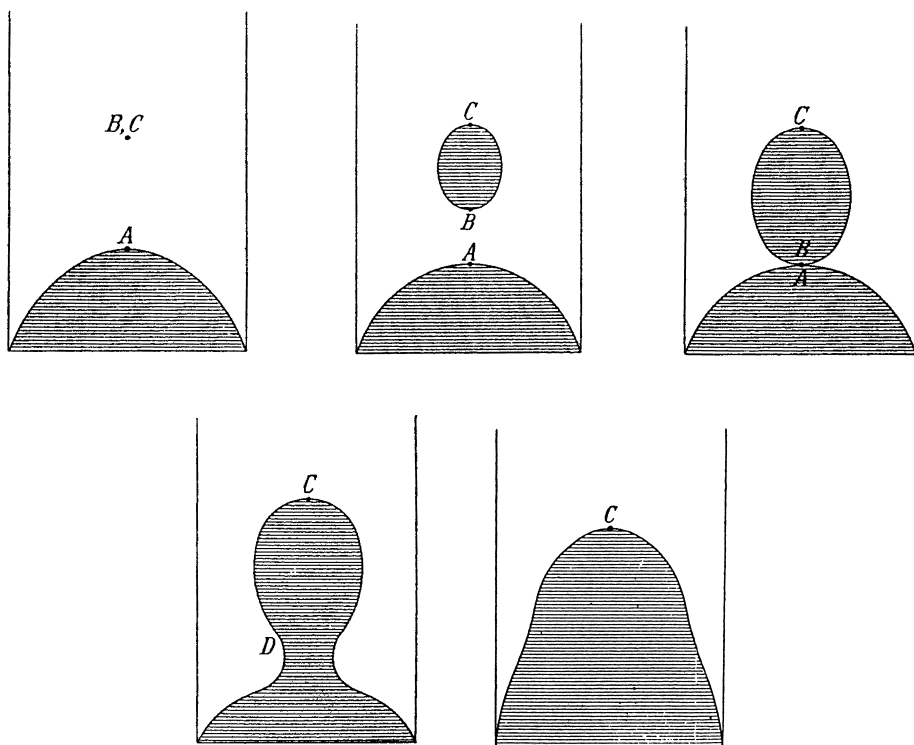


Figure 7.17 T - x phase diagram for binary liquid mixtures with an associating component. Copied from Van Laar (1905a), Figs. 1-7. Depending on the functional form of the temperature dependence of the degree of association, different types of liquid-liquid phase separation result. The top left drawing shows an ordinary longitudinal plait. Above it, however, a homogeneous double plait point B,C has appeared. As the temperature dependence of the association constant is modified, the homogeneous double plait point splits and a region of closed-loop phase coexistence develops (top middle drawing). Further modification of the temperature dependence of association gives rise to the other phase behaviors displayed.

of mixtures. This reinforced the notion of a division into ‘normal’ and ‘anomalous’ substances, which had guided Kuenen’s choice of experimental systems worthy of study. Whether the Van der Waals equation by itself could actually produce the different types found experimentally, away from the pristine starting point of Korteweg’s mixture of identical components, still remained an open question.

7.5.3 ‘*The different forms and transformations.*’ Van Laar (1905b) sketches out how he believes the full phase diagrams resulting from experiments must look. He demonstrates deep insight by remarking that the evolution of phase

diagrams in incompressible anomalous liquid mixtures due to changing the degree of association might likewise be achieved by changing the pressure in compressible fluid mixtures.

Van Laar classifies the phase diagrams found experimentally in three types, using different Roman numerals than K&S. We preferably use the K&S terminology here, but will add (vL) to the Roman numeral when referring to Van Laar's types. The three types postulated by Van Laar, which he claims are in agreement with Kuenen's data, are shown in Fig. 7.18.

This same paper presents an opportunity to admire Van Laar's (1905b) mastery of drawing fluid phase diagrams. Fig. 7.19 shows a dazzling rendering of a Type-III phase diagram in P - T - x space. Van Laar states in a footnote that he first saw this diagram in a presentation by Büchner, a graduate student of Bakhuis Roozeboom, who had not published it. The P - x sections shown, however, are from Van Laar's own hand.

Van Laar's (1905b) last page raises the question of whether, following the classification of a multiplicity of phenomena, a still farther synthesis, a higher unity, could be achieved. Since all fluid phases are following from one equation of state, he claims it should be possible to classify the different phase diagrams solely on the basis of the critical temperatures and critical pressures of the two components. This is what he sets out to do.

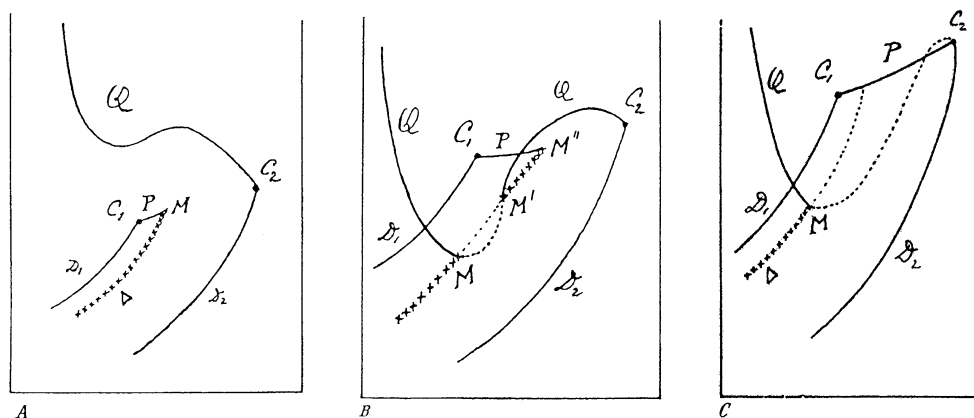


Figure 7.18 Three different types of binary-mixture phase diagrams. Copied from Van Laar (1905b), Figs. 13a-c. The left figure we recognize as Type III_m. Van Laar correctly compares it with Kuenen's plot for the ethane-methanol mixture, our Fig. 7.16. The right one is an odd-looking Type II. The middle figure shows a speculative intermediary between Type II and Type III, and is a correct Type-IV phase diagram. Van Laar compares its upper portion (unjustifiably, as we will see) with Kuenen's plot for the system ethane-propanol, our Fig. 7.15.

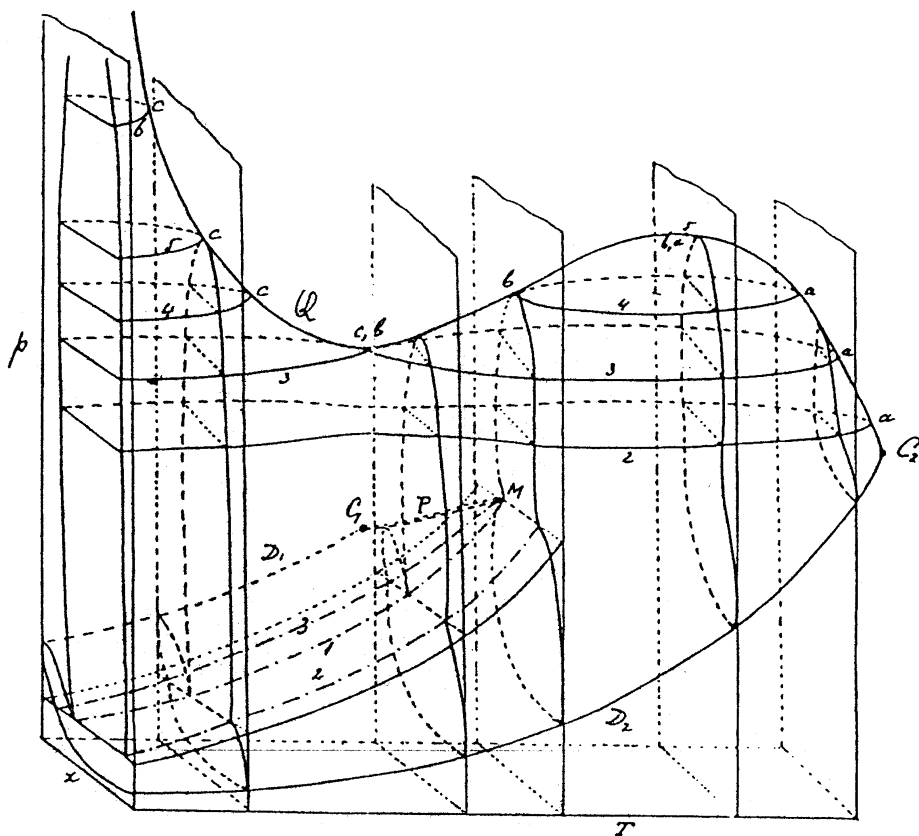


Figure 7.19 P - T - x diagram for a Type-III_m binary mixture. Copied from Van Laar (1905b), Fig. 4. The vapor pressure curve of the first component, D_1 , runs to the critical point C_1 . That of the second component, D_2 , runs to the critical point C_2 . A short piece of critical line runs from C_1 to M , the critical end point. Three phases, 1, 2 and 3, of different composition exist to the left of the critical line C_1M . A critical line starting at C_2 runs to lower temperatures, passing through a maximum and a minimum in pressure before moving to high pressure.

7.5.4 'An exact expression.' Van Laar (1905c) decides to renounce all forms of approximations he made in his earlier paper on liquid-liquid immiscibility, when he created an approximate Gibbs energy. In the first in a sequence of four papers, Van Laar (1905c) derives explicit, closed-form expressions for the isothermal spinodal curves in V - x space, and for the critical line in T , V , x space for the geometric-mean Van der Waals mixture equation. He assumes that the excluded volume interpolates linearly between those of the two pure components. Usually, but not always, b is considered a constant.

Instead of using the Helmholtz energy and finding the spinodal from setting the Hessian equal to zero, Van Laar makes a point of using the Gibbs energy, for which the criticality conditions have a simpler form, Eq. (4.16). His first exact result, obtained for linear dependence of b on composition, is a closed-form expression for the temperature of the spinodal in terms of volume and mole fraction. For each temperature, then, the V - x projection of the spinodal is determined. At this point, Van Laar gives reference to Van der Waals's (1890) paper on mixtures, which indeed gives an implicit expression for the T - V - x relation of the spinodal in Appendix I. It is not immediately transparent that it would reduce to Van Laar's simpler expression under the geometric-mean rule. See, however, Ch. 7.5.5.

Following Van der Waals and Korteweg, and giving credit to the former, he introduces the third critical temperature T_0 , at which a longitudinal plait first appears on the surface at $V = b$; this happens for $x = 1/2$ if the excluded volumes are the same, but favors the component with the smallest excluded volume if this is not the case. Van Laar labels it as C_0 . Next, after extensive formula manipulation, Van Laar obtains an algebraic equation for the projection of the plait point curve (critical line) onto the V - x plane, an expression of the fourth degree in volume and in mole fraction. The plait point temperature as function of volume and mole fraction is then obtained from the expression for the spinodal. It is of the fifth degree in volume and quadratic in mole fraction.

7.5.5 Van Laar finds a singularity in the plait point curve. Van Laar (1905d) belatedly checks the earlier, implicit expression for the spinodal in Van der Waals's (1890) paper on mixtures. Indeed, it agrees with his own expression after the mole fraction derivatives of the mixture parameters occurring in Van der Waals's paper are duly calculated for the geometric-mean assumption. But Van Laar strenuously defends priority for his equation for the projection of the plait point curve on the V - x plane. Van der Waals produced only an approximate rule for its shape, he writes, while Korteweg's expression is much more complicated. The semi-deferential, semi-aggressive tone of the introduction to the paper is a sign that Van Laar is under stress.

Curiously, Van Laar expresses the opinion that his equation is so much simpler because he started from the Gibbs free energy. This cannot be true, however, since the Helmholtz and Gibbs energy are equivalent alternatives. Recent work by Meijer *et al.* (1993), and by Levelt (1995), using computer algebra, proves that the simplicity results from the exclusive use of Van Laar's geometric-mean rule. Van Laar (1905a) considers this rule 'approximately exact.'

The fascinating and profound part of this paper begins in the second section, and is, from now on, restricted to the case of equal excluded volume for

the components and the mixture, and, as always, to the geometric-mean rule for a_{12} . The equations for the temperature of the spinodal and the plait point curves' projections on the V - x plane then simplify to the point that Van Laar can calculate them.

Van Laar uses the third critical temperature T_0 as the unit for his temperature scale, and introduces the parameter φ :

$$\varphi = \sqrt[3]{a_1} / (\sqrt[3]{a_2} - \sqrt[3]{a_1}) \quad (7.6)$$

This parameter represents an alternative way of expressing the difference between the two components, instead of the parameter ζ used by K&S. The smaller φ , the larger the difference between the two components.

In terms of φ , the ratio of T_1 , the critical temperatures of the two components to the third critical temperature is given by

$$T_1/T_0 = (16/27) \varphi^2; \quad T_2/T_0 = (16/27)(1 + \varphi^2) \quad (7.7)$$

Van Laar now calculates the projection of the plait point curve onto the V - x plane for two characteristic values: $\varphi = 1$ ($a_2/a_1 = 1/4$), and $\varphi = 2$ ($a_2/a_1 = 4/9$). Especially for the case of $\varphi = 1$, the second component is extremely volatile, with a critical temperature only $1/4$ of that of the first component. Eq. (7.7) shows that in the case of $\varphi = 1$, the 'third critical temperature' T_0 is between the critical temperatures of the components, while in the case of $\varphi = 2$ it is lower than those of the components. The results of Van Laar's calculation of the plait point line are shown in Fig. 7.20.

Van Laar (1905d) thus has discovered that in the physically accessible region the plait point curve shows two branches. For the smaller φ (large difference between the two components), one branch connects C_2 and C_0 , the other connects C_1 and the point A at zero temperature, for which $V = b$ at $x = 0$. For the larger φ (the substances becoming more alike), C_1 connects with C_2 , and C_0 connects with A. Under the geometric-mean assumption of the Van der Waals equation for equal excluded volumes, there are thus naturally two classes of phase diagrams, depending on whether C_1 connects with C_2 , or not.

Fig. 7.21 shows the critical lines projected onto the V - x plane, according to the symbolic calculations by Levelt (2001). They agree in detail with Van Laar's (1905d) calculations.

The next question is how the transition between the two cases arises. Van Laar (1905d) derives from his equation for the plait point curve an analytic solution for the location of the transition point, where the two curves exchange connectivity. In terms of φ and x , he presents the exact value:

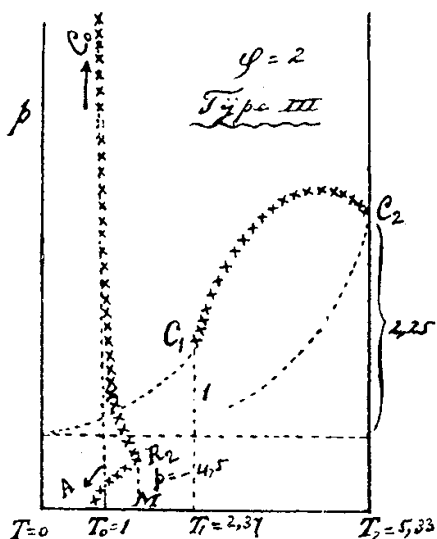
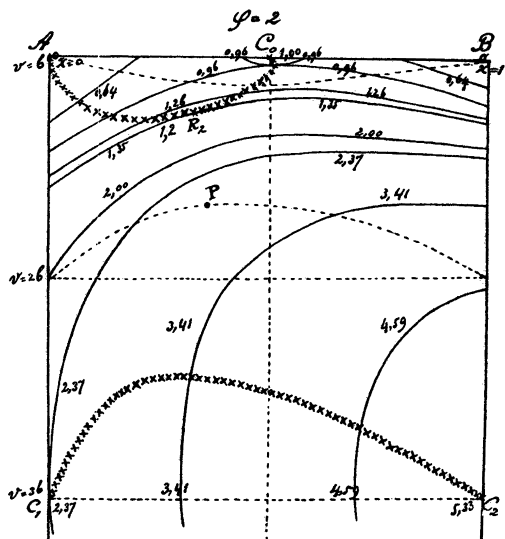
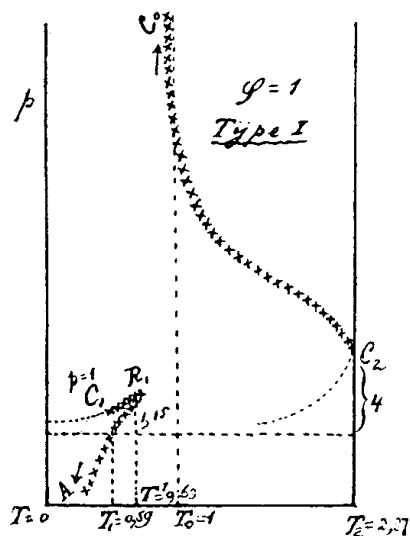
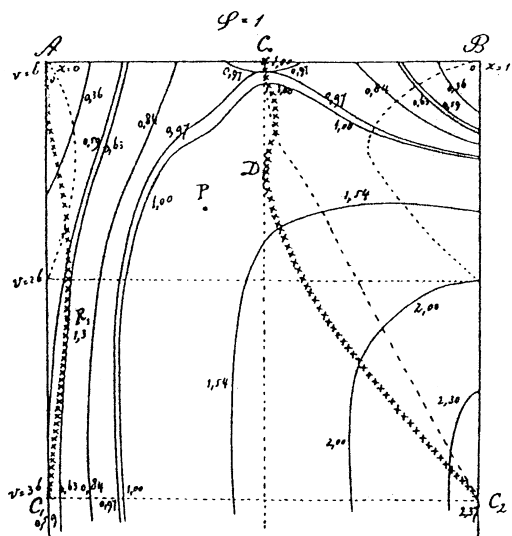


Figure 7.20 Projections of critical lines onto the V - x and P - T planes for two values of the parameter φ . Copied from Van Laar (1905d), Figs. 1, 1a, 2, 2a. The two diagrams on the left are V - x diagrams, the critical volume $3b$ being at the bottom, and the close-packed volume b at the top. The plait point curves are indicated by (xxx). The full curves drawn in the diagrams are isothermal spinodals, and they are labeled by the ratio T/T_0 . C_1 and C_2 mark the critical point of the pure components, C_0 is the critical point as the longitudinal plait enters the diagram at $V = b$. The two diagrams on the right are the corresponding projections of the plait point curves onto the P - T plane.

For $\varphi = 1$, $a_2/a_1 = 1/4$, the case of large difference between the components, the pure-component critical points are not connected. The critical line from C_1 to A touches a spinodal at R_1 . Thus along the plait point line starting at C_1 , the temperature first rises, and then falls, as can be seen from the temperature labels on the spinodals. This causes a cusp in the critical line in the corresponding P - T diagram, displayed below it, claims Van Laar, crediting Korteweg. We recognize this diagram as being of Type III, but note that the unstable part of the critical line is shown in this plot, rather than the three-phase line cutting it off. The critical line from C_2 ends in C_0 at $V = b$, at infinite pressure, and at a temperature between the critical temperatures of the two pure components. The wiggle between C and D is real: the plait point curve passes through a temperature minimum before it reaches C_0 .

In the case of $\varphi = 2$, $a_2/a_1 = 4/9$, with the two components not as different as in the previous case, the critical points of the pure components are connected. The cusp in the liquid-liquid critical line in the corresponding P - T diagram arises from the fact that the curve A- C_0 touches a spinodal in R_2 . This diagram is of Type II.

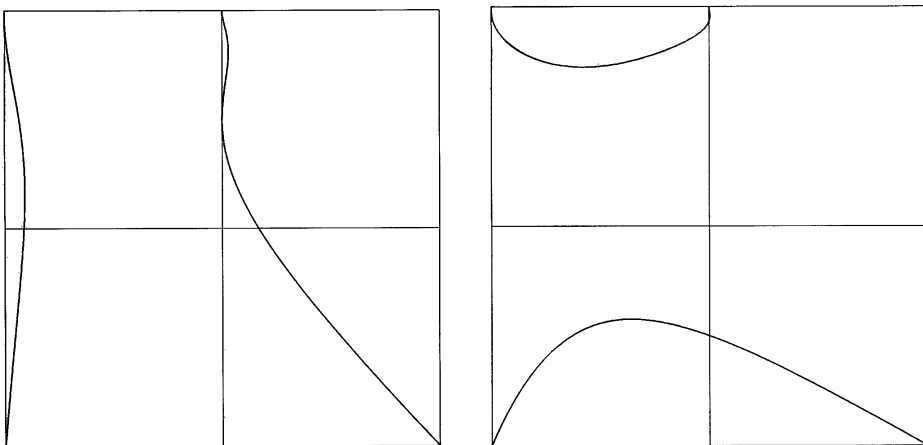


Figure 7.21 Computer-algebra results for the cases $\varphi = 1$ (left) and $\varphi = 2$ (right), by Levelt (2001). The agreement with Van Laar's results in Fig. 7.20 is excellent.

$$\begin{aligned}\varphi &= (1/2)(-1 + \sqrt{2} + \sqrt{6}) (= 1.432) \\ x &= (1/2)\{1 - (1/2)(\sqrt{6} - \sqrt{2})\} (= 0.2412)\end{aligned}\tag{7.8}$$

This corresponds with a ratio of 2.887 for the critical temperatures of the two components. Van Laar calls this point a double point. Following Meijer *et al.* (1990), we call it a *crossing point*. Van Laar's sketch of the V - x diagram at $\varphi = 1.432$ is presented in Fig. 7.22, left drawing.

Van Laar's calculation of the point of intersection is exact. It is obvious, however, that Van Laar's sketch of the phase diagram for the case of the crossing point, center of Fig. 7.22, is just that, a sketch. He did not calculate the critical lines for this value of φ . Although his value for the mole fraction at the crossing point is correct, it is not plotted in the right place. Also, the plot suggests that the two branches are tangent to each other at the crossing point. The computer-generated plots (right) show that this is not the case.

Meijer *et al.* (1993) showed that in a larger space the critical line segments in the physically accessible region of Van Laar's V - x plots are part of a single curve, which intersects itself as found by Van Laar. Meijer has proposed to call it the *Van Laar point*. Strictly speaking, however, he defined the Van Laar point as the intersection of the curves Tr , ADP , and MDP in Fig. 7.6. Only in the case of the Van der Waals equation for equal excluded volumes does the geometric-mean curve for the attraction happen to pass through this special point. In hindsight, Van Laar had an uncanny intuition and an incredible amount of good fortune by assuming the geometric-mean rule, thus being able to locate the transition point that now carries his name.

As mentioned earlier, computer algebra calculations by Meijer *et al.* (1993) and by Levelt (1995) have confirmed the exact result for the Van Laar point. The numerical result of K&S closely agrees with the exact results from Van Laar, Meijer and Levelt, confirming the accuracy of the numerical work of K&S.

7.5.6 The case of unequal excluded volumes. In a tour-de-force calculation, the intrepid Van Laar (1905f) undertakes the problem of calculating the spinodal curve in the case of unequal excluded volumes, be it still under the geometric-mean condition for the attraction. He derives a general equation for the crossing point, and confirms that for the case of equal excluded volumes it reduces to the result obtained previously. Then he treats a second case, in which the two components have the same critical pressure, which implies that $a_1/b_1^2 = a_2/b_2^2$. He finds that the crossing point still exists, but it shifts to an extreme ratio of the critical temperatures of the two components, namely almost 10. It is located on the line $V = b_x$, and at a very small value

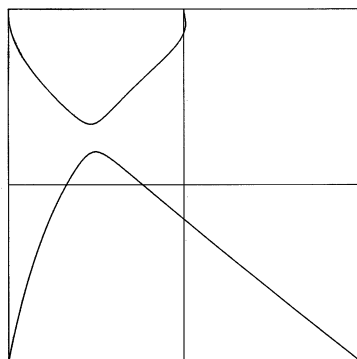
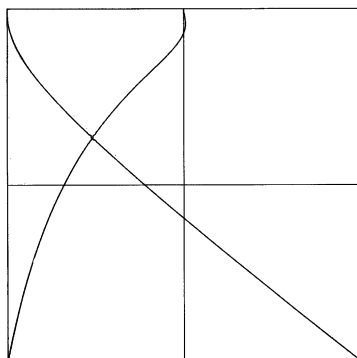
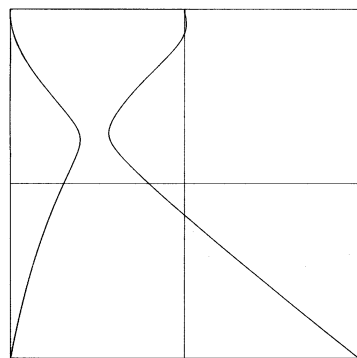
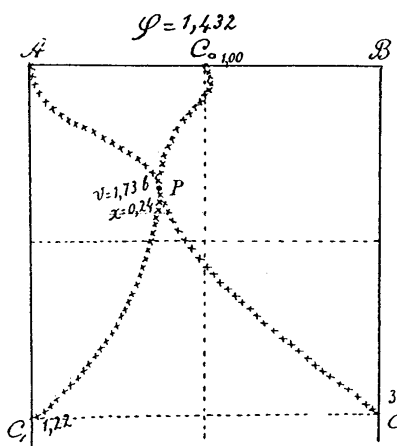


Figure 7.22 Exchange of branches of the critical curves in the V - x plane, by Van Laar (1905d), Fig. 4, left, and by Levelt (2001), right. Left: Van Laar (1905d) shows that the two branches of the critical curve intersect and exchange connectivity at the special point $\varphi = 1.432$. Right: computer algebra results by Levelt, for $\varphi = 1.42$, $\varphi = 1.432$, and $\varphi = 1.44$, from top to bottom.

of x . It seems therefore of little practical interest. For the time being, we just file this result. It will be of relevance in the following section.

7.5.7 The existence of Type IV. In a paper of over 50 pages, Van Laar (1906a) summarizes earlier results and then goes into considerably more detail. Referring to work by Korteweg (1891) that we discussed in Ch. 5.5.7, he shows how an accessory plait is formed from a heterogeneous double plait point in the unstable region, protrudes into the stable region, and exchanges roles with the principal plait by passage through an MDP (Figs. 5.12 and 7.6). Then he returns to K&S Type IV, which he had postulated to occur if the plait point line from C_1 to C_2 touches a spinodal twice, in R_1 and R_2'

He investigates whether that can be the case for the Van der Waals mixture, under the geometric-mean rule for attraction and for equal excluded volumes. After setting up the conditions for such touching, he finds, after lengthy calculation, that the only place this could happen is at the crossing point! But this is mathematically a pathological case. Van Laar concludes:

the spinodal can only touch the curve AC_0 in R_2[K&S Type II]), and a contact in both R_1 and R_2' cannot happen, *so that*....[K&S Type IV] *will be impossible for mixtures of normal substances when $\beta = 0$ ($b_1 = b_2$)* [Translated from the French; italics by Van Laar].

This result is in complete agreement with the K&S global phase diagram (Fig. 7.2), which shows that the geometric-mean curve passes through the Van Laar point, which terminates the Type-IV region.

Then, he works on the case discussed in Ch. 7.5.6: the critical pressure ratio equal to unity, the excluded volumes unequal, under the geometric-mean rule. He finds that for values of φ falling between the double-point value and a certain maximum value Q , there will be two points R_1 and R_2' on the branch from C_1 to C_2 , where the spinodal touches the plait point curve.

The possibility of a contact between the spinodal and the plait point curve – and that twice, as....[present Fig. 7.23] demands – and therefore the possibility of....[K&S Type IV] for the case $\pi = 1$, is hereby proved. [Translated from the French; italics by Van Laar]

In the maximum value Q , the two contact points R_1 and R_2' in Fig. 7.23 coincide and the critical line touches the three-phase line in an actual double critical end point, ADP in Fig. 7.6, so that a transition occurs from K&S Type III to K&S Type IV. Van Laar gives the precise conditions under which this transition takes place.

The second transition, from (metastable) K&S Type IV to Type II, now occurs by passage through a mathematical double point in the unstable region, MDP in Fig. 7.6, for which Van Laar finds the conditions as well.

These two transitions take place for large size ratios of the components, between 4.4 and 9.9, and for a very low mole fraction of the less volatile component, $x \approx 0.01$, but at distinctly different temperatures and molar volumes.

K&S (1980) also report some results on the asymmetric-size case $b_2 = 2 b_1$, and for linear mole-fraction dependence of b . They find that the geometric-mean line no longer passes through the Van Laar point, but traverses region IV. Van Laar recorded a similar traversing of region IV in the first decade of the 20th century, be it for different asymmetric-size cases.

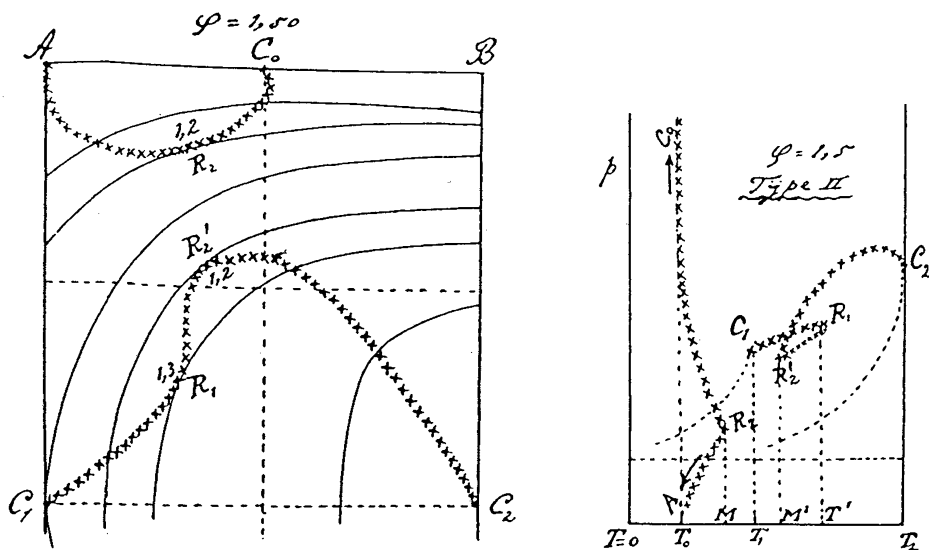


Figure 7.23 The formation of Type IV. Copied from Van Laar (1905d), Fig. 3, 3a. Van Laar makes the assumption that the critical line connecting the critical points C₁ and C₂ of the two pure components touches an isothermal spinodal twice, in the points R₁ and R₂', respectively. In each of these points, the critical line thus passes through an extremum in temperature. In a P - T diagram (right), this results in two cusps. The part of the critical line between R₁ and R₂' is not stable. A three-phase line (not shown) cuts off the metastable and unstable parts of the critical line. The critical line connecting C₀ and A touches a spinodal once, and therefore has one cusp in the P - T diagram, and another unstable part cut off by a three-phase line (not shown).

7.5.8 *An assessment.* It is easy to criticize Van Laar's work as myopic and to disregard it because it is so unappetizingly presented. Myopic, because of his single-minded pursuit of the geometric-mean case, with little attention given to Van der Waals's more general results. Poorly presented, because he does not set out his goals, nor does he state the major results before throwing himself into the calculations, in acute contrast to Korteweg's didactic style.

It is, however, undeniable that Van Laar obtained very important insights on the basis of this felicitous choice of the geometric-mean case. Concentrating on this case allowed him to obtain practical results by the very limited computational means available a century ago. In the process, he obtained profound insight into the different phase behaviors in binary mixtures of unlike components, and a fundamental understanding of how the transitions between the cases of Type II, III and IV take place.

It was a major achievement of Van Laar to demonstrate that the Van der Waals equation for normal (non-associating) compounds is perfectly capable of producing the kind of phase diagrams observed in experiment, with the exception of Type VI. This was contrary to the prevailing opinion that mixtures with an associating component, such as those studied by Kuenen, were outside the purview of the Van der Waals equation.

Given the state of discredit of the Van der Waals equation at that time, one would have expected Van der Waals to be very happy with this demonstration of the power and relevance of his mixture equation. Unfortunately, this was not the case. It was Lorentz who presented the Van Laar (1905d) paper on the shape of the plait point curve to the Royal Netherlands Academy.

8. Barotropic effect and gas-gas equilibria – Kamerlingh Onnes, Keesom, and Van Laar

8.1 *Historical setting – Keesom*

The Physics Laboratory in Leiden entered the 20th century in fine shape. Although the laboratory had lost the race for the liquefaction of hydrogen to Dewar in 1898, the technical advances made by Dewar, and in particular the invention of the double-walled, silver-plated vacuum glass that carries his name, were quickly incorporated into the instrumentation of the Leiden laboratory. Air and hydrogen liquefiers were under construction as an essential step towards the ultimate goal: the liquefaction of helium.

Once liquid hydrogen and a supply of pure helium gas became available by 1906, Kamerlingh Onnes and his group started preparing to take *PVT* data on hydrogen and helium at cryogenic temperatures, so that, with guidance from the law of corresponding states, an estimate could be made of the critical temperature of helium. While working with helium at liquid-hydrogen temperatures, Kamerlingh Onnes made a curious discovery. A vivid account of the discovery can be found in Kipnis (1996), p. 154-155. Here, we have followed the original papers and elaborate on the interpretation of the effect.

In this chapter, we meet a new player, destined to become the world's leading authority on the properties of helium at cryogenic temperatures. Willem Hendrik Keesom (1876-1956), a farmer's son from the island of Texel, began his physics studies at the University of Amsterdam and was a brilliant student. In 1904, he obtained his doctorate in Leiden with Kamerlingh Onnes. He held a research assistant position at the laboratory, where he was deeply involved in the preparations for the liquefaction of helium. From 1917 to 1923, he taught at the veterinary school in Utrecht. In 1923, he received a chair of experimental physics at Leiden University, and he succeeded Kamerlingh Onnes as the director of the Physics Laboratory. He was the first to solidify helium under pressure, in 1926. Over a period of time, he discovered evidence of a phase transition occurring in liquid helium at 2.19 K. In 1932, he measured, with Clusius, the lambda-shaped heat capacity anomaly of helium near

this superfluid phase transition. Keesom was elected to the Royal Netherlands Academy of Arts and Sciences (KNAW) in 1924, and to the Holland Society of Sciences and Humanities (HMW) in 1937.

Keesom's early work, in the time period covered in this book, concentrated on topics related to phase separation in fluid mixtures.

8.2 *A gas that sinks in a liquid*

8.2.1 *A curious experiment.* Kamerlingh Onnes (1906a) presented a two-page communication in the November Academy session about a strange phenomenon that he had observed. He was motivated by the following consideration. Suppose one pressurizes a system composed of a perfect gas and an incompressible liquid with negligible vapor pressure, and that the gas does not dissolve in the liquid. By pressurizing the system, it should be possible to increase the density of the gas enough to exceed the density of the liquid. If, initially, the gas was at the top of the vessel, it would end up at the bottom after enough pressure is applied.

Kamerlingh Onnes found such a system in fluids available to him: liquid hydrogen and compressed helium. He immersed a sturdy glass cell into a bath of boiling liquid hydrogen. The boiling point of hydrogen, 20 K, is far below the hydrogen critical point of 33 K, but far above the critical point of helium, which we presently know to be at 5.3 K. Kamerlingh Onnes filled the cell with a mixture of 6 parts hydrogen and 1 part helium. The system split into two phases, the liquid phase being mostly hydrogen and the vapor phase mostly helium. Kamerlingh Onnes then compressed the mixture. He noted that at 49 atmospheres, the gas phase sank and formed a large bubble at the bottom of the cell. Reducing the pressure to 32 atmospheres, he saw the bubble rise again. It was always clear which phase was the gas phase since the volume of the bubble decreased considerably with pressure, while the volume of the liquid was insensitive to pressure. Kamerlingh Onnes increased the pressure to 60 atmospheres, but the two phases remained.

Intuitively, the explanation of the sinking of the gas phase was relatively straightforward. The molecular weight of helium is twice that of hydrogen. By compressing the gas phase, consisting mostly of helium, one can make it denser than the liquid phase, mostly hydrogen.

Kamerlingh Onnes and Keesom (1906b), in the next Academy session, coined the term *barotropy* for the inversion of the phases. This paper is mostly descriptive. It speculates on the form of the isothermal transverse V - x plait in unit-mass coordinates, which must have a tie line parallel to the x -axis at the barotropic point, where the volumes per unit mass of the two phases are equal. At low enough temperature, however, when the plait runs

across the entire surface, the tie line must become parallel to the volume axis again at $x = 1$, so the system should re-invert at a second barotropic point. Thus, the authors are thinking mostly in terms of a transverse plait, although occasionally one finds an allusion to possible interference by a longitudinal plait.

The paper ends with an interesting question: what if the experiment would be done at a temperature where a solid phase appears? Would the solid phase, preponderantly hydrogen, float on top as the pressure increases? Schouten and Van den Bergh (1986) finally answered this question by studying a mixture of helium and hydrogen in a diamond anvil cell suitable for cryogenic work. Two diamonds, whose faces are separated by a gasket that forms the cell, are squeezed together, and high pressure is thus generated. The cell is the size of the head of a pin, and is observed under a microscope. Under appropriate conditions, the scientists observed three coexisting phases: a gas bubble, mostly helium, at the bottom; a mixed liquid phase, mostly hydrogen; and a tiny crystal of solid hydrogen floating at the top.

8.2.2 Azeotropy and barotropy. One could maintain that barotropy is just a curiosity, since a happenstance equality of mass density in two coexisting fluid phases does not seem to have any special physical significance. The chemical engineer who samples the wrong phase from a still because the phases have inadvertently switched positions might, however, be of a different opinion.

Van der Waals (1907) took an immediate interest in this discovery. His paper, presented in December, 1906, begins as follows 'Kamerlingh Onnes' startling experiment, in which a gas was obtained that sinks in a liquid....' He obviously did not consider it just a curiosity. On the contrary, he produced an elegant argument juxtaposing the cases of azeotropy and that of the sinking of a gas in a liquid. In the case of azeotropy, the two phases have the same mole fraction but different densities. The tie line is therefore parallel to the volume axis in the isothermal V - x plane, and so is the tangent at an azeotropic critical point. In the case of inversion of the phases, the two phases have the same mass density although molar density and mole fraction are different. If, therefore, mass units instead of molar units are used for volume and concentration, then at the inversion point the tie line is parallel to the mass fraction-axis, and so is the tangent at a plait point. The thermodynamic relations of the case of azeotropy, which Van der Waals (1890) developed earlier in his theory of mixtures, can be simply converted to those for the case of phase inversion by exchanging the volume and concentration variables.

No one will deny the significance of azeotropy in the case of fluid mixture behavior (see, for instance, Ch. 4.9, Ch. 5, Ch. 6.7, Ch. 7.2, Ch. 7.3, Ch. 7.4.3), nor its importance in the practice of distillation. Van der Waals

(1907) treated the two phenomena, azeotropy and phase inversion, on the same footing and thus gave azeotropy and barotropy equal fundamental significance. In the process, he developed the conditions for criticality of phases that have equal mass density.

8.2.3 *Quantifying the barotropic effect.* The Leiden researchers had a strong incentive to pursue this matter more deeply. Kamerlingh Onnes (1906a) mentions that even the sign of the parameter a for helium is unknown, and might even be negative, prohibiting liquefaction. From the paper by Kamerlingh Onnes and Keesom (1906b) it is clear that in December 1906, less than two years before the actual liquefaction of helium, they still did not have a reliable estimate of the helium critical temperature. If they could model the observed barotropic effect, that might give them an estimate. A paper by Keesom (1906) follows in the same session, in which such a model is presented. Interestingly, for this purpose the Leiden investigators, for the first time, turn to the Van der Waals equation for mixtures. To begin with, Keesom reformulates the Van der Waals equation for binary mixtures in terms of mass, instead of molar variables. In order to model the system helium-hydrogen, he chooses the molar mass ratio as 2, and assumes that the molar critical volume of helium is $1/4$ that of hydrogen. For this parameter choice, the Van der Waals equation predicts that there is a barotropic point on the gas-liquid plait around the boiling temperature of hydrogen, if the critical temperature of helium would equal $1/20$ that of hydrogen (roughly 1.5 K). A discouraging result indeed! Note, however, that this is a result applying to a transverse plait. At various instances, Kamerlingh Onnes and Keesom, however, do caution that a longitudinal plait might be present.

Keesom (1907) tries to find conditions for a barotropic plait point for the Van der Waals equation that give agreement with the observations of barotropy in the helium-hydrogen mixture. This study still limits itself to a transverse plait, but reference to possible interference with a longitudinal plait is frequent. What values to use for the a and b parameters turns out to be a difficult question. In a 1 $1/2$ page footnote, Keesom struggles to find a and b parameters suitable for describing known hydrogen and helium properties, while giving results compatible with the barotropic experiment, in an effort to estimate the critical temperature of helium.

As in his previous paper, Keesom begins with an excluded volume for helium that is $1/4$ of that of hydrogen per mole ($1/8$ per unit mass), but also tries a value twice as large. What to choose for the value of a for helium is unclear. Keesom expects that the cohesion of helium is very small, and realizes that in that case Van der Waals's mixture equation would give rise to a longitudinal plait. Another unknown in the problem is the composition

dependence of the excluded volume for helium-hydrogen. Even with that many adjustable parameters, it is not possible to make sense of the meager experimental evidence under the hypothesis that there is a transverse liquid-vapor plait. Upper bounds for the helium critical temperature in the paper range from $1/175$ to $1/4$ of the critical temperature of hydrogen, rendering them useless. In writing this paper, however, Keesom is gradually acquiring the insight that the presence of a longitudinal plait must be considered. Further work with Kamerlingh Onnes elucidates what the nature might be of the phase diagram helium-hydrogen (Sec. 8.3).

A final remark about barotropy: this is a phenomenon more general than that of 'a gas sinking in a liquid.' If two liquid phases of almost the same mass density but of different compressibility coexist, a change of pressure can easily lead to phase inversion, to no one's surprise. Historically, however, this feature was first discovered in the more spectacular case of 'a gas sinking in a liquid' and was connected with phase separation in the gas phase.

A reliable value for the critical temperature of helium would be obtained later in 1907, after the first P - V - T data for helium at temperatures around 20 K became available. Using the law of corresponding states and mapping the helium isotherms onto those of hydrogen, Kamerlingh Onnes (1907e) obtained an estimate of 5.3 to 6 K for the critical temperature of helium. As narrated in Sec. 3.3, this estimate enabled the designing and dimensioning of a helium liquefaction apparatus; helium was first liquefied on July 9, 1908.

8.3 *Gas-gas separation*

The Leiden work now takes a different turn. In the next few papers, Kamerlingh Onnes and Keesom (1907a, 1907c; Comm.Leiden Suppl. 15) elaborate on the idea of a mixture in which one component has no cohesion, and investigate the phase behavior of a Van der Waals mixture with $a_2 = a_{12} = 0$. That is, the second component exerts no attractive interactions whatsoever, but *does* have a finite excluded volume. Here subscript 1 refers to the component representing hydrogen, and 2 refers to the component without cohesion, representing helium. In the K&S global phase diagram for equal excluded volumes, Fig. 7.2, this case would correspond with $\zeta = 1$, $\Lambda = 1$. It does fulfill the geometric-mean condition for the attraction.

Contrary to the experiences of Korteweg (Ch. 5, Ch. 7.3) and Van Laar (Ch. 7.5), who ended up with complex models requiring extensive formula manipulations, the two Leiden scientists invented a model that they could handle readily. It shows some interesting physics. There is at most one plait on the isothermal Helmholtz energy surface, a plait that is neither purely transverse, nor purely longitudinal. The second component has no critical

point, so no plait can begin or end there. The two coexisting phases can be considered to both being gas phases, since they may occur above the critical temperatures of both components. In the spring of 1907, the two scientists reached a full understanding of the behavior of the gas-gas plait for the Van der Waals binary mixture.

The 1907a paper begins on a provocative note. First of all, there is a three-line footnote referring to the Van Laar (1905c,d) paper that contain the exact expression for the plait point curve, as discussed in Ch. 7.5.4. The footnote states:

Van Laar treated the projection of the plaitpoint curve on the v, x plane for such a mixture, without, however, further investigating the form of the spinodal curve and of the plait.

This is a rather grievous understatement of the work of Van Laar, who will not take this remark lightly (see below). The Leiden authors further ignore Van Laar's work, and base themselves solely on the Van der Waals (1890) mixture paper.

In the second paragraph Kamerlingh Onnes and Keesom (1907a) state:

Two different phases may be in equilibrium which must both be considered as gasphases. Then the two substances which are the components of these mixtures are not miscible in all proportions even in the gas state.

The italics are theirs. Here we see two good advertisers at work: this sentence is bound to catch the eye of the reader.

Another footnote on the first page refers to an Academy paper by Van der Waals (1894d). In this brief paper (in Dutch) Van der Waals indeed postulates that there might be a longitudinal plait on the Helmholtz-energy surface at temperatures exceeding the critical temperatures of the two components, so that there is no transverse plait on the surface. He expects that this could happen when 'the mixing takes a lot of energy' presumably because the cohesion between unlike components is much weaker than that of each of the components. For Van der Waals's description of the birth and growth of the longitudinal plait, the reader might refer to a picture from Korteweg's work for the symmetric case, see Fig. 7.7 (GTP A_1). This plait moves into the surface from the 'side of the small volumes', $V = b_x$, where the pressure is infinite. Once formed, well above the critical temperature of the components the plait proceeds into the V - x plane towards the larger volumes as the temperature is lowered. It begins at the temperature at which the plait point appears on the line $V = b_x$. We recall that this 'third critical temperature' was introduced earlier by Van der Waals (1890) in his Appendix, as well as by Korteweg (1891b).

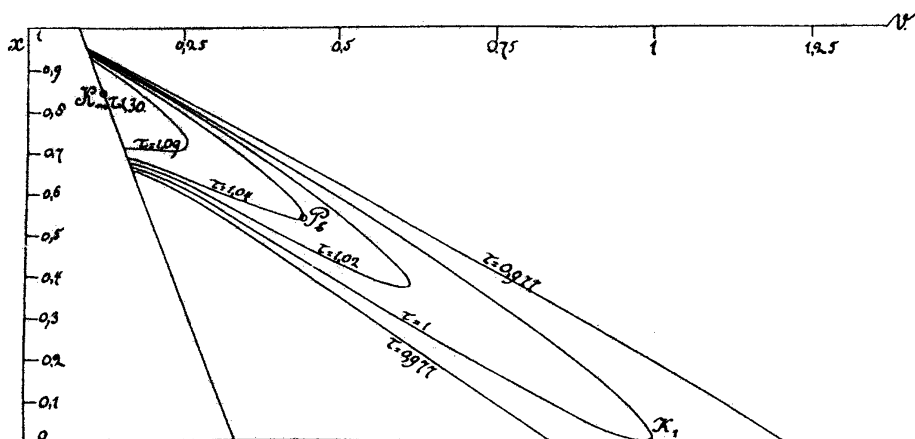


Figure 8.1 The gas-gas plait for a binary mixture, one component having no cohesion. Copied from Kamerlingh Onnes and Keesom (1907a), Plate I, Fig. 1. Several isothermal spinodals are indicated, each labeled with its value of the reduced temperature $\tau = T/T_{K_1}$. The plait starts at K_m , and moves into the V - x surface as the temperature drops. The plait point leaves the surface at K_1 , the critical point of the component that does have cohesion.

Van Laar (1905b, 1905d) used it extensively in his analysis of the various types of phase diagrams, as discussed in Ch. 7.5.4.

In their treatment of the case where one component has a non-zero excluded volume but no cohesion, the two Leiden scientists begin with their version of the Van der Waals equation in mass units, for a molar mass ratio of 2 and a molar volume ratio of 1/4 between the first and second component. Only the first component has a nonzero value of a , and the quadratic mixing rule, Eq. (4.5), is used to calculate a_x . The value of b_x is linearly interpolated between the excluded volumes of the two components. They use the Van der Waals (1890) expression for the spinodal, substitute the chosen values for the parameters, and obtain a relation cubic in volume and mass fraction, and linear in temperature. They solve this equation numerically and obtain the spinodals shown in Fig. 8.1 for a variety of temperatures. The result is a plait running at an angle through the V - x plane. The plait point begins at K_m , their symbol for the third critical temperature, which in this case equals 1.30 on a reduced scale, and ends at the critical temperature of the first component. The plait moves into the plane as the temperature falls. Once the plait point reaches the critical point of the first component, it leaves the surface, and only an open plait is left. Fig. 8.2 shows the progression of the plait in P - x coordinates.

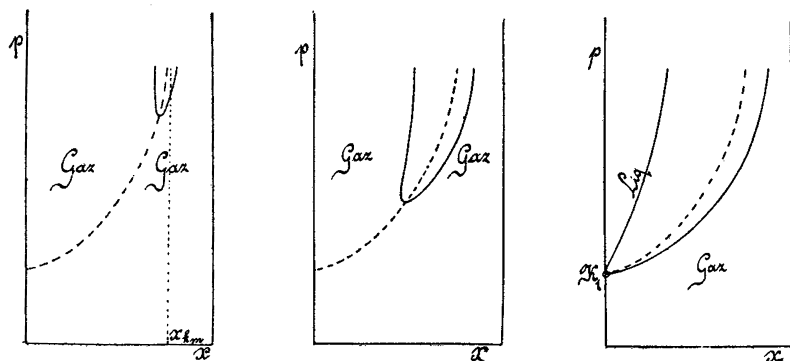


Figure 8.2 A schematic of the gas-gas plait in the pressure-mass fraction plane. The plait moves to the pure-component critical point as the temperature decreases. Dashed curve: projection of the critical line. Full curves: isothermal connodals. Copied from Kamerlingh Onnes and Keesom (1907a), Plate 1 Figs. 3-5.

On the open plait near the critical point of the first component, the two coexisting phases differ in density, and it is still sensible to distinguish a vapor and a liquid phase, even though the temperature may be above the critical temperature of the only component that has a critical point. Near the third critical temperature, however, the phases are both near the close-packed state and differ mostly in mass fraction. The character of the plait thus changes from mostly transverse at the first component's critical point to mostly longitudinal near the close-packed state.

Our Leiden heroes, however, spend many pages arguing that both phases should be called gas phases. At first they use the following criterion: the name gas or liquid is appropriate only if the particular phase can be connected without a phase transition along an isobar or isopleth (curve of constant concentration) to another phase for which the designation gas or liquid is clear. The authors seem to get trapped in convoluted semantics, but finally propose another criterion: that the plait must occur at temperatures above the critical temperatures of both components. The term gas-gas equilibrium is indeed still in use for this case.

In the last part of the paper, presented on March 30, 1907, the authors relax the condition of zero cohesion, and just make the cohesion a_{22} very small. They decline to discuss the complications induced by the presence of the additional critical point for the weakly cohesive second component, referring to Van Laar (1906a, 1906b) in a footnote, but without any discussion of the quoted work. They then discover that the gas-gas plait may split, one part coming in from the critical point of the first component, the other

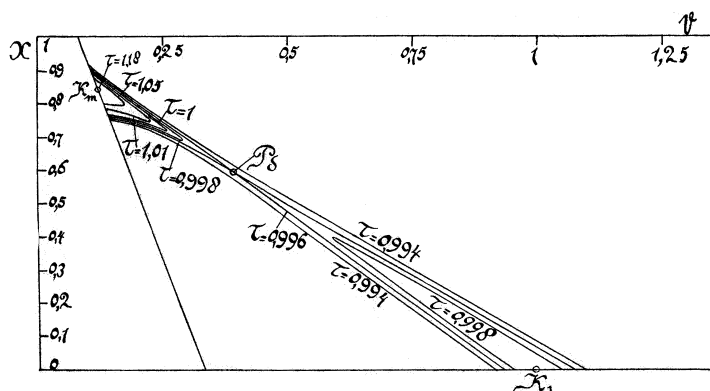


Figure 8.3 The gas-gas plait in the case that one component has small, but nonzero cohesion. Isothermal spinodals are shown, each labeled with the value of $\tau = T/T_{K_1}$. Plaits now enter from K_m and K_1 , and meet at a homogeneous double plait point as the temperature decreases. Copied from Kamerlingh Onnes and Keesom (1907a), Plate II.

part from the line $V = b_x$. As the temperature decreases, the two plaits meet in a homogeneous double plait point, at a temperature minimum, Fig. 8.3. They calculate the conditions for the minimum in terms of the interaction parameters of the two components. They do cite Korteweg in connection with the meeting of the two plaits in a homogeneous double plait point. What is missing from this paper is a connection with previous work by Kuenen, as well as by Van Laar, discussed in Ch. 7, on systems that have a plait point curve running to high pressures. Although Van Laar's (1906a, b) work is cited, it is brushed aside as not relevant to a component with feeble attraction. Shortly after, the authors will receive a forceful reminder of this omission.

8.4 *Matters of priority – Van Laar, Kamerlingh Onnes and Keesom*

A pained reaction by Van Laar (1907a) was presented to the Academy by Lorentz one month after the second of the Kamerlingh Onnes and Keesom (1907a) papers had been communicated. Van Laar wrote the bulk of his paper after he had read the February 23, 1907 presentation (§I-§6), but before he read that of March 30 (§7). Van Laar must have hastily composed this 13-page paper. The large number of typos and aggrieved tone, in addition to the content, point to considerable mental anguish on the part of the author.

In a footnote, Van Laar criticizes the use of the term gas-gas equilibrium for two obviously quite dense phases. He proposes to use Van der Waals's term 'fluid phases.' Van Laar has a point, but history will not be on his side.

Van Laar reminds Keesom that if the cohesion of the second component is weak, the phase diagram is more complicated than the single simple plait the Leiden scientists show, because the volatile component now has a critical point, with a three-phase region nearby.

In the first few pages, Van Laar claims priority regarding the plait described by Kamerlingh Onnes and Keesom (1907a). Keesom's application, with $a_{22} = a_{21} = 0$, is indeed a special case of Van Laar's geometric-mean Van der Waals mixture model, so Van Laar's point seems well taken. In a footnote, Van Laar refers to half a dozen papers from his hand, written in 1905 and 1906. Several of these were discussed in Ch. 7.5.

We recall how Van Laar showed that the two parts of the V - x projection of the plait point line exchange connectivity at a special condition of the interaction parameters (Ch. 7.5.5). If the critical temperature ratio is larger than that corresponding to what we now call the Van Laar point, a plait point curve will run from the plait point of the least volatile component, C_2 , to the 'third critical point' C_0 at $V = b_x$, resulting in what we presently call a Type-III phase diagram (Fig. 7.4). Van Laar himself was fully aware, and mentions again here, that the experimental systems water-ether and ethane-methanol are of this type. He also showed that this feature persists, even when the excluded volumes are unequal. The peculiar limiting case of one component with zero cohesion and therefore no critical point, he writes, may have led to failure on Kamerlingh Onnes's and Keesom's part to connect with Kuenen's and Van Laar's vl Type-I, presently called Type-III phase behavior.

Van Laar is very insistent on a particular aspect of the plait: will this plait run from C_0 to C_2 , (or from K_m to K_l , in Fig. 8.1), as discussed by Keesom? Or could it start as two plaits moving from each end towards each other and meeting in a double plait point somewhere in the middle of the V - x plane? If the latter is the case, the plait point curve from K_l to K_m (from C_2 to C_0) must pass through a temperature minimum. This minimum, where the two parts of the plait meet, is clearly visible in Van Laar (1905d), Fig 1, reproduced in this book in Fig. 7.19. See the two isothermal spinodals join barely below C_0 , in the top left figure, for $\varphi = 1$. Van Laar (1905e) also specified conditions on the ratios of critical pressures and critical temperatures of the two components for the minimum to occur. Unfortunately, the precise location of the minimum, topic of a paper Van Laar (1906a) had submitted to Archives Teyler, was not yet in print when the Kamerlingh Onnes and Keesom (1907a) paper appeared (although the Leiden scientists did cite it, but considered it not relevant). So, in a rush, Van Laar (1907a)

summarizes the Archives Teyler paper in seven or eight pages of dense formulae and calculations.

Van Laar (1907b) added an appendix to his paper after he read the March 30 presentation of Kamerlingh Onnes and Keesom (1907a). For the more general case that a_{22} is small but not zero, the Leiden authors indeed discovered that there is a minimum in the plait point curve, and derived an expression for it. This obliterates part of Van Laar's criticism in the body of his paper. Van Laar (1907b), however, demonstrates in his Appendix that he derived this identical expression a year earlier, see Van Laar (1905g), and mentions that Verschaffelt (1906a) confirmed this result shortly after.

A reply by Kamerlingh Onnes and Keesom (1907c) was not long in coming. Half the first page of their paper is occupied by lengthy footnotes disputing Van Laar's criticisms. They do not agree with his objection to the terminology gas-gas. They feel they did sufficient justice to Van Laar's work on the three-phase equilibrium in the VL Type-I phase diagram by citing a reference to his papers in the last part of their criticized paper. For the 'critical point of complete miscibility' (Van Laar's third critical temperature) they credit Van der Waals (1890). Then they point out that Van Laar treated only one case of a gas-gas line, namely that with a minimum in temperature. In a lengthy discussion demonstrating their familiarity with Korteweg's theory of plaits, they argue that there are several cases with no minimum in the plait, one of which having been discovered by themselves, but overlooked by Van Laar.

In a remarkably meek reply, Van Laar (1907b) concedes the points made by Kamerlingh Onnes and Keesom, and generously acknowledges (in a footnote in the English version of the Proceedings) the priority of Kamerlingh Onnes and Keesom in recognizing different ways the plait may run to the third critical point. Half a page of errata to his preceding paper appears at the end of this paper. These do not refer to typos, but to issues of substance resulting from Van Laar's haste in producing the 1907a paper.

The last paper in the sequence by Kamerlingh Onnes and Keesom (1907d) combines the two themes: barotropy, and mixtures in which one component has only feeble cohesion. It is a very detailed investigation of the kinds of plaits that show barotropy. We will not discuss this paper here, but only mention that constructive references to Van Laar's work are now plentiful and generous, giving Van Laar credit where credit was clearly due.

8.5 *Measuring gas-gas equilibria*

According to their own principles, Kamerlingh Onnes and Keesom had not measured gas-gas separation. This term refers to the case that the plait exists

above the critical temperatures of both components. The Leiden scientists, however, measured the phase separation in the helium-hydrogen system at the hydrogen boiling point, well below the critical point of hydrogen but far above that of helium.

It is common for the critical line to move through a minimum temperature for systems that display this kind of separation. Consequently, a high pressure is needed to then bring the mixture critical temperature to higher values than the critical temperature of the least volatile component.

Krichevskii and Tsiklis (1941) first measured gas-gas separation in the system nitrogen-ammonia. It took a pressure of over 9500 atmospheres to bring the mixture critical temperature above the ammonia critical temperature.

8.6 *A case study of the workings of the Dutch School*

The short episode, less than a year, in which the phenomenon of barotropy was discovered, explained, and generalized to gas-gas equilibrium, provides an interesting example of the mode of operation of the Dutch School. Kamerlingh Onnes himself performed the innovative experiment: compressing a mixture of two components of very different volatility, hydrogen and helium. To explain the existence of a plait persisting to high pressures, Kamerlingh Onnes and Keesom used the 1890 paper by Van der Waals in a straightforward and effective way. In the process, they intruded on territory recently occupied by Van Laar. Van Laar then overreacted, writing a substantial paper before he had completely read the Leiden scientists's paper. Kamerlingh Onnes and Keesom were in good command of all issues, and had indeed found variants of what they called the gas-gas plait that Van Laar had overlooked. The episode ended in harmony, and on a rare conciliatory note by Van Laar. This episode had a high level of intellectual intensity, as evidenced by the large number of academy presentations in such a short time span.

Amidst all this commotion, what was Van der Waals's role? Apparently, his only contribution was the very nice paper on the analogy of azeotropy and barotropy, which we discussed. Throughout these stormy discussions about the plait running to infinite pressure, while his name was invoked repeatedly, Van der Waals plowed away at a five-part series of substantial papers on the theory of binary mixtures and stayed out of the fray.

9. Criticality, capillarity, and critical exponents: Verschaffelt and Van der Waals

In the development of the theory of plaits on surfaces, the prominent role of the critical point was evident right from the beginning. Korteweg's (1891a) paper on plait points is based on the special form of the Taylor expansion of the surface at such a point (Ch. 5.3.4). The assumption of analyticity of the mathematical representation of a thermodynamic surface was as natural and obvious to the Dutch School as the use of Gibbsian thermodynamics. The second half of the 20th century, however, witnessed essential progress in the understanding of criticality in fluids and solids, magnets and model systems. Surprisingly, however, modern theory was found to be in profound disagreement with the predictions of mean-field theories such as that of Van der Waals for fluids, or that of Curie and Weiss for magnetism. The question this chapter answers is: did no one notice early on that something was profoundly amiss?

At least two scientists did notice. Van der Waals (1894), in his work on capillarity, found a discrepancy between his theoretical prediction and the experimental behavior of surface tension. Verschaffelt pinpointed the origin of the discrepancy while working on his doctoral thesis with Kamerlingh Onnes. This happened around 1900, a full half century ahead of the development of modern theory. Since this topic is somewhat specialized, it requires an introduction, which will be followed by a discussion of Van der Waals's contribution, and by the story of Verschaffelt's detective work. Biographical material about Verschaffelt is added at appropriate spots in the narrative. The chapter is based on Levelt Sengers (1976).

9.1 *Characterization of critical behavior*

9.1.1 *What happens at a critical point?* Any experimentalist observing a fluid such as carbon dioxide near its critical point is immediately struck by the appearance of the fluid. When a transparent homogeneous fluid is cooled to within a few tenths of a degree from criticality, the fluid becomes opaque, so that it looks like a thick mist. Then, a meniscus forms near the center of the cell, and the mist

clears after the temperature drops a few more tenths of a degree. This phenomenon is called *critical opalescence*, and it was quite familiar to experimentalists in the 19th century. The opaqueness is caused by strong variations in the refractive index in the cell over distances comparable to the wavelength of light. These are, in turn, due to variations in the fluid density. The wavelength of light is of the order of 1000 molecular diameters, and thus these fluctuations occur on a mesoscopic scale far exceeding molecular dimensions. Clearly there is another length scale in the system. The average radius of the fluctuations is called the *correlation length*. The closer to the critical point, the longer the correlation length. It becomes infinite at the critical point. There is a reason for the emergence of these correlated regions. In the words of Benjamin Widom, a forerunner of the revival of interest in criticality of fluids and major contributor to the field ever since: ‘the system is practicing to split into two phases’ by forming microscopic regions that will become vapor and liquid after the system is cooled through the critical point. Thermodynamically, the compressibility of the system is becoming very large, and therefore, the energy cost of making a density fluctuation is far less than it would be far from the critical point.

Van der Waals’s equation of state was the first formulation of a critical-point phase transition in terms of a molecular model of hard spheres with a range of mutual attraction. The Van der Waals attractive term, however, is proportional to the bulk density. Thus, there is no allowance for the existence of the fluctuations that make the near environment of a molecule different from the bulk.

Einstein was the first to propose an explanation of critical opalescence in terms of the fluid compressibility in the early 20th century, but his result was correct only for the scattering intensity in the forward direction, while overestimating it in all other directions. Two Dutch physicists at the University of Groningen, Professor Leonard Ornstein (1914) and his graduate student Frits Zernike (a future Nobel-prize winner), formulated a theory of critical opalescence that accounted at the mean-field level for the angle-dependence of critical light scattering due to the long-distance correlation of density fluctuations. Their work provided a key contribution to the theory of liquids developed during the 20th century.

Criticality is so interesting because the presence of these long-range fluctuations has strong consequences for the behavior of thermodynamic and transport properties. In near-critical systems, the effects of fluctuations are dominant, and the molecular peculiarities, size, shape, and interactions, are in the background. This leads to great similarity in criticality of diverse systems, far exceeding the class of fluids and fluid mixtures: binary alloys, certain magnetic systems, and statistical-mechanical models. All behave similarly near a critical point as long as the independent and dependent variables are chosen properly. Modern theory calls this similarity in behavior *critical point universality*.

9.1.2 *Power laws and critical exponents.* As we have seen in Ch. 5, the mathematician Korteweg (1891a) provided the foundation for the description of criticality in fluid mixtures.

For a one-component fluid, the procedure is simpler. The Helmholtz energy $A(V, T)$ is expanded, its second and third derivatives with respect to volume being equal to zero, while there is nothing special about the temperature dependence. A double-tangent is drawn, as shown in Fig. 2.3. It is then found that close to the critical point the connodal or binodal (presently called coexistence curve) is a parabola, see Fig. 9.1. Thus, when the temperature T approaches the critical temperature, the density difference between the two phases T_c disappears as $(T - T_c)^{1/2}$. The P - V relation on the critical isotherm is a cubic, the pressure difference with the critical pressure disappearing as the third power of the density difference, see Fig. 9.1. Since the compressibility becomes infinite at the critical point, the inverse compressibility at the critical density has to approach the value of zero proportional to $(T - T_c)$. All these facts were quite well known to the Dutch School.

Presently, these expressions of critical behavior in terms of a power of the distance from the critical point along a specified path go by the name of *power laws*. The exponents characterizing the asymptotic behavior of the coexistence curve (β), the critical isotherm (δ), and the inverse compressibility (γ) are called *critical exponents*. They assume the values $\beta = 1/2$, $\delta = 3$, and $\gamma = 1$, respectively, for equations of state analytic at the critical point, as long as only two volume derivatives of the pressure are equal to zero at this point.

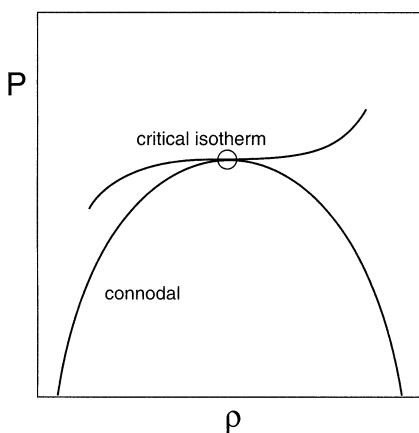


Figure 9.1 The connodal (coexistence curve) and the critical isotherm in the pressure (P) – density (ρ) plane. For the Van der Waals equation and other analytic equations of state, the coexistence curve is a parabola and the critical isotherm is a cubic.

The special form of the power laws is not just a mathematical consequence of the form of the Van der Waals equation. They must hold true for any Helmholtz-energy formulation for which a Taylor expansion exists at the critical point and for which only the second and third derivatives are equal to zero.

The Van der Waals equation served as a model for the Curie-Weiss theory of ferromagnetism, and the curve of spontaneous magnetization as a function of temperature shows the same parabolic shape at the Curie point as the fluid coexistence curve. Because the Curie-Weiss theory assumes that each magnetic spin finds itself in the average field of all spins, this theory, and a fortiori all theories that assume analyticity at the critical point, are called mean-field theories. Alternatively, they are denoted as ‘classical,’ which only refers to their venerable analytical basis, not to a contrast with quantum mechanics.

9.1.3 Modern theory of criticality. Onsager’s (1944) solution of the two-dimensional Ising model marks the beginning of the modern era. This is a model for magnetic spins placed on a lattice. These spins interact solely through nearest-neighbor forces. At low temperatures, all spins are lined up either ‘up’ or ‘down’ and the system is fully magnetized. As the temperature increases, spins start flipping out of order and the spontaneous magnetization diminishes. The more spins flip, the more disordered the system becomes and the easier it is for the next ones to flip. Finally, on average 50% of the spins point up and 50% point down, and the spontaneous magnetization has disappeared. For Onsager, solving this problem required a mathematical tour de force. The rewards were great. To the amazement of the scientific world, the model produced a heat capacity (which is proportional to the second temperature derivative of the Helmholtz energy) that becomes infinite at the critical point logarithmically. This is something an analytic theory could never do – second derivatives of analytic functions just do not diverge. The experimental discovery of the divergence of the isochoric heat capacity of argon by Alexander Voronel and his group, see Bagatskii *et al.* (1962), was an important factor in rekindling physicists’ interest in fluid criticality.

The modern study of criticality came to full bloom in the 1960s, when scientists began to investigate the critical behavior of the three-dimensional Ising model and its lattice-gas variant. The latter is a simple model for a vapor-liquid phase transition, with lattice sites occupied by molecules or ‘holes’ (empty sites). It was found that the coexistence curve of the three-dimensional model was roughly cubic in shape:

$$\rho_l - \rho_v = B(T_c - T)^\beta, \quad (9.1)$$

with ρ_l the liquid, ρ_v the vapor density, and B a substance-dependent coefficient called a critical amplitude. The best modern value of the critical

exponent β for the three-dimensional Ising model equals 0.326, substantially different from the value $1/2$ for a classical or mean-field theory. The best values for fluids agree with this Ising-model value to within their uncertainty, a triumph of the modern principle of critical-point universality.

When the news of the (almost) cubic coexistence curve for the Ising model sank in, scientists remembered a paper by Guggenheim (1945). Guggenheim had analyzed the experimental coexistence curves of several noble gases and found that they were cubic in shape. To this day, the myth is perpetuated that Guggenheim discovered the cubic coexistence curve. Guggenheim rediscovered it and also produced a very convincing plot, reconfirming the adage that a picture is worth a thousand words. The original discovery, however, was made half a century earlier in the Netherlands.

The difference between a parabolic and a cubic coexistence curve is both obvious and of fundamental importance. In appearance, a cubic curve is much flatter than a parabola. Fundamentally, a Helmholtz energy that is analytic at the critical point cannot possibly give a cubic coexistence curve.

9.1.4 *How to measure a coexistence curve.* To find out the asymptotic shape of a coexistence curve, an experimenter needs to be able to measure accurately the densities of coexisting phases as a function of temperature as close to the critical point as possible. Simultaneous density measurement in coexisting phases is not easy to arrange. In the 19th century, an alternative method was developed which is still in use. Densities are measured on each side of the coexistence curve independently. The measured densities of vapor or liquid are plotted as a function of temperature, and an interpolation is made for the true coexisting density values at a chosen temperatures.

The procedure is as follows. A glass cell of known volume is partially filled with a known amount of liquid. The cell is sealed and heated. The temperature is noted at which the meniscus, the interface between coexisting phases, reaches the top or the bottom of the cell. At the temperature at which the meniscus is on the verge of exiting, the cell is filled with a homogeneous fluid of known density, and thus a density value on the coexistence curve is obtained. In the first case, the meniscus reaching the top, the cell is overfilled: it runs out of vapor before the critical point is reached, and a density-temperature value on the liquid side of the coexistence curve is obtained. In the second case, the cell is underfilled, and one obtains a point on the vapor side. It is also possible (and even easier than one might think) to fill the cell in such a way that the meniscus remains near the center of the cell, where it flattens, and finally disappears at the critical point. This is a standard method of measuring the critical temperature of a fluid.

The reader should appreciate that as the temperature rises in the sealed glass vessel filled with a vapor-liquid system, so does the pressure. Typically, critical pressures range from 35 to 50 atmospheres, posing a risk to the glass container. Carbon dioxide, with a critical pressure of 72 atmospheres, and water, with a critical pressure of 220 atmospheres, clearly present an even more serious challenge and risk to experimenters. These difficulties, however, did not discourage the intrepid early investigators of fluid criticality in Europe.

Near the end of the 19th century, it became possible to measure coexisting densities with sufficient accuracy, and one would think that one scientist or another might test the shape of the coexistence curve and find the Van der Waals theory wanting. In fact, history took a more tortuous path.

9.2 *Van der Waals develops the theory of capillarity*

Presently, the use of critical exponents for characterizing the behavior of experimental data on approach to criticality is widespread. Van der Waals (1894c) used this tool in the modern sense in the course of his work on the theory of capillarity in the early 1890s. See Levelt Sengers (1976). Rowlinson (1979) translated Van der Waals's (1894c) article into English. Here we touch on the subject of Van der Waals's theory of capillarity only lightly, because of the availability of a book on this topic by Rowlinson and Widom (1982).

Van der Waals's paper on capillarity was a seminal piece of work. Laplace, who presented the first rigorous treatment of the shape of an interface, had treated the interface as being infinitely sharp. Although Poisson, Maxwell and Fuchs were aware that this could not be the case, Van der Waals was the first to incorporate a smooth density variation through the interface in a rigorous fashion. The loop of his equation of state provided him with inspiration and opportunity. In Van der Waals's theory of capillarity, an interfacial term representing the cost of creating a gradient in density is added to the Helmholtz energy of the system. Van der Waals assumed that this cost, to lowest order, would be proportional to the square of the density gradient. Had it been linear, the term would change sign with the direction of the gradient, which is unphysical.

Van der Waals then calculated the density profile by minimizing the surface free energy. He found that the local free energy and the square-gradient term, integrated over the height of the interface, contributed equal amounts to the surface free energy, so that the surface free energy density, or surface tension, equals twice the contribution from the square gradient term. Van der Waals thus knew the form of the Helmholtz energy, including the square-gradient term, everywhere including the vicinity of a critical point. It was

very important to him to find out what his theory would predict for the behavior of the capillary rise and the surface tension near this point. At the critical point both quantities must be zero, because the difference between the two phases has disappeared.

The standard theory, in which a sharp interface is assumed, was known to give a surface tension approaching zero as the first power of the temperature difference with the critical temperature. Assuming a continuous variation of the density through the interface might give a different exponent. Van der Waals (1894c) carefully did the analysis. He found that the capillary rise itself goes to zero with the first power of the temperature difference with critical, the density difference with the power $1/2$ and thus the surface tension goes to zero with the power $3/2$.

Modern theory obtains the exponents for the capillary rise and the surface tension by considering that near a critical point the thickness of the interface cannot be less than the correlation length ξ , which itself is known to grow according to a critical exponent ν

$$\xi \cong (T - T_c)^{-\nu} \quad (9.2)$$

where ν equals 0.5 in classical theory. The correlation length thus diverges more slowly than the compressibility, with an exponent only about half as large as the exponent γ .

A simple argument yields the critical exponents of the surface tension and the capillary rise in terms of those of the coexistence curve and the correlation length. First, since the surface tension is proportional to the product of the capillary rise and the density difference between the coexisting phases, the surface tension critical exponent must equal the sum of the density and the capillary rise critical exponents. We saw that the surface free energy equals twice the energy stored in the density gradient, averaged over the thickness of the interface. The gradient, however, can be estimated from the density difference divided by the thickness of the interface, or $(\rho_l - \rho_v)/\xi$. Integrating the square of the gradient over the thickness of the interface yields a surface free energy density, or surface tension, which must be proportional to $\xi [(\rho_l - \rho_v)/\xi]^2$, or $(\rho_l - \rho_v)^2/\xi$. This yields a surface tension critical exponent of $2\beta + \nu$, and therefore a capillary rise critical exponent of $\beta + \nu$. In mean-field theory, the first exponent equals $3/2$, and the second equals unity. Both the capillary rise and the surface tension thus approach the value zero at the critical point. For the surface tension σ we have:

$$\sigma \cong (T - T_c)^{2\beta+\nu} \quad (9.3)$$

For a proper understanding of what follows, we provide the non-classical values of these two exponents, which follow from $\nu = 0.62$ and $\beta = 0.326$.

The result is a value of 1.27 for the surface tension exponent, much lower than the classical value of 1.5. For the capillary rise, the value of 0.97 is found, almost indistinguishable from the mean-field value of 1.

9.3 *De Vries measures the capillary rise near a critical point.*

Kamerlingh Onnes knew of Van der Waals's new work on capillarity prior to publication. In the early 1890s, Kamerlingh Onnes assigned his graduate student De Vries the measurement of capillary rise in ether. Capillary rise is larger the finer the capillary. For small surface tensions, such as near a critical point, fine capillaries are used. Measuring the capillary rise requires careful determination of the diameter of the capillary and close temperature control. The coexisting densities must be measured separately in order to obtain the surface tension from the capillary rise.

De Vries took six data points in the range of -100°C to $+160^{\circ}\text{C}$, the critical point of ether being around 194°C . He notes that the plot of the capillary rise versus temperature is not completely linear, as predicted by classical theory, but slightly curved, turning its concave side to the temperature axis, indicating a critical exponent slightly less than unity. The plot of surface tension, however, curves with its convex side towards the temperature axis, indicating a critical exponent larger than unity, which differs from the sharp-interface theories, but is consistent with Van der Waals's theoretical prediction. Kamerlingh Onnes presented De Vries's (1893) results at the Academy meeting, a year before Van der Waals's paper on capillarity was published. A brief remark by Van der Waals follows De Vries's paper. This remark, translated into English from the Dutch, reads:

The result of the experiment, although not quite in agreement with $k(1 - T/T_c)^{3/2}$, is in conflict with the older theories. If one tries to calculate the value of the exponent, one finds, at some distance from the critical point, the value 1.23. However, the values increase on approaching T_c and seem to confirm the proposition that the limiting value may be equal to $3/2$.

A footnote of roughly the same wording can be found in Rowlinson's (1979) translation of Van der Waals's (1894c) paper on capillarity, p. 233, note 7.

Thus, in 1893, Van der Waals used the concept of critical exponent in the modern sense. The first sparse and somewhat crude measurements fell short of the exponent value he predicted. There were indications that his predictions would be found correct on closer approach to the critical point. This hope is expressed very carefully.

It so happened that in the same year, while Van der Waals completed his paper on capillarity, Ramsay and Shields measured capillary rise in nine

organic fluids, some of which had critical temperatures over 200°C. This reputable laboratory produced an extensive and detailed set of data, with about 20 data points per fluid and a range of 60°C to 0.1°C from criticality. Ramsay and Shields needed coexistence curve data to calculate the surface tension from the capillary rise. They did not have to look far, since Ramsay and Young's data were readily available. If one plots the capillary-rise data versus temperature, the same features noted by De Vries appear: the capillary-rise data are slightly concave, whereas the surface tension data are distinctly convex. Nevertheless, Ramsay and Shields (1893), in Section XVI, p. 474 of their paper, chose to represent the surface tension data by an expression linear in temperature, ignoring both the convexity and the data points within the last 6°C. Consequently, the calculated surface tension reached the value of zero 6°C below the known critical point.

In a letter dated November 3, Kamerlingh Onnes (1893) wrote to his friend Van der Waals about Ramsay and Shield's data. He rejected the use of the linear form because De Vries's as well as Ramsay's own data clearly followed a curved path. Furthermore, he found the proposed procedure of subtracting 6°C from T_c 'almost incredible.' This judgment highlights Kamerlingh Onnes's strong conviction that a critical point is a truly exceptional point at which all critical anomalies should be centered.

A few days after receiving Kamerlingh Onnes's letter, Van der Waals (1893b) completed his tests of the surface tension data for ether, benzene and acetic acid, and replied (translation from the Dutch):

Dear friend, On studying the numbers given by Ramsay and Shields, I noticed that for ether, benzene and acetic acid σ is given by the following equation:

$$\sigma = k (T_c - t)^n$$

for ether	$\log \sigma = 8.37014 + 1.27 \log (T_c - t)$
benzene	$\log \sigma = 8.457 + 1.23 \log (T_c - t)$
acetic acid	$\log \sigma = 8.465 + 1.23 \log (T_c - t)$

Here, σ is the symbol for the surface tension and n is the surface-tension critical exponent, predicted to equal 3/2 by Van der Waals's new theory. This letter is shown, in part, in Fig. 9.2. A comparison between the correlating equations and the experimental data is shown in a table, and it is seen that the agreement is close. The exponent, however, ranges from 1.23 to 1.27. For Van der Waals, the exponent value falling midway between that of the older theories and that predicted by his new theory, was undoubtedly bad news. How delighted would he have been if he had known that the best modern theoretical value of the exponent is right in the range he found from experiment.

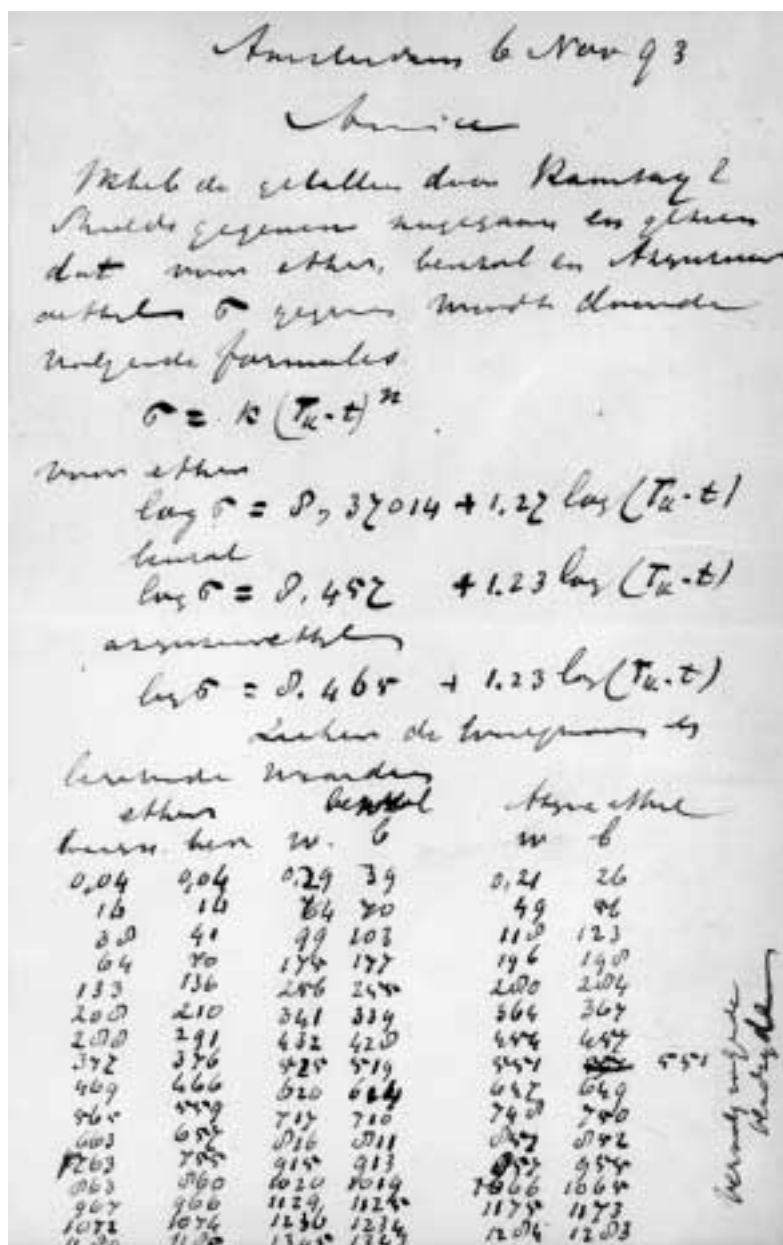


Figure 9.2 Perhaps the oldest references to a critical exponent, in a letter by Van der Waals to Kamerlingh Onnes dated Nov. 6, (1893b). The power law and critical exponent n for the surface tension are defined. The exponent values obtained for three fluids, 1.27, 1.23, and 1.23, respectively, are well below the Van der Waals prediction of 1.5. For each fluid, the observed values, w , are compared with the predicted values, b . Copied, with permission, from Brievenarchief Boerhaave Museum, Leiden.

The letter continues:

The law of corresponding states would require n (1.27, 1.23, 1.23) to be constant. It is, however, remarkable that from De Vries's measurements 1.23 was found as well. Ramsay's observations are perhaps not sufficiently accurate in the vicinity of the critical point. Moreover, I am still of the opinion that in the absolute vicinity of T_c the exponent should be equal to 1.5. In the vicinity of T_c there seems to be a rapid change. From Ramsay's data one calculates indeed a higher value of the exponent in the neighborhood of T_c , and therefore the difference of the first data, between, for instance, 29 and 39, is a consequence of the use of an approximate equation. [Translated from the Dutch.]

Thus, Van der Waals, as early as 1893, introduced the notion of a critical exponent with the purpose of characterizing the manner in which the surface tension disappears as the critical point is approached. By performing a Taylor expansion of the Helmholtz energy at the critical point and including the square-gradient term, he obtained the classical or mean-field values of the critical exponents for the coexisting density difference, the capillary rise and the surface tension. He was also the first to notice that the apparent exponent values obtained from surface tension data from two laboratories were *not* in agreement with his theory. It is quite understandable that, although noting the discrepancy, he hoped it would disappear on closer approach to the critical point. Finally, it is interesting to note his expectation that the observed experimental critical exponent should be universal. He invoked the principle of corresponding states, knowing that its validity might extend beyond that of his equation of state, and, unknowingly, anticipated the modern principle of critical-point universality.

The analysis of the Ramsay and Shield data, plus data for chlorobenzene and carbon tetrachloride, can be found in Appendix 3 of the German and French versions of Van der Waals's (1894c) paper on capillarity. This appendix was not included the Dutch original, nor in Rowlinson's translation into English (1979). For all five substances Van der Waals reports critical exponent values between 1.21 and 1.27, and shows that the extensive sets of experimental data follow the simple power-law expression Eq. (9.3) closely over large temperature regions. Van der Waals notices that in several cases the critical exponent seems to increase in value within the last few °C from the critical point. Quite honestly, however, he states that in other cases the exponent appears to remain constant up to the critical point. He concludes:

Whether the limiting value of B really equals 1.5, cannot be decided on the basis of these observations

This was the first and last time that Van der Waals calculated a critical exponent from experimental data. He did not play any role in the subsequent events discussed below.

9.4 *Verschaffelt finds that mean-field theory fails at the critical point*

9.4.1 *Who was Verschaffelt?* Henriot's biography (1957) for the Belgian Academy, published two years after Verschaffelt's death, reports that Jules-Émile Verschaffelt was born in 1870 to an educated family in Gent. His brother Eduard would later become a professor of plant science at the University of Amsterdam. Verschaffelt began his university studies in Gent in 1888 and completed the doctoral degree in 1893 with distinction. (In the Low Countries, a doctoral degree was the rough equivalent of the present-day American Ph.D. qualifying exam).

Although he was of Flemish origin, his education has been entirely in French. Professor McLeod influenced him to study the plant sciences. McLeod also convinced him not to forego his Flemish heritage, and encouraging him and his brother to learn to speak cultivated Dutch. This skill would serve both of them very well in later life.

After obtaining his doctoral degree, Verschaffelt served as an assistant in the geology department and began his study of physics, crystallography and chemistry. A research project he completed on the refractive index of fluid mixtures won him a 2-year scholarship for studies in the Netherlands. He spent his first year in Amsterdam, taking courses with Van 't Hoff and Van der Waals. In 1894, at the beginning of his second year, he joined Kamerlingh Onnes's laboratory, while taking courses with Lorentz. After his scholarship expired he was hired as a laboratory assistant, and served as such from 1895 to 1898.

9.4.2. *Verschaffelt measures capillary rise.* The unfinished business of the surface tension must have been on Kamerlingh Onnes's mind, for he asked the young Belgian to repeat the measurements of De Vries, and to extend the measurements to higher temperatures. Verschaffelt used the glass capillary-rise apparatus built by De Vries. This apparatus is shown in Fig. 9.3. A fine capillary is mounted inside a glass tube suspended in a thermostated bath, which may be a circulating vapor or a liquid boiling under controlled pressure. In the mid-1890s, the Dewar vessel (now called a thermos bottle: two coaxial silvered glass cylinders, closed at the bottom and fused together at the top, separated by an evacuated space) had not yet been invented, and therefore several nested glass vessels provided insulation. Drying agents were used to prevent the deposition of moisture on the glass. These nested glass tubes also provided some protection to observers if the pressurized apparatus exploded.

Verschaffelt's (1895) publication contains the first fruits of his labor: four data points for CO_2 , three data points for N_2O , none closer than 10°C from

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flict with the mean-field prediction of a symmetric top, and, gave a notoriously poor fit to the data. Verschaffelt, blithely unaware of these difficulties, multiplies the capillary rise data by the appropriate density differences, calculates the surface tension critical exponent and finds 1.311 for CO_2 and 1.333 for N_2O . In addition, he analyzes surface tension data for five of the fluids studied by Ramsay and Shields and reports values between 1.21 and 1.27 for the critical exponent. He concludes that his own critical exponents are closer to the Van der Waals theoretical prediction than those of Ramsay and Shields, and, on this optimistic note, sets out to improve the apparatus for work closer to the critical point.

Verschaffelt improves the homogeneity and stability of the temperature bath to 0.1°C . He adapts the apparatus to measurement of the small surface tensions near criticality by using a much finer capillary than before, with an inner diameter of 0.1 mm. He then takes two independent sets of data for CO_2 , demonstrating perfect reproducibility of the apparatus. Verschaffelt (1896) reminds the reader that, to date, all work on surface tension yielded exponents well below the theoretical value of $3/2$. There seems, however, to be a tendency for exponents to grow on approaching criticality; his purpose is to check whether the exponent will indeed reach the predicted limiting value of $3/2$. He reports six data points between 29.3°C and 30.6°C , the highest temperature being within 0.5°C from criticality.

9.4.3 *Verschaffelt pinpoints a problem with the near-critical surface tension data.*

The new data presented no surprises. The capillary rise data are again linear in temperature, at least up to a degree from criticality. This time, however, Verschaffelt (1896) is much more aware of the problems arising from using literature values for the coexisting densities. For CO_2 , he uses Amagat's new data (1892). Amagat measured coexisting densities up to 0.35°C below critical. In his paper, however, he only presented tabular data at regular temperature intervals. These values were obtained by passing a curve graphically through the experimental data. First, Verschaffelt proposes to test whether a parabolic equation is compatible with Amagat's data. He knows the theoretical foundation for the parabolic law in volume-temperature coordinates, and points out that this same limiting law then must also apply if density-temperature coordinates are used. This is how Verschaffelt (1896) tested the validity of the parabolic law for the coexistence curve (the symbol m represents T/T_c , the symbol τ represents $T - T_c$, and Δ is a finite increment):

In order to submit this first theoretical result to experimental verification I have calculated, from Amagat's densities, the values of the quotient $\Delta \log (\rho_l - \rho_v) / \Delta \log (1 - m)$ which, according to Cailletet and Matthias, must be constant and equal to 0.5, and would reach this value for $m = 1$, according to Van der Waals.

Column 4 of table I shows immediately that the formula of Cailletet and Mathias does not well represent the experiments, for carbonic acid at least. Till 1° from the critical temperature the quotient remains sensibly constant, mean value 0.367, and the experiment can therefore be represented well by

$$\rho_l - \rho_v = A (1 - m)^{0.367},$$

A being a constant.

From $\tau = \pm 1^\circ$ begins a sensible increase of the quotient as required by the theory of Van der Waals, and the last value 0.521 comes very near the theoretical one.

Verschaffelt's table is reproduced in Fig. 9.4. Verschaffelt proceeds to calculate the surface tension, and subjects it to a similar analysis. He finds low exponent values, between 1.2 and 1.4 in most of the range, but increasing to 1.5 within the last degree below the critical point.

The present-day reader is pleasantly surprised by Verschaffelt's method of data analysis: the calculation of an apparent critical exponent value by logarithmic differencing. This particular method was reinvented in the 1960s, and is known as the Kouvel-Fisher (1964) method.

τ	$1 - m$	$\rho_l - \rho_d$	$\frac{\Delta \log (\rho_v - \rho_d)}{\Delta \log (1 - m)}$
$0^\circ, 1$	0,00033	0,075	0,521
$0^\circ, 35$	0,00115	0,144	0,468
$0^\circ, 85$	0,00279	0,218	0,414
$1^\circ, 35$	0,0044	0,264	0,386
$2^\circ, 35$	0,0077	0,327	0,357
$3^\circ, 35$	0,0110	0,371	0,336
$4^\circ, 35$	0,0143	0,405	0,356
$5^\circ, 35$	0,0176	0,436	0,351
$6^\circ, 35$	0,0209	0,463	0,374
$7^\circ, 35$	0,0241	0,489	0,391
$8^\circ, 35$	0,0274	0,514	0,354
$9^\circ, 35$	0,0307	0,535	0,379
$10^\circ, 35$	0,0340	0,556	0,383
$11^\circ, 35$	0,0373	0,575	

Figure 9.4 Verschaffelt (1896) calculates the value of the critical exponent of the coexistence curve by taking logarithmic differences of the measured densities and temperatures. τ is the temperature difference, $1 - m$ the reduced temperature difference with the critical temperature, ρ_l the density of the liquid and ρ_v the density of the vapor. The last column is an estimate for the surface-tension critical exponent. It is close to $1/3$, except for the last degree from critical, where it appears to approach the mean-field value $1/2$.

The conclusion that Verschaffelt believed mean-field behavior to set in one degree from the critical point is proven wrong in the next section of the paper, appropriately named 'Critical Remarks.' Verschaffelt reminds the reader that the densities used for the highest temperatures were not measured but interpolated. Amagat had passed a curve through the data tangent to the ordinate of the critical point.

And as we know that generally a curve has with every tangent a contact of second order, we must confess that the obtained result, though it may really be contained in the experiments, is nevertheless a consequence of the manner of interpolating.

Since capillary ascension is virtually linear in temperature, and a parabolic shape was imposed on the top of the coexistence curve by the manner of interpolating, it was inevitable that the theoretical value of 1.5 would be found for the surface tension exponent.

This verification would therefore be satisfying only then when it was founded quite on observed densities – these observed values however I have nowhere found.

A present-day experimentalist cannot fail to be impressed by Verschaffelt's analysis. His critical attitude towards any input data used in addition to his own observations leads him to the source of the problem posed by the low surface tension exponent: the coexistence curve, contrary to expectations, does not seem to be parabolic. The tendency for exponents to reach the values Van der Waals predicted could be a consequence of the way the top of the coexistence curve was graphed in a region where no data exist. The 1896 paper was not Verschaffelt's last word on the limiting value of critical exponents, but it did conclude his work on capillarity in Leiden.

9.4.4 *Verschaffelt finds non-classical critical exponents very near the critical point.* Around 1897, Verschaffelt became engaged to a Dutch student of physics, Elisabeth Ebert, and started planning for marriage and for a career in the Netherlands. To this end, he would need a Dutch doctorate. Kamerlingh Onnes accepted him as a graduate student and assigned to him an investigation of the properties of dilute fluid mixtures (Ch. 11.4.4, Ch. 11.4.6). He defended his doctoral thesis in 1899, and from 1898 until his appointment as a physics professor at the University of Brussels in 1906, he taught high school physics in Dordrecht. During this period, Verschaffelt retained his collaboration with Kamerlingh Onnes and struck his verdict on mean-field theory.

While dealing with the pressures and responsibilities of marriage, disciplining high school boys, and receiving Kamerlingh Onnes's urgent requests

to speed up his work on mixtures, Verschaffelt (1900a) produced a definitive paper on fluid critical exponents. The problem of the shape of the coexistence curve had never left his mind. A data set came to his attention in 1900 enabling him to settle the question. Sidney Young (1894) had published superb data, P - V isotherms and coexisting densities of isopentane. Young was a student with Ramsay at Bristol, and succeeded him after Ramsay was appointed in London. Both scientists were highly reputable experts in the measurement of properties of fluids, and a stream of excellent data flowed from their laboratories. Verschaffelt (1900a) applied to Young's coexistence curve data the same technique of logarithmic differencing that he had used for CO_2 . He found that the entire body of data was well fitted with a power law with exponent $\beta = 0.3434$. Between 1.8 and 0.8°C from critical, the exponent value was 0.344, and between 0.8 and 0.4°C it was 0.337. Thus the exponent had a steady value near 1/3, with no tendency to grow as T_c was approached.

Therefore for the time being no experimental proof can be given for the supposition, that up to the immediate neighborhood of the critical state $\rho_l - \rho_v = A (1 - m)^{0.3434}$ would not hold instead of the theoretical formula $\rho_l - \rho_v = A (1 - m)^{1/2}$.

Verschaffelt did not limit himself to the coexistence curve, but immediately widened the quest to the form of the critical isotherm:

It now appears that in place of the exponent 1/2 in the difference of liquid and vapor density a less simple fraction must be substituted. Hence as according to Van der Waals' simple supposition the isothermal is a curve of the third degree, I have investigated whether the critical isothermal could not be expressed in an analogous way by means of a fractional exponent. The result I arrived at, was that the observations of S. Young on the form of the critical isothermal of isopentane are well expressed by the formulae

$$\begin{aligned} P &= P_c - P_c [1 - (v_c - b)/(v - b)]^n \text{ for } v > v_c \\ P &= P_c + P_c [(v_c - b)/(v - b) - 1]^n \text{ for } v < v_c \end{aligned}$$

in which $P_c = 32.92$ atm, $v_c = 4.266$ cc, $b = 0.518$ cc and $n = 4.259$. The following table shows that these formulae are in good harmony with the observations.

Here the symbol v stands for the specific volume, and v_c for the specific critical volume. The reader should not be confused by Verschaffelt's use of empirical forms. He had to represent the critical isotherm by two branches, since he expected a nonanalyticity at the critical point. The branches have a point of antisymmetry at criticality. Asymptotically near the critical point, the form in brackets is proportional to $v_c - v$, thus giving rise to a power-law expression for the pressure as function of the volume in the vicinity of the

critical point. The only numerical value of interest is that of the critical exponent $n = 4.259$, which is obviously much larger than the classical value $\delta = 3$.

At the end of his paper, Verschaffelt stresses that his equation for the critical isotherm is purely empirical:

It may be seen that only in a very forced way a division of the pressure into a thermodynamical and a cohesion pressure can be deduced from my formula, which division is the basis of the Van der Waals theory. If therefore my formulae have a theoretical meaning, this seems to be based on a principle somewhat different from Van der Waals's equation of state; I did however not succeed in deducing such a principle.

By 1900, Verschaffelt had discovered a fundamental flaw of classical theory: an inability to describe correctly the critical behavior of fluids. The low value of the experimental surface tension exponent is caused by the low value of the experimental coexistence curve exponent. Verschaffelt sensed that this shortcoming, unlike other weaknesses of a simple two-parameter equation of state, could not be repaired within the framework of mean-field theory. This intuition grew into a conviction in his later life.

9.4.5 Impact, or lack of it. Two opposing remarks are valid regarding the impact of Verschaffelt's findings. On the one hand, empirically, the cubic coexistence curve was confirmed by several investigators, most notably by the Kazan physicist Goldhammer (1910) in a substantial paper in a prestigious journal. Goldhammer, citing Verschaffelt (1896), proposed a cubic law of corresponding states for the coexistence curves of a dozen fluids from Young's laboratory, preempting Guggenheim's (1945) paper by 35 years.

On the other hand, Verschaffelt's findings did not seem to resonate in his scientific environment in any significant way. There is no indication of animosity or any attempt at suppression of evidence on the part of Verschaffelt's supervisor. Kamerlingh Onnes did present at the Academy meetings Verschaffelt's three early Leiden communications that build the case against Van der Waals's theory. He also approved Verschaffelt's papers for publication in *Archives néerlandaises*. Verschaffelt maintained a most cordial relation with Kamerlingh Onnes. Kamerlingh Onnes just never warmed up to the insight that the Van der Waals theory of criticality was in fundamental disagreement with experiment.

To understand the lack of interest in Verschaffelt's ideas, one must know about Kamerlingh Onnes's interests, convictions, and purposes at the turn of the century. Many limitations of the Van der Waals equation came to light long before 1900. It was well known that critical ratios were overestimated by as much as 20%, and that experimental data could be represented at best over limited ranges only by particular choices of values of a and b . The use

of a constant excluded-volume term b had been questioned on theoretical grounds. As early as 1881, Kamerlingh Onnes himself had pointed out that b should be volume-dependent. From that time on, several physicists, including Van der Waals, Lorentz, Van Laar and Boltzmann, worked on improvement of the excluded-volume term by calculating successive contributions from pairs, triplets, etc., of interacting hard spheres.

Shortly after he presented Verschaffelt's (1900a) result, and as discussed in Ch. 3.5, Kamerlingh Onnes (1901) proposed an empirical corresponding-states polynomial representation of P - V - T data, in order to replace the much maligned Van der Waals equation. He may have viewed Verschaffelt's result as yet another shortcoming of this equation.

Kamerlingh Onnes retained his enthusiasm for the study of mixtures and truly appreciated the fundamental role played by the theory of Van der Waals. Since the early 1890's, he was engaged in a lengthy vendetta against half a dozen experimenters who were attacking the Andrews-Van der Waals view of criticality on the basis of questionable data (Ch. 10). Kamerlingh Onnes was convinced that the main problem with the literature data was impurity, and initiated a program of studies of impurity effects near critical points. This is why, in 1896, Kamerlingh Onnes assigned the experimental study of one such mixture, that of a small concentration of H_2 in CO_2 , to Verschaffelt as a thesis project. Around 1900, the mathematician Korteweg, who had been out of the picture for a decade, began an analysis of the behavior of dilute fluid mixtures near critical points (Ch. 11.4.3). One must recall the atmosphere at that time to understand the lack of impact of Verschaffelt's work on critical exponents. Kamerlingh Onnes's was disillusioned with the Van der Waals equation and engrossed in his own work on accurate empirical equations; he was vividly interested in impurity effects; his mind was occupied by a well-planned research project for Verschaffelt; and Korteweg's entrance into the field was a challenge. To Kamerlingh Onnes, Verschaffelt's nonclassical critical exponents must have seemed to be one more sign of the failure of the Van der Waals equation, of whose multitudinous shortcomings he had been convinced for many years. Verschaffelt's insistence must have seemed like beating a dead horse. The fundamental difference between a discrepancy in a critical ratio and that in a critical exponent must have escaped Kamerlingh Onnes.

This hypothesis about Kamerlingh Onnes's attitude is in agreement with all known facts. Although there seems to have been a disruption in the correspondence between Van der Waals and Kamerling Onnes between 1894-1900, the exchange of letters resumed its original high frequency in 1900. Kamerlingh Onnes described to Van der Waals in fair detail the activities of his students and coworkers. The only reference to Verschaffelt in letters of

that year that have been conserved, occurs in that of October 18. Kamerlingh Onnes (1900b) writes:

In the meantime I think I have gotten Verschaffelt to work on the hydrogen-carbon dioxide plait.

This was the year that Kamerlingh Onnes presented Verschaffelt's results about the nonclassical values of critical exponents at the Academy. The subject apparently did not even cross his mind when he wrote to Van der Waals. The only problem he saw was 'getting Verschaffelt to work' on the mixture project. Nevertheless, in the years to follow, several Leiden experimentalists reported approximately cubic coexistence curves. For instance, Keesom (1902) reports an exponent value of 0.3327 for pentane, quotes Verschaffelt, and mentions that the Van der Waals theory gives a value of 0.5.

It is moving to read how Kamerlingh Onnes (1915), replying to what must have been a question by the 78-years old Van der Waals regarding cubic coexistence curves, enthusiastically reports that he has found the origin of the $1/3$ power law, pointing his friend to Goldhammer (1910). But then he carefully explains how, beginning with Verschaffelt's value of 0.3434 for isopentane, several experimenters in his group had found similar exponent values between 1902 and 1910. He appears to accept the validity of the cubic law, but does not mention the intrinsic conflict with the mean-field prediction.

9.5 *Verschaffelt's career in the 20th century*

Verschaffelt was appointed a professor of experimental physics at the Free University of Brussels in 1906. When the First World War erupted in 1914 and the Germans occupied Belgium, he and his family escaped to the Netherlands. Kamerlingh Onnes's appointed him to a research position at the Cryogenic Laboratory in Leiden (Fig. 9.5), and he taught high school again to supplement the family income. Lorentz, then secretary of the Holland Society of Sciences and Humanities (HMW), appointed him as the French-language editor of the *Archives néerlandaises*. For many years he also served as a science secretary for the Institut International de Physique Solvay. This required thorough knowledge of French, German and English, and brought him a huge amount of work.

In 1923 he received an appointment from the University of Gent, which had recently turned Flemish. He became a full professor in 1929 and served until his retirement in 1940. Verschaffelt remained in Belgium during the Second World War. Remaining true to his Flemish origins, he always walked a straight and independent path with respect to the Flemish movement. When this movement compromised itself by seeking German support for its

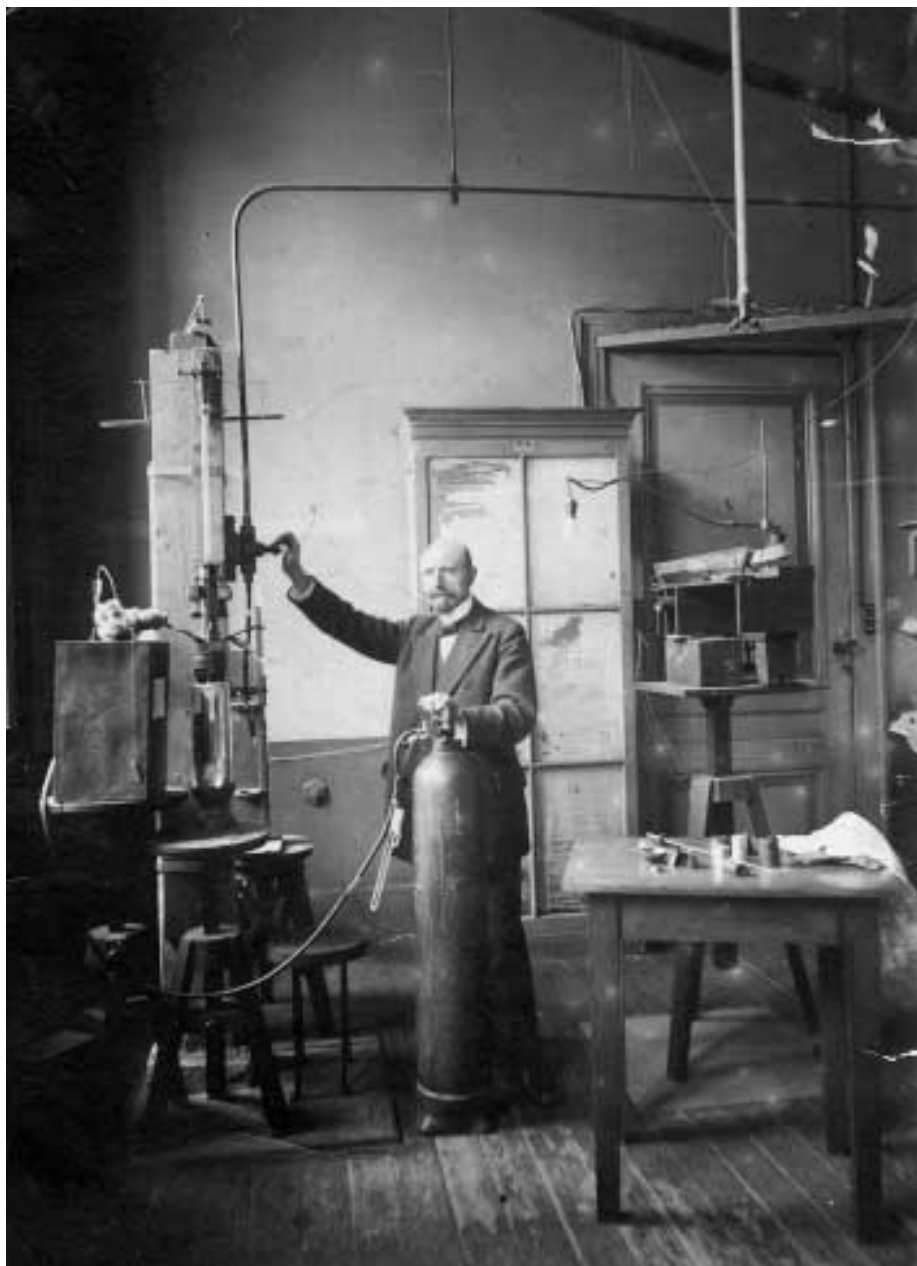


Figure 9.5 Verschaaffelt at work in the Physics Laboratory at Leiden in 1915. The picture was provided by his daughter, Françoise (Fransje) Wiersma-Verschaaffelt, in 1975.

cause, Verschaffelt denounced the movement's student chapter at Gent University and refused an honorary membership. As a consequence he spent some months in jail in 1943, which he endured as an interesting experience. In 1946, after his wife's death, he left for the Netherlands. His daughter Françoise (Fransje) had married Professor Wiersma in Leiden. Throughout his long career and up to the year of his death, he published almost 300 papers on topics of thermodynamics, capillarity, thermochemistry and irreversibility. He became a correspondent of the Belgian Academy in 1909.

9.6 *An unrecognized bridge to the modern era*

Despite the difficulties he encountered throughout his life, Verschaffelt returned repeatedly to his 1900 insights on fluid criticality. Verschaffelt (1901) attempted to replace the classical Taylor expansion of the pressure in terms of volume and temperature around the critical point by one more true to experiment.

$$P = P_1 + m(x - x_1) + a(x - x_1)^n \quad (9.4)$$

Here $x = 1/(v - b)$, x_1 equals the critical value of x , and m is a temperature-dependent coefficient which passes through zero at the critical temperature; n is the critical exponent for the critical isotherm, known to equal at least 4, instead of the classical 3, and a a critical amplitude. Verschaffelt was not too happy with this expression because he had no theoretical justification for it, nor did he see how it could be generalized to mixtures.

Three more publications on critical behavior resulted in the 1920s, see Verschaffelt (1922, 1926, 1927). He tried to describe the critical P - V isotherm, as in his 1901 paper, as two branches of 'fourth degree parabolas,' so that the isotherm is a curve with an analytical discontinuity. We quote from the 1922 paper, translated from the French:

If it is true that the third derivative is zero at the critical point, but not the fourth, then there is a point of discontinuity which equations of the Van der Waals type cannot describe. Thus the critical isotherm could still be expanded, on each side of the critical point, in a power series in which the coefficient of the third power is zero, but it is impossible to represent the entire critical isotherm by a series expansion around the critical point: the critical point presents to such an expansion an insurmountable barrier. Thus an equation as that of Van der Waals cannot serve to represent the isotherms up to the smallest volumes.

Such an equation can only serve in the region of large volumes, where it starts as an extension of the gas laws. Similarly, a series expansion in increasing powers of $1/v$, such as the one employed by Kamerlingh Onnes for representing the isotherms, is only valid up to the critical region, at least if one considers it as a Maclaurin series

beginning at $\delta = 0$; since nothing prevents one, of course, to represent the isotherm, even beyond the critical point, by a polynomial – which is what Kamerlingh Onnes does – but then one must observe relatively large deviations in the vicinity of the point of discontinuity, that is, near the critical point. That is exactly what happens; Kamerlingh Onnes, however, ascribes these deviations to the large compressibility of matter near the critical point, a compressibility which *disturbs* the slope of the experimental isotherms

Thus, in 1922, Verschaffelt had a clear idea of the failure of all analytic equations, including the virial expansion.

Verschaffelt died in 1955, the year that B. Widom and O.K. Rice (1955) proposed an expression for the equation of state near the critical point that is similar to Verschaffelt's (1901). Widom and Rice's paper, in turn, initiated the modern revival of interest in fluid criticality.

9.7 *Verschaffelt vindicated*

We saw in Ch. 9.1.3 that the modern understanding of criticality in fluids has evolved from fundamental work on model systems, such as the Ising model, which could be transformed to a crude model for the gas-liquid phase transition. Theory predicted that criticality in systems with short-range forces should show universal critical behavior, characterized by critical exponents quite different from those given by mean-field theory. Experimental work on near-critical fluids and on liquid mixtures, by refined new optical techniques that became available after the invention of the laser, began in the 1960s and continued throughout the 20th century. It resulted in critical exponent values that ultimately converged with the best theoretical results and are now known with high accuracy. For a review with many references to the literature, see Sengers and Levelt Sengers (1986). The values obtained by Van der Waals for the surface tension critical exponent, and by Verschaffelt for the coexistence curve and the critical isotherm, are consistent with the best modern values to within the more limited accuracy of these century-old results.

10. Challenges to Van der Waals-Andrews criticality: Kamerlingh Onnes, Kuenen, and Verschaffelt

History has demonstrated that it was very difficult for scientists to accept the Andrews-Van der Waals ideas about fluid criticality and continuity of states above the critical point. The older notion that liquid disperses into vapor at the critical point, with liquid and vapor retaining their identities, was firmly ingrained. From 1880 until well into the 20th century, scientists in many European countries challenged the concepts of Andrews and Van der Waals. In response, Kamerlingh Onnes and his collaborators engaged in a spirited battle that flared up time and again, and spent many years refuting these challenges. Later, in the middle of the 20th century, mean-field theories would be found defective on a fundamental level for their neglect of critical fluctuations. In parallel, however, the old theme of persistence of the liquid phase, discredited long ago by the Leiden scientists, resurfaced in new guises.

This chapter, based on Levelt Sengers (1979), may therefore be considered as a vindication of the early insight in fluid criticality achieved by the Dutch School.

10.1 *Andrews-Van der Waals versus older views of fluid criticality*

Chapter 2 describes how Cagniard de la Tour (1822) sealed different quantities of liquid into glass tubes, and heated them until the meniscus left the cell. When the amount of liquid was properly chosen, the meniscus disappeared near the middle of the cell, at a temperature characteristic for the fluid under consideration. At this ‘Cagniard-Latour’ temperature the surface tension between liquid and vapor had disappeared. At that time, however, it was not at all clear what had happened to the liquid. Early experimenters, such as Mendeleev and, at least on some occasions, Faraday, assumed that the liquid ‘dissolved in the vapor’ without actually losing its identity. This is an asymmetric way of considering the vapor-liquid critical point.

Andrews’s experiments in the 1860s, however, led him to describe the vapor-liquid transition in symmetric terms. As we saw in Ch. 2.2, Andrews reduced the volume of carbon-dioxide vapor at constant temperature, and

found that the vapor transformed into a liquid while the pressure remained constant (Fig. 2.1). Only after the vapor had condensed would the pressure rise again. On repeating this process at higher temperatures, the densities of the two phases approached each other, to become equal at what Andrews called the critical temperature. Above the critical temperature, a transition from a dilute to a dense phase occurred gradually with increase in pressure, without the appearance of a meniscus. In his Bakerian lecture, Andrews (1869) insisted that a continuous transition from gas to liquid is possible, and that the two states cannot be distinguished from each other unless they are actually in coexistence. In his words:

...gas and liquid are only distant stages of the same condition of matter and are capable of passing into one another by a process of continuous change.

Van der Waals reinforced Andrews's view (Ch. 2). Based on simple assumptions about excluded volume and mutual attraction of the molecules, his equation of state yielded pressure-volume isotherms, a vapor-liquid phase transition, a critical point, and a continuously varying supercritical state, in qualitative agreement with Andrews's observations. There was no need to ascribe to molecules in the gas phase properties different from those in the liquid.

Obvious as the Andrews-Van der Waals picture may seem to us, it was revolutionary at the time. Notwithstanding its clarity and appeal, it was generally not accepted. Scientists were very reluctant to give up the older idea of the liquid dissolving in the gas. Most opponents of the Andrews-Van der Waals description of the gas-liquid transition believed in some form of persistence of the liquid state above the temperature of meniscus disappearance. Many scientists, even well into the 20th century, felt that the liquid-vapor phase transition could not be understood unless liquid molecules were assumed to be different from vapor molecules. Usually they considered the liquid molecules as products of chemical reactions or association of gas molecules, although an alternative view, that the gas molecule is an expanded version of a liquid molecule, was also voiced. The supercritical fluid was considered to be a mixture of gas and liquid molecules, 'molécules gasogéniques et liquidogéniques' in the words of De Heen (1892b), 'fluidons and gasons' in the words of Traube (1904, 1938). The opposition to the Andrews-Van der Waals view was not merely philosophical. Between 1880 and 1905, experiments all over Europe were claimed to indicate the failure of the theory of the continuity of states.

It took a long time for scientists to appreciate how difficult and error-prone critical-region experimentation is. By the early 1890s, only a few European laboratories – those of Kamerlingh Onnes in Leiden, Gouy in Paris,

Ramsay in London and Young in Bristol – had acquired a sufficient grasp of the principal sources of error. They identified temperature gradients, gravity, impurity, and slow equilibration, by critical evaluations of experiments in other laboratories.

Interpretation of the experiments was virtually impossible before the formulation of Gibbsian thermodynamics and the phase rule in 1877. Arguments raised against the Andrews-Van der Waals concepts were often in contradiction with the phase rule. It took surprisingly long – well into the 1890s – before the implications of Gibbs's work began to be generally known and accepted. Van der Waals, however, had acquainted himself at an early stage with Gibbs's work. Kamerlingh Onnes, through his friendship with Van der Waals, became familiar with Gibbs's ideas as well, and he quickly developed into a staunch defender of the Andrews-Van der Waals position.

10.2 *Overview of controversies*

From 1880 to 1907, experiments were carried out in Europe that disputed the Andrews-Van der Waals view of criticality and of the supercritical state. Between 1880 and 1889, Ramsay, then in Bristol, and Cailletet and coworkers in Paris, carried out imaginative and exciting experiments showing that after a two-phase system is heated through the critical point, the supercritical fluid retains a memory of the preceding two-phase state. The experiments could not be interpreted at that time. Inspired by these results, a rash of experimentation broke out in the early 1890s, involving the Italians Battelli and Zambiasi, the Belgian De Heen, and the Russian Galitzine. These experiments were all used to discredit the Andrews-Van der Waals view. In 1892, the Frenchman Pellat proposed that the Cagniard de la Tour temperature, at which the meniscus disappears, is *lower* than Andrews's critical point at which the densities of the two phases become equal. This particular idea would be repeated for half a century after Pellat first expressed it.

Also during the early 1890s, however, the Frenchman Gouy performed the first reliable studies of the effect of gravity on near-critical fluids and on the rate of equilibration of such systems. Shortly before, Leiden graduate student Kuenen discovered how to perform reproducible measurements in near-critical fluid mixtures (Ch. 6). These experiments would provide necessary clues for understanding the problems affecting the controversial experiments.

Around 1893, Kamerlingh Onnes and his staff took the offensive, repeating several of the controversial experiments and assessing their errors. Ramsay joined Kamerlingh Onnes in this effort, and openly revoked his earlier conclusions. Galitzine and De Heen, however, persisted. As a consequence, De Heen found himself doggedly pursued by Kamerlingh Onnes, who did

not give up until the inadequacy of De Heen's separator was demonstrated. Finally, the Germans Traube and Teichner reported in 1904 a quite elegant experiment that they claimed demonstrated the persistence of the liquid state above the critical point. Kamerlingh Onnes took this attack so seriously that he decided to repeat Teichner's experiment. He also had seasoned staff members perform quantitative estimation of impurity effects near critical points (Ch. 11).

Kamerlingh Onnes did not overreact when he spent considerable effort to demolish, one by one, over a period of fifteen years, the challenges to Andrews-Van der Waals criticality. The idea of persistence of the liquid state above the critical point appears to arise very naturally, *viz.* its re-emergence in the mid-20th century. The more impressive is the unwavering conviction with which Kamerlingh Onnes adhered to the Andrews-Van der Waals concepts, and the lengths to which he went to in order to refute experiments seemingly in conflict with this picture.

In modern work, the presence of critical fluctuations, ignored in mean-field theory, plays an essential role. We will touch on this topic at various occasions, in particular towards the end of this chapter. However, the challenges posed to the Van der Waals theory at the end of the 19th century, with the exception of Verschaaffelt's work, (Ch. 9), were seldom at this fundamental level. In most cases, it was underestimation of the quality controls needed in experiment that led to reports of baffling results.

10.3 *Why experiments near critical points are difficult*

For a proper understanding, it is necessary to explain why experimentation near critical points is difficult, and what are the principal sources of error. We have seen in Ch. 2 that at the critical point, the isothermal compressibility and the isobaric expansion coefficient diverge. As a consequence, the density of the system becomes extremely sensitive to variations of pressure and temperature. If the bottom of the cell is cooler than the top, a steady-state density gradient will develop due to the large expansion coefficient, creating the impression that the liquid state persists. In the early days of critical-region experimentation, the need for excellent temperature stability and homogeneity was not always appreciated. Much of the work was done in organic fluids with critical point near to, or over 200°C, and stability to 0.1°C was considered excellent temperature control. Gouy's work in the 1890s, achieving a stability of 10⁻⁴°C, was a unique and admirable exception.

Due to the large compressibility, the force of gravity is sufficient to generate a sizeable density gradient in a fluid within a few 0.1 K from its critical point, as was first pointed out by Gouy (1892). An interesting consequence is

that the meniscus can disappear at various levels in the cell, depending on the fill density, even though the critical point is an invariant point. Confusion about this point persisted for decades.

Most importantly, impurity effects, topic of Ch. 11, are greatly magnified near a critical point. Thus, even small impurities can have a major effect on the density, depending on how the experiment is conducted. Equilibration of impurities by diffusion is a long and tedious process. Unevenly distributed impurities cause unexpected density gradients. Few experimenters had vacuum pumps at their disposal, so air was an ever-present contaminant. Expelling air from organic liquids by boiling could lead to decomposition.

The effect of impurities could not be properly understood until a theory of mixture behavior near the solvent critical point was developed by Van der Waals (1890), and Kuenen had learned to conduct reproducible experiments on mixtures (Ch. 6). By 1894, the Leiden experimenters were in a position to pinpoint the principal sources of error in many early experiments. Quantification of impurity effects became possible a decade later, thanks to Leiden work that is the topic of Ch. 11. Verschaffelt then estimated the size of density gradients due to unequilibrated impurities, and showed that these gradients reached very large values near the critical point. Thus, with great persistence, the Leiden experimenters demonstrated that the reported conflicts with the Andrews-Van der Waals view of criticality were within the limits of error of the respective experiments.

10.4 *Ramsay finds evidence of gaseous and liquid molecules*

William Ramsay (1852-1916), a British experimental chemist, is best known for his discovery of several of the noble gases. In 1894, jointly with Lord Rayleigh, Ramsay announced the discovery of argon, and in 1895, he isolated terrestrial helium, which up till then had only been known from solar spectroscopy. In 1898, he discovered krypton and neon. He received the 1904 Nobel prize in chemistry.

From 1880 to 1887, he was a professor of chemistry at University College in Bristol. He and his associate Sidney Young performed careful measurements on the critical state of many fluids. Some of these were discussed in Ch. 9. Young succeeded Ramsay at Bristol in 1887, when the latter became a professor of chemistry at University College, London. Ramsay continued his collaboration with Young on fluid criticality until the mid-1890s. Young and his group produced accurate equation-of-state data, critical parameters, and surface tension data for many organic fluids. These data led Verschaffelt to question the adequacy of the Van der Waals equation for describing critical behavior (Ch. 9).

In his early years at Bristol, Ramsay performed a series of experiments on the nature of the supercritical state, which Andrews had carefully avoided calling either vapor or liquid. Ramsay studied several organic liquids of fairly high critical temperatures, near 200°C. He partially filled glass tubes with the liquid under consideration, boiled off part of the liquid to expel air, and sealed the tube. Tubes and thermometers were inserted in holes in a copper block, and observed through slits in the block. (Fig. 10.1), that was heated to a desired temperature.

In a first set of experiments, Ramsay (1880a) found that the temperature of meniscus disappearance decreased considerably, as much as 13°C, as the fill density increased. With Andrews, Ramsay accepted that the densities of gas and liquid became equal at the critical point. He explained the above observations as follows:

...when the tube contains a small amount of liquid the space left for the gas is larger, and consequently more vapour must be given off by the liquid before enough gas can be compressed till it acquires the same specific gravity as the liquid; the temperature at which the meniscus disappears is consequently higher.

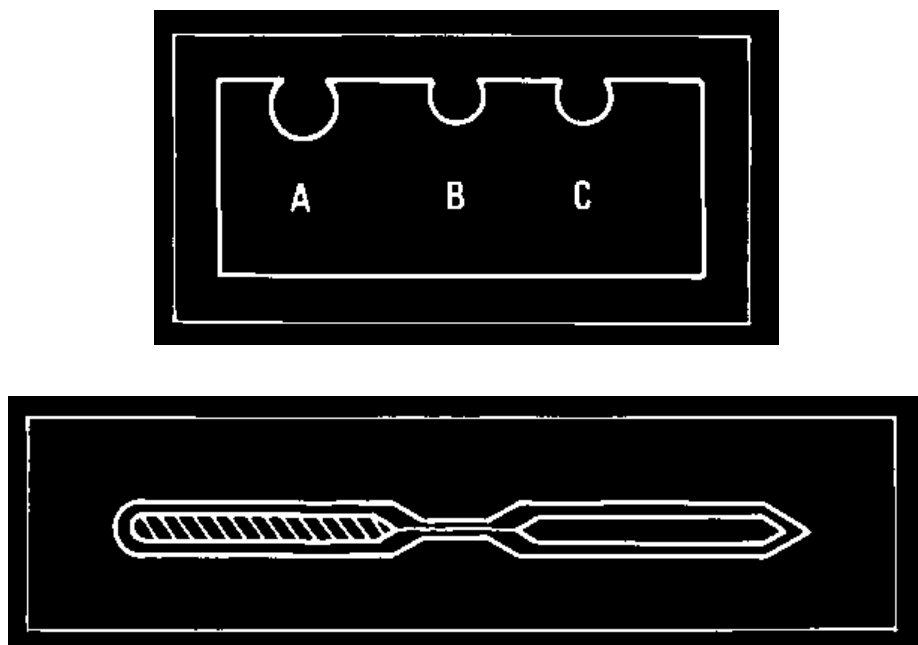


Figure 10.1 Top: a copper block heated by a flame and provided with slotted holes for inserting tubes and thermometers. Bottom: a constricted tube. Copied from Ramsay (1880a), p. 324, 325.

Ramsay's explanation contradicts the invariance of the critical point. In addition, he expresses his belief that gas and liquid maintain their identities after passing through the critical point. At the critical point they merely mix because their densities are equal.

In a second experiment, Ramsay demonstrated the persistence of the liquid using a tube constricted in the middle (Fig. 10.1). After a pass upwards and downwards through the critical point, the liquid always re-condensed in the section of the tube where it had been originally, even if that section was tilted upwards in the supercritical state. Revealingly, Ramsay reports that this memory effect disappeared after the tube was maintained at the supercritical state for half an hour or more.

Ramsay, cleverly using the constricted tube as a cylindrical lens, showed that the part that had originally contained the liquid had a higher refractive index. He concluded that the constriction prevented the mixing of the liquid and the gas.

Apparently, Ramsay's experiments were challenged. At the end of his paper, there is a reply to Professor Stokes, who had criticized the experiment in a letter to Prof. Mills. The latter was a senior colleague of Ramsay's, who had presented his paper to the Chemical Society. Stokes had suggested several possible sources of error, such as air or water impurities, and the presence of temperature gradients between the copper block and the cells. Ramsay replied that his method of filling the tubes made the presence of air impossible. He decribed in detail the great effort he made to dry his samples. He was sure that temperature gradients do not exceed 0.5°C. The critical temperatures of two samples filled to the same volume fraction, as well as the repeatability of the experiment, were within this tolerance.

In the same year, Ramsay (1880b) published P - V - T measurements on ether, benzene and an equal-weight mixture of these compounds, in an apparatus similar to those of Andrews and Cailletet. After the liquids were dried and partially boiled off in order to expel air, they were confined to a glass tube. Mercury separated the liquid from an air manometer on which pressures were read. The thermostat, again, was a heated copper block, temperature-controlled to about 0.1°C. The volume of the liquid was obtained by observing the position of the mercury level through a slit in the block. For several of the sub-critical benzene and mixture isotherms, Ramsay reported that close to the liquid branch the pressure actually *decreased* with diminishing volume. He apparently did not realize that this violates thermodynamic stability. Instead, he claimed Andrews had never seen such effect because the carbon dioxide the latter used had not been pure enough. Ramsay (1880b) explained this effect as follows:

...the molecules, when the gas has been compressed to a certain extent (very shortly before all gas is condensed to liquid), begin to exert some attraction for each other, and consequently relieve the pressure.

Ramsay compared the gas-liquid transition with the dissociation of a compound. In evaporation of a liquid, complex molecules dissociate into simpler ones. Liquid and gas molecules do not mix until the disappearance of the surface tension signals that the densities of the two phases have become equal. At supercritical temperatures, the fluid consists of a mixture of liquid and gas molecules, the relative amounts depending on the total volume available. Mixing can be prevented temporarily by use of a constriction.

Apart from variations in detail, Ramsay's point of view typifies the idea of persistence of the liquid state. Justly, therefore, Ramsay would be quoted as the originator of this idea, much to his later chagrin. The experimental findings usually are: a critical temperature that depends on the fill density, and the persistence of density differences above the critical point. The explanation of these effects is, usually, that liquid and vapor molecules have different identities. At the critical point, mixing occurs because the *densities* of liquid and gas become equal. In principle, however, liquid and vapor molecules are distinguishable, and can be separated even above the critical point.

In hindsight, the early experimenters were not always aware that their sample purity, temperature control, and equilibration times might be insufficient for experimentation near a critical point. The implications of the phase rule, formulated by Gibbs during the 1870s, were not yet common knowledge amongst experimentalists in 1880. Echos of Ramsay's arguments, however, will be heard until well into the 20th century.

10.5 *Cailletet liquefies mixtures*

On many occasions in this book, we have encountered Cailletet, well known for his work on liquefying gases, including the 'permanent' gas oxygen. His advanced technological skill and his bold spirit produced pioneering research on the behavior of fluids at high pressures. In Ch. 4.2, we saw Cailletet (1880a,b) studying the condensation of a mixture of five parts of carbon dioxide and one part of air. On various isotherms below 20°C, the mixture began to condense at modest pressure. Condensation would proceed as the pressure was raised. At pressures between 150 and 200 atmospheres, however, the meniscus became hazy and disappeared. It did not reappear on further compression. He noted that when the pressure was slowly reduced, a thick mist appeared in the tube and a meniscus formed. His description and explanation of the observations is the same as that used by other scientists of that

time when describing a critical-point phase transition in one-component fluids. The problem is that according to the phase rule a mixture of fixed composition has an invariant critical point. Therefore, the meniscus disappearance and reappearance observed by Cailletet over a range of temperatures cannot, in general, have been a critical-point phase transition.

In the absence of a practical model for phase transitions in fluid mixtures, an understanding of Cailletet's experiment was out of the question. Cailletet himself did little more than present the observations and express the opinion that the liquid and the gas had dissolved into one another, forming a homogeneous phase. Van der Waals reported similar observations in the same system that year (Ch. 4.2).

A compatriot of Cailletet, Jamin (1883) was less cautious. He did accept Andrews's result that at the critical point the vapor no longer 'takes refuge at the top' and the liquid no longer falls to the bottom. The liquid, persisting at its vapor pressure, 'swims' in the gas and is no longer visible. The vapor pressure keeps on increasing with temperature, until all liquid is exhausted and a truly dry vapor results. According to Jamin, this explanation was not only in agreement with Cagniard de la Tour's and Andrews's experiments, but it could also explain Cailletet's experiments on mixtures. Thus, on compressing a mixture of air and carbon dioxide, the latter component begins to condense when its vapor pressure is reached. On further volume reduction, carbon dioxide remains at constant vapor pressure, but the pressure of air continues to increase. Finally, a point is reached at which the density of the vapor is as high as that of the liquid. The liquid now leaves the bottom of the cell and spreads itself out through the vapor. One could imagine, ventured Jamin, that on further increase of pressure the density of the liquid, increasing less fast than that of the vapor, might be overtaken by that of the vapor, after which the liquid would separate out again and collect at the top of the vessel. Jamin's explanation might seem to forecast the so-called barotropic effect, later discovered by Kamerlingh Onnes and Keesom in mixtures of helium and hydrogen, and discussed in Ch. 8. The focal point of the argument is, however, that two fluid phases mix because they have reached equal density. This argument will be heard repeatedly, even after being challenged by Duhem in 1888 (Ch. 10.8).

Ramsay considered Jamin's explanations an infringement on his own priority in this field, and reacted immediately. In the *Comptes Rendus* of the same year as Jamin's paper, Ramsay (1883) pointed out that he had voiced the ideas now presented by Jamin three years earlier. He repeated statements in his earlier papers. At the critical point gas and liquid mix because they have the same density. Above the critical point, a gas, consisting of small molecular aggregates, and a liquid, consisting of more complex aggregates, can mix in all proportions.

10.6 Cailletet and Collardeau demonstrate the persistence of the liquid state

Cailletet and Collardeau (1889) thought of an interesting way to demonstrate the persistence of the liquid state. They deposited a drop of iodine on the wall of a test tube into which they compressed carbon dioxide. As soon as the liquid level reached the iodine, the latter dissolved, giving the liquid a purple color. When the fluid was heated above the critical point, the meniscus disappeared, but the purple color persisted at the bottom of the cell, fading out over a range of a few millimeters of height. The authors considered the persistence of the purple color evidence of the persistence of the liquid state.

This refutation of one of Andrews's premises opened the field to further challenge. Cailletet and Collardeau (1889) made a serious effort to confirm Jamin's prediction (Ch. 10.5) that a compressed homogenized binary mixture should separate again if the pressure were sufficiently increased to make the gas denser than the liquid. Despite their efforts, however, the experimenters were unable to verify this prediction. They then ventured that perhaps Andrews's concept of equality of liquid and vapor densities at the critical point had to be questioned in the first place! Cailletet and Collardeau had the original idea of testing equality of densities first in a partially miscible binary liquid mixture. Duclaux (1876) had experimented with binary and ternary liquids at the point where two phases of equal volume become identical, and the interface disappears. Cailletet and Collardeau recognized the similarity of the meniscus disappearance in the binary liquid and in a one-component gas. Measuring the densities of the two liquid phases at the point of meniscus disappearance, they found them to be unequal. In order to demonstrate that a similar inequality of densities existed at the critical point of a one-component fluid, Cailletet and Collardeau used a device that Cailletet and Mathias (1886) had designed for measuring coexisting densities: a glass tube in the form of a letter O, containing some sulfuric acid at the bottom. The apparatus was filled with CO_2 . By cooling one side, the CO_2 was made to condense there. The sulfuric acid showed a level difference, indicating the density difference of liquid and vapor. After heating the O tube through the critical point, however, the level difference, although diminishing, persisted, and was still visible several degrees above the critical point. Apparently, the liquid had not completely evaporated after the meniscus disappeared.

The O-tube experiment would be a source of inspiration to subsequent investigators. (This device, however, has a serious problem with equilibration: when CO_2 condenses in one side of the tube, the volatile impurities are forced to the other side, and will be very slow to mix.)

The authors concluded that the critical point is not the point at which the liquid suddenly evaporates completely. Nor does it occur at the temperature

at which liquid and vapor attain the same density. It is the temperature at which liquid and gas acquire the property of dissolving into one another in all proportions, forming a homogeneous mixture after stirring. Continuity of states is guaranteed by modifying the proportion of liquid to gas in the supercritical fluid in a continuous fashion.

So, almost two decades after Andrews's experiments, the premises that vapor and liquid become identical at the critical point and do not persist above it were put into question by one of France's leading high-pressure experts, Cailletet.

10.7 *Pellat: Andrews's critical temperature is not that of Cagniard de la Tour*

The experiments of Cailletet and Collardeau led Pellat (1892) to question whether Andrews's critical temperature, at which liquid and vapor densities become equal and the P - V isotherm has a horizontal inflection point, is indeed the same as that of Cagniard de la Tour's temperature of meniscus disappearance. Since the experiments showed that density differences apparently persist above the temperature of meniscus disappearance, Pellat concluded that Andrews's critical temperature was higher than that of Cagniard de la Tour. He also observed that the meniscus disappears inside the cell for quite a range of fill densities, whereas, according to Andrews, this should happen at only one density. (We recognize that this is Gouy's gravity effect mentioned in Ch. 10.3.) Pellat concluded that the meniscus disappears somewhere in the interior of Andrews's coexistence dome, and that at such a point gas and liquid densities are not yet equal (Fig. 10.2). Different versions of this plot will reappear during the next half-century.

10.8 *Blurring of the Andrews-Van der Waals view*

Cailletet's 1880 experiment on condensation of mixtures puzzled scientists in the field, especially Van der Waals, who independently reported similar experimental results in the same year (see Ch. 4.2). Both authors described the reappearance of the meniscus on expansion of the homogeneous mixture at various temperatures in terms that suggested an analogy with the critical phase separation of a one-component fluid. A correct explanation of this experiment had to wait for Van der Waals's development of his theory of mixtures in 1890, (Ch. 4), and for Kuenen's verifications of this theory in 1892 (Ch. 6). The French physicist, historian and philosopher Pierre-Maurice-Marie Duhem (1861-1916) made a distinct step in the right direction. Duhem (1888) was the first to apply Gibbs's principles to Cailletet's experiment. He pointedly remarked that equality of density alone is not a sufficient

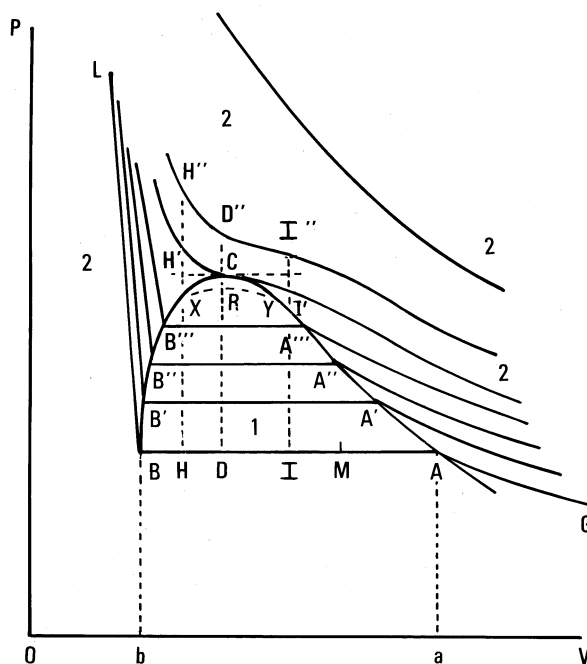


Figure 10.2 Sketch of the curve of meniscus disappearance XRY inside Andrews's coexistence dome BCA. Copied from Pellat (1892), Fig. 1.

reason for mixing of the phases in binary fluids, citing Plateau's work as a counterexample. Plateau (1873) had suspended oil drops in a water-alcohol mixture of matching density in order to eliminate the effect of gravity. Although the droplets had the same density as the surrounding fluid, they obviously did not mix with it.

Nevertheless, the colorful experiments of Cailletet and Collardeau aroused the imagination of many scientists, and resulted in a flood of new experiments. Unfortunately, Cailletet and Collardeau also set the tone for the interpretation of these experiments. This process, once in motion, would be hard to stop.

10.9 Experiments by Zambiasi, De Heen, Battelli and Galitzine

In the early 1890s, scientists in several European countries reported observations of critical behavior in fluids. The Italian Zambiasi (1892), for instance, repeated Cailletet's O-tube experiment in an apparatus of modified shape (Fig. 10.3).

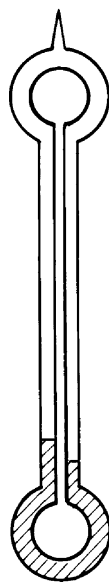


Figure 10.3 Zambiasi's (1892) version of the O-tube experiment.

He confirmed that the level differences persisted above the critical temperature. Contrary to Ramsay, Ch. 10.4, however, he reported that the temperatures of meniscus disappearance and meniscus reappearance were the same.

The Belgian De Heen (1892a), working at the Physics Institute of the University of Liège, observed temperatures of meniscus appearance and disappearance in tubes filled with varying amounts of ether and heated in a bath of sulfuric acid. Contrary to Ramsay (Ch. 10.4), he found that the temperature of meniscus disappearance *rose* with fill density. De Heen (1892b) also calculated the density of the vapor from the position of the meniscus, the fill density, and the density of the liquid, as determined in a separate experiment. To his surprise, the vapor density in the two-phase system varied by as much as 50% at a fixed temperature. De Heen concluded that the density of the saturated vapor may assume a range of values at a given temperature.

The Italian Battelli (1893) filled glass tubes with varying amounts of ether or alcohol and sealed them while the fluid was boiling. The tubes were heated in vapors of boiling kerosene (Fig. 10.4), of which he had prepared eight fractions boiling at 10°C intervals. He found that the temperature of meniscus reappearance was below that of meniscus appearance, but that it was *lower* the higher the fill density. Battelli showed that one or the other of his

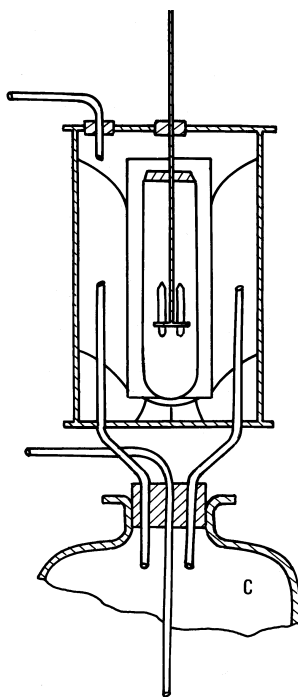


Figure 10.4 Sealed glass tubes inside a glass jar surrounded by vapors from kerosene boiling in the vessel C. Copied from Battelli (1893), Fig. 1.

findings was in contradiction to the experiments or conclusions of at least one of his predecessors in the controversy: Zambasi, De Heen, Cailletet, Ramsay, Jamin and Cagniard de la Tour. For details, see Levelt Sengers (1979). Battelli presented a new explanation: the meniscus disappears at the point that cohesive forces are no longer capable of holding liquid molecules together. These molecules then fly out into the vapor phase where they keep on dividing into smaller and smaller groups. Occasionally they meet and melt together forming chains. These are the 'striae,' the refractive-index streaks observed in critical-region experiments. (They are presently considered a sign that a near-critical system is not in thermal equilibrium.)

Boris B. Golitsyn (1862-1916) spells his name as Galitzine in French publications. A descendant of St. Petersburg nobility, he studied physics and mathematics at the University of Strasbourg and joined the faculty at Moscow University in 1891. He was intrigued by Pellat's idea that Andrews's and Cagniard de la Tour's critical temperatures might not be the same. Galitzine (1893) published a paper based in part on work he had carried out while at Strasbourg.

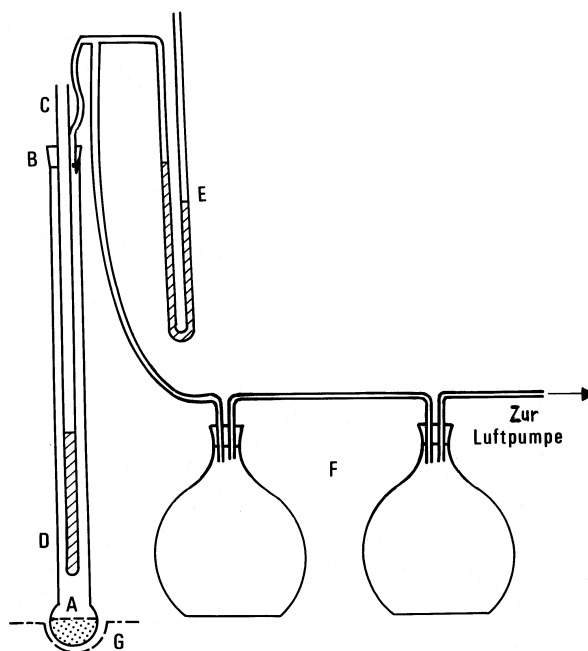


Figure 10.5 Tubes, partially filled with ether, are heated in a cylinder C filled with glycerine and surrounded by naphthalene vapor A boiling under reduced pressure in vessel D. Copied from Galitzine (1893), Fig. 1.

He had prepared about ten tubes with various amounts of ether, paying special attention to expulsion of all air. He heated the tubes in an elaborate vapor thermostat, Fig. 10.5. In contrast to Zambiasi, De Heen and Battelli, he found that the temperature of meniscus disappearance was *independent* of the fill density. This may be considered a tribute to the purity of his samples. Although he had no method for measuring the Andrews critical temperature, he states that it was substantially above those of meniscus appearance or disappearance. He was able to observe meniscus disappearance inside his tubes for a range of initial liquid fill volumes between 0.31 and 0.48 of the cell volume.

Next, Galitzine performed some studies of the supercritical state. He used a glass U-tube with mercury at the bottom (Fig. 10.6), with one side filled completely with liquid ether, the other only partially, and found that the mercury levels did not equalize above the critical point. According to Andrews criticality, they should, each leg being filled with a supercritical fluid at the same pressure and temperature. (Unlike in the O-tube experiment, however, equality of pressure on the two separate sides of the U-tube

device is not guaranteed. Persistence of a temperature-dependent level difference is therefore not in conflict with the Andrews-Van der Waals concepts.)

Galitzine also calculated that the densities on the two sides differed by as much as 20% at supercritical temperatures. To prove that residual air could not have caused these phenomena, Galitzine showed that they were unaltered after a large amount of air was admitted to one side of the vessel. The reader will find this hard to believe, and so did the Leiden group, as we will see in Ch. 10.13. Finally, he claimed that the ‘new ideas’ about the disintegration of molecular complexes could readily explain his experiments.

Thus, by 1893, all insights of Andrews and Van der Waals had been challenged and disproved by several experimenters. Andrews’s deep grasp of the experimental situation was given up in favor of a mass of mutually conflicting observations. Van der Waals’s molecular theory was pushed aside in favor of intuitive ‘explanations.’ These explanations claimed to be based on more modern theories of molecular constitution in vapors and liquids, but were never quantified. Fortunately, a few experimentalists kept their heads cool. The year 1892 would prove to be a turning point in experimentation near critical points.



Figure 10.6 A glass U tube has mercury at the bottom, and is partially filled with liquid ether on one side, but completely filled on the other side. Copied from Galitzine (1893), Fig. 6.

10.10 Gouy studies gravity effects near the critical point

The skilled experimenter Louis-Georges Gouy (1854-1926) was an expert in optics and a professor at the University of Lyons, France. Gouy (1892) published a 3-page note on the effect of gravity in a near-critical fluid. He pointed out that even though the pressure exerted by the force of gravity is minute compared to the critical pressure, gravity has a large effect on the density because of the divergence of the compressibility.

Gouy's note clarified a fact that tends to confuse experimenters: due to the action of gravity, the critical state, even though it is invariant, can be realized at some level in a cell even if the cell is not precisely filled to the critical density.

This gravity effect is present in all fluids, and had already been described by Gibbs. Due to the very large compressibility of a near-critical fluid, even a small gravitational pressure head can have a large effect on the density. Thus, the near-critical fluid in a vertical cell assumes a range of states. The gravitational contribution to the chemical potential, gh , increases linearly with the height h , and therefore the intrinsic fluid contribution, μ , must decrease linearly with height, so that the total chemical potential remains constant. The fluid contribution is calculated readily from a formulation of the Helmholtz free energy or the equation of state of a fluid. The result for the density is a sigmoid curve as a function of height, with an inflection point at or near the level where the density equals the critical density, and where the meniscus will appear when the cell is cooled through the critical temperature. As long as the inflection point remains within the cell, the critical-point meniscus disappearance can be observed at a range of levels, but always at the same temperature, the critical.

It is much to Gouy's credit that he quantified the density profile in a tall tube on the basis of the Van der Waals equation. According to Gouy's estimate, the fluid in a cell 8 cm high would become critical at some level inside the cell for fill densities from 3% below to 3% above the critical density. Gouy's estimate was not decisive in the raging controversies because most experimenters reported density gradients much larger than could be explained by gravity effects alone.

In the next year, Gouy (1893) reported the first accurate observations of equilibration near the critical state. He used 25 cm tall cells filled with carbon dioxide. He felt that, in view of the great sensitivity to temperature disturbances, temperature control to 10^{-4}°C would be required. This goal was two orders of magnitude beyond what was considered the best achievable at that time, and is still competitive today. He built a 100 l bath, insulated it with down, stirred it thoroughly, and provided it with an electric on-off control. He shook his tubes, inserted them in the bath, and watched the meniscus

drift and settle. He found that the position of the meniscus was independent of the previous states of the sample, and always the same at a fixed temperature. He was able to make the meniscus vanish at a level inside the cell by choosing liquid-to-vapor volume ratios from 0.73 to 0.93 at 17°C. Density differences did indeed persist at slightly supercritical temperatures, but Gouy ascribed those to the action of gravity on the highly compressible medium.

He then took a tube equilibrated at 20°C and placed it in a bath at the critical temperature, without shaking the tube. The meniscus now formed in the wrong place, indicating too high a density for the liquid phase. The position of the meniscus drifted. It had not yet reached its final state after a *week*. Gouy ascribed this very slow transition from a transient to a final state in a tall tube to the diffusion of a small amount of air.

In these two papers, Gouy demonstrates an advanced understanding of the pitfalls of critical-region experimentation. All major sources of error, temperature gradients, gravitational stratification, impurities, and slow equilibration, are recognized and understood.

Gouy (1880) is best known for inventing an elegant optical interference technique, still in use, for measuring diffusion coefficients in liquid mixtures. He made use of the refractive index gradient accompanying the concentration gradient. A parallel light beam impinging on the cell gets deflected, and an interference pattern results, which evolves in time as diffusion decreases the existing concentration gradients. In an interesting twist, Wilcox and Balzarini (1968) adapted the Gouy method to the measurement of density profiles caused by gravity in one-component fluids near critical points. Hocken and Moldover (1976) used this method to prove that fluids behave like the Ising model if the vapor-liquid critical point is approached within a fraction of 1 K.

10.11 *Kuenen explains Cailletet's early experiments on phase separation of mixtures*

While controversy raged, Kuenen discovered how to make reproducible measurements in fluid mixtures, and Van der Waals produced the first mixture equation of state. Shortly after he finished his doctoral thesis (Ch. 6), Kuenen (1893b) felt confident enough about his understanding of criticality in fluid mixtures to offer an explanation of the early experiments of Cailletet (1880a, b) on compression of mixtures of carbon dioxide and air, discussed in Ch. 10.5. First of all, unless the contents of the vessel containing the mixture are vigorously stirred, the system does not reach an equilibrium state. Cailletet, however, had not stirred. Secondly, Kuenen describes what happens when a near-critical two-phase binary mixture is compressed. Fig. 10.7, from Kuenen's doctoral thesis, shows the isothermal liquid-vapor plait, including

the tie lines, in the V - x plane. The concentration is plotted on the vertical axis, and the volume on the horizontal axis. The critical point, where the length of a tie line shrinks to zero, is indicated by C. Consider the connodal points on the tie line closest to C. If the two-phase system is compressed at constant temperature, at first each state moves to the left, to a smaller volume, at constant composition. Kuenen shrewdly observes that both states thus move into the stable region. Though not in equilibrium with each other, the states will tend to persist in the absence of stirring. Only near the interface some exchange of matter will occur, which will eventually wash out the interface by diffusion, just as Cailletet had observed. This, however, has nothing to do with criticality.

Thus, by 1893, the Leiden scientists had achieved a sound theoretical and experimental understanding of liquid-vapor criticality in pure fluids and fluid mixtures. From then on, Kamerlingh Onnes and his staff took the lead in defending the Andrews-Van der Waals concept of criticality.

It should be mentioned that the prestigious Russian physicist Stoletov, aware of Kuenen's and Gouy's work on stirring and equilibration near critical points, did not let Galitzine's refutations of Andrews-Van der Waals criticality pass without comment. Between 1892 and 1894, Stoletov published in Russian a series of papers that criticized experiments by Galitzine and by many others for reasons of impurity, partial decomposition of samples, and lack of equilibrium. See Kipnis et al. (1996), p. 186, for details.

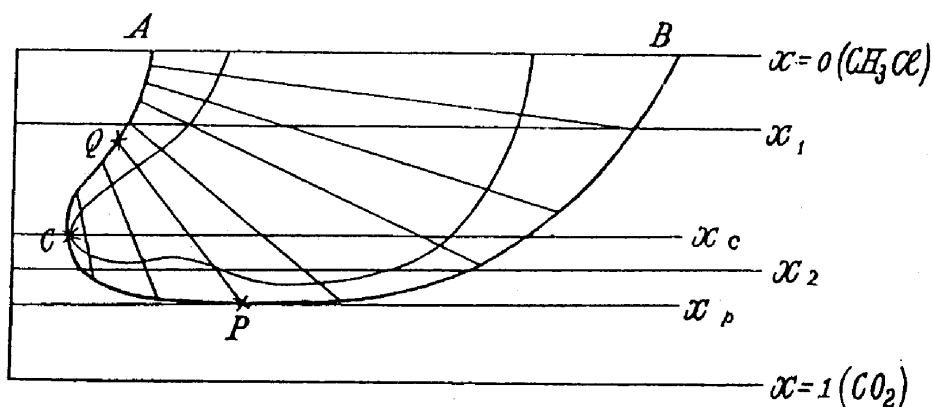


Figure 10.7 A plait for a binary mixture in the isothermal volume-composition plane. Shown are the connodal AQCPC and several tie lines. The vertical axis represents the concentration, and the horizontal axis the volume. C is the critical point, branch A-C the liquid, branch B-C the coexisting vapor. Copied from Kuenen (1893c), p. 378.

All opponents of the Andrews-Van der Waals concept of fluid criticality began their reports by quoting Ramsay (1880a) as the originator of the new ideas. By 1890, however, Ramsay, Young, and their coworkers were immersed in accurate determinations of coexistence curves of organic liquids. Ramsay's experience preparing pure samples and his growing awareness of the effects caused by even small impurities made him realize that his earlier point of view was mistaken. Much to his credit, Ramsay (1894a) openly recalled his former position.

Unfortunately, my name is often cited as a proponent, yes even as an originator of such ideas; and I feel compelled to repent once more, by taking the occasion to declare that I no longer believe in such nonsense. [Translated from the German.]

This humble acknowledgement of his fallibility was immediately followed by full-scale criticism of the experiments of Battelli, Zambiasi, Galitzine and De Heen. Ramsay and Young (1894b) pointed out the inconsistencies between the various experiments with respect to the variation of the temperature of meniscus disappearance with fill density (Ch. 10.9). They also noted that the critical temperatures reported by De Heen for several fluids differed greatly from those reported for the same substances by other groups, in one case even by as much as 46°C. As one possible source of error, they indicated temperature variation, certainly in the cases of Battelli and De Heen, whose work was put aside as 'very inaccurate.' They pointed out this might also be the case in Galitzine's experiment if the naphthalene he used in his bath was impure. Ramsay and Young emphasized that striae are never seen if the temperature is truly constant.

Next, they turned their attention to the claimed persistence of the liquid state. Not denying the possible existence of molecular complexes, they knew these should not affect the homogeneity of the supercritical state. The only reason for density gradients is the gravity effect discussed by Gouy. Thus, sample impurity must have been a major reason for the aberrant results. Ramsay and Young deplored the fact that scientists were now attempting to improve Van der Waals's simple formula on the basis of these untrustworthy observations.

De Heen and Galitzine immediately reacted to this criticism. De Heen (1894) repeated his statement that pressure and temperature do not always define the state of a supercritical fluid, and challenged Ramsay and Young to point out his errors of reasoning and experimentation. He felt that Gouy's gravity effect could not explain his observed density gradients, since gravity effects should be immediate and not take a day to develop. Galitzine's (1894)

reply was more to the point. He claimed he had made sure the experimental temperature was uniform and that he had not seen any striae. He also felt he had taken great pains in eliminating air from his ether samples. In their reply, Ramsay and Young (1894b) took Galitzine's position seriously, but suggested alcohol as a possible contaminant of ether, and warned him about fluid decomposition or contamination from sealing the tube. In reply to De Heen, the authors showed that the reported critical temperatures for methyl formate and methyl acetate spanned a range of no more than 10°C. De Heen's critical temperatures for these substances, however, differed from the averages by more than 40°C. Given these huge discrepancies, Ramsay and Young simply refused to take his work seriously.

10.13 *Kuenen disproves Galitzine's experiments*

Kuenen (1893b) claimed that even before knowing about Gouy's work on transient states he was convinced that the history dependence and hysteresis effects reported by Cailletet, Zambiasi and De Heen indicated a process of 'retardation.' He had completed experiments with carbon dioxide and found that using a stirrer provides reproducible results. Also the meniscus disappeared inside the cell for a rather narrow range of densities, just as Gouy predicted. The reason for the retardation clearly had to be sought in the presence of impurities. Suppose a two-phase system contains a little air.

Slowly according as air is absorbed by the liquid and spreads through it by diffusion equilibrium will be attained.

This explanation was so satisfactory, Kuenen felt, that the development of new theories for the critical behavior of simple substances seemed unnecessary.

Kuenen (1894a) then examined the new theories purporting that liquid and vapor molecules retain their identities in supercritical states. If it is assumed there are indeed two different kinds of molecules, either these two types of molecules can transform into one another, or they cannot. If they can transform, the fluid must behave as a one-component system. Thus, the specific volume must be fixed once temperature and pressure are given in the one-phase state. This hypothesis, therefore, does not explain Galitzine's observations that density differences persist in the one-phase state. Likewise, coexisting fluid phases must have well determined densities at a given temperature, in contradiction to De Heen's experiments.

On the other hand, if one assumes that liquid and gas molecules cannot pass into one another, some of Galitzine's experiments could perhaps be explained. But who wants to make the assumption of two different species of ether molecules, for which no evidence has ever been found in any other experiment?

Although this argument alone would have been sufficient, Kuenen decided to repeat Galitzine's U-tube experiment. Kuenen quickly found that close to a critical point the U-tube served as a sensitive thermometer, reacting to the lightest temperature differences between the two legs. He estimated that temperature differences below the level of detection could cause a good part of the density differences in the supercritical state he and Galitzine observed. Subsequently, Kuenen (1894b) showed that the remaining density differences must be ascribed in part to difference in the mercury level, and in part to an admixture of a permanent gas. He also demonstrated that his own results, in contrast to Galitzine's (Ch. 10.9), changed drastically when he admitted air to one side of the U-tube. He estimated that 0.1 volume% of air readily explained the residual density differences in his own experiments.

10.14 *De Heen separates the liquid-like from the gas-like molecules*

Not discouraged by Ramsay's and Kuenen's criticism of his earlier experiments, De Heen (1896) decided to build a device for separating 'liquidogeneous' from 'gasogeneous' molecules in the supercritical state. Two cylindrical vessels, provided with sampling valves, were placed one above the other and connected by a capillary containing a shut-off valve. Each reservoir contained a piston; the pistons moved in tandem, keeping the total volume constant. In a typical experiment, the two reservoirs were filled with liquid carbon dioxide, the connecting valve was closed, the top vessel emptied, and the connecting valve reopened. The system was then heated above the critical point and the valve closed. On sampling the two vessels, large density differences were found in the supercritical state. In de Heen's view, the top vessel contained gasogeneous, the bottom one liquidogeneous molecules. The narrow connection between the two vessels prevented mixing. In a second set of experiments, he restricted mixing even further by heating the system with the valve closed. Above the critical point, the valve was opened and closed a few times. A density ratio of 1.44 was now found between the two reservoirs.

Surprising are the seriousness with which Kamerlingh Onnes took De Heen's work, and the alacrity with which he reacted. The sequence of events can be reconstructed from a detailed paper by Kamerlingh Onnes (1901a). Kamerlingh Onnes first contacted De Heen with questions about sample purity. When De Heen did nothing to check or improve purity, Kamerlingh Onnes asked him to send his apparatus to Leiden, and he asked his assistant Verschaffelt to repeat the experiment. When the latter disassembled De Heen's apparatus, a smell of grease was detected, originating from valve packing material that was in direct contact with carbon dioxide. Kamerlingh Onnes then abandoned the original apparatus, and built a simplified version.

The pistons were omitted, and thermocouples were installed for checking temperature equilibrium. Repeating De Heen's first experiment with 20 ppm pure carbon dioxide, he found the density difference was within the bounds expected given his rather crude temperature control.

Before repeating De Heen's second experiment, Kamerlingh Onnes pressed De Heen on the time scales involved in opening and closing the valves. De Heen (1898) replied that the valve was cracked open 4 or 5 times for 4 or 5 seconds each. Kamerlingh Onnes quickly showed that after each equalization of pressure an equivalent temperature difference builds up, while little if anything happens to the density. Repeating De Heen's second experiment, he again found that the density differences observed could be explained by the temperature gradients in the system. In a letter responding to Kamerlingh Onnes's (1901a) paper, however, De Heen (1901) considered the matter far from settled and proposed that he, Kamerlingh Onnes, Verschaffelt, Mathias, and Galitzine conduct the experiment with the same substance in the same apparatus. There is no evidence that the parties mentioned accepted the challenge.

10.15 *Persistence of the concept of liquidogens*

Notwithstanding the efforts of Gouy, Kuenen and Kamerlingh Onnes, doubts about the correctness of the Van der Waals-Andrews ideas persisted. At the prestigious Congrès International de Physique in Paris, Galitzine (1900) presented a paper on the critical refractive index in which he reaffirmed that, in the supercritical fluid, large density differences persist, which cannot be explained by temperature differences, gravity, or impurity effects. Above its critical point a substance can assume a range of densities at fixed given temperature and pressure.

More striking was the Frenchman Mathias' attitude. Cailletet and Mathias are known as co-discoverers of the well known law of the rectilinear diameter (1886). The law states that the average of the coexisting vapor and liquid densities is a linear function of temperature, and is frequently used to estimate the elusive critical density. In later years, Mathias would become a frequent guest at the Leiden laboratory. At the international conference in Paris referred to, Mathias (1900) submitted a paper on the determination of the critical density and temperature. In this paper, he emphatically states that at the temperature of meniscus disappearance the density of the liquid is larger than that of the vapor. In his book on the critical point of pure fluids, Mathias (1904a) treats Andrews's theory and the theory of the persistence of the liquid state on an equal footing, without rejecting one in favor of the other. In a letter to Van der Waals about his book, Mathias (1904b) writes:

From my book on the critical point of pure fluids, you may have seen that I remain faithful to the classical theory of fluids, in particular on the point of univariance of saturated equilibrium states.

The most serious discrepancy, in fact, the only one, between the classical theory and reality is formed by the phenomenon Cagniard-Latour, namely that the saturated states stop being monovariant a little below the true critical temperature. [Translated from the French.]

After a few diplomatic words about the possibility of reconciliation between the two points of view, Mathias reveals his inability to accept the identity of gaseous and liquid molecules:

The great defect, in my view, of your theory of identity of liquid and gas molecules is that one cannot understand at all the simple phenomenon of liquefaction of gases. You begin with a gas in which the molecules are equidistant on the average: you decrease the volume at constant temperature, the molecules remain equidistant on the average; there is no reason why that would ever stop and why the liquid should be partitioned in two phases, a liquid and a gas.

With the idea of liquidogens, however, the explanation is very simple, since the reason for the discontinuity required for the production of a separation in to two phases at a given moment, is that a group of gasogeneous molecules can form a single liquidogeneous molecules below the critical temperature. [Translated from the French.]

Mathias ignores Kuenen's argument that whether molecules associate or not in the liquid phase makes no difference to the critical behavior. He makes, however, an interesting point by graphically expressing the heart of the mean-field assumption: gaseous molecules remain equidistant on compression of the gas. His uneasy feeling about this assumption is justified. Statistical physics developed during the 20th century shows that in molecular systems interacting with short-range forces, the local density around a chosen molecule in a gas exceeds the average density, contrary to the mean-field assumption.

10.16 *The use of floats as probes of local density*

10.16.1 *An experiment by Teichner.* A professor at the Technische Hochschule, Charlottenburg, Germany, J. Traube (1902a, 1903a,b) published a series of papers proposing a new theory of the vapor-liquid phase transition. In contrast to the prevailing views on liquid-like and gas-like molecules, Traube assumes that the former, which he calls fluidons, are much smaller than the latter, called gasons. In his view, when a fluidon evaporates from the liquid phase, it expands into a larger gason. There are, therefore, two values for the

Van der Waals co-volume: a small one for the liquid and a large one for the vapor. He does not quantify this theory. In a letter Traube (1902b), whose ideas had raised considerable controversy, asks for Van der Waals's blessing. We do not know whether the master granted this request, but chances are slim. Traube (1903b) credits Van der Waals for pointing out that the excluded volume decreases with density (for completely different reasons, see Ch. 2.4), and, in the same breath, scolds the master for not giving priority to Traube as the discoverer of the shrinking gasons.

Traube had his student Teichner (1904) investigate the supercritical fluid by an ingenious and elegant new method. Small hollow glass spheres, a few mm in diameter, were suspended in a glass tube filled with near-critical carbon tetrachloride. The average densities of the floats had a range spanning the critical density of carbon tetrachloride. Each float would seek the level of matching density in the fluid, and since the densities of the floats were calibrated, the density distribution in the cell was thus made directly visible (Fig. 10.8). In view of the high value of the critical temperature of carbon tetrachloride, 282.2°C, special care was taken to insulate the glass thermostat, which was of the same type as those used by Young and by Galitzine. Teichner carefully prepared his samples, and noted that stirring affected the location of the meniscus as well as the temperature of meniscus disappearance.

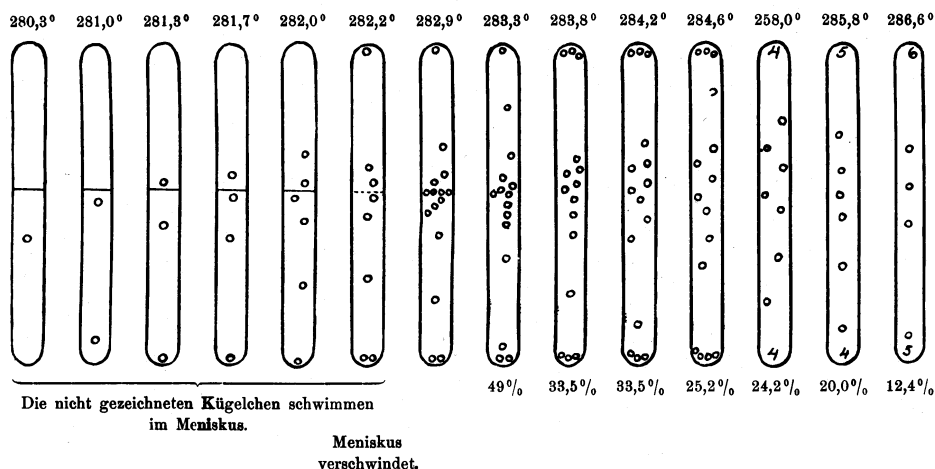


Figure 10.8 Calibrated glass floats indicate the density profile in carbon tetrachloride when heated through its critical point. On the left, below the critical point, spheres not shown have collected at the interface. For supercritical states, on the right, the density difference between top and bottom is indicated in %. Copied from Teichner (1904), Fig. 2.

Fig. 10.8 shows the course of a typical experiment and the resulting density distribution, with the fluid, starting from the right, passing through the critical point on heating. Stirring made the large density difference in the supercritical state disappear. Nevertheless, Teichner concluded that his experiments were in complete agreement with those of Galitzine and De Heen, and he deemed it unlikely that Andrews's theory was correct.

Teichner was prepared for criticism on the points of temperature stability and purity. He conceded that temperature differences as large as a few tenths of a degree could be present, but these could never cause density gradients as large as 25%, as observed. Purity was a different story. In a paper by Traube (1904) and a letter by Young (1905) to Verschaffelt, it transpires that Young had been in contact with Teichner in the early stages of the experiment and in 1903 investigated the tube in which the large density differences were found. He noted that the fluid turned brown on heating, indicating decomposition. On opening the tube he found a large amount of permanent gas. Young repeated the experiment with a sample he considered pure, and found no evidence of anomalously large density gradients. He sent this tube to Teichner with elaborate instructions as to sample preparation. When Traube and Teichner repeated the experiment with Young's sample, they found that the density differences increased after each passage through the critical point. Young thought this was evidence of progressive decomposition of the fluid.

Teichner (1904) was pessimistic about the chances of his experiment being accepted as disproving Andrews's view of criticality. He realized that proponents of this view would always invoke the presence of impurity or the occurrence of decomposition.

One wonders why Traube and Teichner made things difficult for themselves by using carbon tetrachloride in an otherwise interesting experiment. Carbon dioxide would have been a much better choice, given its lower critical temperature, its availability in highly pure form, and the substantial knowledge already available about its properties.

10.16.2 *A quantitative treatment of impurity effects near critical points.* Around the turn of the 19th century, it became clear to Kamerlingh Onnes that controversies around the experiments 'proving' persistence of the liquid state would never end if the influence of impurities could not be quantified. He initiated a program to study such effects, to be described in Ch. 11. Verschaffelt (1899a-d, 1900a,b) measured P - V - T - x relations for the system carbon dioxide-hydrogen. From these measurements, the behavior of a condensable substance, such as carbon dioxide, in the presence of a small amount of a permanent gas, such as hydrogen, can be estimated. Verschaffelt used a corresponding-states model for comparing the properties of a dilute mixture

with those of the pure host at the same pressure and temperature. Verschaffelt (1904) calculated that at the host's critical pressure and temperature, a 0.1% impurity could cause as much as 30% difference in density. A reduction of the impurity level by a factor of 10 cuts the density difference only in half, as a result of strong nonlinearity of the impurity effect at the critical point. Density differences of several percents must still be expected at 3°C above critical. In tall cells such differences, which are caused by unevenly distributed impurities, will persist almost indefinitely and disappear only on stirring. Verschaffelt explained that the entire course of Teichner's experiment could be understood completely on the basis of small, slowly diffusing impurities.

Young (1905) was very impressed with Verschaffelt's analysis and sent him a congratulatory letter. After describing his frustrating interactions with Traube, he wrote:

I am therefore particularly glad that you have taken the matter up and shown so clearly that the observed differences in density can be explained by the presence of minute quantities of impurities.

Verschaffelt's wife sent a copy of this letter to Kamerlingh Onnes (1905), who, within days, wrote an equally enthusiastic reply:

Dear friend, with much interest and joy I read Young's letter regarding your latest paper. It was so kind of your wife to copy it for me; she can be pleased with her effort. Of course both of you are delighted with the letter, and you may count me in as well....and congratulations that such a well-known authority as Young is no less pleased with your work than H. Kamerlingh Onnes. [Translated from the Dutch.]

10.16.3 *Kamerlingh Onnes repeats De Heen's and Teichner's experiments.* This story has reached the years immediately preceding the liquefaction of helium in Leiden, which took place in 1908. One might think that after the repetition of Galitzine's and De Heen's experiments, and after giving a quantitative account of Teichner's experiments as an impurity effect, Kamerlingh Onnes might consider matters closed and turn to more pressing affairs. This is not so. Clearly dissatisfied with his crude repetition of De Heen's experiment and believing that verbal arguments against Traube and Teicher must be supported by facts, Kamerlingh Onnes decided to repeat both experiments.

Repeating De Heen's experiment (Ch.10.14) more carefully, Kamerlingh Onnes and Fabius (1907b) showed that the small density differences they found between the cells 3°C above the critical point were consistent with Verschaffelt's estimate, given the purity of their samples. This was a conclusive test that De Heen's reported large density differences were spurious.

Reviewing Teichner's experiment, Kamerlingh Onnes decided that carbon dioxide would be a better choice than carbon tetrachloride. The lightweight floats required must have been a challenge to Leiden's glass blowers. The temperature stability in the experimental cell was at the mK level. In an extensive series of experiments, Kamerlingh Onnes and Fabius (1907b) showed that the densities of liquid and vapor were within 5% of each other when the meniscus disappeared at a level inside the cell. After heating through the critical point, the densities were equalized to within 3% slightly above critical, but it took about six hours to reach equilibrium. According to Verschaffelt's estimate, an unequilibrated impurity of only 0.01% could cause density gradients as large as 12% this close to critical. Kamerlingh Onnes concluded that the small density difference he found was explained by residual impurities.

Not to be deterred, Traube (1914) commissioned his student Hein to repeat the Teichner experiment in carbon dioxide under the best-controlled circumstances. Grudgingly, Traube admitted that Hein's results agreed better with those of Kamerlingh Onnes and Fabius than with those of Teichner. Nevertheless, he stuck to his assumption that there are two types of molecules, fluidons and gasons. He again rejected Van der Waals's 'one-phase theory,' which he disparagingly refers to as the 'old classical theory.' Traube claimed that Van der Waals's occasional remarks, such as his Nobel lecture of 1911, confirm the persistence of fluidons. Traube's pugnacious mood continued for another quarter century.

10.17 *History repeats itself*

10.17.1 *Fallow years and rebirth.* Just prior to the liquefaction of helium in 1908, the Leiden researchers had completed their proof of the validity of the Andrews-Van der Waals view. After the liquefaction of helium, physicists turned their attention to the exciting world of superconductivity and superfluidity, leaving the study of fluid phase equilibria to chemists, geologists, metallurgists and engineers. At the 1937 Amsterdam meeting commemorating the centennial of Van der Waals's birth, for instance, there was extensive coverage of Van der Waals forces, but only two papers were presented on the gas-liquid transition and criticality. One was Lennard-Jones's paper on the phenomenological cell theory of liquids, which has had merit as a simple approximation method for estimating properties of liquids, but which has not opened new vistas. The other was written by Born, who referred to Mayer's new theory of condensation, which was just appearing in print at that time. This latter theory indeed marked the onset of a new era in the study of phase transitions in fluids.

Joseph Mayer was a professor of statistical physics at the University of Chicago and the spouse of a Physics Nobel-Prize winner, Maria Goeppert-Mayer, with whom he wrote a widely used textbook on statistical mechanics. Mayer showed how to derive the virial expansion for the pressure of an imperfect gas from first principles of statistical mechanics, namely the Ursell cluster expansion.

Mayer (1937, 1938) and his student Harrison (1938) investigated properties of large clusters and identified the condensation point as a point of singularity of the cluster expansion. With this promise of rigor, the subject of condensation became a concern worthy of the attention of physicists. Born and Fuchs, as well as Uhlenbeck and Kahn, inspired by Mayer's approach, improved and generalized his theory of condensation. Set in motion by Mayer, further rigorous statistical-mechanical work on phase transitions followed, such as that by Van Hove, Van Kampen, and by Yang and Lee. For a review of these developments, see De Boer (1949).

10.17.2 *The derby hat and the flat top.* Applying their theory of condensation to the critical region, Harrison and Mayer (1938) predicted that above the temperature of meniscus disappearance a region of infinite compressibility exists, which was later affectionately referred to as the 'derby-hat region' (Fig. 10.9). Above the Cagniard-Latour temperature of meniscus disappearance, T_m in Fig. 10.9, there is a region in which different densities can be realized for given temperature and pressure. This was an old theme, several examples of such anomalous regions having appeared in print in the preceding 50 years. See, for instance, Fig. 10.10, a picture taken from Traube (1903).

Note that the density is plotted on the vertical axis in the Traube picture, so that it appears turned by 90° compared to that of Harrison and Mayer, Fig. 10.9.

Mayer and Harrison were aware that such reports existed and also that the reported anomalies had been ascribed to temperature gradients, impurity, or gravity. However, it so happened that just at the time Mayer was developing his theory of condensation, the experimental group of Maass at McGill University in Montreal was involved in full-scale critical-region experimentation. Their specialty was local density measurements by means of a highly sensitive spring-and-float technique. They reported many curious effects in the critical region of fluids. Almost invariably they observed hysteresis effects on repeated passage through the critical point. In the one-phase region above T_c they measured large density differences at fixed temperature and pressure. See for instance, Tapp et al. (1933), Maass and Geddes (1937), and Maass (1938). Naldrett and Maass (1940) reported that the coexistence curves of ethylene, in stirred samples, had a flat top, see Fig. 10.11.

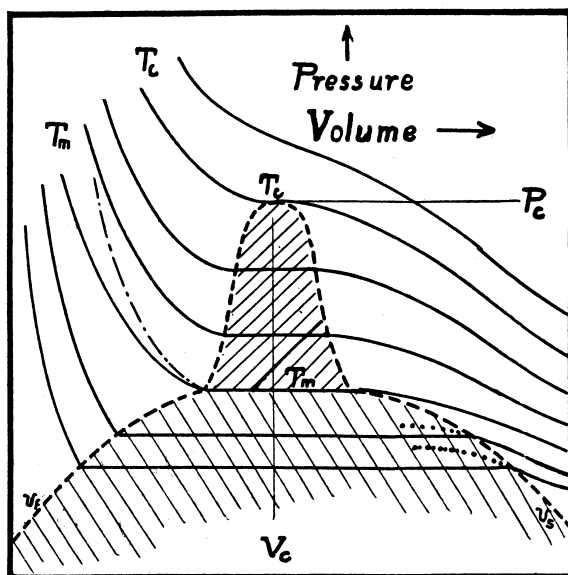


Figure 10.9 The 'derby-hat' region, a postulated region of infinite compressibility above the temperature of meniscus disappearance T_m . Several pressure-volume isotherms are shown. The meniscus disappears at T_m , the horizontal section of the isotherms disappears at T_c . Copied from Harrison and Mayer (1938), Fig. 1.

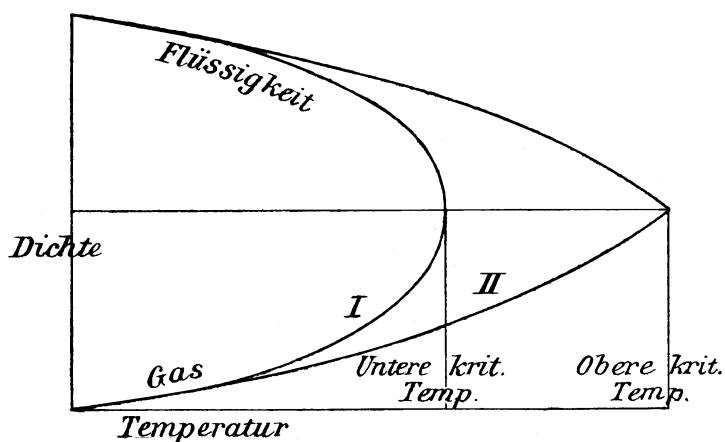


Figure 10.10. A sketch of the curve of coexisting densities in a stirred (I) and in an unstirred system (II). The vertical axis represents the density, the horizontal one the temperature. At the lower critical temperature the meniscus disappears, but only at the upper one the densities become equal. Copied from Traube (1903a), p. 570.

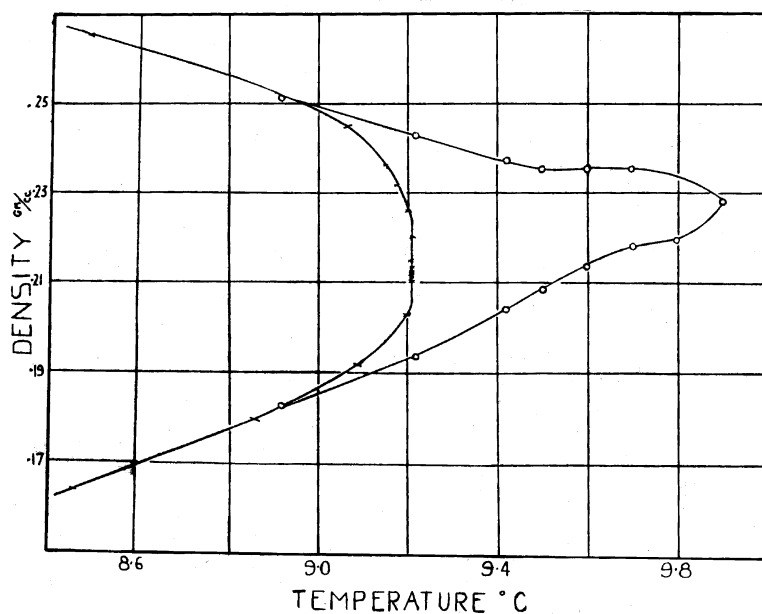


Figure 10.11 The flat-top coexistence curve of ethylene. A stirred system shows the inner flat-top coexistence curve. The curve marked by o indicates the region in which P - V isotherms show a flat portion. Copied from Naldrett and Maass (1940), Fig.1.

The descriptions of their findings, and the titles of their publications, such as ‘Persistence of the liquid state of aggregation above the critical temperature,’ are oddly reminiscent of the work done around 1900. Maass and coworkers knew these effects had been seen before, and took sides with Galitzine, Teichner and Traube, see Tapp et al. (1933). Traube (1938) gladly accepted this endorsement of his work and offered his two-phase theory as an explanation:

O. Maass and his collaborators have used this hypothesis of the structure of liquids to explain those questions of critical phenomena, and the present author agrees with them. He is of the opinion that the particles of liquids form complexes – orientated aggregates which are closely packed, whereas the gas particles are less closely packed groups or single particles. Thus we may, if we wish, speak of a theory of two phases instead of a theory of continuity. At the critical temperature and above and below that temperature there exists an equilibrium of different states of matter closely and less closely packed, which we call liquidogene and gasogene, and this equilibrium is responsible for the deviations from the Andrews-van der Waals’ theory observed by so many investigators.

Modern researchers who simulate molecular arrangements in supercritical states by computer will immediately recognize the picture that Traube paints here, of denser and less dense regions in the supercritical fluid, as akin to their own results. For such a simulation, see Figure 10.12 in Ch. 10.18. Traube's 1938 description, however, differs considerably from his early-1900 hypothesis that fluidons were small molecules and gasons big ones. By indiscriminately lumping together the many investigators 'who observed deviations,' Traube ignores the careful separation of the wheat from the chaff achieved by the Leiden scientists.

Maass and coworkers considered the supercritical fluid to be a 'dispersion' of a liquid in a vapor, in contrast to the idea of continuity of states, and thought that a liquid-like structure persisted above T_c , see Maass (1938). As was the case with Mathias and with Traube, the emphasis on the structure of the supercritical state gives a foretaste of modern developments, although the rejection of continuity of states is misplaced. As happened around 1900, Maass and coworkers invoked 'modern theory' for an explanation of their results. In this case, that was the theory of Mayer and Harrison. Krichevskii and Rozen (1947), however, two Russian investigators thoroughly familiar with the work

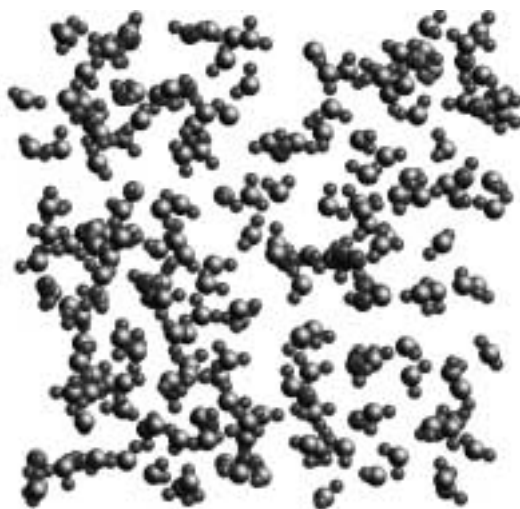


Figure 10.12 Computer simulation of supercritical water near its critical density. The molecules occupy a 3-D box. The fluid density is 12% below the critical, and the temperature is 5% above critical. The molecules do not occupy space uniformly, but form clusters. From Mountain (1997).

of Andrews and Van der Waals, pointed out that such a one-phase region of infinite compressibility is thermodynamically impossible. They also analyzed Mayer's series expansions and indicated several instances where Mayer's arguments could have failed. They expressed the opinion that the experiments were likewise in conflict with thermodynamics. Mayer (1952), however, still maintained that the coexistence curve had a flat top.

Although a new set of accurate and detailed P - V - T data for carbon dioxide, obtained by Michels and coworkers (1937) at the Van der Waals Laboratory in Amsterdam, was available and showed none of the effects reported by the Canadian group, Maass's results were not seriously questioned in the West.

By the mid-1950s, however, due to excellent experimental work by Schneider and coworkers at the National Research Council in Canada, it was shown that the flat top was an artifact entirely due to gravity. See, for instance, Habgood and Schneider (1954). Along with the flat top, the derby hat quietly faded away.

A new era began in which the fundamental role of critical fluctuations was brought to the light. Mean field theory's neglect of these fluctuations would be exposed as its insurmountable weakness.

10.18 *A modern view of the supercritical state*

Confusion about the critical state in the last part of the 19th century was due to two factors: under-appreciation of the difficulty of experimenting near this state, and unfamiliarity with Gibbs's phase rule

After the turn of the century, however, when the existence of molecules was no longer in doubt, the structure of the supercritical state remained a puzzle and source of confusion. Many authors describe this state as a mixture of liquid-like and gas-like structures, but mean-field theory is in no position to deal with such a state. Incorporating the fluctuations became the objective of the modern theory of criticality and took place in the second half of the 20th century.

At the end of this chapter, it seems appropriate to comment on the modern view of the structure of the supercritical fluid. Fig. 10.12 shows a computer simulation by Mountain (1997) of the positions and orientations of a collection of water molecules in a 3-dimensional box. The attractive energy between the polar water molecules is represented fairly realistically, so that the model yields properties such as the vapor pressure curve, the critical point, and the dielectric constant reasonably well compared to those of real water.

The particular state shown is that of supercritical 'computer water' about 12% below its critical density, and about 5%, or 35 K, above its critical temperature, not particularly close to its critical point. The most striking feature is the clustering of the water molecules. They seem to search each

other's company, leaving parts of space unfilled. The average cluster may be four or five molecules in diameter, so the correlations are not particularly long-ranged, but their extent agrees with what one would estimate on the basis of the power law for the correlation length at this condition, Eq. (9.2). This clustering persists and grows even more pronounced at the lower densities. Therefore it is not solely a critical effect. This clearly illustrates the failure of the mean-field assumption setting the local density around a molecule equal to the average density.

The clustering effect strengthens when a strongly interacting solute is inserted into the supercritical solvent. It collects the solvent molecules around it in a thick blanket, at a density much higher than the bulk. This effect is not just an interesting computer-generated artifact. Modern spectroscopic techniques allow the study of solute molecules in supercritical solvents and can deduce the local density from changes in the absorption or fluorescence spectrum of the solute molecules. Invariably, the solvent density around the solute is found to be higher than the bulk density, thus directly disproving the mean-field assumption.

Must one now conclude that the Van der Waals-Andrews picture of fluid criticality is incorrect? Yes, according to present-day understanding of criticality. It neglects the critical density fluctuations whose effects can be seen, and which are caused by short-ranged molecular interactions.

Were Kamerlingh Onnes and his staff misguided in their unflinching defense of the Andrews-Van der Waals view? Most certainly they were not. The shortcomings of the controversial experiments, their interpretations, and the rejection of the Andrews-Van der Waals concept of criticality had nothing to do with this subtle but fundamental flaw of the mean-field assumption.

Did the Leiden group overreact, spending too much effort on experiments better ignored? Perhaps it is wise to let Kamerlingh Onnes judge. He had a better and closer feel for the scientific climate of the time than can be developed over a century later. He must have sensed a genuine threat to sound scientific principles and reliable experimental practice.

Must we conclude that so much effort spent on defending a mean-field model was not worth it? This would be very shortsighted, in view of the essential role mean-field theory has played and still plays. Mean-field theory is always useful when the effect of fluctuations is minor. For theoretical models, the mean-field approximation is often the first step, giving the researcher a feel for what qualitative behavior to expect. In dimensions of two and higher, it does not give nonsense. For calculating fluid phase diagrams, it is unsurpassed. Even the nonclassical renormalization-group calculations of critical exponents use the mean-field expansion of the free energy as a starting point for the incorporation of the effect of critical fluctuations.

II. Dilute near-critical mixtures – Van 't Hoff, Van der Waals, Korteweg, Verschaffelt, Keesom, and Van Laar

II.1 *Introduction*

In this last chapter on topics studied by the school of Van der Waals and Kamerlingh Onnes, almost all members encountered earlier gather around a common interest: the behavior of dilute mixtures near critical points. Why was this? One reason was that the universal laws for the thermodynamic behavior of dilute solutions had moved to the center of attention at that time. What happens to these laws near the solvent's critical point was a natural and compelling question for the Dutch School, which was uniquely equipped to address it. Another motivation was the need to quantify the effect of impurities in experiments near critical points, as discussed in the previous chapter. It became urgent to model impurity effects. In the process, it was found out that the effect of impurity on the fluid density is exceptionally large near the solvent critical point.

This chapter begins with the behavior of dilute mixtures away from criticality. Near infinite dilution, such mixtures have very special and interesting characteristics elucidated in the 19th century, with major contributions by Jacobus Henricus Van 't Hoff, a chemistry professor at the University of Amsterdam from 1877 to 1896. He won the first Nobel prize in chemistry, the centennial of which was celebrated in 2001. It seems fitting to pay tribute to Van 't Hoff in this chapter, even though his interactions with Van der Waals were minimal.

The emphasis of the chapter then shifts to the behavior of dilute solutions near critical points. After an introduction from the modern perspective, contributions by Van der Waals, Korteweg, Verschaffelt, Keesom and Van Laar will pass review. Each of them approaches the problem in a way reflecting his special expertise and interest. The chapter closes with remarks regarding the revival of interest in dilute near-critical mixtures triggered by a topic widely studied in the last part of the 20th century, that of supercritical fluids as solvents.

11.2 *Van 't Hoff and mixtures near infinite dilution*

11.2.1 *Biographical.* E. Cohen (1912), a former pupil, colleague and friend of Van 't Hoff, published an extensive biography (in German) the year after the latter's death. Recently, Cordfunke (2001) published (in Dutch) a succinct overview of Van 't Hoff's life and the significance of his work. These sources have provided the following facts. Jacobus Henricus (Henry) Van 't Hoff (1852-1911) originated from an upper-middle-class family, his father being a physician in Rotterdam. The family had a comfortable existence, but since he and three younger brothers would all receive a university education, finances were sometimes tight. A precocious and brilliant student in high school, he studied calculus and technology at the Delft Polytechnic, and physics with Professor Rijke in Leiden in 1871 and 1872. He took classes along with Lorentz and Van der Waals, the latter being 15 years his senior. After his 1872 candidaats exam (roughly equivalent to a bachelor's degree), he studied abroad for a while, which was not customary for beginning graduate students in those days. He spent the academic year 1872/73 in Bonn, Germany, with the chemist August Kekulé, famous for his proposition of the ring structure of benzene. He then returned to the Netherlands and obtained his doctoral exam (roughly equivalent to a Ph.D. qualifying exam) at the University of Utrecht in December, 1873. Then he spent another six months in France, where Adolph Wurtz and Joseph Achile Le Bel at the faculty of medicine in Paris strengthened his interest in structural organic chemistry. By the summer of 1874, Van 't Hoff returned to the Netherlands, applying in vain for a HBS teaching position. He felt fortunate when he acquired a teaching position at the Veterinary School in Utrecht, where he found he had plenty of time to spend in the laboratory.

In the fall of 1874, at the age of 22, Van 't Hoff proposed, in an 11-page Dutch manuscript, the hypothesis that forms the foundation of organic chemistry and the life sciences: the tetrahedral arrangement of the bonds of the carbon atom. He did this on the basis of the known number of isomers of substances containing an 'asymmetric' carbon atom, one that was bonded to four different atoms or groups. If the bonds were in a plane, there should be three different isomers, and no mirror images. In a tetrahedral arrangement in space, however, there should be only two isomers, and these two would be optically active mirror images of each other. It was known that the latter was the case. This proof was brilliant, but its force escaped some of the learned professors that reacted to his paper. Although the hypothesis intrigued them, they advised Van 't Hoff to go back to the laboratory and find out experimentally whether his hypothesis was really true, see Cohen (1912).



Jacobus Henricus van 't Hoff.
Copied with permission of the Boerhaave Museum, Leiden.

The tetrahedral model raised the level of reality of molecules, just at the time that thermodynamics experts such as Ostwald and Mach considered molecular existence unproven, and the molecular hypothesis unnecessary. Before Van 't Hoff's hypothesis, a chemical formula such as H_2O could still be interpreted in minimalist way, as representing a reaction of two volumes of hydrogen with one volume of oxygen, forming a new compound. The young Van 't Hoff, however, had the vision to ascribe a spatial arrangement to the bonds of a molecule, and proved its validity.

Van 't Hoff had a meteoric career. When the Amsterdam Athenaeum was converted to a university in 1877, he was appointed a lector of chemistry, and in 1878 he received a professorship, becoming a colleague of the much older Van der Waals. He was elected to the Royal Netherlands Academy of Arts and Sciences (KNAW) in 1885, and to the Holland Society of Sciences and Humanities (HMW) in 1890. His talent was widely recognized and appreciated both in

Holland and in Germany. Repeatedly, he received offers for prestigious positions abroad. In particular, he used an offer from Leipzig University in 1887 to obtain a new chemistry building at the University of Amsterdam, which cost the city an exorbitant amount of money. (As a student, the author of this book took some of her chemistry classes in this cavernous building, but it burned down in 1987.) In 1896, however, Van 't Hoff accepted an offer from the Prussian Academy of Sciences in Berlin, as the teaching load in Amsterdam was too much for him. In 1901 he received the first Nobel prize in chemistry. Surprisingly, it was not given for the asymmetric carbon atom, although this work was highlighted in the laudatory speech by Dr. Odhner, President of the Royal Swedish Academy of Sciences, but for Van 't Hoff's work on the chemical thermodynamics of dilute solutions. Van 't Hoff indeed laid the thermodynamic foundation for the physical chemistry of solutions and for reaction chemistry, by equations that carry his name and that are used by chemists to the present day.

Although the tenures of Van der Waals and Van 't Hoff at the University of Amsterdam overlapped for 20 years, they did not collaborate. Nevertheless, Van 't Hoff immediately grasped the importance of Van der Waals's work on mixtures for extending osmotic theory to higher concentrations. As a co-editor, with Ostwald, of the *Zeitschrift für Physikalische Chemie*, he arranged for translation into German and rapid publication of Van der Waals's (1890) paper on mixtures before the original French version of 1891 went to press, see Kipnis *et al.*, (1996) 114-115. Van der Waals's profound influence on the Amsterdam chemists came to the fore only after Van 't Hoff left for Berlin, to be succeeded by Bakhuis Roozeboom in 1897.

Van 't Hoff received the Nobel prize in 1901, at the age of 49. Van der Waals would have to wait for another decade, and was in his seventies when he was finally so rewarded.

11.2.2 *What is magic about dilute solutions?* In order to explain the importance of Van 't Hoff's work, we make an analogy with ideal-gas law, $PV = RT$. This law is universal, since it contains no particulars of the gases it applies to. No actual gas, however, obeys the law exactly. At low density, there are usually small positive or negative departures between PV and RT . Near a critical point, however, the departures are huge, and condensation cannot be described at all. Nevertheless, the law is of utter importance in theory and in practice. It serves as an anchor point in the limit of zero density (infinite molar volume). Any theoretical equation of state needs to be thus anchored. Experimental data that appear to miss this limit are thereby suspect.

Ch. 4.1 introduced Dalton's generalization of the ideal-gas law to mixtures, $P = \sum P_i = \sum n_i RT$, Eq. (4.1). Each component i is assumed to exert a partial

pressure P_i independent of the others, given by Boyle's law and therefore proportional to the mole number n_i of component i . The total pressure equals the sum of the partial pressures. Again, this low-density limiting behavior serves as an anchor point for the description of the behavior of gas mixtures.

The ideal-gas laws are valid to the extent that the interactions between the molecules of the gas can be neglected, that is, at low density. The focus of the school of Van der Waals, however, was on departures from the ideal-gas law caused by the molecular interactions.

One may characterize Van 't Hoff's work as the development of a set of anchors for solutions, analogous to the ideal-gas law. A solution is a special type of mixture in which one component, the solvent, is a liquid usually well below its boiling point, with low compressibility and a vapor pressure far below an atmosphere. The other component, the solute, may be solid, liquid or gas, and is usually assumed to be present in relatively small amounts. In such a case, the interactions between solute molecules can be ignored, but interactions between molecules of the solvent, or between solvent and solute, are strong and ever present. Nevertheless, at low solute concentration, the solution becomes ideal, and the properties of the solution and the characteristics of chemical reactions between solute molecules assume a simple and universal concentration dependence. Chemistry owes this profound insight in large measure to Van 't Hoff.

As early as the 1880s it was quite well known that adding a volatile solute to a solvent, such as water, lowers the vapor pressure and therefore lowers the freezing point and increases the boiling point. On the basis of his experiments, Raoult, in 1887, proved that for low concentrations those effects are proportional to the mole fraction of the solute, but entirely independent of its nature. (For dissociating solutes, it is not the number of moles, but the number of independent entities that counts.) These universal dilute-mixture effects are called *colligative* properties. Eq. (4.2), $(P_0 - P)/P_0 = x_i$, for the lowering of the vapor pressure of a solution due to an admixture, is an example of a colligative property.

The colligative property studied by Van 't Hoff was osmosis, an effect known from the 18th century. If a solution, such as sugar in water, is covered by a layer of pure water, the sugar will slowly spread through the water until the concentration is the same throughout. If a sturdy membrane is put between the sugar solution and the water such that water can pass through, but sugar cannot, water is driven to the side of the solution, and pressure builds up in the solution until it stops further transport of water to the solution. Van 't Hoff called this measurable pressure buildup through a semi-permeable membrane the *osmotic pressure* Π . Van 't Hoff, as well as other chemists in the late 19th century, measured the osmotic pressure as a function

of concentration and found that, for low concentrations, it was proportional to the concentration and independent of the nature of the solute. Careful measurement established, moreover, that the osmotic pressure equals.

$$\Pi = c RT; \quad c = n_2/V \quad (11.1)$$

with V the volume of the solution, n_2 the moles of solute, and c the concentration of solute. Van 't Hoff derived this law in 1885. He pointed out its implication: the osmotic pressure equals the pressure that an ideal gas would exert in the cell if would contain as many moles per unit volume as the solute in the solution, independent of the character of the solute.

Van 't Hoff put the laws governing colligative properties on a thermodynamic basis by imagining appropriate thermodynamic cycles, while making use of semi-permeable membranes to move components in and out reversibly. In his design of such cycles, he always used the ideal-gas law for vapor phases, and assumed a state of high dilution in the solution. He invented his proofs afresh, avoiding the use of Gibbsian thermodynamics and the phase rule. His most important work was in the field of chemical reactions. He postulated by intuition, see Cordfunke (2001), the famous relations for the change of the chemical equilibrium constant with temperature and pressure in terms of the standard-state heat and volume of reaction. These relations were proved to be exact, and they form the foundation of chemical thermodynamics. In solution chemistry, a commonly used standard state from which to measure departures from ideality is that at infinite dilution of the reacting solutes.

11.2.3 Critique. The laws derived by Van 't Hoff for the osmotic pressure, Eq. (11.1), as well as for other colligative properties, were defined in terms of concentration dependence, and were strictly valid only in the limit of infinite dilution. Van 't Hoff was well aware of this, but many of his followers were not. As clearly stated by Gibbs (1876, 1878), the key is in the chemical potential of the solvent, which must be equal on both sides of the membrane. If interactions between solute molecules can be neglected, the most important concentration-dependent contribution to the chemical potential of the solvent comes from the Gibbs mixing term, which for small concentration assumes the simple universal form of $-RTn_2/n_1$; here n_1 equals the moles of solvent in the volume V . In addition, the (small) increment of pressure, Π , on the side of the solution contributes $(V/n_1)\Pi$ to the solvent chemical potential. Setting the sum of these contributions to zero keeps the chemical potential of the solvent in the solution equal to that of the pure solvent on the other side of the membrane and results in Eq. (11.1). For small Π , the pressure buildup must therefore be proportional to c , independent of the nature of the solute.

It is understandable that enthusiastic followers immediately began to apply this law at any concentration. Worse, Van 't Hoff's observation that the osmotic pressure happens to equal the pressure that the solute molecules would exert if they would be moving freely in the volume occupied by the solvent, was widely interpreted by German chemists as a physical explanation of the origin of osmotic pressure. These developments drove the Amsterdam chemist Van Laar to a high pitch of strident indignation. For the rest of his life, he conducted a one-man crusade against the concept of osmotic pressure, and against the German 'Osmotic School,' see Snelders (1984). He did not mellow with age. In 1915, he attacked Ehrenfest, who had had the temerity to write an article on the kinetic interpretation of osmotic pressure. To Van Laar, the driver of osmotic effects is the difference in chemical potential of the pure water and the water in the solution. The story of sugar molecules, unencumbered by the solvent, flying around in the cell and impinging on membranes, was anathema to him.

Van Laar, of course, justly criticized this interpretation. A sound basis for describing both the colligative effects and the corrections needed for systems not at infinite dilution could only be found by systematically applying Gibbsian thermodynamics. Curiously, the only references to Van der Waals in Cohen's (1912) voluminous biography are exactly about this point. Van 't Hoff, while careful about the fact that the laws proposed by him are valid only in the limit of infinite dilution, repeatedly refers to Van der Waals as the one who would know how to proceed away from this limit. From this perspective, the present chapter makes the point that 'moving away' from the infinite – dilution limit is very different if the solvent is at its critical point, rather than in an incompressible liquid state.

Van 't Hoff, who shunned the complex mathematical machinery being put into place by Van der Waals and who did not appreciate Bakhuis Roozeboom's phase theory, was able to obtain the fundamental limiting laws of chemical thermodynamics by simple means and sound intuition. These laws bear his name, and, properly generalized, find application to this very day. The Nobel prize was well deserved, even if not given for the asymmetric carbon atom.

11.3 *A solute added to a solvent at its critical point*

In this section, we introduce from a present-day perspective the concepts and properties that will be encountered in the historic narrative to follow. For details, reviews and references, see Levelt Sengers (1991, 1993).

11.3.1 *Solute-induced phase separation.* Near infinite dilution, adding a solute to a solvent results in changes in the solvent properties that are proportional to the amount of solute and of a universal nature. This is not always so if the

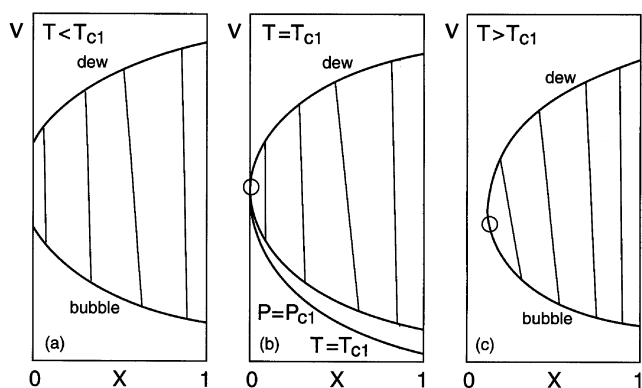


Fig. 11.1 The plait and its tie lines for a low-volatility solute, in the V - x diagram, for a temperature just below (a), at (b), or above (c) the solvent critical point. The isothermal connodal (coexistence curve, or dew-bubble curve) is shown. The tie lines slant, but become vertical at $x = 0$ and $x = 1$. In (b), not only the connodal, but also the curve of constant pressure ($P = P_{c1}$, $T = T_{c1}$) has been shown. The circles indicate the solvent critical point (b), or the plait point (c).

solvent is at its critical point. One reason is that the solute may induce a phase transition, which is a catastrophic effect rather than a smooth change proportional to the amount of impurity.

To explain why this is so, we draw in Fig. 11.1 isothermal V - x plots, with V the molar volume, and x the mole fraction of the solute. These plots are shown for the cases that the principal component, the solvent, is just below (a), just at (b), or just above (c) its critical temperature, while the solute, far less volatile, is way below its critical point. The feature at $x = 0$ is the one to watch first. In case (a), the solvent is just below its critical temperature, so at $x = 0$ there are coexisting liquid and vapor phases that have almost, but not quite, the same molar volume. In case (b), the critical temperature, these two volumes have just become equal. In case (c), the solvent is above its critical point, and there is no longer vapor-liquid coexistence at $x = 0$. The behavior on the $x = 1$ axis, however, is entirely unremarkable. The solute is way below its critical point, and therefore a small-molar-volume liquid and a high-molar-volume vapor are coexisting at all three temperatures.

We now pay attention to the plait on the surface. In case (a), the transverse plait simply runs across the entire diagram. This is not necessarily so: azeotropy, or the occurrence of an additional fluid or solid phase, may interrupt the plait (Fig. 6.6). We assume the absence of such interruptions here, so as not to complicate the argument. In case (b), the plait comes in from the

right, and just closes at the pure-solvent critical point on the $x = 0$ axis. In case (c), the plait comes in from the right and closes at a critical point before it reaches the $x = 0$ axis.

To find the critical point of the mixture, we pay attention to the tie lines. Since the solute is of low volatility, we expect it to shun the vapor and concentrate in the liquid. Thus, the tie lines should slant from top left to bottom right. There is an exception: at $x = 0$ and at $x = 1$, the tie lines must be vertical, because only one of the components is present and its mole fraction is unity in both phases. This leads to the tie lines shown schematically in Figs 11.1. The mixture critical point in Fig. 11.1c is the point where the tie line shrinks to zero, and we would not be surprised to find it slightly off to lower volumes in this particular case of an involatile solute and an uncomplicated plait.

Thus by adding an involatile solute to a slightly supercritical solvent, a two-phase region is entered. This is a disruptive event instead of a smooth change proportional to the amount of impurity.

11.3.2 *What happens to the plait point?* As the impurity is added, the plait point shifts in general to a slightly different temperature T_{pl} and pressure P_{pl} . In the particular example of a nonvolatile solute, Fig. 11.1c, for instance, we notice that the plait point temperature must be above that of the solvent, but in practice a downward shift is just as common. We will see that both the Amsterdam and Leiden scientists invested ingenuity and effort in calculations of the derivatives dT_{pl}/dx and dP_{pl}/dx . They found that the shift of the plait point temperature and pressure is linear in x for small x , but most certainly not universal. In the process, they found a number of interesting relations between these shifts and a variety of derivatives of the Helmholtz energy or the pressure evaluated at the solvent critical point.

11.3.3 *The shape of the isothermal coexistence curve.* The most interesting case is that when the solvent is at its critical point, Fig. 11.1b. First of all, near $x = 0$, the coexisting phases still have different molar volumes, but they have almost the same mole fraction. For mean-field equations of state, the conodal (coexistence curve) is a parabola tangent to the volume axis. At the solvent critical point, therefore, the roles of V and x are distinctly different. A small amount of solute added at the solvent critical temperature leads to a split into two phases of considerably different density. For instance, at the solvent critical point, a 1%-level addition of impurity leads to two phases with a density difference of the order of 10%.

11.3.4 *The shape of the critical isotherm-isobar.* The Leiden researchers were most interested in the question of the difference in density between a pure

fluid at its critical point, and that of a dilute mixture at the same pressure P_c and temperature T_c . The answer will reveal what density differences can persist due to un-equilibrated impurities in a fluid at its critical point.

For a nonvolatile solute, the isotherm-isobar at the solvent critical point must run in the liquid phase, as shown in Fig. 11.1b. For a mean-field equation of state it is part of a cubic, with a vertical tangent at the solvent critical point. Mathematically, this can be expressed in the following way:

$$\text{At } P = P_c, T = T_c, \text{ near } x = 0: (V - V_c)^3 \approx x \quad (\text{II.2})$$

This implies that the derivative $(\partial V/\partial x)_{P,T}$ becomes infinite at the solvent critical point. This derivative serves to define the partial molar volumes of solvent and solute, V_1 and V_2 , given by

$$\begin{aligned} V_1 &= V - x (\partial V/\partial x)_{P,T} \\ V_2 &= V + (1-x) (\partial V/\partial x)_{P,T} \end{aligned} \quad (\text{II.3})$$

Here V is the molar volume of the solution.

The partial molar volumes, as a characteristics of solvent and solute, were used by Bakhuis Roozeboom, but not by Van der Waals and Kamerlingh Onnes. The partial molar volume is one of many similarly defined partial molar properties introduced early in the 20th century for characterizing mixture behavior, and presently universally used. See, for instance, Rowlinson and Swinton (1982). In dilute mixtures, partial molar properties usually have very simple behavior, the partial molar properties of the solvent approaching those of the pure solvent, and those of the solute approaching a finite limit. At the solvent critical point, however, this simple behavior no longer prevails. It is clear from Fig. 11.1b, for instance, that when x approaches 0 at the solvent critical point, the partial molar volume of the solute, V_2 , becomes infinite. The same conclusion follows from the mathematical identity

$$(\partial V/\partial x)_{P,T} = - (\partial P/\partial x)_{V,T} (\partial V/\partial P)_{x,T} = (\partial P/\partial x)_{V,T} (V K_T) \quad (\text{II.4})$$

Since $(\partial P/\partial x)_{V,T}$ is finite and non-zero, it follows that in the limit of infinite dilution the partial molar volume of the solute diverges just like the compressibility K_T of the pure solvent. The sign and strength of the divergence are determined by the derivative $(\partial P/\partial x)_{V,T}$, see Ch. 11.3.5.

The fact that the isotherm-isobar is a cubic with vertical tangent is the reason that near the solvent critical point a small impurity causes a disproportionately large density change, which is not linear in the concentration. It implies that, at the critical pressure and temperature of the pure host, a 1 part in 1000 impurity causes a density increase of the order of 10%! This is a huge effect, quite contrary to the usual linear departure

from infinite dilution. It easily explains the strange phenomena observed in so many laboratories where sample purity was not a high priority (Ch. 10). The Leiden researcher Verschaffelt found a way of estimating the size of this effect in the early 1900s.

At the solvent critical point, therefore, the simple rules for colligative properties, that effects are proportional to concentration, must fail. Rightly, Van 't Hoff pointed to Van der Waals holding the key to formulation of the thermodynamic behavior of mixtures not infinitely dilute, and with vapor phases that are not ideal.

11.3.5 Some other useful derivatives. The critical-point value of the derivative $(\partial P/\partial x)_{V,T}$, introduced in Eq. (11.4), is a well defined, finite, generally non-zero, non-universal quantity in mean-field theory. It reveals how much the pressure falls or rises if in a fluid at its critical point, kept at constant volume, a small number of solvent molecules are exchanged for solute molecules. If the solute is highly volatile, such as hydrogen in carbon dioxide at its critical point, an increase in pressure is to be expected and the derivative $(\partial P/\partial x)_{VT}$ is positive. A low-volatile solute, such as a salt in near-critical water, will lead to a decrease in pressure, so that the derivative is negative.

When a solute is added to a solvent at its critical point, a mixture critical line develops starting at $x = 0$. In Fig. 11.2 we show this situation in a P - T diagram. There are two important slopes in this picture: that of the vapor pressure curve, $(dP/dT)_\sigma$, of the pure solvent at its critical point, and that of the incipient critical line, dP_{pl}/dT_{pl} . As to the first one, Van der Waals (1905b) showed that for pure fluids, $(dP/dT)_\sigma$ equals the slope of the critical isochore, $(dP/dT)_V$. See Ch. 11.4.5 and 11.4.8. This means that in Fig. 11.2, the pressure-temperature relation for the one-component fluid at its critical density does not change slope when the fluid passes through its critical

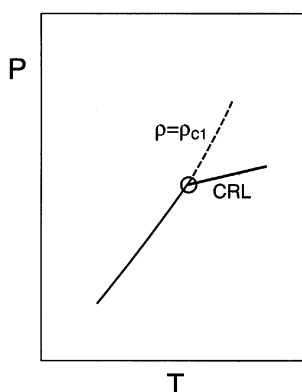


Fig. 11.2 In the P - T diagram, the vapor pressure curve and the critical isochore $\rho = \rho_{c1}$ of the pure solvent, (1), are shown, along with the beginning of the critical line, CRL. The circle indicates the solvent critical point.

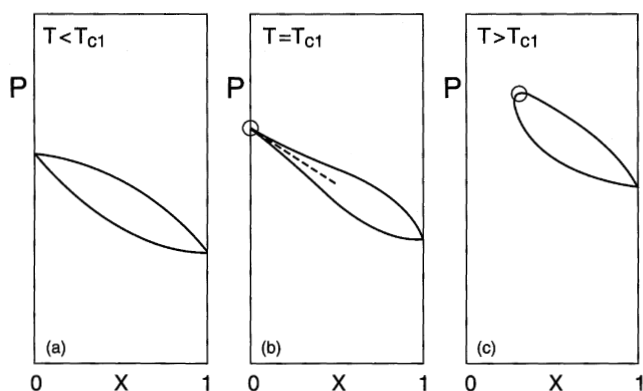


Fig. 11.3 Near-critical isothermal dew-bubble curves in the P - x diagram, for a solute of low volatility. The behavior is shown (a) just below, (b) at, and (c) above the critical temperature of the solvent. The circle indicates the solvent critical point (b), or the plait point (c). At the critical point, the dew-bubble curve narrows to a 'bird beak.'

point. The derivatives dP_{pl}/dT_{pl} , dT_{pl}/dx and dP_{pl}/dx obey a simple thermodynamic relationship, see Ch. 11.4.5.

11.3.6 The shape of the mixture dew-bubble curve in the P - x plane. In Fig. 11.3, we draw attention to a peculiarity of the dew-bubble curve in the vicinity of the solvent critical point for the case of a solute of low volatility. Just below the solvent critical point, case (a), the dew-bubble curve has the normal appearance, with a finite angle between the two branches. Above the solvent critical point, case (c), the dew-bubble curve does not reach the $x = 0$ axis any more. At the critical point, case (b), the two branches have a common tangent with, in general, finite non-zero slope. Van der Waals (1905b) proved this 'bird-beak' feature. It was rediscovered by Wheeler (1972), see Ch. 11.5.

11.4 The Dutch school and dilute near-critical mixtures

11.4.1 Overview. Van der Waals (1895a,b) derived, as exact thermodynamic relationships, the first limiting laws for the shift of the critical pressure with temperature due to an admixture. The first experiments and modeling of impurity effects began in Leiden shortly before the turn of the century. Verschaffelt and Keesom were principal players. The experimental data they used for tests were those Verschaffelt had obtained around 1900 for the system carbon dioxide with small fractions of hydrogen. For the modeling, they used

various forms of the law of corresponding states, in keeping with the Leiden tradition of preferring this law over the Van der Waals equation.

Around 1900, the mathematician Korteweg, who had been silent on the matter of fluid mixtures for a decade, took an interest in the problem of impurity effects near criticality. He produced a calculation of impurity effects in the V - x diagram on the basis of the Van der Waals equation for mixtures, in his own systematic fashion. Korteweg (1903) published this work in French and in English. A large color graph is part of his paper.

At roughly the same time, Keesom and Verschaffelt independently began deriving expressions for the initial slopes of the plait point curve. This effort stranded because of the impossibility to obtain from experiment with any degree of reliability the second derivatives occurring in their various expressions. Verschaffelt (1906a) then turned around and, quickly and effectively, developed a reliable method for estimating impurity effects, based on the superposition of nets of experimental P - V isotherms for the pure solvent and a dilute mixture of constant composition. Van Laar (1905e,h) derived simple expressions for the shift of the plait point temperature with concentration for his specialty: the van der Waals geometric-mean mixture model. Van der Waals (1905a,b) reminded all parties involved that he had worked on this problem ten years ago, but he did use the opportunity to publish a number of proofs of interesting and relevant identities that had been lying in his desk drawer for a long time.

After briefly reviewing Van der Waals's (1895) papers, we will first discuss Korteweg's (1903) pictures, the results of Keesom (1901) and Verschaffelt (1902a, 1902b, 1903, 1906a,b), and finally, the work of Van Laar (1905e,h) and Van der Waals (1905a,b).

11.4.2 *Van der Waals and the slope of the critical line.* Van der Waals's (1895a,b) papers give an exact expression for the derivative $dP_{\text{pl}}/dT_{\text{pl}}$ for any concentration along the plait point curve in terms of second derivatives of both the energy and the Helmholtz energy. Also, Van der Waals gives the analogous result for the limit of infinite dilution. With no direct link to experiment, Van der Waals's relations, although exact, were not particularly useful. Keesom (1901) rewrote these equations for dilute mixtures, replacing the energy and Helmholtz energy derivatives by the more convenient derivatives of the pressure, to be discussed in Ch. 11.4.5. This is the reason we do not give Van der Waals's expression here.

11.4.3 *Korteweg's mathematical analysis of the Van der Waals model near the solvent plait point.* A picture is the centerpiece of the Korteweg (1903) paper. Fig. 11.4 shows the top part of the large-scale graph in the back of his paper.

There are eight possible locations of the dilute-mixture plait point with respect to the pure-fluid critical point. One such case was introduced in Ch. 11.3.1 and was shown in Fig. 11.1. Korteweg considers all possible cases for the Van der Waals model for mixtures.

Korteweg displays the condition of a dilute mixture, kept at a constant temperature close to but not equal to the critical temperature of the solvent, in an isothermal V - x plane. The point K indicates the critical volume of the pure solvent, while P indicates the plait point volume and concentration. K - P is the projection onto the V - x plane of the initial part of the critical line, which itself is, of course, not isothermal. The full curve is the isothermal connodal or coexistence curve, ending in P , and the dashed curve is the isothermal spinodal through P . The point R is the largest concentration reached on the connodal. Its location with respect to P determines the nature of the retrograde behavior (Ch. 6.6).

Considering the four pictures in the left column, we note that they represent situations as in Fig. 11.1c, where the temperature is slightly *higher* than the critical temperature of the solvent: the plait does not intersect the V axis, and thus there are no solvent coexisting phases present. The solute is far *below* its critical point, and much less volatile than the solvent. As the temperature decreases, the plait will touch the $x = 0$ axis at the solvent critical temperature. Below this temperature, the plait point disappears and the plait runs over the full length. On the left, Korteweg has collected all possible arrangements of K , P and R for this case.

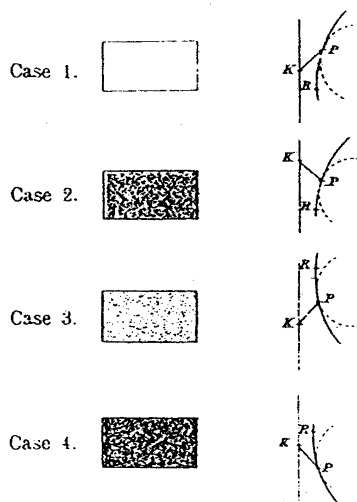
Considering now the four isothermal pictures on the right, we note that the temperature is below the critical point of the solvent. The plait intersects the V -axis at $x = 0$ in two points, which represent a low-volume liquid phase and a high-volume vapor phase, with the critical volume somewhere in the middle. The plait disappears at P , the plait point, and, if it does not reappear as x increases, it will not reach the $x = 1$ axis (the case of azeotropy is an example of reappearance of the plait). The solute is *above* its critical temperature, and thus in general more volatile than the solvent. As the temperature drops towards the critical point of the solvent, the plait point P moves towards K . Below the solvent critical temperature, there is no plait on the surface.

A further division of Korteweg's eight cases is based on the location of the plait point P with respect to the solvent critical point K . P is located at a higher volume than K in all odd-numbered plots, and at a lower volume than K in all even-numbered cases.

We now address the relation of the extremum R to the type of retrograde condensation. Take, for example, case 6. Coming down along a vertical path of fixed composition passing between points P and R , a mixture, on expanding, develops a drop of liquid when it enters the plait on the dew side of the

SIDE OF THE LARGE VOLUMES.

Temperature slightly *higher* than the critical temperature of the solvent.



SIDE OF THE LARGE VOLUMES.

Temperature slightly *lower* than the critical temperature of the solvent.

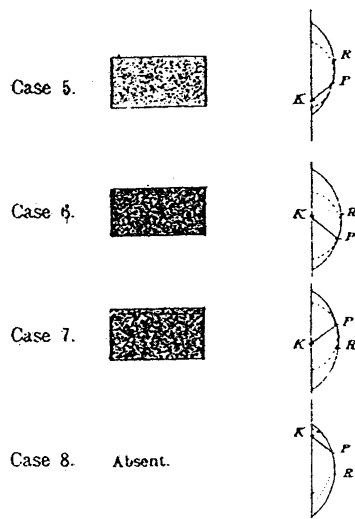


Fig. 11.4 Eight possible ways in which a plait forms by addition of a small amount of a second component to a fluid near its critical point. The vertical axis is the volume axis, the horizontal one the concentration. K is the critical volume of the first component, P is the mixture plait point, the full curve is the connodal, R is the extremum on the connodal, and the dashed curve is the spinodal. Copied from Korteweg (1903), Fig. 1.

connodal. On continued expansion, the amount of liquid grows, reaches a maximum, and then shrinks, to disappear when the mixture passes out of the plait, again on the dew side of the connodal. This is retrograde condensation of the first kind, as discovered and explained by Kuenen, see Ch. 6.6. Cases 3-6 are in this category.

In a case such as 7, on the other hand, the low-volume mixture of fixed composition will now enter and exit the two-phase region through the bubble curve. Thus it will form a gas bubble, which will disappear again on further expansion. This is retrograde condensation of the second kind, which Kuenen tried in vain to find experimentally (Ch. 6.7). Cases 1-2 and 7-8 fall in this category.

Korteweg derived these cases from the Van der Waals binary-mixture equation by expanding the isothermal Helmholtz energy at the critical point of the solvent in terms of concentration and volume. Korteweg needs to con-

sider only two parameters, a_{12} and b_{12} , since the application is to a dilute mixture to lowest order in concentration, when solute-solute interactions can be neglected, Korteweg introduces the lowest-order parameters

$$\kappa = a_{12}/a; \quad \gamma = b_{12}/b \quad (11.5)$$

and proceeds to calculate in which ranges of κ , γ space the individual cases shown in Fig. 11.4 prevail. Note that this is the quite general 'global' problem, be it near the limit of infinite dilution. The geometric-mean rule is not assumed, nor is any restriction placed on the strength of the unlike excluded volume b_{12} .

A large color graph of these ranges and their borders in κ , γ space accompanies the paper. A reduced-size copy, be it in black and white, is shown in Fig. 11.5. Even though the color of the original is lost, Fig. 11.5 is still easy to read, since the labels of the regions correspond to those in Fig. 11.4. Regions of negative κ or γ have no physical meaning.

Korteweg's (1903) paper gives the details of the calculations of the border curves in Fig. 11.4 to second order in concentration, based on a Taylor expansion at the plait point of the solvent, and finding the plait point of the mixture as discussed before, Ch. 5.3.6. Korteweg gives expressions for the initial shift of the plait point concentration as a function of temperature, and the shift of the plait point volume as a function of concentration. We will not discuss these derivations here. One result is that case 8 does not follow from the Van der Waals equation, which is the reason one does not find it in Fig. 11.5. A second result is that points on the border between regions with plaits open to the left and plaits open to the right, such as case 2 and case 6, correspond with a double homogeneous plait points (Ch. 5.4.2) at the solvent critical point. In Fig. 11.5, there is one point where six regions meet. This is the point where the mixture interaction parameters equal those of the solvent, $\kappa = 1$, $\gamma = 1$, a pathological case, physically speaking, requiring a higher-order treatment.

Korteweg's work on the general dilute Van der Waals mixture is exact and exhaustive. It is to be regretted that it evolved independently from Verschaffelt's and Keesom's work. Korteweg refers often to their work and even refrains from claiming priority:

We do not, however, give them [the mathematical relations Korteweg presents] as new, as they must essentially agree with similar equations obtained by Keesom (1901) and Verschaffelt (1903).

An early collaboration with the Leiden scientists, especially Verschaffelt, might have made all parties involved more effective. Kamerlingh Onnes seems to have viewed Korteweg as a competitor, see Ch. 11.4.6.

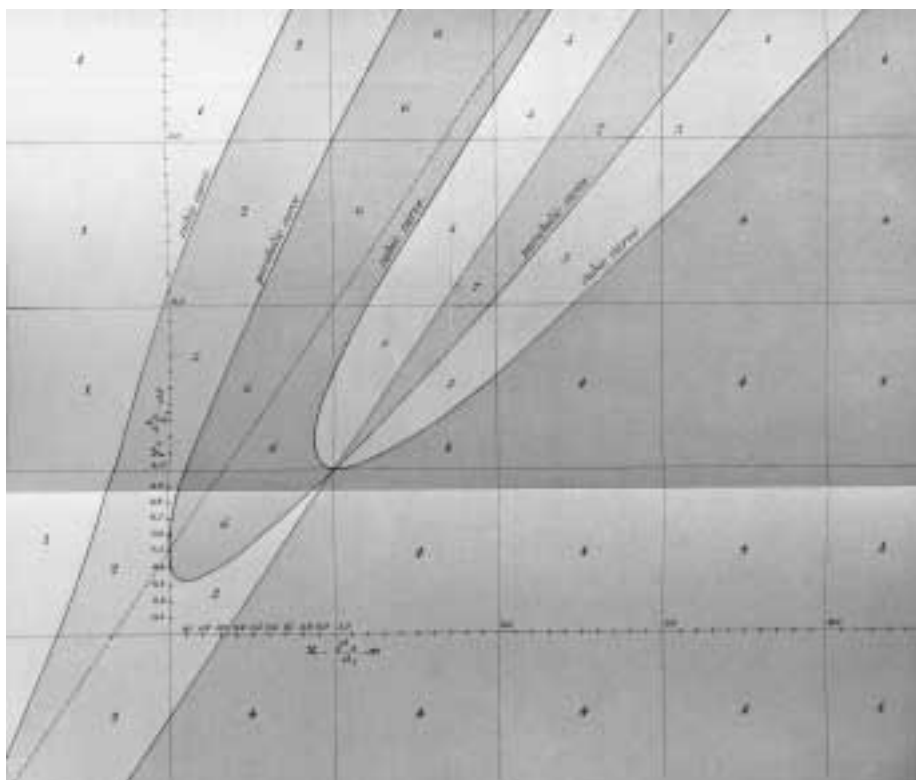


Fig. 11.5 'Global' diagram for mixture behavior near the solvent critical point according to the Van der Waals equation. The regions in x, γ space, with $x = a_{12}/a$ and $\gamma = b_{12}/b$, in which the various scenarios shown in Fig. 11.4 prevail according to the Van der Waals equations for mixtures. The numbers in Fig. 11.4 correspond to those in Fig. 11.5. Case 8 in Fig. 11.4 does not occur in Fig. 11.5. In the point $x = 1, \gamma = 1$ six regions meet. Regions of negative x and γ have no physical meaning. Copied from Fig. 1, in color, of Korteweg (1903). The horizontal line just below the center is an artifact due to a fold in the original.

11.4.4 *Verschaffelt: an experiment on dilute near-critical mixtures, and its interpretation.* We introduced Verschaffelt in Ch. 9, after he began to work on his doctorate at the Physical Laboratory in Leiden. Kamerlingh Onnes wanted him to study the system carbon dioxide-hydrogen. The initial objective seems to have been a more detailed study of retrograde condensation than Kuenen had done (Ch. 6.6). Another goal was to test the validity of the principle of corresponding states for mixtures. Serendipitously, the system became a model for impurity effects in which Kamerlingh Onnes was interested,

embroiled as he was in conflicts about the nature of criticality (Ch. 10). There were some experimental constraints. The critical pressure of carbon dioxide is over seventy atmospheres to begin with, and Verschaffelt noticed right away that adding 5 mol% hydrogen led to a huge increase in vapor pressure as the mixture condensed. The study of this system in glass cells near the carbon dioxide critical point was therefore by necessity going to be limited to small fractions of hydrogen.

A large difference in volatility will enhance impurity effects. So the system carbon dioxide – hydrogen was an excellent choice: the first component has a critical temperature of 404 K, while that of hydrogen is only 33 K.

Measurements were performed as described in Ch. 6.4. The highest pressures Verschaffelt (1899a) reports for a 5 mol% mixture are close to 120 atmospheres. *P-V* isotherms were measured at seven temperatures from 15 to 31°C. One striking result is the huge increase in pressure required to make the mixture condense. At 15°C, for instance, pure carbon dioxide condenses at about 50 atmospheres. The 5% mixture, however, begins to condense at 57 atmospheres, but fully converts into liquid only at 103 atmospheres. This clearly demonstrates the fierce resistance to mixing of these two components. The plait point temperature decreases about 4°C for a 5% admixture of hydrogen. Verschaffelt found clear evidence of retrograde condensation of the first kind.

Next, Verschaffelt (1899b) reports some results for the nominal 10 mol% and 20 mol% mixtures. For these, he could only measure short stretches of the *P-V* isotherms, because the pressure limit of his apparatus was quickly reached. From the data, he constructed the dew-bubble curves and the plait point curve. The latter keeps on moving to lower temperatures and to steeply higher pressures.

It is clear to us that Verschaffelt has inadvertently discovered a Type-III phase diagram (Ch. 7 and Ch. 8), with a critical line running to high pressure and lower temperatures. At that time, Kuenen had not yet published his work on such a system. Verschaffelt does wonder about the course of the plait point line. He thinks it will rise equally steeply from the hydrogen side and speculates that it may go through a very high maximum, suggesting an uninterrupted mixture critical line (Type I). Much later, however, in the French translation of his thesis, in 1906, he quotes Kamerlingh Onnes as suggesting that two branches of the critical line might rise steeply from the carbon-dioxide and hydrogen critical points and move to infinite pressure. This was just about the time Van Laar investigated the longitudinal plait, making connection with Kuenen's Type-III phase diagram (Ch. 7.5), although just before gas-gas equilibrium was discovered and explained in Leiden (Ch. 8). Verschaffelt (1906a), however, in a model described in Ch. 11.4.6, still calculates the critical line for the mixture of carbon dioxide and hydrogen as a continuous curve with a very

large pressure maximum. For the present application, the inappropriate phase diagram presents no problem, because only the part of the critical line close to the carbon-dioxide critical point is under consideration.

Verschaffelt (1900b) performs a test of the law of corresponding states by plotting the P - V isotherms for pure carbon dioxide by Amagat, and for the 5%, 10%, and 15% mixtures he himself has obtained, on large-scale logarithmic plots, shifting these with respect to each other to make them superimpose, which he is able to do quite well. This procedure is an example of the use of empirical scale factors discussed in Ch. 3.5.

It is important to realize that the test is limited to a narrow range of temperatures, about 15°C, and that only the 5% mixture has substantial overlap with the isotherms of pure carbon dioxide. After superposition, even the closest 5% mixture isotherm is 7°C from the critical temperature of pure carbon dioxide; all other isotherms are further away after superposition. Verschaffelt notes some departures at densities higher than critical.

Verschaffelt obtains values for the critical parameters P_{xk} , V_{xk} , and T_{xk} of each of the mixtures, the point at which the mixture would have become critical if a pure fluid, had it not become materially unstable. He calls these fictitious parameters the *critical parameters of the homogeneous mixture*. They will play a substantial role in Keesom's subsequent work.

Verschaffelt finds the concentration dependence of the scale factors. He also derives from the fictitious critical parameters the mixture parameters a_x and b_x that the Van der Waals equation would give, and finds that they can be represented as quadratic functions of the composition according to the mixing rules proposed by Van der Waals, Eq. (4.4).

II.4.5 *Keesom: dilute mixtures and the law of corresponding states.* Keesom (1901) wants to find out how the plait point shifts as an impurity is added to a pure host.

He first derives useful relationships between these slopes and derivatives of the pressure that could, in principle, be obtained from experiment. In the back of his mind is Verschaffelt's experiment, in which P - V isotherms were obtained for mixtures of constant concentration. Although such experiments readily yield the 'fictitious plait point,' they give no clue as to the location and shift of the real plait point.

Keesom first performs a service to science by writing Van der Waals's (1895) expression for the initial slope of the plait point temperature in a more convenient way. He replaces Van der Waals's second derivatives of the energy and free energy by derivatives of the pressure. Keesom then produces the following relation for the initial change of the (real) plait point temperature with composition:



W.H. Keesom and J.P. Kuenen posing at the rear of the Physics Laboratory, Leiden in 1909. Keesom is the tall bearded man next to the door.
Kuenen is the one flanking the woman (Miss G.L. Lorentz).
Collectie Academisch Historisch Museum, Universiteit Leiden.
Copied with permission.

Lim ($x \rightarrow 0$, solvent critical point)

$$dT_p/dx = - \frac{(\partial P/\partial x)^2_{VT} + RT (\partial^2 P/\partial x \partial V)_T}{RT (\partial^2 P/\partial T \partial V)_T} \quad (11.6)$$

Keesom's equation thus permits evaluation of the initial slope of the plait point temperature from first and second derivatives of the pressure, evaluated at the solvent critical point. Alternatively, once an equation of state is given for the dilute mixture, the derivatives at the solvent critical point can be evaluated. Although the sign of the denominator is always negative, the plait point temperature may rise or fall depending on the sign of the second term in the numerator and the magnitude of this second term compared to the first. Keesom's nice result was forgotten and derived anew by American chemical engineers Redlich and Kister (1962).

Keesom (1901) presents an expression similar to Eq. (11.6) for the initial change of the plait point pressure (his Eq. 1C, p. 295) with concentration. The two derivatives are related by the expression:

$$\lim (x \rightarrow 0, \text{ solvent critical point})$$

$$dP_{\text{pl}}/dx = (\partial P/\partial x)_{VT} - (\partial P/\partial T)_{Vx} dT_{\text{pl}}/dx \quad (11.7)$$

with dT_{pl}/dx standing for the right-hand side of Eq. (11.6). Keesom's more elaborate expression represents Eq. (11.7) with dT_{pl}/dx substituted from Eq. (11.6).

In the limit $x \rightarrow 0$, the derivative $(\partial P/\partial T)_{Vx}$ equals $(\partial P/\partial T)_V$, the limiting slope of the critical isochore, which is the locus $V = V_c$ of the pure solvent. Keesom now makes use of the fact that in the P - T plane at the critical point, the critical isochore and the vapor pressure curve of a one-component fluid are confluent, see Fig. 11.2. He mentions that Van der Waals proved this interesting equality in his lecture notes, and that Van Laar and others also noted it. In part 3 of his paper, Keesom (1901) copies three proofs given to him by Van der Waals. Later, Van der Waals (1905b) will finally publish these proofs, see Ch. 11.4.8. Keesom uses the equality of $(\partial P/\partial T)_V$ and $(dP/dT)_\sigma$ at the critical point for numerical estimations of one or the other of the two. Usually the latter is easier to obtain from experiment. If $(dP/dT)_\sigma$ is substituted for $(\partial P/\partial T)_V$, Eq. (11.7) could have been written as

$$\lim (x \rightarrow 0, \text{ solvent critical point})$$

$$dP_{\text{pl}}/dx = (\partial P/\partial x)_{VT} - (dP/dT)_\sigma dT_{\text{pl}}/dx \quad (11.8)$$

Keesom retains the right-hand side of Eq. (11.6) for dT_{pl}/dx in his expression.

Krichevskii (1967) derived Eq. (11.8) anew. Krichevskii, who rekindled the interest in dilute near-critical mixtures in the modern age, led a large experimental group in the area of fluid mixtures in the former Soviet Union. This group is known for several firsts, such as the measurement of gas-gas equilibrium above the component critical points (Ch. 8), and of the tricritical point (Ch. 7.2.4). The infinite-dilution critical value of $(\partial P/\partial x)_{VT}$, a non-diverging characteristic indicator of dilute-mixture behavior near the solvent critical point, is presently called the *Krichevskii parameter*.

Keesom (1901) now proceeds to estimate the various derivatives in Eq. (11.6) in order to test his relationship. He estimates numerical values for the slopes of the vapor pressure curve and the critical isochore from experiment. For carbon dioxide, he reports a value near 7, in reduced units, with a 10% spread. The spread makes him unhappy. Discreetly, Keesom does not mention that the Van der Waals equation gives a value of only 4 for $(dP/dT)_\sigma$.

After 1900, everyone involved, including the master himself, seems to be content with the experimentally derived value of 7 for this slope.

For the derivative in the denominator of Eq. (11.6), $(\partial^2 P / \partial T \partial V)_T$, Keesom derives a value from Amagat's data on carbon dioxide, which happens to agree closely with that from the Van der Waals equation. (If, however, the value of $(\partial P / \partial T)_V$ is uncertain by 10%, there is no way he could have derived the volume derivative of this quantity with an uncertainty even approaching 10%.)

More seriously, but unknown to Keesom, or anyone else at that time, this particular second derivative must be *zero* in a real fluid at its critical point because of the failure of mean-field theory at the critical point, (Ch. 9). Thus, Eq. (11.6) is not applicable to real fluids. If care is used in taking the infinite-dilution limit, however, Eqs. (11.7) and (11.8) do retain their validity for real fluids.

Having been unsuccessful in a direct test of Eq. (11.6) due to circumstances beyond his control, Keesom decides to rewrite this equation in terms of the law of corresponding states. He uses the fictitious gas-liquid critical parameters mentioned in connection with Verschaffelt's work to make the pressure, volume, and temperature dimensionless

$$\pi = P/P_{xk} \quad \tau = T/T_{xk} \quad \omega = V/V_{xk} \quad (11.9)$$

In these reduced coordinates, the mixture obeys the same equation of state as the pure fluid. Keesom expresses all derivatives on the right-hand side of Eq. (11.6) in terms of these reduced coordinates, in the limit of small x near the solvent critical point, and obtains the following result:

$$(1/T_k) (dT_{pl}/dx) = \alpha - \frac{[\beta - \alpha (\partial\pi/\partial\tau)^2]}{C (\partial^2 \pi / \partial \omega \partial \tau)} \quad (11.10)$$

with a corresponding expression for the initial slope of the pressure along the plait point curve. The constant C represents the value of the inverse critical ratio. The derivative dT_{pl}/dx and dP_{pl}/dx are thus expressed in terms of derivatives of the reduced, one-component equation of state, with two parameters characteristic of the mixture:

$$(1/T_k) (dT_{xk}/dx) = \alpha; \quad (1/P_k) (dP_{xk}/dx) = \beta \quad (11.11)$$

At first sight, it seems a step backward to express the concentration dependence of the *real* plait point temperature in terms of that of the *fictitious* plait point. The advantage of Eq. (11.10) is, however, that the derivatives involved are those of a pure component. Contrary to Eq. (11.6), no concentration derivatives are involved. Moreover, Verschaffelt (1900) had already

shown the way to obtaining the fictitious plait point parameters, namely by superimposing the measured P - V isotherms of the mixture of constant composition onto those of the pure solvent using two scale factors. Keesom also derives a simple relation for the location of the real plait point in P - T space with respect to the fictitious plait point for small x :

$$\frac{P_{\text{pl}} - P_{xk}}{T_{\text{pl}} - T_{xk}} = (dP/dT)_{\sigma} \quad (11.12)$$

This is a result that Van 't Hoff should have appreciated: since the right-hand side is a pure-solvent property, the ratio on the left must be the same for all solutes in the same solvent. Keesom estimates the left-hand side of Eq. (11.12) using Verschaffelt's values (1899c, 1900b) for 10% and 5% hydrogen in carbon dioxide. He is content with a 20% mutual agreement of the left-hand and the right-hand side of Eq. (11.12).

Although he had already demonstrated the futility of pinning down second pressure derivatives, he wrestles through the computations required to calculate the shift of the plait point *volume* with composition in the last pages of this paper. This leads to a formula occupying a full three lines on a page. It contains various third derivatives of the reduced pressure, and can obviously not be tested.

The paper ends with the honest admission that there are not enough sufficiently accurate data to test the expressions derived for the shift of the plait point parameters. For the comparison of observation and calculation, Keesom considers the simple Eq. (11.12) the most important result for the time being. That so much effort has yielded such minimal returns must have been a painful conclusion for the Leiden proponents of the law of corresponding states.

11.4.6 Verschaffelt models dilute near-critical mixtures. Shortly after Keesom's (1901) work was published, Verschaffelt (1902a, 1902b, 1903) took up the same problem. Inspired by Keesom's work, Verschaffelt (1902a) decides to use the law of corresponding states in the form of the two-scale-factor empirical virial equation developed by Kamerlingh Onnes (Ch. 3.5) that was fitted accurately to data for several pure fluids.

Verschaffelt then develops a Taylor expansion of the virial equation for the pure solvent at the critical point, and proves that the coexistence curve is a parabola to lowest order. Verschaffelt does not show any reluctance to do this, even though he was the only person to know that such an expansion is not possible (Ch. 9.4.4), and he does not allude to his finding that this curve is a cubic.

Next, Verschaffelt expands the mixture equation of state, at constant composition, around the fictitious critical point. He expresses the expansion coefficients in terms of the shift of the critical parameters, which he knows empirically from his superposition of isotherms. Alternatively, he can obtain them from Kamerlingh Onnes's reduced virial equation.

Although Korteweg (1903) would calculate the coefficients of the expansion from the Van der Waals equation, Ch. 11.4.2, while Verschaffelt uses the empirical virial equation, once the expansion is performed, further mathematical procedures are the same. Nevertheless, the Amsterdam mathematician and the Leiden physicist worked independently during the same time period. Verschaffelt's work can be considered to be the more general because it is not based on the Van der Waals equation.

Verschaffelt's (1902a, 1902b) papers, published as Leiden Comm. 81, consist of a thick sheaf of calculations of the behavior of a dilute mixture near the solvent's critical point. Verschaffelt could have learned from the clarity of presentation that marks Korteweg's work.

A letter from an unhappy Kamerlingh Onnes (1903) to Verschaffelt, dated January 24, reveals that there is a problem with the draft of Leiden Communication 81, which was to bundle Verschaffelt's (1902a, 1902b) papers. Korteweg had presented his results in the December 1902 meeting of the Academy, and apparently reported that there were some discrepancies with Verschaffelt's results. Korteweg (1903), however, while referring repeatedly to the work of Verschaffelt and Keesom in the publication, did not mention any discrepancies. We quote from Kamerlingh Onnes's (1903a) letter to Verschaffelt:

You have everywhere expanded to a power one higher [than Korteweg]. You remember that I explicitly cautioned you about this approach, because lots of powers might then be needed, and you understand that I do not have the time to do such a thing, or check it. But I do advise you to check once more all calculations....

...Could you not work through all of Korteweg's essay with your new results, expressing all of Korteweg's coefficients in yours and then comparing all of Korteweg's conclusions with yours? This would be very useful by itself. But it would be very useful indeed if you would in time discover a mistake in your calculations, as far as they don't agree with Keesom's and the latter have been checked. Surely it is also desirable for you to draw your cases in the xV plane and it is regrettable that you have not worked right away on the representation in the ψ [Helmholtz energy] plane, but have let yourself be distracted by other problems, because since Korteweg has entered this field, you should understand that it would have been desirable that you would have made of it what you could.....I am holding back Comm. 81 for the time being. [Translated from the Dutch.]

(The ‘other problems’ must refer to Verschaffelt’s discovery, discussed in Ch. 9.4.4, of the failure of mean-field theory at the critical point.) In a letter of Kamerlingh Onnes (1903b) to Verschaffelt dated February 18, it appears that Verschaffelt had great difficulty trying to fit the adjustable parameters of the virial-equation corresponding-states model. When fitted to all data, the resulting critical point was in the wrong place. Kamerlingh Onnes agrees that there is something discrepant between the behavior of the fluid in general and near a critical point (something Verschaffelt had tried to convey to him repeatedly, Ch. 9).

There is definitely something irreconcilable between the critical region and the isotherms further away. The conflict between what follows from the isotherms further away and the observations nearby the critical temperature indicates that in the critical region the observations are dominated by influences not yet clarified. [Translated from the Dutch.]

He feels, however, that reasonably close to a critical point the virial model should still be able to represent qualitatively the difference between pure-fluid and mixture behavior, since if there is deviant behavior, it would be the same for all substances. Dutifully, Verschaffelt (1903) carries out the substantial chore of an intercomparison with Korteweg’s results, substituting Korteweg’s Van der Waals equation for mixtures by his own empirical virial equation. After correcting a few mistakes in his 1902 papers, he finds complete agreement with Korteweg’s results. Later, however, Verschaffelt (1906b) published yet another erratum: he had found that some small terms were omitted in the starting expansion of the mixture free energy.

Verschaffelt must be pitied. Keesom had worked on this problem, and had already decided that the data were not good enough to obtain the necessary values of pressure derivatives. Verschaffelt had to work with a model that he alone knew was wrong at the critical point. Fitting the data in a reasonable way appeared impossible. A monstrous amount of formula manipulation had to be carried out. He found himself in a race with Korteweg and under pressure by Kamerlingh Onnes.

As stated in Ch. 10.16.2, Verschaffelt (1904) totally redeemed himself in Kamerlingh Onnes’s estimation by making the first useful estimate of the size of impurity effects in Teichner’s (1904) questionable experiment. He used a net of isotherms for mixtures of carbon dioxide and oxygen determined by Keesom in the work for his doctoral thesis; Keesom had superimposed these isotherms following Verschaffelt’s example (Ch. 11.4.5), and had estimated the parameters α and β in Eq. 11.11. A pure fluid and a dilute mixture at the same pressure and temperature are at slightly different values of the reduced coordinates. To lowest order, the reduced temperatures differ by αx , and the reduced

pressures by βx . The corresponding density differences can then be directly obtained from the reduced plot of the P - V isotherms. Verschaffelt estimates that, in the absence of stirring, Teichner must expect a density gradient of the order of 30% over the length of the tube if there is a concentration difference of 0.001 mole fraction between the ends. Thus, Verschaffelt obtained by simple means a useful estimate of the magnitude of impurity effects in near-critical fluids. Kamerlingh Onnes's praise for this work was quoted in Ch. 10.16.2.

11.4.7 *Van Laar uses the geometric-mean Van der Waals model.* Van Laar (1905h) felt compelled to react to a paper by Van 't Hoff (1903) about the rise of the critical (plait point) temperature due to the addition of a solute in the limit of infinite dilution. True to form, Van 't Hoff had stated that this rise was universal, the same for a mole of any solute. Van Laar (1905h), however, derived an approximate expression for the rise of the critical-point temperature, which clearly depended on the Van der Waals parameters of the solute in question and thus lacked Van 't Hoff-like dilute-mixture universality. Dissatisfied about a very unreasonable assumption he had to make in order to fit his expression to known data, Van Laar (1905e) begins anew. He knows about Keesom's exact expression, Eq. (11.10), based on the law of corresponding states, but criticizes it as containing too many derivatives that have to be obtained empirically. He, in his turn, uses his own exact expression (Ch. 7.5.4) for the plait point curve for Van der Waals mixtures obeying the geometric-mean rule, Eq. (4.7), for mixtures of arbitrary a and b . After elaborate calculations, he obtains a compact expression for the change of the critical temperature with composition at infinite dilution:

$$(1/T_1) (dT_{pl}/dx)_{x=0} = \theta \pi^{-1/2} \{ \theta \pi^{-1/2} (3/2 - \pi^{-1/2}/2)^2 - 1 \} \quad (11.13)$$

with $\theta = T_{c2}/T_{c1}$, the ratio of the critical temperature of the solute to that of the solvent, and $\pi = P_{c2}/P_{c1}$, the ratio of the critical pressures. This expression is not only simple, it is also highly useful, since the rise of the critical temperature is now expressed for the first time in terms of directly measurable pure-fluid critical properties only, be it under the restriction of the geometric-mean rule. The expression simplifies even more if it is assumed that the critical pressures of the host and the impurity are the same. Then, the right-hand side reduces to $\theta(\theta-1)$.

Van Laar (1905e) makes an interesting comparison of Eq. (11.13) with experiment. It so happened that Bakhuis Roozeboom's graduate student Büchner had performed one of the first experiments on supercritical solubility. Five organics of low volatility, such as naphthalene and tribromomethane, were dissolved in carbon dioxide near its critical point. The solubility is, by definition, the concentration at which the solution saturates in

the presence of an excess of the solute. At saturation, the plait point curve reaches a critical end point that is usually close to the critical point of the solvent. From the solubility and the temperature at the critical end point, Van Laar readily obtains an estimate of the value of $(1/T_1) dT_{pl}/dx$. In order to calculate θ , the critical temperature of the solute is needed, which was not known for any of these solutes. Van Laar poses as a rule of thumb that the critical temperature equals twice the melting temperature. Van Laar finds agreement between the experimental value of $(1/T_1) dT_{pl}/dx$, and his $\theta(0-1)$ rule on the level of 20% or better. Why was he so lucky? For one, he refrained entirely from calculating any property involving the volume, which would have come out poorly. For another, there was no need for him to take derivatives of experimental data. This was a nice piece of work, with an interesting new application.

11.4.8 *Van der Waals has the last word.* Van der Waals (1905a,b,c) begins a series of three papers in the following irritated vein:

..., by a remark by Van 't Hoff, and by Van Laar's calculations, a discussion has been carried on on the rise of the critical temperature of a substance in consequence of an admixture. In this it has been perfectly overlooked that already more than ten years ago, the principal properties of the critical line, and also the properties at the beginning and the end of the line were discussed and determined by me.

In this first paper, Van der Waals begins with his 1895 expression referred to in Ch. 11.4.1, which gives the initial rise of the critical temperature in terms of second and third derivatives of the Helmholtz free energy. Using his mixture equation of state, he is able to obtain an expression in terms of infinite-dilution concentration derivatives of the characteristic parameters a and b , valid for the case that b is a constant. He spends some effort reworking it, approximating some of the terms, and trying to compare with Keesom's experimental data on the mixture of carbon dioxide and oxygen. That leads him to an expression akin to that Krichevskii would derive much later, Eq. (11.8), except that instead of the initial slope of the plait point curve, his expression is derived for the initial slope of the line of *fictitious* critical points. This leads him into the same blind alley as Keesom and Verschaaffelt.

The paper suffers from repeated switching between calculations based on the Van der Waals pure-fluid and mixture equation of state, and comparisons based on empirical fact. The fact that the excluded volume must shrink as the density increases, for instance, is not incorporated in the equation of state, leading to a 30% overestimate of the critical volume. Furthermore, Van der Waals uses the empirical fact that the slope of the pure-fluid vapor pressure curve is around 7, while his equation of state gives a value of only 4.

In the second paper, Van der Waals (1905b) follows a much more satisfactory path. Apparently, he paid attention to Keesom's remark that all kinds of useful but unpublished thermodynamic relations at the solvent critical point could be found in Van der Waals's lecture notes (see Ch. 11.4.5), and he sets out to neatly derive these relations one by one. Thus, there is a proof of the pure-fluid property that the critical isochore and the vapor pressure curve in the P - T plane have the same slope at the critical point.

In the same paper, a number of interesting dilute-mixture properties are described that would be slowly rediscovered in the 1960s and 1970s (see Ch. 11.4.5). First, there is the proof that the dew and bubble curves in the P - T plane have a common tangent at the pure-solvent critical point, the 'bird-beak' effect, see Fig. 11.3, (b). It is also shown that this slope is equal to the derivative $(\partial P/\partial x)_{V,T}$ at the solvent critical point.

Another interesting relation is that between this derivative, the solute concentrations x_1 , x_2 in coexisting phases, and the molar volumes V_1 , V_2 of the two phases near the solvent critical point:

$$(\partial P/\partial x)_{V,T} = RT [(x_2 - x_1)/x_1] [1/(V_2 - V_1)] \quad (11.14)$$

Since the left-hand side of Eq. (11.14) remains finite as x_1 and x_2 tend to zero, $x_2 - x_1$ must approach the value of zero faster than $V_2 - V_1$ does. This was noted in Ch. 11.3.3, and shown in Fig. 11.1, (b).

The last of the three papers is an excruciating attempt to fit expressions for limiting behavior to measured mixture properties. Van der Waals (1905c) makes no secret of the fact that, although he needs an equation of state to evaluate several of the derivatives in his expressions, large deviations must be expected especially in volume-related properties, due to the neglected volume dependence of the excluded volume b . The large departure of the experimental slope of the vapor pressure curve from that predicted by his equation is also referred to. A number of attempts to obtain numerical estimates for infinite-dilution properties follow, with Van der Waals alternating between the equation of state and empirical parameters, interspersed with data comparisons. There do not seem to be new results in this paper and it ends without a firm conclusion.

11.4.9 An evaluation. Van 't Hoff's work honed scientists' interest in dilute solutions. Almost all members of the Dutch School participated in the studies of dilute mixture effects near critical points described in this chapter. The results fall into three classes: thermodynamic relationships between various properties of dilute mixtures near the plait point; calculations by means of the Van der Waals equation for mixtures; and calculations by means of the law of corresponding states.

As to the thermodynamic relationships, Van der Waals was clearly the leader, setting the tone with his early formulae for the change of temperature and pressure along the plait point curve, and later, proving interesting relations for properties of coexisting phases in a mixture near the host's critical point. Keesom contributed heavily by rewriting Van der Waals's formulae in terms of experimentally accessible variables.

The calculations based on variants of the Van der Waals equation for mixtures are relatively simple, because the interactions between solute molecules are negligible to lowest order. Korteweg's application is general, elegant and complete. The mathematician was not as close to experiment as Van Laar and his Leiden colleagues, which limited the impact of his work. Van Laar's geometric-mean Van der Waals model is both simple and applicable.

Keesom's and Verschaffelt's contributions on the basis of variants of the law of corresponding states were sound in principle, but application was a disappointment. This was due in part to the impossibility of estimating reliable values for second derivatives of experimental data. More seriously, however, the inadequacy of a mean-field description of near-critical states in pure fluids and in mixtures played a role. Verschaffelt and Kamerlingh Onnes sensed this, but more than half a century would pass before this issue was resolved. From a modern perspective, P - V isotherms of fluid mixtures of constant concentration cannot be expected to superimpose near a critical point: a field variable, not a density, must be kept constant for critical-point universality to hold.

For a rough estimation of impurity effects, Verschaffelt's and Van Laar's shortcuts paid off. Verschaffelt's repeat of Korteweg's calculations for a corresponding-states model, this time to third order, however, was not a good idea. Given the limited computational means of the times, mistakes were unavoidable. More seriously, Keesom had already shown the inadequacy of that approach even at the second-order level.

The present-day reader is appalled by the extraordinary calculative efforts made at that time. Modern computers do the work carried out with so much dedication a century ago, and our appreciation for such 'drudgery' is very limited. We should not forget that the Dutch school generally kept proper perspective, and that new concepts and deep insights emerged from the many pages of calculations. Appreciation of the historical work returns when one watches the old concepts and insights slowly rediscovered in modern times.

11.5 *Supercritical fluids*

In the 1980s there was a strong surge of interest in the behavior of mixtures near the pure-solvent critical point. The interest was driven by the unusual solvent properties of supercritical fluids, which could be made good use of in chemical process design. A decade earlier, however, Krichevskii and his experimental group in the Soviet Union did significant work, as did the American theoretical chemist John C. Wheeler.

From reviews by Krichevskii (1967) and Khazanova and Sominskaya (1971), it is clear that Krichevskii's group had spent considerable effort in order to obtain an experimental and a theoretical understanding of the behavior of dilute near-critical mixtures. A collaborator, Rozen (1976), worked out the thermodynamics of such systems by means of a classical Taylor expansion around the solvent critical point, in the way Korteweg or Van Laar could have done it. In the introduction to this paper, Rozen describes how Krichevskii was questioning whether the dilute-mixture laws would hold at the solvent critical point as early as 1943. Rozen then showed that the partial molar volume of the solute, instead of varying linearly in the concentration, diverges as $x^{-1/3}$. This follows immediately from Eqs. (11.3) and (11.4). Initially, Krichevskii refused to believe this, but measurements from his own group confirmed the divergence. Even stranger, these measurements also demonstrated that the partial molar volume of the solvent does not simply become equal to the molar volume of the solvent, but has different limits at the solvent critical point depending on the path of approach. Rozen (1976) worked out these different limits under the mean-field assumption.

Wheeler (1972) had reached this same conclusion on the basis of a non-classical theoretical model. An expert on decorated lattice gases, he calculated the partial molar volume near criticality for a modern nonclassical version of the decorated lattice gas. The partial molar volume of the solute indeed diverges, be it with a different exponent than in Rozen's case for the mean-field fluid. Wheeler (1972) also rediscovered the 'bird-beak' behavior of the dew-bubble curve, Fig. 11.3, (b). In addition, Wheeler confirmed that the limiting value of the *solvent* partial molar volume depends on the path to the solvent critical point, and he gave the proof for his model.

The partial molar properties of the solute are the mainstay of solution chemical thermodynamics. They are directly connected to the infinite-dilution standard state first characterized by Van 't Hoff, and are extensively tabulated for many aqueous systems. This unanticipated divergence of the standard state was an unpleasant surprise. It implies that at the solvent critical point, the departures of the solution from the infinite-dilution state do not depend linearly on the concentration of the solute, but are unexpectedly large.

Many experiments performed in the 1980s have confirmed these divergences of the solute's partial molar properties at the solvent critical point. Highly accurate measurements of partial molar enthalpy and heat capacity of aqueous salt solutions, performed close to the water critical point at 647 K, revealed steep changes at low concentration, and the more so the closer to the water critical point. For reviews and references, see Levelt-Sengers (1991, 1993).

A satisfactory formulation of the properties of solutions near the solvent critical point will be difficult to come by. Models such as those of Korteweg and Rozen are consistent and incorporate the anomalous behavior correctly at the mean-field level. However, if an accurate representation of the real, nonclassical fluid behavior is desired, an approach based on mean-field equations, or on the use of the traditional law of corresponding states must fail. For non-electrolytes, nonclassical mixture models are presently available, but most of these are limited to regions close to the critical point. The appropriate renormalization-group calculations incorporating charge screening effects in electrolyte solutions have not been performed as yet.

The Dutch scientists studied a problem with implications and challenges that they could not have foreseen. The difficulties they encountered when comparing with experiment resulted to a great extent from the nonclassical behavior of real fluids, only dimly perceived at that time. The Dutch School had reached the limits of mean-field theory, but did not have the means to transcend it.

12. Impact of the Dutch School

12.1 *Overview.*

There are many and diverse paths leading from the studies of fluid mixture phase separation and fluid criticality of the Dutch School at the turn of the 19th century to present-day science and technology. Some are quite direct and obvious, others are more tortuous and diffuse. Some paths were major excursions: they crossed geographical boundaries, and at their far end, a new scientific endeavor began. Some never evolved, or were forgotten. A new path was created later, and only afterwards it was found to have existed much earlier. From what was initially a strictly scientific enterprise, the emphasis shifted to engineering applications, but the century-old roots of the modern disciplines are still recognizable and traceable.

The effect of Van der Waals's work on molecular science in the 20th century was direct and fundamental, as is well recognized and extremely well documented, due in large part to books by Rowlinson (1988), and by Kipnis *et al.* (1996). This chapter summarizes the achievements of the Dutch School highlighted in previous chapters, as well as insights lost and rediscovered later. Then, it sketches connections perhaps less known. Three of these have been chosen. First, the history of fluid property and phase equilibrium studies in the Netherlands passes review, including the bifurcation of phase equilibrium and fluid property studies that occurred early in the 20th century. Secondly, we show the impact of the Dutch School on physical chemistry, geology and metallurgy in Russia. Finally, we recall the debt owed to the Dutch School by the 20th-century chemical process industry.

12.2 *Lasting intellectual contributions*

By introducing parameters characterizing molecular size and attraction in constructing his equation of state, Van der Waals set the tone for molecular physics of the 20th century. That molecular aspects such as size, shape, attraction, and multipolar interactions should form the basis for mathematical

formulations of the thermodynamic and transport properties of fluids is presently considered an axiom. The Van der Waals forces between molecules, much weaker than chemical bonds but present universally, play a fundamental role in condensed-matter science and in surface science. Elucidation of the nature of the Van der Waals forces between molecules has remained a scientific effort from Van der Waals's days to the present.

The law of corresponding states, first derived by Van der Waals from his equation of state and generalized by Kamerlingh Onnes, was a key concept of lasting significance. This law is still the method of choice for estimating properties of poorly characterized compounds within families of related substances.

The ability of the equation of state to qualitatively describe phase separation in fluid mixtures is another major and lasting achievement. The cubic character simplifies these calculations. This is why, notwithstanding the enormous advances in computer technology, cubic equations retain their niche in the modeling of chemical processes. The virtues of cubic equations for calculation of phase equilibria of multicomponent fluid mixtures are so great that efforts to improve them have lasted through the 20th century. In a sense, the cubic equations are the first and the last word in global phase equilibrium calculations. Any refining of the equation of state due to increased knowledge of intermolecular forces leads to greater complexity. This diminishes the ability to explore the phase behavior fully and may produce phase diagrams not present in real fluid mixtures. There is, as yet, no match for this achievement of the Dutch School a century ago.

The mean-field assumption, another fundamental contribution by Van der Waals, has turned out to be a mixed blessing. Its strength is the major simplification of the conceptual and computational work. For the application to global phase diagram calculations, there is no substitute for the mean-field approach, which is still the method of choice for a first exploration of any theoretical model in statistical mechanics. This method fails, however, when fluctuations become important. The method does not work, for instance, in fluid mixtures of very different molecular attraction and size, in which the surroundings of a chosen molecule differ considerably from the bulk concentration. Chemists and chemical engineers have developed approximations to account for local-composition variation while retaining the character of analyticity of the equation of state.

The neglect of large-scale fluctuations existing near critical points because of the large compressibility of the fluid cannot be repaired this way. Van der Waals and Verschaffelt noted the failure of the Van der Waals equation near the critical point a century ago, and Verschaffelt knew this failure was a general feature of analytic equations of state. It was only in the second half of the 20th century that the critical fluctuations were quantitatively studied, and

limited-range scaled fundamental equations, accurately fitting fluid data near the critical point, where proposed to replace those based on the mean-field theory. Crossover theory offers means to repair existing mean-field equations near the critical point. However, an equation of state valid over large ranges of fluid phase behavior, which is accurate in region where fluctuations are large, and which is capable of predicting realistic fluid mixture phase behavior, is still a distant goal.

12.3 *Knowledge lost and rediscovered*

12.3.1 *Important insights that were forgotten.* Much, but not all, of the mathematician Korteweg's work on plaits and plait points was lost and gradually rediscovered. His insight in the origin and development of plaits on analytic surfaces, including the unstable regions, was qualitatively familiar to Van der Waals as well as to Dutch chemists such as Scheffer, who show plots of accessory plait formation in their papers. The Taylor expansion of the Helmholtz energy near critical points (plait points) of pure fluids and fluid mixtures were familiar to the Dutch School, and the criticality conditions formulated by Korteweg for fluid mixtures made it into the modern literature. This was primarily due to Rowlinson's influential book on liquids and liquid mixtures (1958). Physicists in general, and Soviet physicists in particular (see Ch. 12.5), however, were unaware of Korteweg's work. Taylor expansions near critical points, the basis for renormalization-group calculations that incorporate the effect of fluctuations, are universally credited to Landau (1937).

Van der Waals's equation of state lost its luster at an early stage as its many deficiencies and inaccuracies became apparent. By the middle of the 20th century it was considered useless beyond the confines of a freshmen physical chemistry class. The work by Van Konynenburg and Scott (1980) on the global phase diagram of Van der Waals mixtures, however, proved how much valuable qualitative insight can be obtained from this equation. Rowlinson's (1988) translation of Van der Waals's thesis, preceded by an extensive discussion of the impact of this work, has led to a renewed appreciation by the scientific community. Van der Waals's definition of critical exponents for mean-field theory, along with Verschaffelt's discovery of nonclassical critical exponents, was a concept lost and not rediscovered until half a century later.

Van der Waals's fourth major achievement is his theory of capillarity of 1894. Though not discussed in this book, it is another example of historic amnesia. Only after Cahn and Hilliard (1958) completed their influential work on the free energy of nonuniform systems (in which they *did* cite Van der Waals's (1894) value of the experimental surface tension critical exponent) did they discover that Van der Waals had developed the theory of capillarity

based on a continuous density profile through the interface more than sixty years earlier.

One wonders what caused this loss of valuable knowledge. There are probably many contributing factors. What presently seems highly significant may not have appeared that way at the time it was first discovered, or was overshadowed by developments considered more important or exciting.

12.3.2 *Language barriers.* Speakers and writers of Dutch are for the most part limited to the native Dutch, Flemish and South-African populations. Due to the foreign-language proficiency of the educated Dutch, however, this should not have been a major impediment to dissemination of the work of the Dutch School. Very few of the relevant papers are available exclusively in the native language. It is very common to find several versions of a paper of the Dutch School in one or more of the foreign languages: German, French and English. The practice of publishing in English took a firm hold in the Netherlands as early as 1900. Before that time, Academy Proceedings appeared in Dutch, while German was the language of preference for publications following these presentations. Kamerlingh Onnes, however, was far ahead of his time, by publishing the Leiden Communications in English from the very beginning.

Korteweg, on the other hand, published his two substantial papers on plaits in the French-language Archives néerlandaises. Only one of these was also published in the German-language proceedings of the Academy of Vienna. Van Laar published part of his work on the geometric-mean Van der Waals model in French in Archives du Musée Teyler. History just might have taken a different course had Van der Waals published his four major works in English instead of German.

12.3.3 *Other impediments to dissemination.* Korteweg the mathematician, even though highly focused on applications and held in high esteem, may have been somewhat of an outsider. The very limited referencing by other members of the Dutch School did not work in his favor. The Leiden colleagues apparently preferred to go by the far less explicit but more accessible results in the appendix of Van der Waals's 1890 paper on mixtures. The esoteric qualities of the Van der Waals symmetric mixture may have been a strike against Korteweg. As we saw in Ch. 7.5.10, Korteweg's model was re-explored in the second half of the 20th century by Meijering (1951), Straley and Fisher (1973), Das and Griffiths (1979) and others in the context of phase separation in three-component liquids or solids and the three-state Potts model. Only Meijering, however, cites Korteweg's work.

Van Laar's work on fluid phase equilibria remains mostly unread. The reasons are obvious to those who have tried. Van Laar, an educated man with

strong interest in literary endeavors, did not know how to bring his points across effectively, and significant results drowned in an ocean of formulae. Van Konynenburg and Scott (1980) recognized his contributions to the global phase equilibrium calculations of the geometric-mean Van der Waals equation for mixtures. Meijer *et al.* (1989, 1993), however, were the first to note that Van Laar had actually performed exact calculations for this case.

Van Laar's work did find a place in chemistry. Van Emmerik (1991) discusses his equation for the heat of mixing based on the geometric-mean rule. Hildebrand used and modified it as input to the influential theory of regular solutions. As a consequence of his feud with Van 't Hoff and the osmotic school, Van Laar was the first to introduce what are currently called activity coefficients for non-ideal solutions.

12.3.4 *The new physics.* By the end of the 19th century modern physics was borne. The discovery of radioactivity broke open the indivisible atom of Demokritus, and directed the focus onto the atomic nucleus. Spectroscopy presented electromagnetic and atomic theory with the challenge to explain the spectral lines, characterizing the different elements, in terms of electrons orbiting the nucleus. Early notions of quantization of energy were to blossom into the new discipline of quantum mechanics. The liquefaction of helium opened the field of cryogenics. Superconductivity and superfluidity were discovered and studied intensively. With so much energy and intensity devoted to the new fields of science, interests in phase behavior of fluid mixtures slipped into the background, out of the focus of physicists.

12.4 *Heritage of Van der Waals and Kamerlingh Onnes in the Netherlands*

The universities of Leiden and Amsterdam were the centers of study of fluid phase behavior around 1900. In the Leiden physics department, Kamerlingh Onnes held the reins. Fluid mixture phase equilibria were a topic of active interest, with the liquefaction of helium marking the end of this period. The mysterious properties of the coldest liquid on earth, and the many new research opportunities offered by the then-ultimate cryogenic coolant, set new directions for the laboratory. Nevertheless, some members of the staff, supplemented by visitors such as Mathias, continued work on P - V - T properties of fluids until the 1920s. They worked mostly on one-component cryogenic fluids such as argon, and the work no longer had the novelty and vibrancy prevalent in the days of Kuenen and the early Keesom. After the Second World War, however, fine experimental work on the molecular physics of fluids, in particular the effect of magnetic fields on transport properties of molecular fluids, was carried out in Jan Beenakker's group.

In Amsterdam around 1900, Van der Waals not only was involved in his theoretical work on fluid mixtures, but also ran a modest-scale laboratory in the Physics Department, where he studied fluid phase equilibria in mixtures at elevated pressures. In 1898, at the occasion of the 25th anniversary of his doctorate, Van der Waals's friends established a fund allowing him to expand his laboratory. Van der Waals decided to use this opportunity to extend the pressure range. Up to that time, experimental pressures in the Amsterdam and Leiden laboratories were limited by the strength of glass.

Van der Waals purchased a press and several deadweight gages in 1900. In 1911, Van der Waals retired and Philipp Kohnstamm, his closest pupil, took over his laboratory. Capabilities for P - V and phase equilibrium measurements were put into place. The pressure limit was set at 3000 atmospheres, following Amagat, the leading French high-pressure expert. Kohnstamm is mainly remembered for his co-authorship with Van der Waals (1912) of a two-volume text on thermodynamics. This is a compendium of Van der Waals's lecture notes on the thermodynamics of fluids and fluid mixtures. It is clearly written, in a somewhat elaborate and flowery style, and was still an obligatory text for physics and chemistry students in Amsterdam in the 1920s.

After 1915, Kohnstamm's interest took a different direction, and the laboratory was moribund by the end of the First World War. The laboratory was rescued from oblivion by Anthonius M.J.F. Michels (1891-1969), Kohnstamm's assistant and later his successor. He shaped the Van der Waals laboratory into a premier high-pressure institute, where the thermophysical properties of fluid were measured with unsurpassed accuracy. During that period, relatively few studies were carried out in fluid mixtures and the pressure limit remained at 3000 atmospheres. In the last part of the 20th century, however, Schouten and collaborators expanded the pressure range in a major way, and pioneered the observation of phase separation in fluid mixtures in diamond anvil pressure cells, work that was referred to in Ch. 8. For more details on the history of the Van der Waals Laboratory, see Levelt Sengers (1993, 2001).

The chemistry department in Amsterdam became a world-renown center of phase studies under the direction of Bakhuis Roozeboom, who succeeded Van 't Hoff in 1897. Van der Waals had triggered the interest in the phase rule when Bakhuis Roozeboom was still a student in Leiden. Until his death in 1907, Bakhuis Roozeboom directed an active experimental group, with the study of phase equilibria in chemically active systems including solid phases as a primary objective. He, too, carried out these studies at elevated pressures, and to rather high temperatures. Phase theory became the principal focus of the department. Van 't Hoff characterized Bakhuis Roozeboom

in a memorial speech shortly after the death of this very devout man: 'To the Almighty in his [BR's] philosophy of life, corresponded the phase rule in chemistry.' See Cohen's (1913) biography of Van 't Hoff.

Bakhuis Roozeboom (1901) wrote the first two books in the series 'Heterogeneous Equilibria from the Perspective of the Phase Rule.' Over the years, his former pupils F.A.H. Schreinemakers, A.H.W. Aten and E.H. Büchner added volumes. By that time, they were all professors of chemistry. This book was highly influential. It introduced Gibbs's phase rule as a foundation for disciplines such as metallurgy, mineralogy and geophysics. Schreinemakers was a professor of chemistry in Leiden, and is well known for 'Schreinemaker's rule,' which sets limits on the angles at which phase boundaries can meet in a phase diagram.

Van Laar could have been a natural mediator between the scientific interests of the physicist Van der Waals and the chemist Bakhuis Roozeboom, but Van der Waals resisted. Thus, early in the 20th century, the two groups diverged, with the chemists becoming the world's experts on phase theory including solid phases, and the Van der Waals laboratory turning to accurate property measurements at high pressures, mostly in pure fluids.

The Delft Polytechnic Institute was only a minor player in this field in the early 1900s. Notwithstanding the difference in curricula between the Polytechnic Institute and the academic institutions, however, there was always an exchange of graduate students and professors. Kamerlingh Onnes, for instance, was an assistant to physics professor Bosscha in Delft from 1878 to 1882. Korteweg began his studies at the Delft Polytechnic and then transferred to Amsterdam. The Polytechnic Institute firmly entered the field of fluid phase equilibria studies in 1917, when it appointed the chemist Scheffer as a professor of analytical and organic chemistry. Scheffer was a research assistant at Van der Waals's Laboratory, having obtained his doctorate with Bakhuis Roozeboom. Scheffer was a professor at Delft from 1917 to 1953, and created a bridge from the work of Van der Waals and Bakhuis Roozeboom to the modern age. He also aided the transfer of the purely scientific knowledge acquired in the early part of the 20th century to chemical process technology. The impact of his textbook on this topic could have been larger, had it been written in English instead of Dutch.

The textbook by the industrial chemist J. Zernike (1955) is a practical, English-language compilation of the work of the Dutch School.

The phase equilibria studies in fluid mixtures on the basis of the method of the Cailletet tube continue to the present day. The Delft group of De Swaan Arons, Peters, and De Loos has made numerous contributions to chemical process technology, in particular to the natural gas industry, polymer processing, and processing by means of supercritical solvents.

In addition to the work in these experimental groups, a high degree of expertise in statistical mechanics, kinetic theory, non-equilibrium thermodynamics and molecular physics accumulated at several of the Dutch universities and science institutes, growing naturally from the foundations laid by Van der Waals and Kamerlingh Onnes. Ornstein and Zernike's (1914) influential treatment of fluctuations was mentioned in Ch. 9. Theorists such as Ehrenfest, Kramers and Uhlenbeck in Leiden, De Boer in Amsterdam (Ch. 3.7.4), and Van Hove and Van Kampen in Utrecht, all built strong theory groups, entertaining a steady stream of foreign visitors and lecturers. De Groot and Mazur's (1962) book on nonequilibrium thermodynamics is a classic.

The chemists Kruyt and Overbeek at the University of Utrecht founded modern colloid science in the early part of the 20th century, in strong interaction with industry. Kruyt raised Casimir's interest in the role of Van der Waals forces between colloid particles, resulting in the calculation of what is presently known as the Casimir effect. Experiments by Vrij and by Lekkerkerker on solutions of colloidal particles of controlled shape and charge in the later part of the 20th century have demonstrated a variety of novel phase separations.

Koningsveld and Kleintjens at the laboratory of the Dutch State Mines pioneered the use of lattice models for modeling phase separation in polymeric fluids. Meijering at Philips Laboratories adapted Korteweg's methods to phase separation in solids. The ground prepared by the Dutch School around the turn of the 19th century has indeed proved its fertility throughout the 20th century.

12.5 *The Dutch School and physical chemistry in Russia*

Kipnis et al. (1996) describe in detail the influence of the Dutch School of fluid phase behavior on Russian scientists. Since two of the authors are Russian, their story is a treasure-trove of interesting facts not well known in the West. A summary relevant to this book follows, supplemented by additional information.

The cosmopolitan physicist A.G. Stoletov (1839-1896), who studied at several major universities in Germany before becoming a professor at Moscow University, taught his students about the Van der Waals equation shortly after the German translation of Van der Waals's thesis appeared in print in 1881. Famous Russian chemists D.I. Mendeleev and D.P. Kononov also studied the thesis. As early as 1886, Kononov took a stand in favor of Van der Waals and against the view that molecules in the liquid are compounds different from those in the vapor. Kononov became an expert on the properties of coexisting phases in liquid mixtures and a strong force in carrying over Van der Waals's ideas to Russian physical chemistry. M.P. Avenarius, a professor of physics at the University of Kiev, was the first to publish an account

of critical opalescence in 1873. We encountered Golotsin (Galitzine) in Ch. 10, one of many scientists reporting experiments that disagreed with Andrews and Van der Waals's view of criticality. Stoletov was one of the first to criticize Galitzine's work. In Ch. 9, we introduced a pupil of Stoletov, D.A. Goldhammer, who, as early as 1910, formulated a corresponding-states coexistence curve equation for pure fluids with a non-classical critical exponent of $1/3$.

N.M. Vittorf (1869-1929), an organic chemist at the Artillery Academy, spent the year 1903/04 in Göttingen, where he met Bakhuis Roozeboom. In 1909, Vittorf published a detailed account of the geometric approach to phase diagrams, as developed by Bakhuis Roozeboom, and used it to construct and classify phase diagrams of alloys. He defined nine classes, five of which had been found by Bakhuis Roozeboom. Thanks to Vittorf's translation, the series of books by Bakhuis Roozeboom and his pupils has had a major and well recognized influence on the development of metallurgy and mineralogy in Russia.

Between 1910 and 1960, the interest of physicists in phase behavior of fluids waned in Russia just as it did in the West, but physical chemists kept the tradition alive. One of these, A.V. Rakovskii (1879-1941) at Moscow University, edited the Russian translation of the book by Van der Waals and Kohnstamm in 1927.

Physical chemist I.R. Krichevskii (1901-1993), whose long life spanned most of the twentieth century, formed a key conduit between the Dutch School and the modern age. At the Institute of the Nitrogen Industry in Moscow, he built a large-scale laboratory for the study of phase equilibria under high pressure. Krichevskii was thoroughly familiar with the work of the Dutch School, and always displayed the two volumes by Van der Waals and Kohnstamm on his desk. He and his group of mostly female researchers were the first to measure gas-gas equilibrium in the strict sense, namely, above the critical temperatures of both components (Ch. 8). They also were the first to study an asymmetric tricritical point (Ch. 7.2.4). They criticized the work on the derby-hat region by Mayer and Maas (Ch. 10) and studied dilute-mixture properties near critical points (Ch. 11.3.6, 11.4.5). In the 1960s, Krichevskii hosted a seminar at his Institute attracting many external speakers and visitors.

It is well known that Russian physicists such as Landau and Voronel led the revival of interest in fluid criticality in the Soviet Union and in the world. Curiously, the work of physical chemists and physicists had diverged to such an extent that the knowledge passed from the Dutch School to Russian physical chemists was completely unfamiliar to physicists. Thus, Landau's work on the Taylor expansion of the free energy at the critical

point, mentioned above, did not build on the foundation laid by Korteweg, but was developed independently. The physics community in Moscow, very active in the field of critical phenomena, kept itself aloof from physical chemistry in general, and from Krichevskii in particular. Physicist Alexander Voronel was an exception. His discovery of the divergence of the isochoric heat capacity in argon near its critical point in 1962 (Ch. 9) brought fluid criticality back to the center of interest. Voronel was a regular participant at the seminar and fully appreciated Krichevskii's knowledge and expertise. Krichevskii, on the other hand, immediately recognized the importance of Voronel's experiment. The physical chemist Mikhail Anisimov, at that time postdoctoral researcher with Voronel and another regular at Krichevskii's seminar, helped bridge the gap separating Soviet physicists and physical chemists, and contributed to the generalization of the modern ideas on critical-point universality to fluid mixtures. Thus, by a circuitous route, the Dutch School seeded Russian physical chemistry and ultimately cross-fertilized Russian physics.

12.6 *The Dutch School and the chemical process industry*

In the Netherlands, phase equilibria studies shifted to the Delft Polytechnic Institute, and a similar change of direction took place in other countries.

In the United States, a prolonged silence followed Gibbs's pioneering work on the equilibrium of heterogeneous substances. After the First World War, however, chemical engineers and physical chemists set up the scaffolding for the modern approach to fluid phase equilibria. Lewis and Randall, in a classic textbook first published in 1923, introduced the universally adopted characterization of fluid mixtures by means of activity coefficients and partial molar properties. Between the two World Wars, studies of the properties and phase equilibria of hydrocarbon and their mixtures flourished in the United States, driven by the practical needs of the explosively growing petroleum industry. As oil and gas drilling extended to greater depth and higher pressures, the phenomenon of retrograde condensation was rediscovered, rekindling interest in Kuenen and the Dutch School. During the Second World War, a study of several years took place at the University of Michigan, collecting all material on the behavior of hydrocarbons under pressure in records dating back to 1860. The report by Katz and Rzasa (1946) contains literature references and reprints of the most important papers by European scientists in this field from 1875 to 1910. A large part of this report is taken up by the work of the Dutch School presented in this book.

In the United Kingdom, Rowlinson served as an effective conduit between the Dutch School and the chemical process industry. Rowlinson's

(1958) book extensively references work of the Dutch School on fluid mixtures, and introduces Korteweg's equations for fluid mixture criticality in terms of the Helmholtz energy. Rowlinson enlightened engineers drilling for gas in the North Sea on Kuenen's retrograde condensation. Freeman and Rowlinson (1960) studied lower critical end points in polymeric solutions, and drew attention to the fact that Kuenen and Robson first observed this type of phase behavior.

Thus, the fundamental contributions by the Dutch School, although perhaps not always explicitly recognized, permeate the modern chemical process industry, providing the framework for understanding and modeling the phase behavior of multicomponent fluid mixtures.

Notes on referencing

Conventions used. The year following the author's name in the text is printed bold-face, again in parentheses, in the corresponding reference in the following list. The references are listed alphabetically by last name of the first author. If an author has more than one paper referred to in a given year, these papers are ordered chronologically to the extent possible, and distinguished by lower-case letters a, b, *etc.*

In frequent cases of multiple versions of a particular paper, the version quoted in the text corresponds with the one carrying the boldface year in the reference list.

Most papers by the Dutch School were published in more than one language. Not all versions of a given paper are given in the reference to it. In case an English-language version is available, this is the primary, and often only reference given. If no English version is available, or if the English version appeared considerably later than the original version, the bold-face version quoted, and referred to in the text, has been chosen in the following order of preference: German, French, or Dutch.

Referencing to the periodicals of the Royal Netherlands Academy of Sciences. The 'Verslagen' and 'Proceedings' of the Academy are printed as issues, each covering a monthly session. The issues are bundled in volumes, which are numbered in chronological order and usually cover an academic year. Within a volume, pages are numbered consecutively. At the beginning of each volume, the starting page numbers for the individual session issues are prominently displayed. Each session issue, in turn, is preceded by a one-page detailed listing of all the communications in the session. Therefore, in this book the references to 'Verslagen' and 'Proceedings' are given for the session under which the particular article is published. This date may occasionally differ from that of the session in which the article was actually communicated. If this is the case, the date of communication is added to the reference. Since the date of print of the session is, at best, indicated inconspicuously in a hard-to-find place at the end of the session issue, this date is not given in this book.

From 1898 onwards, an English version of the Academy presentations, the *Proceedings*, was published. For Academy presentations from 1898 onwards, only the English version is given in the reference.

The 'Verhandelingen' of the Academy are usually more substantial papers, which may or may not have been presented in individual sessions. Roughly half a dozen 'Verhandelingen' are published in a volume, in which each 'Verhandeling' is numbered

starting with page 1. A listing of the papers appearing in a volume is included in the Volume, but the papers are not always numbered. They are therefore somewhat awkward to find or to refer to. In this book, the volume number, year, and page numbers (1-X) are given, and, if it is known, the session in which the paper was presented.

Referencing to the Communications of the Physical Laboratory at Leiden. The Leiden Communications bundle all of the publications of the Physical Laboratory starting around 1890. They were printed in English almost exclusively, and are numbered sequentially. For almost all Dutch-language Academy presentations published by Kamerlingh Onnes and his laboratory, a corresponding English-language Communication exists. If it does, it serves as the prime reference. In the case of the English-language Academy Proceedings, the Leiden Communications number, if known, is included in the reference.

Particular usages. Dutch last names are alphabetized while skipping definite articles and propositions such as De, Den, Van, Van de, Van der, Van 't. Examples: Van 't Hoff is found under H, and Van der Waals is found under W. Note that, following present-day custom in the Netherlands, the first of the articles or prepositions that are part of the last name are capitalized in the text and references as long as only the last name is stated. If the first name or first initial is included, the articles/propositions are not capitalized. In the case of a double last name, the reference is alphabetized according to the first letter of the first of these two names. Thus, Kamerlingh Onnes is found under K, and Levelt Sengers is found under L.

Frequently used sources for biography and bibliography. *The Dictionary of Scientific Biography* has been a major source of biographical information given in this book. The *Dictionary* is an 18-volume series published, under various editors, by Scribner's Sons, New York, from 1970 to 1990. In addition, the following biographies have been consulted. Each of these contains a complete bibliography. For Van der Waals, that by Kipnis *et al.* (1996) – for Van 't Hoff, that by Cohen (1912) – for Van Laar, that by Van Emmerik (1991) – and for Verschaffelt, that by Henriot (1957).

Journal Abbreviations

Ann. Acad. Roy. Belg.	Annuaire de l'Académie Royale de la Belgique
Ann. Chim. et Phys.	Annales de Chimie et de Physique
Ann. Physik	Annalen der Physik
Ann. Physik und Chem.	Annalen der Physik und Chemie
Ann. Rev. Phys. Chem.	Annual Review of Physical Chemistry
Arch. Musée Teyler	Archives du Musée Teyler
Arch. néerl.	Archives néerlandaises des sciences exactes et naturelles

Ber. Bunsenges. Physik. Chem.	Berichte der Bunsengesellschaft für Physikalische Chemie.
Bull. Acad. Roy. Sci. Belg.	Bulletin de l'Academie Royale des Sciences de la Belgique
Bull. Inst. Liège	Bulletin de l'Institut de Liège
Can. J. Res.	Canadian Journal of Research
Chem. Rev.	Chemical Reviews
Chem. Weekblad	Chemisch Weekblad
Comm. Phys. Lab. Leiden	Communications of the Physical Laboratory at Leiden.
Comptes Rendus Acad. Sci. Paris	Comptes rendus hebdomadaires des séances de l'Academie des Sciences (Paris)
Fluid Phase Equil.	Fluid Phase Equilibria
J. Am. Chem. Soc.	Journal of the American Chemical Society
J. Chem. Phys.	Journal of Chemical Physics
J. de Phys.	Journal de Physique et le Radium
J. Math. Phys.	Journal of Mathematical Physics
J. Phys.	Journal of Physics
J. Phys. Chem.	Journal of Physical Chemistry
J. Stat. Phys.	Journal of Statistical Physics
Philips Res. Rep.	Philips Research Reports
Phil. Mag.	Philosophical Magazine
Phil. Trans. Roy. Soc. London	Philosophical Transactions of the Royal Society of London
Physik. Z.	Physikalische Zeitschrift
Phys. Rev.	Physical Review
Phys. Rev. Lett.	Physical Review Letters
Proc. Roy. Soc. London	Proceedings of the Royal Society of London
Proc. Kon. Akad.	Koninklijke Nederlandse Akademie van Wetenschappen. Proceedings of the Section of Sciences.
Pure and Appl. Chem.	Pure and Applied Chemistry
Rep. Progr. Phys.	Reports on Progress in Physics
Russ. J. Phys. Chem.	Russian Journal of Physical Chemistry. Translation of. Zhurnal Fizicheskoi Khimii
Sitzungsber. Akad. Wissensch. Wien	Sitzungsberichte der mathematisch-naturwissenschaftlichen Klasse der Königliche Akademie der Wissenschaften zu Wien.
Soviet Phys. JETP	Soviet Physics, JETP. Translation of Zhurnal Eksperimentalnoi i Teoreticheskoi Fizika
Trans. Connecticut Acad.	Transactions of the Connecticut Academy
Trans. Farad. Soc.	Transactions of the Faraday Society
Verh. Kon. Akad.	Verhandelingen van de Koninklijke Nederlandse Akademie van Wetenschappen

Versl. Kon. Akad.

Z. Anorg. Algem. Chem.

Z. Anorg. Chem.

Z. Physik. Chem.

Koninklijke Nederlandse Akademie van Wetenschappen. Verslagen van de gewone vergaderingen der Wis- en Natuurkundige Afdeling.

Zeitschrift für Anorganische und Allgemeine Chemie

Zeitschrift für Anorganische Chemie

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