

Application of Molecular Modeling to Vapor-Liquid Equilibrium of Water with Synthesis Gas

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In the Integrated Gasification Combined Cycle (IGCC) process for electricity generation, the hot synthesis gas may be quenched with water. The amount of water vaporized in this step has a large influence on the process economics, but is difficult to predict with typical thermodynamic models that are not designed for such systems. The most important factor in this phase-equilibrium problem is the nonideality of the vapor, which we model with the virial expansion. Second virial coefficients for water with synthesis gases are derived from state-of-the-art pair potentials obtained from quantum chemistry. When combined with Henry’s law for the liquid phase, reliable results are obtained. Our results show that the vapor nonideality significantly enhances the water content of the vapor. Perhaps surprisingly, the Peng-Robinson equation, with a water-specific “alpha” function, is also able to provide reasonable values for the amount of water vaporized.

Introduction

Concern about global climate change and other environmental issues is leading to increased interest in “greener” ways of generating electricity from coal. One such process under consideration is the Integrated Gasification Combined Cycle (IGCC), in which a synthesis gas (mostly H₂, CO, and CO₂) is made from coal, purified, and eventually burned in a gas turbine, whose waste heat drives steam turbines. An advantage of the IGCC is that it is possible, with some penalty in efficiency, to incorporate CO₂ capture and sequestration in the pre-combustion part of the process.

A typical IGCC configuration with CO₂ sequestration would involve quenching the hot synthesis gas with water. This quench serves to knock out some undesirable substances such as particulates from the gas. It also adds water to the synthesis gas, which is needed for a water-gas shift reaction later in the process that converts CO to CO₂ and makes H₂ the main energy carrier in the process. The amount of water in the quenched gas is an important variable in the process economics, but it is hard to model with typical engineering thermodynamics approaches.

In this work, the vapor-liquid equilibrium is modeled with approaches tailored to each phase. The vapor is modeled with the virial expansion,

while the liquid is modeled with Henry’s law. This is sufficient to perform the phase-equilibrium calculation with a high degree of accuracy. We briefly describe these calculations here; more details may be found in a NIST Report [1].

Thermodynamic Modeling

The phase-equilibrium calculation requires a model for the fugacity of each component in each phase. Once the models are established, the “flash” calculation for vapor-liquid equilibrium (VLE) for a given feed composition, absolute temperature T , and pressure p is straightforward; our method for performing that calculation is described in [1].

The fugacity of gaseous solutes in the liquid phase is described by Henry’s law. The Henry’s constant k_H is defined by

$$k_H = \lim_{x_i \rightarrow 0} (f_i / x_i), \quad (1)$$

where f_i and x_i are the fugacity and mole fraction, respectively, of solute i . For VLE in single solvents, it is sufficient to consider k_H as a function of temperature only along the saturation curve of the solvent. Values of $k_H(T)$ were taken from a recent critical evaluation [2] for common solutes in water covering a wide range of temperatures.

At low solute gas pressures, Eq. (1), with the limit removed, would be sufficient for the VLE calculation. At the pressures of interest in this work, a correction for pressure, as described in [3], becomes marginally significant (affecting the gas solubility in liquid water by a few percent or less). This correction requires infinite-dilution partial molar volumes for each solute; these are computed as described by Fernández-Prini and Japas [4,5].

Under the conditions considered here (dilute solution of solute gases), the fugacity of water in the liquid phase is well approximated by the product of the mole fraction and the fugacity of pure water at the temperature and pressure of interest. The fugacity of pure liquid water was computed from the IAPWS standard for water’s thermodynamic properties [6] as implemented in a NIST database [7].

For fugacities in the vapor phase, we use the virial equation truncated at the level of the second virial coefficient. The virial equation provides a systematic series of corrections to the ideal-gas law:

$$\frac{p}{\rho RT} \equiv z = 1 + B\rho + C\rho^2 + \dots, \quad (2)$$

where p is the pressure, ρ the molar density, R the molar gas constant, and T the absolute temperature. The second virial coefficient B is a function of temperature (and of composition for a mixture), and depends only on interactions between pairs of molecules. The third virial coefficient C depends on interactions among three molecules, and so forth.

For phase-equilibrium calculations, the key quantity is the fugacity. If the virial expansion is truncated at B , the fugacity coefficient ϕ_i for species i is given by [3]

$$\ln \phi_i \equiv \ln \left(\frac{f_i}{y_i p} \right) = 2\rho \sum_j y_j B_{ij} - \ln z, \quad (3)$$

where y is the vapor-phase mole fraction. The B_{ij} are second virial coefficients characterizing the binary interaction between components i and j ; for $i=j$ this is a pure-component property. For a given pair, the B_{ij} are functions of temperature only.

Values of $B(T)$ for pure water were taken from the correlation of Harvey and Lemmon [8], while for other pure components they were taken from the NIST Refprop database [9].

For pairs not involving water, values of $B_{ij}(T)$ were calculated from the correlation developed by Tsionopoulos [10]. The binary parameter k_{ij} in the Tsionopoulos correlation was fitted to experimental B_{ij} data where available, as described in [1].

For the interaction of water with CO_2 , B_{ij} data of reasonable accuracy exist in the temperature range

of interest here [11]. These data were fitted to a simple function of temperature as described in [1].

For interactions between water and Ar, H_2 , N_2 , and CO , $B_{ij}(T)$ were taken from recent work [12-15] in which *ab initio* quantum mechanics was used to define the potential-energy surface between the molecules. Obtaining $B_{ij}(T)$ from these potential-energy surfaces is a straightforward numerical integration. The surfaces are produced with uncertainty estimates, which can be propagated through the calculations to provide uncertainties for $B_{ij}(T)$.

Because advances in quantum chemistry now allow for highly accurate potential-energy surfaces to be generated for pairs of small molecules, and because experimental measurement of B_{ij} is difficult for such systems, the uncertainties from this approach are typically smaller than can be obtained by experiment. Another advantage of this approach is that, once a potential-energy surface is generated, B_{ij} can be calculated at any temperature, whereas experimental information typically covers a limited temperature range.

Alternative Vapor Fugacity Models

In order to provide a comparison of our results to more typical chemical engineering calculation methods, such as might be employed in commercial process simulation software, two additional models were used for calculating vapor-phase fugacities.

The first model was the ideal gas, which simply involves setting all the fugacity coefficients ϕ_i to unity at all conditions. This would not be expected to be very accurate at the pressures of interest in this application, but it is often the “default” calculation method in engineering software.

The second model was the Peng-Robinson equation of state [16]. Because of the importance of water in the system of interest, the special “alpha” function for water introduced later by Peng and Robinson [17] was employed. The calculation of fugacity coefficients from the Peng-Robinson equation of state is described elsewhere [1,16].

Definition of Conditions for Calculation

A “baseline” set of conditions was established for the calculations, based on sponsor input and representing one proposed IGCC design. This baseline condition was a temperature of 495 K, a pressure of 4.5 MPa, and the following dry composition of synthesis gas: 41 % CO ; 39 % H_2 ; 18 % CO_2 ; 1 % Ar; 1 % N_2 . While the result of

Table 1: Equilibrium Liquid (x_i) and Vapor (y_i) Mole Fractions for the Baseline Case (495 K, 4.5 MPa), with Vapor Fugacities Computed by the Ideal-Gas (IG), Virial (Vir), and Peng-Robinson (PR) Methods.

i	$x_i(\text{IG})$	$x_i(\text{Vir})$	$x_i(\text{PR})$	$y_i(\text{IG})$	$y_i(\text{Vir})$	$y_i(\text{PR})$
H ₂ O	0.9986	0.9988	0.9989	0.4817	0.5731	0.5666
Ar	6.87×10^{-6}	6.15×10^{-6}	5.96×10^{-6}	0.0052	0.0043	0.0043
H ₂	2.98×10^{-4}	2.72×10^{-4}	2.68×10^{-4}	0.2026	0.1668	0.1693
N ₂	4.89×10^{-6}	4.38×10^{-6}	4.32×10^{-6}	0.0052	0.0043	0.0043
CO	2.87×10^{-4}	2.56×10^{-4}	2.53×10^{-4}	0.2131	0.1754	0.1780
CO ₂	7.58×10^{-4}	6.32×10^{-4}	6.14×10^{-4}	0.0922	0.0762	0.0774

most interest (H₂O mole fraction in the equilibrium vapor phase) is relatively insensitive to the total amount of water in the system (as long as there is enough for a liquid phase to form), all calculations assumed five moles of H₂O per mole of dry gas.

In order to examine a range of conditions, flash calculations were performed along the 495 K isotherm at pressures above and below 4.5 MPa, and along the 4.5 MPa isobar at temperatures above and below 495 K.

Results

Table 1 shows the calculated vapor-liquid equilibria for the baseline case, not only for the model developed here but also for the two alternative vapor-phase fugacity models.

Figures 1 and 2 show the calculated water content in the vapor phase along the 4.5 MPa isobar and along the 495 K isotherm, respectively. The trend with temperature in Figure 1 is expected; the increase of vapor pressure of water with temperature results in more water in the vapor phase. Similarly, the trend with pressure in Figure 2 makes sense; the partial pressure of water is determined primarily by its vapor pressure as a

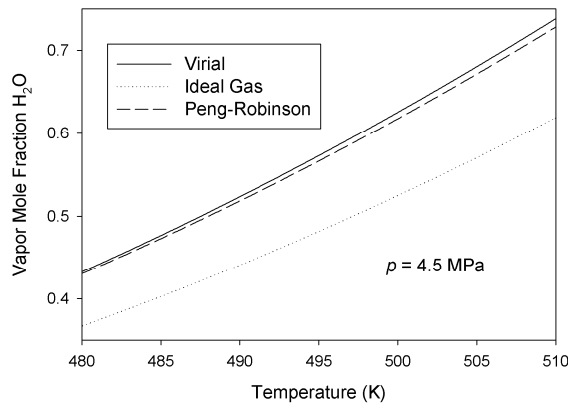


Figure 1: Effect of temperature on equilibrium mole fraction of water in vapor at 4.5 MPa.

function of temperature, so any increase in pressure must come from increasing the amount of other components in the synthesis gas.

The more interesting result is the difference among vapor fugacity methods. The rigorous calculation from virial coefficients produces a vapor mole fraction of water much larger than would be obtained from an ideal-gas assumption. In thermodynamic terms, this can be understood by looking at the fugacity; the function $f_i = \phi_i y_i p$ must be equal in the equilibrating phases. The vapor-phase nonideality in this case reduces the fugacity coefficient ϕ_i of water below its ideal-gas value of unity (to about 0.8 at these conditions), requiring a higher mole fraction of water y_i to produce the same fugacity required by the condition of equilibrium with the liquid phase.

Perhaps surprisingly, the Peng-Robinson equation, which is typically considered unreliable for aqueous systems, gives vapor-phase water contents very close to those from the more rigorous calculation. Apparently the inclusion of the special water “alpha” function, which serves to describe pure-water properties correctly, captures most of the important influences on the vapor fugacity of water in these mixtures.

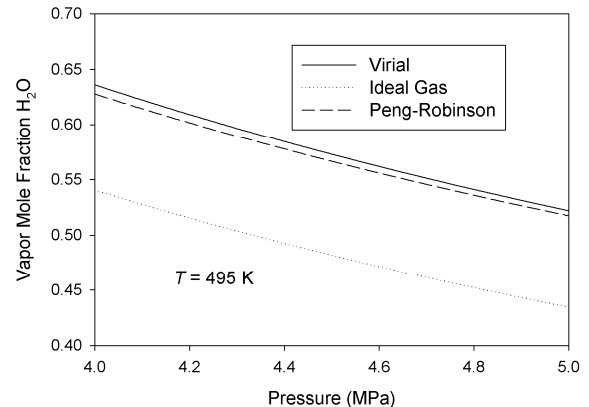


Figure 2: Effect of pressure on equilibrium mole fraction of water in vapor at 495 K.

Uncertainty and Sensitivity Analysis

There are a variety of uncertainties in the liquid-phase fugacity model, such as in the Henry's constants for gas solubility. However, these produce negligible uncertainty in the equilibrium water content of the vapor phase, which is the quantity of interest here.

The vapor-phase model has two main sources of uncertainty (all uncertainties in this paper are expressed as expanded uncertainty with coverage factor $k=2$, which corresponds approximately to a 95 % confidence level). The first is the uncertainty in the virial coefficients; in most cases, these uncertainties were available from the original sources. These were also relatively small, with the largest contribution being from the second virial coefficient for pure water [8], which contributes about 0.002 to the uncertainty for the water vapor mole fraction.

The largest source of uncertainty is the truncation of Eq. (2) after the second virial coefficient B . The magnitude of possible error can be estimated by using approximate values for the third virial coefficient C ; in particular, enough information exists to make this estimate for the H₂O-CO₂ binary mixture. As a result of this calculation, it can be estimated that the omission of higher virial coefficients causes an uncertainty of 0.005 to 0.01 in the water vapor mole fraction. Most of this is due to omission of the higher virial coefficients of pure water, and the test calculations suggest that our calculations truncated at the second virial coefficient probably slightly underestimate the true equilibrium water content of the vapor.

The sensitivity of the vapor-phase water content to synthesis gas composition was also examined by perturbing the input gas composition and examining the resulting changes. It was found that such effects are small, with additional CO₂ (leaving constant the relative proportions of the other gases) slightly increasing the water in the vapor, additional H₂ slightly reducing it, and additional CO having almost no impact.

More details of the uncertainty and sensitivity calculations are found in [1].

Comments on Practical Calculations

While the scope of this project was limited to calculations at fixed temperature and pressure, a closer approximation to the industrial situation would be what is known as an "adiabatic" flash calculation, in which the inlet vapor and liquid

streams are brought together at a fixed pressure and the outlet temperature and vapor and liquid compositions are determined under the constraint of constant enthalpy. We can offer some qualitative guidance regarding how the results of this work would translate into such a situation.

Because the solubility of the synthesis gas in the water is small, the enthalpy balance will be dominated by the vaporization of the water. More vaporization will result in more evaporative cooling; this will be attenuated somewhat by the lower vapor pressure of the water as the temperature decreases. For a given ratio of quench water to synthesis gas, methods that underestimate the equilibrium water content of the vapor at a fixed temperature and pressure (such as the ideal-gas assumption) will overestimate the outlet temperature from the quench step in an adiabatic situation.

Another consideration for practical use is the common use of process simulation software, which typically would not have available the rigorous calculations used in this work. However, most simulation software would have the Peng-Robinson equation, which as we have shown is adequate for this calculation provided the water-specific "alpha" function [16] is used. It is likely that other modern equations of state (Soave-Redlich-Kwong, etc.) that had been modified in their attractive term to give accurate properties for pure water would be similarly adequate, but no additional equations of state were tested in this work.

It should be noted, however, that it is typical in process simulation usage to use the Peng-Robinson equation (or similar equations of state) not only for the vapor fugacity but also for the liquid phase. Such an approach would give results significantly in error for the solubility of the gases in the liquid phase (test calculations indicated that solubilities could be in error by a factor of 2). If the liquid-phase solubility is not a quantity of interest, then that is not a problem. If accurate solubilities are needed, it will be necessary to use a more accurate liquid-phase model – this could involve use of Henry's law or perhaps adjustment of binary Peng-Robinson parameters to match data for Henry's constants at the temperatures of interest.

Industrial situations will also contain other components in trace amounts, such as H₂S and NH₃. The inclusion of H₂S in the present model would be straightforward; its Henry's constant in water is known with fair accuracy [2], and the vapor-phase interactions could be estimated. Including NH₃, however, would be significantly more difficult due to its acid-base reaction with CO₂ and/or H₂S when

dissolved in water. Rigorous modeling of systems with NH_3 would involve superimposing the liquid-phase chemical reaction on the phase-equilibrium calculation, perhaps in the same manner as for “sour water” systems [18,19]. However, in cases where the liquid composition is not of interest and the number of moles of NH_3 is small compared to the number of moles of acid gases, it could be acceptable to ignore these acid/base effects.

Summary and Conclusion

Vapor-liquid equilibrium calculations, rigorous at the level of the second virial coefficient, have been performed for a representative synthesis gas with water. Such calculations can help in the design of IGCC power plants.

For these calculations, key data are the cross second virial coefficients $B_{ij}(T)$ for pair interactions involving water. These data are for the most part not available experimentally, but they can be calculated with suitably small uncertainties from potential-energy surfaces obtained from *ab initio* quantum methods. This illustrates the utility of computational chemistry for deriving accurate thermodynamic properties for systems containing small molecules, particularly for mixtures containing water.

The calculations show that an ideal-gas assumption seriously underestimates the amount of water in the equilibrium vapor. With nonideality correctly taken into account, the water content in the vapor can be determined with an uncertainty of 1 % or less at typical conditions. The commonly used Peng-Robinson equation of state can also provide accurate results, as long as a water-specific “alpha” function is used.

The main room for improvement in these calculations would be the inclusion of higher-order virial coefficients. The most important of these for this particular problem would be the third virial coefficient $C(T)$ for pure water, for which limited experimental data exist. The improvement that could be obtained would be limited by the relatively large uncertainty of $C(T)$, as evidenced by the fact that two sources for correlated values [6,20] differ by roughly 25 % in the temperature range of interest here.

For many engineering purposes, the approximately 1 % uncertainty obtained in this work (and the uncertainty obtained from the Peng-Robinson equation of state, which seems to be similar) should be sufficient, especially for the preliminary evaluation of design alternatives.

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