## The need for reliable data in computational thermodynamics

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#### Abstract

Computational methods have become indispensable tools for efficient development and processing of new materials and have led to the new discipline of integrated computational materials engineering (ICME). The CALPHAD (calculation of phase diagrams) method has been identified as one of the pillars of ICME. The CALPHAD method, originally developed to model thermodynamic properties and phase diagrams, uses extrapolation methods for the functions of binary and ternary systems that enable the calculation of the properties of higher order systems. The CALPHAD functions are built to a large extent on available experimental data for these binary and ternary systems. To ensure reliability of the results from CALPHAD calculations, it is necessary to critically evaluate the experimental data that are being used for developing the CALPHAD functions. This review presents a brief overview of the CALPHAD method and its models, summarizes the data that are needed and the criteria that need to be applied for the evaluation of these data.

Keywords: CALPHAD, computational thermodynamics, computational data, experimental data, phase equilibria data, thermochemical data, thermophysical data

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#### **1 INTRODUCTION**

Phase diagram data provide essential information for materials and process development. However, most phase diagrams are two-dimensional representations of binary and ternary systems with composition, temperature or pressure as variables, while most engineered materials consist of four or more components. Because of this, classic phase diagram representations can only provide initial guidance. The calculation of phase equilibria or computational thermodynamics is extremely well suited to overcome this limitation because the conditions for the calculation can deal with higher order systems. Since the calculation of phase equilibria is based on the thermodynamic properties of the phases in the system the calculation can also provide data of the thermodynamic properties, such as enthalpy, heat capacity and chemical activities.

The methods employed in computational thermodynamics can be grouped into three categories: firstprinciples or ab initio methods, atomistic calculations or simulations and calculations using semiempirical approaches. While the first two approaches operate on the atomistic level and primarily treat single phases, semi-empirical approaches deal easily with the properties of the multiphase macroscopic body. Semi-empirical approaches are also computationally significantly less expensive than the atomistic level methods. Each of these methods needs experimental data for validating the results from the calculations and some also need data to develop the functions that are being used in the calculations.

The methodologies used by the semi-empirical approaches depend greatly on the class of material being modeled. The present article will focus on the semi-empirical modeling using the CALPHAD (calculation of phase diagrams) method and the data that are needed for model parameter development. Since its inception, the CALPHAD method has evolved into an essential tool for computational materials and process development [1]. The strength of this method is its predictive power for multicomponent-

multiphase systems with solution phases. CALPHAD databases were originally thermodynamic databases with a collection of the descriptions of the Gibbs energy functions of the individual phases. However, with time the properties covered by CALPHAD-type databases have been expanded to include other phase-based data, such as diffusion mobilities and molar volume, and the extension to other phase-based properties is being discussed [2]. The functions in these databases describe the properties of the unary, binary and, maybe, ternary sub-systems constituting the full multicomponent system, and are usually obtained by fitting model parameters to experimental data. High-quality databases are key for reliable predictions.

For reliable description of solution phases, it is essential that the model functions describe the phases from 298 K to 6000 K [3] and over the entire composition range even if a phase does not occur as stable phase at all compositions and temperatures. This poses a significant challenge for the parameter development. For reliable description of phases outside their stability range, experimental data for the metastable states are invaluable. In recent years, experimental data have been increasingly supplemented by data from other computational methods, such as density functional theory (DFT). Although such first-principles methods can predict data with little a-priori input, comparison of their predictions with data from experimental measurements is still needed for validation.

It should be noted that the CALPHAD method focusses on modeling of inorganic materials, particularly alloys, similar approaches are used for other material classes, such as geochemical systems [4] or small organic molecules [5].

#### **2 THE CALPHAD METHOD**

Phase diagrams are graphical representations of the minimum of the Gibbs energy in the compositiontemperature-pressure space. Therefore, modeling the thermodynamics, i.e., the Gibbs energy functions of phases, enables calculation of phase equilibria and boundaries between different equilibria. The

CALPHAD method uses a number of different models to describe the Gibbs energies of the individual phases that are based on the underlying physics. The model parameters are fitted to experimental and computational data, a process which is often called thermodynamic assessment or optimization of a system. Descriptions of unary, binary and ternary systems are collected in a file that is usually referred to as a CALPHAD database. To build databases for multicomponent systems, it is imperative that a consistent description of the pure elements is used in all the multicomponent systems in which they occur. Currently, most assessments use the 1991 SGTE (Scientific Group Thermodata Europe) database of the pure elements [3, 6]. The descriptions of binaries can be combined for the prediction (extrapolation) of ternary systems which then can be combined for the prediction of quaternary systems and so on.

For the calculation of phase equilibria, the Gibbs energy of the entire system is minimized for the given conditions. Different approaches have been used, such as the use of a Lagrange function [7, 8], grid minimization [9] or a combination of both [10]. The calculation of metastable equilibria is possible by removing one or more of the stable phases from the calculation. A list of free and commercial<sup>†</sup> CALPHAD software is provided in Table 1. Most commercial software suppliers offer databases for commercial alloy classes and a number of free databases, such as the COST 507 database for light metal alloys [11] or the open MatCalc databases [12] can be found on the internet.

#### 2.1 The CALPHAD hierarchy

CALPHAD databases are collections of the descriptions of the unary, binary, ternary and, maybe, quaternary systems constituting a multicomponent system. A ternary system is described by combining the descriptions of the three binary sub-systems and, if necessary, adding ternary phases and ternary

<sup>&</sup>lt;sup>+</sup> Commercial products are identified in this paper for reference. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

excess parameters to the description to describe deviations from the extrapolation. For the description of a quaternary system the descriptions of the four ternary sub-system are combined. For quaternary systems it is rarely necessary to add quaternary excess parameters because experience has shown that quaternary excess parameters are rarely needed to fit available data. This hierarchical structure of the description of a multicomponent system is very efficient for the development of databases for the application to commercial alloys that may contain six or more elements. Unfortunately, this convenience comes also at a price because each multicomponent system depends on the individual subsystems constituting it, i.e., a number of ternary systems in a multicomponent database will have one binary system in common and, therefore, the descriptions of all these ternary systems must be based on the same description for this binary system to enable calculations in the multicomponent system. The CALPHAD hierarchy is illustrated in Fig. 1. The same applies of course to the descriptions of the unaries making it potentially necessary that the descriptions of systems need to be re-adjusted if parameters of sub-systems are changed. This hierarchy may be viewed as a major weakness of the CALPHAD method. However, it is also its strength because the same hierarchy provides knowledge about higher component systems just from the descriptions of binary and, maybe, ternary sub-systems constituting them. This knowledge can be used to identify critical composition-temperature regimes for efficient experimental investigation of a system.

## 2.2 CALPHAD model structure

Most CALPHAD models for the composition dependence are based on the compound energy formalism (CEF) [13] where different species, i.e., atoms, molecules, ions or vacancies, occupy the sublattices in a phase. Commonly used models are actually special cases of the CEF. For example, stoichiometric phases are phases with only one species on each sublattice and regular-type solutions have only one sublattice. Some models describe phases with internal equilibrium, e.g., charged or molecular species or the same species occur on several sublattices in the CEF.

The general equation for the Gibbs energy of a phase,  $G^{arphi}_m$  , is:

$$G_m^{\varphi} = {}^{srf} G_m^{\varphi} + {}^{cfg} G_m^{\varphi} + {}^{phy} G_m^{\varphi} + {}^{exs} G_m^{\varphi}$$
(1)

where  ${}^{srf}G^{\varphi}_{m}$  is the surface of reference (or contribution of the pure end-members),  ${}^{cfg}G^{\varphi}_{m}$  is the configurational term, assuming ideal mixing of the constituents on each sublattice,  ${}^{phy}G^{\varphi}_{m}$  is a term describing physical phenomena, such as magnetism and  ${}^{exs}G^{\varphi}_{m}$  describes deviations relative to the first three terms. The gas phase lacks deviations from the first three terms and has only one sublattice. All these terms can be functions of temperature, pressure and composition although pressure is rarely used in CALPHAD descriptions.

The excess Gibbs energy is composed of the contributions of the excess Gibbs energies of the constituent binary, ternary, and maybe quaternary, sub-systems of a multicomponent systems:

$${}^{exs}G^{\varphi}_{m} = \sum_{i}^{\frac{n!}{2!(n-2)!}} {}^{exs}_{bin}G^{\varphi}_{i} + \sum_{i}^{\frac{n!}{3!(n-3)!}} {}^{exs}_{tern}G^{\varphi}_{i} + \dots$$
(2)

The excess parameters are frequently represented by polynomials of species compositions.

It is beyond the scope of the present paper to present details of the individual CALPHAD models. The temperature dependence of the Gibbs energy is either described by a polynomial [3] or by an Einstein or Debye model in combination with a simple polynomial [14] for the solid state and a two-state model for the liquid [15]. The Debye model is rarely used because it requires integration of the function which can only be done numerically. The pressure dependence of the Gibbs energy of the condensed phases is rarely considered for the modeling of alloy systems but becomes important when systems are modeled for geological applications [16]. Two workshops were dedicated to the modeling of the temperature and pressure dependence in 1995 and 2013 [17, 18].

The composition dependence of most phases is described with the CEF [13]. Specific variants of the CEF describe ordered and disordered states of phases [19, 20] or short-range order in the liquid phase [21]. Other models such as the modified quasi-chemical model for the liquid phase [22, 23] or the cluster site approximation for order-disorder transformation in close packed phases [24] are specific to certain CALPHAD software. A recently developed variant of the CEF, the effective bond energy formalism [25], holds promise to better predict the phases when only functions form the binary systems are used in the description of the multicomponent system.

Since heat capacity data are not commonly available for solutions and intermediate phases the model parameters are usually the enthalpy and entropy of the end-member compounds and the Neumann-Kopp rule [26], i.e., the average value of heat capacities of the pure elements, is used to describe the heat capacity.

## 2.3 Model parameters

Originally the model parameters of the Gibbs energy functions were determined from experimental data for the system. Phase diagram and thermochemical data are considered to obtain an optimized model parameter set that fits all types of data. Increasingly experimental data are being supplemented by computational data from atomistic methods [27, 28]. Data from these computational methods are particularly valuable if they are needed for the model description but cannot be determined experimentally, such as the Gibbs energy of formation of a hypothetical metastable end-member compound in a CEF model description. The available data must be critically evaluated and assigned a weight to obtain a meaningful description of the system. The model parameters are usually adjusted using mathematical methods by fitting them to selected data. Mathematical methods, such as the leastsquares method of Gauss [29, 30], the Levenberg-Marquardt method [26] or Bayesian estimation method [31, 32], are efficient and have been implemented in various CALPHAD software. These

methods are particularly needed for the parameter optimization in complex systems and/or systems for which a multitude of data is available. It is imperative to verify the validity of the thermodynamic descriptions of the individual phases during the assessment. It is equally important that the phase diagram and thermochemical properties are reproduced without artifacts over wide temperature and composition ranges and that metastable phase diagrams where one or more phases are absent are reasonable [33]. Since one set of functions is used to calculate thermochemical and phase equilibria data, the data are self-consistent. Recently work has begun to add uncertainty quantification to the results from CALPHAD parameter assessments [32, 34, 35].

## 2.4. The CALPHAD challenge

For the use of CALPHAD descriptions in the calculation of multicomponent alloy systems the descriptions of most phases must cover the entire composition and temperature space of a system. This has as a consequence that descriptions of the different states of the pure elements are needed for temperature regimes where they are not stable, e.g., liquid below the melting temperature. This is illustrated in Fig. 2 for the Al-Ni system. The face centered cubic (FCC) solid solution which occurs on both sides of the phase diagram is described as mixture of FCC-Al and FCC-Ni. Although pure Al melts at 933 K it is dissolved in the Ni-rich solid solution which is stable to 1728 K. Likewise, the liquid is described as mixture of liquid-Al and liquid-Ni with Ni which freezes as pure Ni at 1728 K being dissolved in Al-rich liquid freezing in a eutectic at 913 K.

This requires that the descriptions of the pure elements need to be extrapolated far outside the stability ranges of the different phases and must also include the amorphous phase for the liquid state. This poses an enormous challenge since experimental data for these metastable regimes are hard, if not impossible, to obtain. However, simple extrapolation of the functions of the stable regions may result in undesired artifacts, such as the solid becoming stable again far above the equilibrium melting

temperature or the liquid becoming stable far below the equilibrium melting temperature. In 1991 SGTE [3] adopted an "interim" solution for the unaries by forcing the heat capacity function of the solid to approach that of the liquid above the melting temperature and that of the liquid to approach that of the solid below the melting temperature. Although this resulted in unphysical kinks and bumps in the heat capacity curves these descriptions worked sufficiently well to enable the development of multicomponent thermodynamic databases for commercial alloy systems. Still, many phases are described using the Neumann-Kopp rule [26] and these unphysical kinks and bumps also occur in the heat capacity curves of these phases. Figures 3(a) and 3(b) show the heat capacity curves of pure Al and Ni. The heat capacity curves for three compositions in the binary Al-Ni system resulting from the Neumann-Kopp rule are shown in Fig. 3(c). The curves show that the kinks and bumps occur in the stable regions of the solution phases. This prompted efforts to develop new formalisms for the pure elements [14, 15]. However, development of the new unary descriptions will be a multi-year effort for the CALPHAD community and because new descriptions of the unaries may require that already existing descriptions of some binary and higher order systems need to be at least readjusted. Therefore, great care must be taken to develop the highest quality descriptions possible and data from methods other than conventional experimental methods are needed.

#### 2.5 More phase-based properties

The CALPHAD name indicates that this method was originally established for the calculation of phase diagrams and thermodynamics. However, the general approach taken in this method is suitable to describe many other phase-based materials properties using models that are based on the underlying physics. The CALPHAD method was first expanded to describe multicomponent diffusion processes in terms of the product of diffusion mobility functions and thermodynamic factors [36]. The thermodynamic factor is obtained from CALPHAD thermodynamics and the mobility functions are obtained from separate diffusion assessments like those being carried out for the thermodynamics. The

CALPHAD description of the liquid phase has been employed in the determination of surface tension [37] and viscosity of liquid alloys [38] and slags [39]. Not too long ago the CALPHAD method was further expanded to include molar volume, thermal expansion and bulk modulus. The CALPHAD modeling of these properties can be done either within the framework of an equation of state [40] or independent phase properties [41]. The general approach taken by the CALPHAD method also makes it suitable to describe other, non-thermodynamic phase-based properties, such as electric and thermal conductivity, optical, thermoelectric or acoustic properties of materials [42]. However, little or no work has been carried out using the CALPHAD method for the modeling of these properties.

Some phase-based properties can be anisotropic depending on the crystal structure of the phase. For proper modeling of these properties it needs to be decided whether the properties of the bulk, i.e., averaged directional properties, or the directional dependence of these properties is considered. In addition, for modeling the behavior of real materials interphase properties must also be considered [42]. Although modeling of these properties will gain importance it is beyond the scope of this article to review the data that are needed for the parameter assessment of these properties.

## **3 DATA FOR PARAMETER ASSESSMENT**

#### 3.1. Experimental data

The hierarchy of the CALPHAD method necessitates that the description being used for database development are of the highest quality and consistency possible. The quality of a description is determined by how closely the selected model represents the underlying physics and how well the description can reproduce the experimental data. Therefore, high quality experimental data are the essence for developing high quality CALPHAD descriptions. Derived data, such as those obtained from a Gibbs-Duhem integration, should be avoided because they are prone to have accumulated errors. It is highly desirable to use only data that were directly measured and are reported in numerical form.

Unfortunately, data are too often only communicated as fitted functions and/or in graphical form resulting in a loss of data quality. A fitted function may hide variations in the original data that may have a physical meaning and digitization of data from graphical representations is likely to increase the error.

Data are not only needed for the parameter determination they also play an important role in the model selection, i.e., crystallographic data for solids to determine the number of sublattices and their occupation or data for properties that indicate short-range order for liquids, such as enthalpy of mixing or viscosity. Therefore, a critical evaluation of the available experimental data is at the core of a CALPHAD parameter assessment. In addition to data for the equilibrium state, data for metastable states are of great importance because they ensure reasonable extrapolation behavior of the CALPHAD functions.

The data that are commonly used for the model parameter development are phase diagram, thermochemical and thermophysical data and the experimental methods commonly used for their determination are summarized in Table 2. Only quantities that can be directly obtained from the experimental method are listed in the table. References for individual methods are also provided in Table 2 as examples. The ASM handbook on materials characterization [59] and the book by Zhao [60] cover many methods that are used for the determination of phase equilibria.

#### 3.1.1 Data from containerless methods

Containerless methods have the great advantage that they can be used to measure properties under conditions that would be not possible if the materials would have to be encapsulated or contained in a crucible. Without the presence of encapsulation or crucible material there cannot be any chemical reaction with the container materials because of very high temperatures, or heterogeneous nucleation from sites in the material. Pulse heating methods allow measurements at extremely high temperatures

while levitation methods make it possible to measure the properties of extremely undercooled liquids. Data obtained from these methods will be extremely valuable for the development of the new Gibbs energy functions for the unaries. For example, these methods can provide heat capacity data for refractory materials far above their melting temperature or for undercooled liquids far below their freezing temperature. Fig. 4(a) shows the experimental specific enthalpy of liquid Ti-6Al-4V (percent mass fraction) measured with a pulse heating method from 1700 K to 700 K above the melting temperature [61] compared to values calculated using the description from Lindahl et al. [62]. The description by Lindahl et al. is an extrapolation of the descriptions of the binary sub-systems and the Neumann-Kopp rule was used to describe the heat capacity. The difference in slopes between the calculated and measured values for the liquid phase indicates that either the heat capacity functions of the pure elements need to be re-evaluated or a term to describe the excess heat capacity needs to be introduced. Ternary excess terms for enthalpy and entropy may be necessary to correct the discrepancy in melting temperatures. Fig. 4(b) shows the experimental heat capacity [63] of undercooled liquid Au compared to results using a description with the new CALPHAD formalism for the liquid phase [15]. With the new CALPHAD model the heat capacity tends to increase below the melting point and experimental data are needed to evaluate how realistic this trend is.

#### 3.1.2 Data evaluation

For a CALPHAD assessment it is desirable to collect all relevant data from the literature for a critical evaluation. Criteria for the evaluation of experimental data are:

#### Purity of starting materials:

For many metals the amount of impurities stated by the supplier does not include interstitial elements, for example, 99.99 % (metal basis) Cr may contain 0.5 % (atomic) oxygen resulting in about 1 % (volume)  $Cr_2O_3$  in the microstructure.

- Reactions with the environment
  - Evaporation
  - Reaction with crucible and/or encapsulation material
  - Reaction with impurities in protective gas atmosphere
- Sample preparation prior to the measurement
  - Heat treatment: Sufficient to reach equilibrium?
  - Quenching: Sufficient to freeze in high temperature state?
- Quality of reference materials
- Calibration of the instrument
- Analysis of the measurement results
- Report of error bars or confidence intervals
- Use originally measured data, never derived data, such as data from a Gibbs-Duhem integration

During the evaluation of the data it is necessary to keep in mind that newer data do not necessarily imply that the quality of the data is better and always to ask what could have gone wrong during the experiment. This may help to find possible causes if inconsistencies between phase diagram data and thermochemical data are noticed and help with the decision of which data set should be removed from the parameter assessment.

## 3.2 Computational data

Today the data used for the assessment of CALPHAD model parameters are increasingly supplemented by data from atomistic computational methods, such as density functional theory (DFT) [27, 64], phonon calculations [65, 66] or atomistic/molecular simulations [15, 67]. Results from DFT calculations have been proven to be very useful for obtaining values for the formation enthalpies for the end-member compounds of the CEF, particularly since the majority of these end-member compounds are hypothetical and not stable. Results from phonon calculations have been used to develop the extension

of the 1991 SGTE functions from 298 K to 0 K [68] and Gibbs energy functions for polymorphs [69]. Atomistic/molecular simulations can provide values for the liquid and amorphous phase [15] and the superheated solid [70]. However, data from computational methods still need, whenever possible, experimental verification and should, therefore, be used with some caution.

## **4 SUMMARY**

Computational thermodynamics is an essential tool for fast exploration of the materials and processing space during the development of new materials. The CALPHAD methods takes a special role among the computational thermodynamics methods in that it is currently the only method that can treat multicomponent-multiphase systems with solution phases. In addition, since the CALPHAD method is mostly based on experimental data, i.e., phase diagram and thermochemical data, makes it possible to obtain realistic phase diagrams and other data.

Computational methods and experimental measurements are linked closely: computational methods enable identification of regimes where critical experiments will provide a maximum of information, help in the analysis of experimental data while experimental data are indispensable for model parameter development and validation and verification of the results.

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# TABLES

Table 1: CALPHAD software (web sites viewed 2019-07-19)

Software	Web site		
Free software			
OpenCalphad	http://www.opencalphad.com/		
pycalphad	https://pycalphad.org/docs/latest/index.html		
Commercial software			
CaTCalc	http://www.materials-design.co.jp/catcalc/index_E.html		
FactSage	http://www.factsage.com/		
MatCalc	https://www.matcalc.at/		
MTDATA	http://resource.npl.co.uk/mtdata/downloads.htm		
Pandat	http://www.computherm.com/		
Thermo-Calc	https://www.thermocalc.com/		

Table 2: Methods of data determination

Classes of methods	Properties	Reference	
Phase diagram data			
Thermal analysis (TA):	Phase transitions	General:	
Differential thermal analysis (DTA)		Speyer [43]	
Differential scanning calorimetry		Höhne et al. [44]	
(DSC)			
Thermogravimetry (TG)			
Dilatometry			
Interferometry			
Microscopy:	Number of phases	Amelinckx et al. [45]	
Optical microscopy	Phase identities	Hawkes and Spence [46]	
Scanning electron microscopy		Goldstein et al. [47], Leng	
Transmission electron microscopy		[48]	
Diffraction methods:	Number of phases	Mittemeijer and Welzel [49]	
X-ray diffraction (XRD)	Phase identities		
Neutron diffraction			
Electron backscatter diffraction		Randle [50]	
(EBSD)			
Spectroscopy methods:	Phase compositions,	Goldstein et al. [47]	
Wavelength dispersive X-ray	Tie lines	Leng [48]	
spectroscopy (WDS)			
Energy dispersive X-ray spectroscopy			
(EDS)			
Electron probe microanalysis (EPIVIA)			
Calorimetry:	Enthalpy of mixing	Gallagher [51]	
Solution calorimetry	Enthalpy of formation		
Drop calorimetry	Enthalpy content		
Reaction calorimetry	Real Capacity		
Differential scanning calorimetry	Transformation Enthalpy	Höhne et al [44]	
	Heat capacity		
Flectromotive force measurements	Activity	Inser et al [52]	
(emf)	Partial Gibbs energy		
Vapor pressure measurements	Vapor pressure	Ipser [53], Hilpert [54]	
	Partial Gibbs energy		
Containerless methods:	Many thermopysical	Cezairliyan et al. [55]	
Pulse heating methods	properties	Boivineau and Pottlacher [56]	
Levitation methods		Millot et al. [57]	
		Brillo et al. [58]	

#### **FIGURE LEGENDS**

Fig. 1: The CALPHAD hierarchy for a 6-component (senary) system. Modification of the description of one element affects the descriptions of 5 binary and 10 ternary systems and modification of one binary affects 4 ternaries.

Fig. 2: The Al-Ni phase diagram [19]. The vertical lines at  $x_{Ni} = 0.10$  and  $x_{Ni} = 0.90$  indicate the temperature range where the description of metastable liquid Ni and FCC-Al is needed.

Fig. 3: Heat capacity curves for (a) pure Al and (b) pure Ni showing an unphysical slope change at the melting temperature [3]. (c) The slope changes in the heat capacities seen at the melting temperatures of pure Al and Ni of solution phases in the Al-Ni system are artifacts of the application of the Neumann-Kopp rule. The heat capacity shown for  $x_{Ni} = 0.1$  and  $x_{Ni} = 0.5$  above the solidus temperature and that for  $x_{Ni} = 0.9$  below the eutectic temperature is that of the metastable phase.

Fig. 4: (a) Experimental specific enthalpy of Ti-6Al-4V (percent mass fraction) from Boiniveau et al. [61] compared to data calculated with the description of Lindahl et al. [62]. No excess parameters were used for the heat capacity. (b) Heat capacity of liquid Au with experimental data [63] for the undercooled liquid compared to results using the new CALPHAD formalism [15].

**FIGURES** 



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(a)



(b)



(c)

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(a)



(b)

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