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SHORT COMMUNICATION

On the Information and Methods for Computing Phase Equilibria and Thermodynamic Properties

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Abstract−The Helmholtz free energy or an equation of state relating temperature, pressure, volume and composition plays a key role in the calculation of phase equilibria and thermodynamic properties. Such information is usually available for vapor, partially available for liquids, and rarely available for solids. Depending on the information available, different methods are used for properties calculation. In this study, various methods were systematically presented and their relations with available information were comprehensively discussed.

Key words: Helmholtz Free Energy, Equation of State, Excess Gibbs Function, Phase Equilibria, Thermodynamic Properties

INTRODUCTION

Thermodynamic analysis requires the computation of phase equilibria and/or physical properties such as volumes, enthalpies, entropies, etc., of real pure fluids and their mixtures. The temperature dependence of a property is simply evaluated along a path of the ideal gas state with the ideal gas heat capacity and we concentrate on the residual properties that reflect the isothermal change from the ideal gas to real fluids. Given a PVT equation of state (EOS) that describes the PVTx behavior for a wide range of density from the ideal gas to solid, residual properties are readily calculated by well-established methods [Prausnitz et al., 1998]. Information needed for phase equilibria and properties may be obtained from an EOS such as SRK or PR developed on empirical bases. However, the PVT EOS is not a fundamental equation and the derivation of equations for other thermodynamic properties is less convenient. Various mixing rules were proposed to describe mixture properties more accurately in using EOSs.

Instead of an EOS, the Helmholtz free energy may be given for fluids. Most recent EOS models that have statistical mechanical basis are derived from Helmholtz free energy. Residual properties are also derived from Helmholtz free energy. The fundamental and comprehensive information is given by Helmholtz free energy as a function of temperature, volume and composition for fluid phases. Since these variables are canonical variables, other thermodynamic properties are obtained most readily. The statistical mechanical derivation of real fluid properties begins with the configurational partition function [Reed and Gubbins, 1973]. Once the configurational partition function is known, the Helmholtz free energy is derived, from which expressions for other thermodynamic properties follow. The configurational partition function is solved for low-density gases to give the virial equation of state [Reed and Gubbins, 1973]. However, the solution is a formidable task even for simple dense fluids. Thus, a general practice for complex molecules in fluid phases is to represent the configurational Helmholtz energy in the mean field approximation as a sum of various contributions. Recently, the applicable ranges of these methods have been extended to polymers, hydrogen-bonding systems and electrolyte solutions. The contributions from the hard sphere interaction, the dispersion interaction, the chain formation, and the association are included in the SAFT model [Chapman et al., 1989]. Alternatively, starting from molecular chains in a lattice frame various contributions are incorporated to describe real fluid behaviors as in lattice fluid models [Sanchez and Lacombe, 1976; You et al., 1994; Yoo et al., 1995; Yeom et al., 1999; Oh et al., 2003]. Also, EOSs for electrolytes are developed by further adding long-range interactions.

For liquid phases we may not have an adequate EOS or Helmholtz free energy representation. Empirical PVT correlations are available for pure liquids. But they are generally not suitable for mixtures. Then we would need an excess Gibbs function model, vapor pressure and the saturated liquid volume. Although Gibbs free energy is also a generating function for thermodynamic properties when expressed as a function of temperature, pressure and composition, complete information on Gibbs free energy is usually unavailable. In principle, the pressure derivative of the excess Gibbs function yields the excess volume. However, the excess Gibbs function is generally represented as a function of temperature and composition. The pressure effect on volume is ignored. Thus, it does not have all the information that an EOS has and does not give information on the excess volume. It is used mainly for low-pressure liquids in phase equilibrium calculations.

The Helmholtz free energy or an EOS for fluids does not extrapolate to solid phases. If a solid component constitutes a phase, other information is needed such as vapor pressure, molar volume, heat capacities, the enthalpy change on melting, and/or the triple point temperature. A solid mixture may form a solid solution, in which case the problem becomes more complex.

Thus, depending on the information and the phase of interest, different methods or formulations are developed for property evaluations. Properties calculation methods presented in a research paper or a textbook tend to deal with a specific problem separately and could lead to confusion on the underlying principles, particularly for phase equilibria. The present work is intended to comprehen-

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sively present and discuss the relations for phase equilibria and properties depending on the level of information available.

MOLAR VOLUME

If the Helmholtz free energy is given, a PVT EOS is derived to give,

$$P=-(\partial A/\partial V)_{T,n} \tag{1}$$

The EOS is represented the pressure as a function of temperature, volume and composition for both gases and liquids.

$$P=P(T, v, \{x_i\}) \tag{2}$$

For given T, P, and $\{x_i\}$ the EOS is solved for the molar volume v, which is then used to obtain other thermodynamic properties. In the two-phase region, we can choose the volume either for the saturated liquid or for the saturated vapor. Depending on the choice we have either liquid properties or vapor properties. Alternatively, for an empirical EOS developed without Helmholtz free energy representation we begin with Eq. (2) to solve for v given T, P, and $\{x_i\}$. Molar volumes are needed in the evaluation of chemical potential or fugacity coefficient for phase equilibrium calculations. If an EOS is not available for liquids, we use empirical correlations for pure liquids and for excess volumes at constant temperature or pressure. The primary concern of some models like the PR EOS is to calculate phase equilibria. Thus the calculated liquid volume is generally not accurate.

ENTHALPY AND ENTROPY

Expressions for thermodynamic properties are derived from the Helmholtz free energy. For enthalpy and entropy,

$$H=-T^2(\partial(A/T)/\partial T)_{V,n}+PV \tag{3}$$

$$S=-T(\partial A/\partial T)_{V,n} \tag{4}$$

Or we may start with an EOS to have [Prausnitz et al., 1998]

$$H=\int\left(P-T\left(\frac{\partial P}{\partial T}\right)_{V,n}\right)dV+PV+\sum n_i u^0_{pure,i} \tag{5}$$

$$S=\int\left(\frac{nR}{V}-\left(\frac{\partial P}{\partial T}\right)_{V,n}\right)dV+R\sum n_i \ln\frac{V}{n_i RT}+\sum n_i s^0_{pure,i} \tag{6}$$

where the quantities with the superscript zero denote properties of ideal gases at 1 bar. These equations are used for property changes including those on phase transition and mixing.

When an EOS or Helmholtz free energy is not available for liquid, we use empirical correlations or the excess Gibbs function for excess properties rather than residual properties.

$$H^E=-T^2(\partial(G^E/T)/\partial T)_{P,n} \tag{7}$$

$$S^E=-T(\partial G^E/\partial T)_{P,n} \tag{8}$$

Kehiaian et al. [1991] calculated the excess enthalpy using an excess Gibbs function model. Kang et al. [1998] reported on the EOS approach for excess properties among others. In both approaches the simultaneous calculation of excess enthalpy and phase equilibria were discussed.

PHASE EQUILIBRIA

The condition for phase equilibria is well established.

$$\mu_i^\alpha=\mu_i^\beta \tag{9}$$

If we begin with the Helmholtz free energy, we have the chemical potential by the relation,

$$\mu_i=(\partial A/\partial n_i)_{T,V,n_j} \tag{10}$$

To use the chemical potential relations, the chemical potential difference is often convenient. Subtracting the pure ideal gas chemical potential at the same temperature and 1 bar from both sides of this equation we have

$$\mu_i^\alpha-\mu^0_{pure,i}=\mu_i^\beta-\mu^0_{pure,i} \tag{11}$$

If β phase is pure solid, sometimes following equation is more convenient.

$$\mu_i^\alpha-\mu^0_{pure,i}=\Delta\mu^{sl}_{pure,i}+\mu^l_{pure,i}-\mu^0_{pure,i} \tag{12}$$

The chemical potential change from liquid to solid is discussed later in this paper. For solid solutions an activity term is added on the right hand side.

Instead of chemical potential relation, a fugacity relation is often used, particularly with an empirical EOS. Fugacity is related with chemical potential by the relation,

$$\mu_i=\mu_i^r+RT\ \ln(f_i/f_i^r)=\mu_i^r+RT\ \ln a_i \tag{13}$$

where the superscript r denotes the a reference state. The fugacity ratio is defined as activity. From Eqs. (9) and (13) we have the phase equilibrium conditions written for fugacities [Prausnitz et al., 1998]

$$f_i^\alpha=f_i^\beta \tag{14}$$

regardless of the reference states that are the same or not.

Chemical potential and fugacity are functions of temperature, volume, and composition. Eqs. (9) or (14) are solved for phase equilibrium calculations together with an EOS to find phase volume. The fugacity relation is more convenient with an empirical EOS and they do not depend on reference states. For Helmholtz free energy based models the chemical potential relation is more conveniently derived and used. There are instances in which inter-conversion between different methods are needed.

Chemical potential of phase π is easily converted to fugacity or vice versa.

$$f_i^\pi=P^0\exp[(\mu_i^\pi-\mu^0_{pure,i})/RT] \tag{15}$$

If we have an EOS instead of the Helmholtz free energy, the following relation conveniently determines the fugacity.

$$f_i^\pi=Px_i^\pi\phi_i^\pi \tag{16}$$

where the fugacity coefficient is given by [Prausnitz et al., 1998],

$$RT\ln\phi_i^\pi=\int_\infty^V\left(\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}-\frac{RT}{V}\right)dV-RT\ln\frac{PV}{nRT} \tag{17}$$

An alternative method for obtaining fugacity coefficient is to use chemical potential. From Eqs. (15) and (16),

$$\phi_i^\pi=P^0\exp[(\mu_i^\pi-\mu^0_{pure,i})/RT]/(Px_i^\pi) \tag{18}$$

This method applies to any component in vapor or liquid phase regardless of the stable phase of the pure component at the condition. Thus, the hypothetical liquid state of a pure solid component may be characterized by vapor pressure and molar volume of super-cooled liquid as in the calculation for vapor phase. For low-pressure applications, the ideal gas phase may sometimes be assumed.

We can still write the fugacity of a component in a condensed phase using activity coefficients even if we do not have an EOS or chemical potential.

$$f_i^{\pi}=f_{pure,\,i}^{\pi}x_i^{\pi}\gamma_i^{\pi} \tag{19}$$

where the activity coefficient is from an excess Gibbs function model,

$$RT\ln\gamma_i^{\pi}=(\partial G^E/\partial n_i)_{T,\,P,\,n_j} \tag{20}$$

Since liquid density is only a weak function of pressure in condensed phases, the pressure dependence of activity coefficients is usually ignored.

To obtain the reference fugacity for pure liquid components in Eq. (19), we use Eq. (15) for a pure component if we have chemical potential for pure fluid or Eq. (16) with an EOS.

$$f_{pure,\,i}^{l}=P^0\exp[(\mu_{pure,\,i}^{l}-\mu_{pure,\,i}^{0})/RT] \tag{21}$$

$$f_{pure,\,i}^{l}=P\phi_{pure,\,i}^{l} \tag{22}$$

When chemical potential or EOS is not available, the fugacity of a pure liquid is readily written for a sub-critical fluid component as

$$f_{pure,\,i}^{l}=f_i^{sat,\,l}\exp[\nu_i^l(P-P_i^{sat,\,l})/RT] \tag{23}$$

To use this equation we need vapor pressure, liquid volume and the fugacity coefficient of pure liquid. Phase equilibrium conditions dictate that the fugacity coefficient for saturated liquid is the same as that for saturated vapor. Therefore, we only need EOS for vapor. They cannot be determined experimentally for a supercritical component, but may be obtained by extrapolating vapor pressure and the saturated liquid volume along the vapor-liquid coexistence curve to supercritical region. Based on this concept, Eq. (23) is modified to give

$$f_{pure,\,i}^{l}=f_{pure,\,i}^{l}(P^r)\exp[\nu_i^l(P-P^r)/RT] \tag{24}$$

The fugacity values of a pure component at the reference pressure of 1 bar are available for some common gases as functions of the reduced temperature [Prausnitz et al., 1998]. The relation enables the pure component fugacity at a reference pressure be corrected for high pressures.

Activity coefficients are also obtained from chemical potential or fugacity coefficient. By comparing Eq. (15) and (19) we have

$$\gamma_i^l=\exp[(\mu_i^l-\mu_{pure,\,i}^{l})/RT]/x_i^l \tag{25}$$

and comparing Eqs. (16) and (19) we have

$$\gamma_i^l=\phi_i^l/\phi_{pure,\,i}^{l} \tag{26}$$

The pure component fugacity obtained by using either Eq. (23) or (24) depends on temperature and pressure. The activity coefficient given by Eq. (20) depends on temperature and composition, while that given by Eq. (25) or (26) depends on temperature, pressure and composition. In fact, an excess Gibbs function model generally depends on temperature and composition but not on pressure. Thus, its use is generally limited to low pressure liquids in which the pressure dependence of volume is negligible.

In the Henry's law based applications for a sparingly soluble component in liquid phases, the component fugacity may also be written by the relation.

$$f_i^l=H_ix_i^l\gamma_i^{l*} \tag{27}$$

where H_i is the Henry's constant. The activity coefficient is now in the asymmetric convention, which is related to that in symmetric convention by the relation,

$$\gamma_i^{l*}=\gamma_i^l/\lim_{x_i\to 0}\gamma_i^l=\gamma_i^l/\gamma_i^{l\infty} \tag{28}$$

Comparing Eq. (27) with Eq. (19) we have

$$H_i=f_{pure,\,i}^{l}\gamma_i^{l\infty} \tag{29}$$

Both Henry's law constants and activity coefficients in the asymmetric convention are related with the chemical potential

$$H_i=P^0\exp[(\mu_i^{l\infty}-\mu_{pure,\,i}^{0})/RT] \tag{30}$$

$$\gamma_i^{l*}=\exp[(\mu_i^l-\mu_i^{l\infty})/RT]/x_i^l \tag{31}$$

or with the fugacity coefficients

$$H_i=P\phi_i^{l\infty} \tag{32}$$

$$\gamma_i^{l*}=\phi_i^l/\phi_i^{l\infty} \tag{33}$$

where the superscript ∞ denotes the state at infinite dilution. Clearly, the Henry's constant depends on temperature, pressure and the composition of the solute-free solvent. To correct the Henry's constant at a reference pressure for high-pressure applications, the following relation analogous to Eq. (24) is used.

$$H_i=H_i(P^r)\exp[\nu^{-l\infty}(P-P^r)/RT] \tag{34}$$

This corresponds to the Krichevsky-Kasarnovsky equation [Prausnitz et al., 1998]. The availability of the partial molar volume at the infinite dilution is limited. Unless we have experimental data, we need an equation of state applicable to liquids to obtain the partial molar volume. But then we would not use the Henry's law based method.

Again, a Helmholtz free energy equation or an EOS is needed for solid phases, which is not generally available. Thus, in the well-known method for a pure solid phase, the component chemical potential is calculated by using sublimation pressure and molar volume.

$$\mu_{pure,\,i}^{s}-\mu_{pure,\,i}^{0}=RT\ln(f_{pure,\,i}^{s}/P^0)=RT\ln(P_i^{sat,\,s}\phi_i^{sat}/P^0)+\nu_{pure,\,i}^{s}(P-P_i^{sat,\,s}) \tag{35}$$

from which the following equation is obtained.

$$f_{pure,\,i}^{s}=f_i^{sat,\,s}\exp[\nu_i^s(P-P_i^{sat,\,s})/RT] \tag{36}$$

This equation is similar to Eq. (23) and convenient for use in solid-vapor equilibria if sublimation pressure is available. It can also be used in solid-liquid equilibria if liquid phase fugacity is represented by Eq. (19). The sublimation pressure is usually very low and the fugacity coefficient is assumed to be 1. Fugacity of a pure solid cannot be determined by an equation analogous to Eq. (22) because an EOS does not extend to solid phase.

Another way of representing the fugacity of a pure solid is to use the sub-cooled liquid state and the chemical potential difference between the sub-cooled liquid and solid.

$$f^{s}_{pure,i}=f^{l}_{pure,i}\exp(\Delta\mu^{sl}_{pure,i}/RT) \tag{37}$$

In this form, the equation is conveniently used for a solid component in solid-liquid equilibria where excess Gibbs function models are used for liquid solutions and pressure is low. The fugacity ratio of pure solid to that of pure liquid cancels out when used with Eq. (19). This equation is also useful when we have EOS or Helmholtz free energy for pure sub-cooled liquid that is extrapolated from real saturated liquid. The pure liquid fugacity is evaluated by using Eq. (22), and the chemical potential difference is evaluated as described below. This equation does not involve sublimation pressure and can be used even if the sublimation pressure is negligible. This method was applied for calculating the solubility of essentially nonvolatile solids in supercritical gases [You et al., 1993].

The chemical potential difference between a solid and the hypothetical liquid of the same component is calculated by extending the method of Prausnitz et al. [1998] to high pressure systems along the path: (1) from the system T and P to the saturated solid isothermally, (2) to the triple point along the solid-vapor equilibrium line, (3) the transition form solid to liquid at the triple point, (4) from the triple point to super cooled liquid at the system T along the extrapolated vapor-liquid equilibrium line, and (5) from the super cooled liquid T to the system T and P isothermally.

$$\begin{aligned}\Delta\mu^{sl}_{pure,i}&=\Delta h^{sl}_{pure,i}(T_t)\left(1-\frac{T}{T_t}\right)+\int_{T_t}^{T}\Delta C_p dT\\&\quad-T\int_{T_t}^{T}\frac{\Delta C_p}{T}dT+v^{s}_{i}(P-P^{sat,s}_{l})-v^{l}_{i}(P-P^{sat,l}_{i})\end{aligned} \tag{38}$$

This equation can also be used even if vapor pressures of solid and the hypothetical liquid are negligible. The heat capacity contribution and the phase transition volume are usually small and the equation may be further approximated for low-pressure applications or negligible volume differences by

$$\Delta\mu^{sl}_{pure,i}\approx\Delta h^{sl}_{pure,i}(T_t)(1-T/T_t)=\Delta h^{sl}_{pure,i}(T_t)-T\Delta s^{sl}_{pure,i}(T_t) \tag{39}$$

For low-pressure applications T_m is approximately equal to T_t in above equations. However, at high pressures the dependence of T_m on P may not be negligible and the pressure effect on the chemical potential difference similar to the last term on the right hand side of Eq. (38) need to be included.

If the solid phase is not pure, then a solid solution is assumed.

$$f^{s}_{i}=f^{s}_{pure,i}x^{s}_{i}\gamma^{s}_{i} \tag{40}$$

For the activity coefficient we would need an excess Gibbs function model for solid solutions. An apparent solid mixture may or may not form a solid solution. We have limited information on the non-ideality of solid solutions at present.

ELECTROLYTE SOLUTION

Electrolyte solution merits further attention. Equilibria involving electrolytes are dissociation or dissolution. Volatile electrolytes may be in vapor-liquid equilibria, in which case species in equilibrium is molecular species that is not dissociated in liquid solutions. We begin with dissociation or dissolution equilibrium of an electrolyte $M_{n+}X_{n-}$ and define the mean ionic chemical potential.

$$\mu_{MX}=\nu_{+i}\mu_{+i}+\nu_{-i}\mu_{-i}\equiv\nu_{\pm i}\mu_{\pm i} \tag{41}$$

where $\nu_{\pm i}=\nu_{+i}+\nu_{-i}$. In most electrolyte solution models, McMillan-Mayer frame is used, which is not adequate for pure molten salt reference states. Thus, the infinite dilution reference state at the system temperature and the standard pressure is commonly adopted for solutes instead of the pure component reference. Subtracting the chemical potential at infinite dilution from both sides of Eq. (41), we have

$$\begin{aligned}\mu_{MX}-\mu_{pure,MX}+\mu_{pure,MX}-\nu_{\pm i}\mu^{l\infty}_{\pm i}&=\Delta\mu^{\infty}_{MX}+RT\ln a_{MX}\\&=\nu_{\pm i}\mu^{l}_{\pm i}-\nu_{\pm i}\mu^{l\infty}_{\pm i}=\nu_{\pm i}RT\ln a_{\pm i}\end{aligned} \tag{42}$$

where

$$a^{\nu_{\pm i}}_{\pm i}=\exp[\nu_{\pm i}(\mu^{l}_{\pm i}-\mu^{l\infty}_{\pm i})/RT]=x^{l\nu_{\pm i}}_{\pm i}(\phi^{l}_{\pm i}/\phi^{l\infty}_{\pm i})^{\nu_{\pm i}}=x^{l\nu_{\pm i}}_{\pm i}\gamma^{*\nu_{\pm i}}_{\pm i} \tag{43}$$

In writing this equation we used Eq. (13) and following definitions.

$$x^{\nu_{\pm i}}_{\pm i}=x^{\nu_{+i}}_{+i}x^{\nu_{-i}}_{-i} \qquad \phi^{\nu_{\pm i}}_{\pm i}=\phi^{\nu_{+i}}_{+i}\phi^{\nu_{-i}}_{-i} \qquad \gamma^{*\nu_{\pm i}}_{\pm i}=\gamma^{*\nu_{+i}}_{+i}\gamma^{*\nu_{+i}}_{-i} \tag{44}$$

The equilibrium relation follows from Eq. (42)

$$K=\exp(\Delta\mu^{\infty}_{MX}/RT)=a^{\nu_{\pm i}}_{\pm i}/a_{MX} \tag{45}$$

This equation is applicable for dissociation and dissolution of electrolytes, in which case the activity of the electrolyte becomes unity.

For the calculation of activity coefficients, a Helmholtz free energy model or an EOS model for electrolyte systems is needed. If they are not available, activity coefficients for electrolyte solutions are also obtained by using Eq. (20) from an excess Gibbs function model.

More often than not, molality scales are used in electrolyte solutions.

$$\mu^{l}_{\pm i}-\mu^{l\infty}_{\pm i}=RT\ln a_{\pm i}=RT\ln m_{\pm i}\gamma^{(m)*}_{\pm i} \tag{46}$$

where

$$m^{\nu_{\pm i}}_{\pm i}=m^{\nu_{+i}}_{+i}m^{\nu_{-i}}_{-i}=m^{\nu_{\pm i}}_{i}(\nu^{\nu_{+i}}_{+i}\nu^{\nu_{-i}}_{-i}) \qquad \gamma^{(m)*\nu_{\pm i}}_{\pm i}=\gamma^{(m)*\nu_{+i}}_{+i}\gamma^{(m)*\nu_{-i}}_{-i} \tag{47}$$

$$\gamma^{(m)*}_{\pm i}=\exp\left[\frac{\mu^{l}_{\pm i}-\mu^{l\infty}_{\pm i}}{RT}\right]/m_{\pm i} \tag{48}$$

In some electrolyte G^E models, activity coefficients are directly obtained with concentrations in molality. Otherwise, we can use the relation between two different activity coefficients by comparing Eqs. (42) and (46).

$$\gamma^{(m)*}_{\pm i}=\gamma^{*}_{\pm i}x_{\pm i}/m_{\pm i} \tag{49}$$

Often non-ideality of solvent in electrolyte solution is expressed in terms of osmotic coefficient in the molality scale.

$$\varphi^{(m)}=-\frac{\ln a_s}{0.001m_iM_S} \tag{50}$$

CONCLUSION

Various methods were systematically presented for the calculation of phase equilibria and thermodynamic properties and their relations with available information were discussed. The Helmholtz free energy or an EOS suffices for all properties of any phases. When they are not available, supplementary information is needed and different methods are adopted. Inter-relations between fugacity, fugacity coefficient, activity coefficient and chemical potential were clarified. Particular attention was given to the fugacity of a component that is not stable at the given condition in its pure state.

NOMENCLATURE

A : Helmholtz free energy
P : pressure
S : entropy
T : temperature
V : volume
f : fugacity
n : number of moles
s : molar entropy
u : molar internal energy
v : molar volume
$\bar{v}$: partial molar volume
x : mole fraction
φ : fugacity coefficient
μ : chemical potential

Superscripts

E : excess properties
l : liquid phase
s : solid phase
sl : property change on solid-liquid transition
sat : saturated liquid or solid
v : vapor phase
α, β, π : a phase
0 : ideal gas state at 1 bar
∞ : infinite dilution state
* : activity coefficient normalized for the infinite dilution reference state

Subscripts

i : a component
pure, i : a component at the pure state

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