ON THE INFORMATION AND METHODS FOR
COMPUTING PHASE EQUILIBRIA AND THERMDYNAMIC PROPERTIES

Chul Soo Lee
Department of Chemical Engineering
Korea University, Seoul 136-701, Korea

ABSTRACTS

The helmholtz free energy or an equation of state plays the key role in the calculation of phase equilibria and properties. Such information is usually available for vapor, partially available for liquids, and rarely available for solids. When it is not available, supplementary information is needed. Thus different methods are in use for the phase of interest. In this study, various methods were systematically presented and their relations with available information were discussed.

INTRODUCTION

Thermodynamic analysis often requires the computation of phase equilibria and properties such as volumes, enthalpies, entropies, etc. of real pure fluids and their mixtures. These properties are usually supplied by various calculation methods that depend on information available. Given the ideal gas heat capacity and the PVT equation of state that describes the PVT behavior for a wide range of density from the ideal gas to solid, a property change of a substance from T_1 and P_1 to T_2 and P_2 at the constant composition can be evaluated along a path; from the real substance at T_1 and P_1 to the ideal gas at T_1 and 1 bar, to ideal gas at T_2 and 1 bar, and to real substance at T_2 and P_2. Since the ideal gas portion of the path is simply evaluated with the heat capacity, we concentrate on the isothermal change from the ideal gas to real fluids, for the evaluation of which an equation of state is needed. Such information is usually available for vapor, partially available for liquids, and rarely available for solids. If they are not available, supplementary information is needed. Thus depending on the information and the phase of interest, different methods 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 confusions on the underlying principles.

The fundamental and comprehensive information is given by the Helmholtz free energy as a function of pressure, 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 of the configurational partition function 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 from; the hard sphere

interaction, the dispersion interaction, the chain formation, and the association as in SAFT (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, Yeom et al., 1999). Recently the applicable range of these methods are extended to polymers and hydrogen-bonding systems.

Information needed for phase equilibria and properties calculation may also be supplied by an equation of state such as SRK or PR developed on empirical bases. These equations may be used to derive the Helmholtz free energy, which in turn becomes the basis for obtaining other property equations. However, the PVT equation of state is not a fundamental equation and the derivation of equations for other thermodynamic properties is less convenient. Complex mixing rules were proposed to describe mixture properties more accurately.

For liquid phases we may not have and equation of state. Then we would need an excess Gibbs function model, vapor pressure and the saturated liquid volume. 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 equation of state has and does not give information on the excess volume. It is used mainly for low-pressure liquids.

The Helmholtz free energy or an equation of state for fluids does not extrapolate to solid phases. If a solid component constitutes a phase, other information is needed such as heat capacities, the enthalpy changy on melting, and the triple point temperature. A solid mixture may forms a solid solution, in which case the problem becomes more complex. The present work is intended to discuss and to present the computation methods for phase equilibria and the properties depending on the information we have.

PHASE VOLUME

When pressure is given as a function of temperature, volume and composition by a PVT equation of state valid for both gases and liquids,
$$P = P(T, v, \{x_i\}) \tag{1}$$
the equation is solved for phase volumes at the given P, T, and $\{x_i\}$. If the Helmholtz free energy is given, the equation of state is derived to give,
$$P = -\left(\partial A / \partial V\right)_{T,n} \tag{2}$$
For given T, P, and $\{x_i\}$ the equation of state 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.

The primary concern of some models like the PR equation of state is to calculate phase equilibria. Thus the calculated volume is not very accurate. Excess Gibbs function models do not yield the information on volume.

ENTHALPIES AND OTHER PROPERTIES

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

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

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

Or we may start with an equation of state to have (Prausnitz et al., 1999)

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

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

These equations are used for property changes including those on phase transition and mixing. The excess Gibbs function may be used to have the excess enthalpy.

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

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

The excess enthalpy calculation was reported by Kehiaian et al. using an excess Gibbs function model (Kehiaian et al., 1991). The equation of state approaches is reported by Park et al. (1999) among others. In both approaches the simultaneous calculation of the excess enthalpy and phase equilibria were discussed.

PHASE EQUILIBRIA

The condition for phase equilibria is well established.

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

The chemical potenential is related with the fugacity by

$$\mu_i = \mu_i^r + RT \ln(f_i / f_i^r) \tag{10}$$

where the superscript r denotes the a reference state. From eqns (9) and (10) we have

$$\mu_i^{r\alpha} + RT \ln(f_i^\alpha / f_i^{r\alpha}) = \mu_i^{r\beta} + RT \ln(f_i^\beta / f_i^{r\beta}) \tag{11}$$

Thus, regardless of the reference states that are the same or not, we have the phase equilibrium conditions written for fugacities (Prausnitz et al., 1998).

$$f_i^\alpha = f_i^\beta \tag{12}$$

Either eqn (9) or (12) may be used for phase equilibrium calculations. However, the fugacity relation is more convenient since they do not depend on reference states.

FUGACITY

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

$$\mu_i = \left(\partial A/\partial n_i \right)_{T,V,n_j} \tag{13}$$

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

$$\mu_i^\alpha - \mu_{pure,i}^0 = \mu_i^\beta - \mu_{pure,i}^0 \tag{14}$$

This relation is easily converted to the fugacity relation. Since the fugacity of a component in a phase π is related with chemical potential by

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

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

$$f_i^\pi = Px_i^\pi \phi_i^\pi$$
(16)

where the fugacity coefficient is given by (Prausnitz et al., 1998),

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

We can still write the fugacity of a component in a condensed phase even if we do not have an equation of state.

$$f_i^\pi = f_{pure,i}^\pi x_i^\pi \gamma_i^\pi$$
(18)

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

$$RT \ln \gamma_i^\pi = \left(\partial G^E / \partial n_i \right)_{T,P,n_j}$$
(19)

and

$$f_{pure,i}^\pi = P_i^{sat} \phi_{pure,i}^{sat} \exp\left[V^\pi (P - P_i^{sat})/RT \right]$$
(20)

To use this equation we need vapor pressure, equation of state for vapor phase, and the molar volume of the condensed phase. A supercritical component does not have vapor pressure. The vapor pressure of a solid component may be too low to measure. Then we need methods to cope with such situations. We will return to these problems.

VAPOR PHASE

The vapor phase fugacity of a component is readily obtained using eqn (15) from the Helnholtz free energy

$$f_i^v = \exp[(\mu_i^v - \mu_{pure,i}^0)/RT]$$
(21)

or using eqn (16) from an equation of state

$$f_i^v = Px_i^v \phi_i^v$$
(22)

This method applies to any component in vapor phase regardless of the stable phase of the component at the condition. A Helmholtz free energy equation or an equation of state is needed. For low-pressure applications, the ideal gas phase may sometimes be assumed.

LIQUID PHASE

With an equation of state the fugacity of a liquid phase is written by eqn (15) or (16) as done for a component in vapor phase regardless of the species' stable state.

$$f_i^l = \exp[(\mu_i^l - \mu_{pure,i}^0)/RT]$$
(23)

or

$$f_i^l = Px_i^l \phi_i^l$$
(24)

An equation of state may not be available for liquid phases. Then the liquid phase fugacity is written by

$$f_i^l = f_{pure,i}^l x_i^l \gamma_i^l \tag{25}$$

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

$$RT \ln \gamma_i^l = \left(\partial G^E / \partial n_i \right)_{T,n_j} \tag{26}$$

Now the problem is how to obtain the pure component fugacity. For a subcritical fluid component, the fugacity of a pure fluid is readily written as

$$f_{pure,i}^l = P_i^{sat} \phi_i^{sat} \exp[v_i^l (P - P_i^{sat}) / RT] \tag{27}$$

However, the evaluation of the pure component fugacity presents difficulties for a supercritical component or for a solid component.

It is interesting to compare eqns (24) and (25).

$$f_{pure,i}^l = P \phi_{pure,i}^l \tag{28}$$

and

$$\gamma_i^l = \phi_i^l / \phi_{pure,i}^l \tag{29}$$

The pure component fugacity obtained using either eqn (27) or (28) depends on temperature and pressure. The activity coefficient given by eqn (26) depends on temperature and composition while that given by eqn (29) 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 applications.

To use eqn (27) we need vapor pressure or the liquid molar volume. 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, eqn (27) is modified to give

$$f_{pure,i}^l = f_{pure,i}^l (P^r) \exp[v_i^l (P - P^r) / RT] \tag{30}$$

The fugacity values of a pure component at the reference pressure of 1bar 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.

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

$$f_i^l = H_i x_i^l \gamma_i^{l*} \tag{31}$$

where

$$H_i = P \phi_{pure,i}^{l\infty} \tag{32}$$

$$\gamma_i^{l*} = \phi_i^l / \phi_{pure,i}^{l\infty} \tag{33}$$

The superscript ∞ denotes the state at the 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 is used.

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

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 for them, we need an equation of state applicable to liquids to obtain

the volume. But then we would not use the Henry's law based method.

For a solid component in liquid state we are usually interested in properties for a wide range of composition up to its solubility. Thus the Henry's law based representation is not used. We first calculate the chemical potential difference of a solid and the hypothetical liquid of the same component 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 extended vapor-liquid equilibrium line, (5) from the super cooled liquid T to the system T and P isothermally [7].

$$\Delta\mu_{pure,i}^{sl} = \Delta h_{pure,i}^{sl}(T_t) + \int_{T_t}^{T} \Delta C_p dT - T\left(\frac{\Delta h_{pure,i}^{sl}(T_t)}{T_t} - \int_{T_t}^{T}\frac{\Delta C_p}{T}dT\right) + (V_i^s - V_i^l)P \quad (35)$$

Since the heat capacity contribution and the phase transition volume are usually small, the equation may be approximated by

$$\Delta\mu_{pure,i}^{sl} \approx \Delta h_{pure,i}^{sl}(T_t)\left(1 - \frac{T}{T_t}\right) \quad (36)$$

We now have the fugacity ratio.

$$\frac{f_{pure,i}^l}{f_{pure,i}^s} = \exp\left(-\frac{\Delta\mu_i^{sl}}{RT}\right) \quad (37)$$

This equation is particularly convenient and generally used for solid-liquid equilibria since the same fugacity ratio appears in the equilibrium conditions.

SOLID PHASE

Equations of state are not generally available for solid phases. For solid-liquid equilibria we have discussed the fugacity ratio, eqn (37), in the section on the liquid phase. The ratio cannot be used for gas-solid equilbria. We need to evaluate the fugacity of a solid component in solids. With the chemical potential, the fugacity of a pure component may be written,

$$f_{pure,i}^s = \exp[(\mu_{pure,i}^s - \mu_{pure,i}^0)/RT] \quad (38)$$

For a component in the pure solid phase the common approach is to use the chemical potential difference that is readily found when the sublimation pressure and molar volume are known,

$$\mu_{pure,i}^s - \mu_{pure,i}^0 = RT \ln f_{pure,i}^s = RT\ln(P_i^{sat}\phi_i^{sat}) + V_{pure,i}^s(P - P_i^{sat}) \quad (39)$$

If the vapor pressure is very small and unknown, we can still proceed assuming essentially zero vapor pressure,

$$\mu_{pure,i}^s - \mu_{pure,i}^0 = (\mu_{pure,i}^s - \mu_{pure,i}^l) + (\mu_{pure,i}^l - \mu_{pure,i}^0) = \Delta\mu_{pure,i}^{sl} + (\mu_{pure,i}^l - \mu_{pure,i}^0) \quad (40)$$

where the first term in the right hand side of the last equality is discussed and presented by eqn (35). It may also be approximated by eqn (36). This relation may also be written as

$$f_{pure,i}^s = \exp[\Delta\mu_{pure,i}^{sl}/RT]f_{pure,i}^l \quad (41)$$

To apply this method we need an equation of state and use eqn (28) since the liquid phase property is for hypothetical fluids. This method was applied in calculating the

solubility of essentially nonvolatile solids in supercritical gases (You et al., 1993).

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

$$f_i^s = f_{pure,i}^s x_i^s \gamma_i^s \tag{42}$$

An apparent solid mixture may or may not form a solid solution. We have limited information on the non-ideality of solid solutions.

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 equation of state suffices for all properties. Supplementary information and different methods were presented when they are not available. Particular attention was given to the fugacity of a component that is not stable at the given condition in its pure state.

NOTATIONS

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
$*$	activity coefficient normalized for the infinite dilution reference state

subscripts

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

REFERENCES

Chapman, W,G., Gubbins, K.,E., Jackson, G. and Radosz, "SAFT: Equation of State Model for Associating Fluids", *Fluid Phase Equil*., **52**, 31 (1989)

Kang, J.W., Kim, J.Y., Yoo, K.-P. and Lee, C.S., "Excess Enthalpy and Vapor Liquid Equilibrium Prediction Using Non-Random Lattice Fluid Equation of State", *Fluid Phase Equil*., **150**, 199 (1998).

Kehiaian, H.V., Gonzalez, J.A., Garcia, I., Cobos, J.C., Casanova, C. and Cocero, M.J., "Prediction of Vapor-liquid and Liquid-liquid and of Excess Enthalpies of Mixing in Linear Carbonates +n-Alkanes or +Cyclohexane Mixtures Using DISQUAC", *Fluid Phase Equil*., **64**, 1 (1991).

Prausnitz, J.M., Lichtenthaler, R.N. and de Azevedo, E.G., Molecular Thermodynamics of Fluid Phase Equilibria, 3rd ed., Prentice Hall, New Jersey (1998).

Reed, T.M. and Gubbins, K.E., Applied Statistical Mechanics, McGraw Hill, New York (1973).

Sanchez, I.C. and Lacombe, R.H., "Statistical Thermodynamics of Fluid Mixtures", *J. Phys. Chem*., **80**, 2352 (1976).

Yeom, M.S., Park, B.H., Yoo, K.-P. and Lee, C.S., "A Nonrandom Lattice Fluid Theory for Phase Equilibria of Associating Systems", *Fluid Phase Equil*.,**158**, 143 (1999).

You, S.-S., Lee, C.S. and Yoo, K.-P., "Modeling of Supercritical Fluid Phase Equilibria Using A Nonrandom Lattice Fluid Theory-based Equation of State", *J. Supercritical Fluids*, **6**, 69 (1993).

You, S.-S., Yoo, K.-P. and Lee, C.S., "An Approximate Nonrandom Lattice Theory of Fluids. Mixtures", *Fluid Phase Equil*., **93**, 215 (1994).