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### Solvation and chemical engineering thermodynamics

Shiang-Tai Lin<sup>1,\*</sup>, Chieh-Ming Hsieh<sup>2</sup>, Ming-Tsung Lee<sup>3</sup>

Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan Received 12 March 2007; accepted 1 August 2007

#### Abstract

With the continued advances in computational chemistry, solvation calculation from first principle methods is becoming a promising route for phase equilibrium modeling. However, except in a few instances, such an approach has not been widely adopted, which may be a consequence of the abstractness of solvation itself and also of the lack of a simple bridge between solvation and other thermodynamic properties. Here, we establish and summarize the relationship between solvation and other properties frequently used in phase equilibrium modeling. An important quantity, called the total solvation free energy, is introduced so that one can easily derive engineering thermodynamic models (such as an equation of state) from solvation models, or vice versa. The equations presented here are of general validity and would be useful for obtaining existing model parameters from solvation calculations and for developing new models stemming from the ideas of molecular solvation.

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### 1. Introduction

The term "solvation" implies the consideration of a solute molecule being surrounded (solvated) by other molecules, called the solvent. This physical picture of solution, frequently used by chemists and chemical physicists (Ben-Naim, 1987; Burger, 1983; Dogonadze *et al.*, 1985; Krestov, 1991), provides a useful means for understanding solvent effects on the structure, spectra, equilibrium, and dynamic properties of a solute. Therefore, there is continued effort in the development of solvation theories and models which will allow for a quantitative description of solvation properties. For example, remarkable progress has been made over the past two decades in the computational approach for solvation properties based on quantum mechanical continuum solvation models (Cramer and Truhlar, 1999; Orozco and Luque, 2000; Tomasi and Persico, 1994; Tomasi *et al.*, 2005).

Solvation properties, in particular the Gibbs free energy of solvation, are closely related to the chemical potential and fugacity that are necessary in phase equilibrium calculations. Combined with QM based solvation calculations, it is possible to make a priori phase equilibrium predictions, i.e., without input of any experimental data. With the enhancement of accuracy and efficiency in computational solvation theory, modeling phase equilibria from first principles is becoming practical. For example, Lin and Sandler (1999a,b, 2002a,b) and Nanu and co-workers (Nanu and De Loos, 2004; Nanu et al., 2004) determined the infinite dilution activity coefficient and Henry's law constant from a group contribution solvation (GCS) model. Klamt (Banerjee and Khanna, 2006; Klamt, 1995, 2005), followed by Lin and Sandler (2002a,b) and by Grensemann and Gmehling (2005), developed a liquid activity coefficient model, Conductor-like Screening Model for Real Solvent (COSMO-RS), for vapor-liquid equilibrium predictions. The COSMO-type models have also been combined with an equation of state model for high-pressure vapor-liquid or liquid-liquid predictions (Constantinescu et al., 2005; Shimoyama et al., 2006). There have also been attempts to develop equations of state from solvation models (Lin, 2006; Panayiotou, 2003a,b).

Despite these successful examples, utilization of solvation calculation for phase equilibrium calculations appears to be relatively limited compared to the amount of effort made in development solvation theory (mostly by chemists). One plausible reason is that the theory of solvation is rather abstract and difficult. This is evidenced by the many debates on the

<sup>\*</sup> Corresponding author. Tel.: +886 2 3366 1369; fax: +886 2 3366 3065. *E-mail address:* stlin@ntu.edu.tw (S.-T. Lin).

<sup>&</sup>lt;sup>1</sup> 林祥泰

<sup>2</sup>謝介銘

<sup>3</sup> 李旻聰

S
energy parameter in van der Waals equation
of state
size parameter in van der Waals equation of
state
Boltzmann constant
product of rotational, vibrational, and
electronic partition functions of a single
molecule
position vector
potential energy
mole fraction
compressibility factor
Helmholtz free energy
binding energy
molar concentration
Gibbs free energy
enthalpy
equilibrium constant of chemical reaction
number of molecules
pressure or the probability density
canonical partition function
gas constant
entropy
temperature
volume
configuration integral

### Greek symbols

 $\alpha$  coefficient of thermal expansion

 $\mu$  chemical potential

 $\rho$  number density

γ activity coefficient

v stoichiometric coefficient of chemical reaction

 $\Lambda$  de Broglie wavelength

#### Special notations

partial molar property (partial molar Gibbs free energy)

\_ property per mole (molar Gibbs free energy)

pseudo property, i.e., the property of solute when it is not allowed to translate (pseudo chemical potential)

### Subscripts

c critical propertyi molecular species ir reduced property

ij binary interaction property between species i and j

i/j solvation property of solute i in solvent j

S1,S2 solvent 1 or solvent 2

### **Superscripts**

ex excess property vap vapor pressure

sol	solvation property
L	liquid phase property
V	vapor phase property
CONF	configuration or residual property
IM	ideal mixture property
IG	ideal gas property
IGM	ideal gas mixture property

physical ingredients of solvation energy (Ben-Naim, 1978; Graziano, 2003; Vitha and Carr, 2000) and confusion as to its relationship with other thermodynamic properties (Pliego, 2003). Furthermore, the terms used in solvation theories are unfamiliar to most chemical engineers.

The purpose of the present work is to establish the relationship, summarized in Fig. 1, between solvation properties and other thermodynamic quantities that are more familiar to chemical engineers. Since solvation thermodynamics, consolidated by Ben-Naim (1987), is based on statistical mechanics, the connection has to be made with statistical thermodynamics. In other words, we derive equations that allow one to go between three realms: classical thermodynamics (represented by the compressibility factor z), statistical thermodynamics (represented by the configurational Helmholtz free energy  $A^{\text{CONF}}$ ), and solvation thermodynamics (represented by the total solvation free energy  $\Delta G^{*sol}$ ), i.e., the three apices in Fig. 1. The molecular solvation free energy (at the center of the triangle in Fig. 1) can be easily derived from any of the three realms. The connection between classical and statistical thermodynamics has been established previously by Sandler (1985) and Abbott and Prausnitz (1987). Our main contribution is to develop the relationships between solvation and the others. In addition, we also derive the expressions for thermodynamic properties frequently seen in phase equilibrium calculations in terms of molecular solvation free energy. Finally, we validate the equations developed here using the van der Waals equation of state.

### 2. The statistical mechanical thermodynamics

Statistical mechanics (Hill, 1986; McQuarrie, 1976; Tien and Lienhard, 1971) is a powerful theory relating macroscopic properties of materials to microscopic molecular interactions. Therefore, it is most useful for establishing the relationship between properties of solvation and other thermodynamic quantities. The canonical partition function for a mixture system of volume V at temperature T is:

$$Q(N_1, N_2, \dots, V, T) = \prod_{i} \left[ \frac{1}{N_i!} \left( \frac{q_i}{\Lambda_i^3} \right)^{N_i} \right] Z(N, V, T)$$
 (1)

where  $N_i$  is the number of molecules of species i,  $N = \sum N_i$  is the total number of molecules,  $q = q_{\rm r}q_{\rm v}q_{\rm e}$  is the product of the rotational, vibrational, and electronic partition functions of a

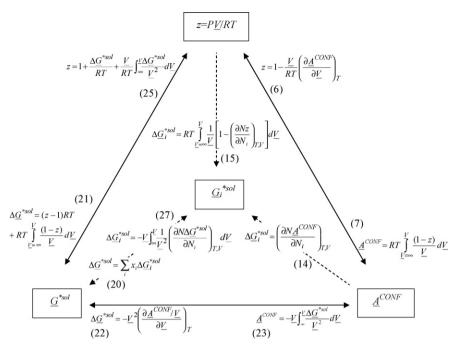


Fig. 1. The mathematical relations between equations of state, configuration Helmholtz free energy, and solvation free energy. The numbers in parenthesis indicate the corresponding equation number in the text.

single molecule,  $\Lambda$  is the de Broglie wavelength, and

$$Z(N, V, T) = \int \cdots \int \exp \left[ -\frac{u(\mathbf{r}_1, \mathbf{r}_2, \dots, r_N)}{kT} \right] d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N$$
 (2)

is the configuration integral which is an integration of the system potential energy  $u(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$  over all possible molecular configurations  $(\mathbf{r}_j)$  is the position vector of molecule j). The evaluation of Z is nontrivial and has been the focus of many fluid theories (McQuarrie, 1976). Our interest here is to stress that, once the configuration integral is available (and thus, the partition function Q), the Helmholtz free energy is readily determined as:

$$A(N_1, N_2, \dots, V, T) = -kT \ln Q(N_1, N_2, \dots, V, T)$$
(3)

from which all other thermodynamic properties can be easily derived (Hill, 1986; McQuarrie, 1976; Michelsen and Mollerup, 2004; Tien and Lienhard, 1971).

It is a common practice for chemical engineers to separate ideal gas contributions in the thermodynamic properties. The configuration Helmholtz free energy (Sandler, 1985) (sometimes called the residual property (Abbott and Prausnitz, 1987)) is defined as the difference in A between a real system and an ideal gas of the same volume, temperature and composition:

$$A^{\text{CONF}}(N_1, N_2, \dots, V, T)$$

$$= A(N_1, N_2, \dots, V, T) - A^{\text{IG}}(N_1, N_2, \dots, V, T)$$
(4)

Therefore, the configuration Helmholtz free energy is related to the configuration integral as:

$$A^{\text{CONF}} = -kT \ln \frac{Q}{Q^{\text{IG}}} = -kT \ln \left[ \prod_{i} \left( \frac{q_i}{q_i^{IG}} \right)^{N_i} \frac{Z}{V^N} \right]$$
 (5)

where the configuration integral for an ideal gas is simply  $V^N$ . Since the ideal gas properties in general are known (or if not, can be easily calculated using modern computational chemistry (Foresman and Frisch, 1996; Ochterski, 2000)), the knowledge of  $A^{\rm CONF}$  is the key for obtaining the other thermodynamic quantities. For example, the compressibility factor or, equivalently, the PVT equation of state can be obtained from  $A^{\rm CONF}$  as:

$$z = \frac{PV}{NkT} = \frac{V}{N} \frac{\partial \ln Q}{\partial V} = 1 - \frac{V}{NkT} \left(\frac{\partial A^{\text{CONF}}}{\partial V}\right)_{N,T}$$
 (6)

It has been shown that most engineering thermodynamic models can be derived just from the knowledge of  $A^{\rm CONF}$  under different assumptions (Sandler, 1985). Conversely, the configuration Helmholtz free energy can be obtained from the integration of z (Abbott and Prausnitz, 1987):

$$A^{\text{CONF}}(N, V, T) = NkT \int_{V=\infty}^{V} \frac{(1-z)}{V} \, \mathrm{d}V$$
 (7)

We will show in the following that the configuration Helmholtz free energy is also the key for solvation property calculations.

### 3. The solvation free energy

According to the definition given by Ben-Naim (1987), the Gibbs free energy of solvation is the work needed to relocate a

molecule from a fixed position in an ideal gas to a fixed position in a solution at constant temperature and pressure. In order to evaluate the work for such a hypothetical molecular process, Ben-Naim first wrote the expression for chemical potential in terms of the binding energy  $B_0$  between the added molecule (located at position  $\mathbf{r}_0$ ) and all other molecules in the system [Appendix A]:

$$\mu_i = -kT \ln \left\{ \frac{q_i V}{(N_i + 1)\Lambda_i^3} \left\langle \exp\left(-\frac{B_0}{kT}\right) \right\rangle \right\}$$
 (8)

where the bracket in Eq. (8) indicates the Boltzmann average. The factor V comes from the integration of the position  $(V = \int_V d\mathbf{r}_0)$  of the newly added molecule over the volume of the system. Suppose that the newly added molecule is fixed at a certain position, the translation partition function and the volume integration of such a molecule would be unity. In this case, Eq. (8) becomes the so-called "pseudo" chemical potential (denoted by the superscript \*) [Appendix A]:

$$\mu_i^* = -kT \ln \left\{ q_i \left\langle \exp\left(-\frac{B_0}{kT}\right) \right\rangle \right\} \tag{9}$$

If the solution is in the ideal gas state, the binding energy  $B_0$  is zero and the pseudochemical potential is simply the molecular partition function (rotational, vibrational, and electronic only), *i.e.*,  $\mu_i^{\text{IG},*} = -kT \ln q_i^{\text{IG}}$ . From Eqs. (8) and (9), we have the chemical potential and pseudochemical potential related to each other as:

$$\mu_i = \mu_i^* + kT \ln(\rho_i \Lambda_i^3) \tag{10}$$

where  $\rho_i = (N_i + 1)/V \approx N_i/V$  is the number density of species *i*. Eq. (10) states that the work needed to insert a molecule to a system (*i.e.*, the chemical potential) is the sum of work needed for inserting the molecule to a fixed location ( $\mu_i^*$ ) and the work gained after releasing the molecule ( $kT \ln \rho_i \Lambda_i^3$ , also known as the liberation free energy). With the solvation process defined by Ben-Naim,  $\Delta G_i^{*\rm sol}$  is just the difference between the pseudochemical potential in the solution phase and the ideal gas phase at the same T and P:

$$\Delta G_i^{*\text{sol}}(T, P, \underline{x}) = \mu_i^*(T, P, \underline{x}) - \mu_i^{*, \text{IG}}(T, P)$$

$$= -kT \ln \left\{ \frac{q_i}{q_i^{\text{IG}}} \left\langle \exp\left(-\frac{B_0}{kT}\right) \right\rangle \right\}$$
(11)

Thus, we can see that the solvation free energy takes into account the changes (due to the presence of the solvent) in the rotational, vibrational, and electronic partition functions of the solute  $(q_i/q_i^{\text{IG}})$  in addition to the solute–solvent binding interaction  $(B_0)$ .

# 4. The solvation properties from configuration Helmholtz free energy

In the derivation above, Ben-Naim introduced the concept of pseudochemical potential (chemical potential of a fixed molecule) in order to obtain the expression for solvation free energy. This is necessary because the liberation free energy  $(kT \ln \rho_i \Lambda_i^3)$  in the solution and the ideal gas phase are typically different at the same temperature and pressure. If the solvation process is taken under conditions of constant temperature and molar volume, the liberation free energy in both phases would be the same and the same expression for the solvation free energy can be obtained without the need for pseudochemical potential, which is unfamiliar to most chemical engineers.

To show this, let us consider a different solvation process of transferring a molecule from an ideal gas to a solution at constant temperature and volume (without fixing the molecule in both phases). The work needed for such a process is the difference in chemical potential of the molecule in the two phases:

$$\mu_{i}(T, V, \underline{x}) - \mu_{i}^{IG}(T, V, \underline{x})$$

$$= \left(\frac{\partial A}{\partial N_{i}}\right)_{T, V, N_{j \neq i}} - \left(\frac{\partial A^{IG}}{\partial N_{i}}\right)_{T, V, N_{j \neq i}} = \left(\frac{\partial A^{CONF}}{\partial N_{i}}\right)_{T, V, N_{j \neq i}}$$
(12)

It can be shown (Appendix B) that the partial derivative of  $A^{\text{CONF}}$  with respect to  $N_i$  can be expressed in terms of the binding energy  $B_0$  as:

$$\frac{\partial A^{\text{CONF}}}{\partial N_i}\bigg|_{TV} = -kT \ln \left[ \frac{q_i}{q_i^{\text{IG}}} \left\langle \exp\left(-\frac{B_0}{kT}\right) \right\rangle \right]$$
 (13)

which is identical to the expression for solvation free energy in Eq. (11). Thus, we see that the solvation free energy can also be obtained from the partial derivative of configuration Helmholtz free energy with respect to the number of molecular species:

$$\Delta G_i^{*\text{sol}} = \mu_i(T, V, \underline{x}) - \mu_i^{\text{IG}}(T, V, \underline{x}) = \left(\frac{\partial A^{\text{CONF}}}{\partial N_i}\right)_{T, V}$$
(14)

Eq. (14) is important as it provides the basis for deriving solvation free energy from any statistical mechanical model (for  $A^{\text{CONF}}$ ) without the need of pseudochemical potential. Together with Eq. (7), the solvation free energy of chemical species can then be obtained from any PVT EOS as:

$$\Delta G_i^{*\text{sol}} = kT \int_{V=\infty}^{V} \frac{1}{V} \left[ 1 - \left( \frac{\partial Nz}{\partial N_i} \right)_{T,V} \right] dV$$
 (15)

We will illustrate this practice using the van der Waals equation of state later.

Since the temperature derivatives of  $\Delta G_i^{*sol}$  give the entropy and enthalpy of solvation, these two quantities can also be derived from  $A^{CONF}$  as:

$$\Delta S_{i}^{*\text{sol}} = -\left(\frac{\partial \Delta G_{i}^{*\text{sol}}}{\partial T}\right)_{N,P} = -\left(\frac{\partial \Delta G_{i}^{*\text{sol}}}{\partial T}\right)_{N,V}$$

$$-\left(\frac{\partial \Delta G_{i}^{*\text{sol}}}{\partial V}\right)_{N,T} \left(\frac{\partial V}{\partial T}\right)_{N,P}$$

$$= -\frac{\partial}{\partial T}\left|_{N,V} \frac{\partial A^{\text{CONF}}}{\partial N_{i}}\right|_{T,V,N_{j\neq i}} - \alpha V \frac{\partial}{\partial V}\left|_{T,N} \frac{\partial A^{\text{CONF}}}{\partial N_{i}}\right|_{T,V,N_{j\neq i}}$$
(16)

and

$$\Delta H_i^{*\text{sol}} = -\left(\frac{\partial(\Delta G_i^{*\text{sol}}/kT)}{\partial T}\right)_{N,P} 
= \frac{\partial A^{\text{CONF}}}{\partial N_i} \bigg|_{T,V,N_{j\neq i}} - T\frac{\partial}{\partial T} \bigg|_{N,V} \frac{\partial A^{\text{CONF}}}{\partial N_i} \bigg|_{T,V,N_{j\neq i}} 
- T\alpha V\frac{\partial}{\partial V} \bigg|_{T,N} \frac{\partial A^{\text{CONF}}}{\partial N_i} \bigg|_{T,V,N_{j\neq i}}$$
(17)

where  $\alpha = (\partial V/\partial T)_{N,P}/V$  is the coefficient of thermal expansion of the system. Since  $\alpha$  diverges (approaches infinity) at the critical point, both  $\Delta H_i^{\rm *sol}$  and  $\Delta S_i^{\rm *sol}$  diverge at this condition.

## 5. Thermodynamic properties from molecular solvation free energy

In the previous section, we showed how the solvation free energy can be obtained from the configuration Helmholtz free energy (which can be provided from an existing thermodynamic model). Of equal importance is to, conversely, obtain all thermodynamic properties of our interest from the solvation free energy. To proceed, let us rewrite  $\mu_i$  in Eq. (14) in terms of partial molar Gibbs free energy:

$$\Delta G_i^{*\text{sol}}(T, P, \underline{x}) = \overline{G}_i(T, V, \underline{x}) - \overline{G}_i^{\text{IG}}(T, V, \underline{x})$$

$$= \overline{G}_i(T, P, \underline{x}) - \overline{G}_i^{\text{IG}}(T, P, \underline{x}) + kT \ln z$$
(18)

where we have used  $G^{IG}(T, P, N) - G^{IG}(T, NkT/V, N) = NkT \ln z$  in the above derivation. For a pure fluid, the above equation reduces to:

$$\Delta \underline{G}_{i}^{*\text{sol}}(T, P) = \underline{G}_{i}(T, P) - \underline{G}_{i}^{\text{IG}}(T, P) + RT \ln z_{i}$$
(19)

on a molar basis. If we define the total solvation free energy of a system (having temperature T, pressure P, volume V, and composition  $\underline{x}$ ) as the sum of contribution from each individual molecule:

$$\Delta G^{*\text{sol}} = \sum_{i} N_i \Delta G_i^{*\text{sol}} \tag{20}$$

the total solvation free energy is related to the configuration Helmholtz free energy as (Appendix C)

$$\Delta G^{*\text{sol}} = A^{\text{CONF}} + (z - 1)NkT \tag{21}$$

Substituting the compressibility factor with that in Eq. (6), we have:

$$\Delta G^{*\text{sol}} = \Delta A^{\text{CONF}} - V \left( \frac{\partial A^{\text{CONF}}}{\partial V} \right)_{T,N}$$
$$= -V^2 \left( \frac{\partial A^{\text{CONF}}/V}{\partial V} \right)_{T,N} \tag{22}$$

Compared to Eq. (14) where molecular solvation free energy  $\Delta G_i^{*\mathrm{sol}}$  is determined from  $A^{\mathrm{CONF}}$ , Eq. (22) provides a way to obtain the total solvation free energy from  $A^{\mathrm{CONF}}$ . The above

partial differential equation can be solved exactly to obtain:

$$A^{\text{CONF}} = -V \int_{-\infty}^{V} \frac{\Delta G^{*\text{sol}}}{V^2} \, dV \tag{23}$$

Here, we have used the boundary condition that  $A^{\text{CONF}}$  is zero at infinite volume condition (the ideal gas limit). Therefore, the canonical partition function can also be expressed in terms of the total solvation free energy as:

$$Q(N_1, N_2, \dots, V, T) = Q^{\text{IG}} \exp \left[ \frac{V}{kT} \int_{\infty}^{V} \frac{\Delta G^{*\text{sol}}}{V^2} \, dV \right]$$
 (24)

Eq. (24) thus provides the basis for obtaining all thermodynamic properties from any molecular solvation model. For example, the compressibility factor from Eq. (6) becomes:

$$z = 1 + \frac{\Delta G^{*\text{sol}}}{NkT} + \frac{V}{NkT} \int_{-\infty}^{V} \frac{\Delta G^{*\text{sol}}}{V^2} \, dV$$
 (25)

It should be noted that, unlike the partial molar properties, the differentiation of  $\Delta G^{*\text{sol}}$  with respect to  $N_i$  at constant T and P does not give the molecular solvation free energy unless the partial molar volume of species i is equivalent to the molar volume of the solution.

$$\left(\frac{\partial \Delta G^{*\text{sol}}}{\partial N_{i}}\right)_{T,P,N_{j}\neq i} = \frac{\partial}{\partial N_{i}} \left(G(T,P,\underline{x}) - G^{\text{IGM}}(T,P,\underline{x}) + NkT \ln z\right) 
= \Delta G_{i}^{*\text{sol}}(T,P,\underline{x}) + kT \left(\frac{\overline{V}_{i}}{\underline{V}} - 1\right) \neq \Delta G_{i}^{*\text{sol}}(T,P,\underline{x})$$
(26)

The proper method to obtain molecular solvation free energy  $\Delta G_i^{*\rm sol}$  from the total solvation free energy  $\Delta G^{*\rm sol}$  is to first calculate  $A^{\rm CONF}$  from Eq. (23) and then substitute into Eq. (14), *i.e.*:

$$\Delta G_i^{*\text{sol}} = -V \int_{-\infty}^{V} \frac{1}{V^2} \left( \frac{\partial \Delta G^{*\text{sol}}}{\partial N_i} \right)_{TV} dV$$
 (27)

Thus, we have established all of the equations presented in Fig. 1.

### 6. Thermodynamic properties for phase and chemical equilibrium calculations

Here, we derive the expression in terms of molecular solvation free energy for some of the thermodynamic properties that are frequently used in phase equilibrium calculations. It is useful to first rewrite Eq. (18) and express all the quantities on a molar basis (Lin and Sandler, 1999a,b):

$$\overline{G}_{i}(T, P, \underline{x}) = \Delta \underline{G}_{i}^{*\text{sol}}(T, P, \underline{x}) + \overline{G}_{i}^{\text{IGM}}(T, P, \underline{x}) - RT \ln z$$
(28)

The fugacity coefficient, the deviation of the partial molar Gibbs free energy from an ideal gas mixture at the same T, P,

and composition, is easily derived from Eq. (28) as:

$$\ln \frac{\bar{f}_i}{x_i P} = \frac{\overline{G}_i(T, P, \underline{x}) - \overline{G}_i^{\text{IGM}}(T, P, \underline{x})}{RT} = \frac{\Delta \underline{G}_i^{*\text{sol}}(T, P, \underline{x})}{RT} - \ln z$$
(29)

The vapor pressure can be derived from the equality of fugacity in the liquid and the vapor phase  $f_i^{\rm L}(T,P^{\rm vap})=f_i^{\rm V}(T,P^{\rm vap})$ . For systems away from the critical points  $\Delta G_{i/V}^{\rm *sol}\sim 0$ ,  $z^{\rm V}\sim 1$ ,  $z^{\rm L}=P\underline{V}^{\rm L}/RT$  the vapor pressure becomes (Lin *et al.*, 2004; Wang *et al.*, 2006):

$$\ln P^{\text{vap}} = \frac{\Delta G_{i/i}^{*\text{sol}}(T, P^{\text{vap}})}{RT} + \ln \frac{RT}{V_i^L}$$
(30)

By definition, the Henry's law constant is the ratio of fugacity and mole fraction in the limit of infinite dilution (Lin and Sandler, 2002a,b):

$$H_i(T, P) = \lim_{x_i \to 0} \frac{\overline{f}_i}{x_i} = \frac{\Delta \underline{G}_{i/S}^{*sol}(T, P)}{RT} + \ln \frac{RT}{V^S}$$
(31)

where we have used subscript i/j to denote the solvation property of solute i in solvent j. The excess Gibbs free energy of a mixture fluid can also be obtained from Eq. (28):

$$\underline{G}^{\text{ex}} = \sum_{i} x_{i} (\overline{G}_{i} - \Delta \overline{G}_{i}^{\text{IM}})$$

$$= \sum_{i} x_{i} (\Delta \underline{G}_{i/S}^{*\text{sol}} - \Delta \underline{G}_{i/i}^{*\text{sol}} + RT \ln \frac{z_{i}}{z})$$
(32)

where  $z_i$  and z are the compressibility factor for the pure fluid i and the mixture S at temperature T and pressure P. The activity coefficient can be obtained from taking the partial derivative of Eq. (32) with respective to  $N_i$  (Lin and Sandler, 1999a,b; Sandler  $et\ al.$ , 2002):

$$\ln \gamma_{i/S} = \frac{\overline{G}_i^{\text{ex}}}{RT} = \frac{\overline{G}_i}{RT} - \frac{\overline{G}_i^{\text{IM}}}{RT} = \frac{\Delta \underline{G}_{i/S}^{*\text{sol}} - \Delta \underline{G}_{i/i}^{*\text{sol}}}{RT} + \ln \frac{z_i}{z}$$
(33)

Therefore, the distribution coefficient, defined as the concentration ratio of a solute in two immiscible (or partially miscible) fluids becomes (Lin and Sandler, 1999a,b):

$$\ln K_{i} = \ln \frac{C_{i}^{S1}}{C_{i}^{S2}} = \ln \frac{x_{i}^{S1}/z_{S1}}{x_{i}^{S1}/z_{S1}} = \ln \frac{\gamma_{i/S2}}{\gamma_{i/S1}} = \frac{\Delta \underline{G}_{i/S2}^{*\text{sol}} - \Delta \underline{G}_{i/S1}^{*\text{sol}}}{RT}$$
(34)

In addition to the above phase equilibrium properties, the chemical equilibrium criteria  $\sum_i v_i \overline{G}_i = 0$  can be expressed in terms of solvation free energy as:

$$\sum_{i} \upsilon_{i} \Delta \underline{G}_{i/S}^{*\text{sol}} + \sum_{i} \upsilon_{i} \underline{G}_{i}^{\text{IG}} + RT \sum_{i} \upsilon_{i} \ln x_{i}$$
$$-RT(\ln z) \sum_{i} \upsilon_{i} = 0$$
(35)

where  $v_i$  is the reaction coefficient for species *i*. Therefore, the equilibrium constant in terms of molar concentration becomes

(Pliego, 2003):

$$\ln K_C = \sum_{i} \nu_i \ln C_i$$

$$= -\sum_{i} \frac{\nu_i \Delta G_{i/S}^{*\text{sol}}}{RT} - \sum_{i} \frac{\nu_i \underline{G}_i^{\text{IG}}}{RT} - \left(\ln \frac{P}{RT}\right) \sum_{i} \nu_i \quad (36)$$

We can see that, except for the partition coefficient and chemical equilibrium constant, it is necessary to have the compressibility factor z (or the molar volume  $\underline{V}$  at a given T and P) to derive most thermodynamic properties in terms of solvation free energy at the same condition. Therefore, a solvation model which allows for the evaluation of z from Eq. (25) or the estimation of molar volume is generally necessary.

### 7. Solvation free energy from an EOS

We use the van der Waals equation of state to illustrate the use of the equations developed here. The compressibility factor of a pure van der Waals fluid is:

$$z = \frac{PV}{RT} = \frac{V}{V - b} - \frac{a}{RTV} \tag{37}$$

According to the principle of corresponding states, the constants a and b can be obtained from the critical properties of the fluid ( $a=27R^2T_{\rm c}^2/64P_{\rm c}$  and  $b=(RT_{\rm c})/(8P_{\rm c})$ ). The configuration Helmholtz free energy is obtained from Eq. (7)

$$\underline{\underline{A}^{\text{CONF}}} = RT \int_{V=\infty}^{\underline{V}} \frac{(1-z)}{\underline{V}} \, d\underline{V} = RT \ln \frac{\underline{V}}{\underline{V} - b} - \frac{a}{\underline{V}}$$
 (38)

and the solvation free energy is obtained from Eq. (14):

$$\Delta \underline{G}_{i}^{*\text{sol}} = \frac{\partial N \underline{A}^{\text{CONF}}}{\partial N} = RT \ln \left( \frac{\underline{V}}{\underline{V} - b} \right) + RT \frac{\underline{b}}{\underline{V} - b} - \frac{2a}{\underline{V}}$$
(39)

The variation of solvation free energy with reduced volume  $(\underline{V}_r = \underline{V}/\underline{V}_c)$  and reduced pressure  $(P_r = P/P_c)$  can be obtained and is illustrated in Fig. 2 for three reduced temperatures  $(T_r = T/T_c)$  0.5, 1.0, and 10. Except for systems under high temperature  $(e.g., T_r = 10)$  or high pressure (large  $P_r$  or small  $\underline{V}_r$ ), the solvation free energy is negative, indicating that work is gained in the solvation process. At  $T_r = 0.5$ , the vapor  $(P_r = 0.028, \underline{V}_r = 45.98, \Delta \underline{G}_i^{*sol}/RT = -0.08)$  and liquid  $(P_r = 0.028, \underline{V}_r = 0.41, \Delta \underline{G}_i^{*sol}/RT = -4.81)$  phases that are in equilibrium are connected by the dashed lines (tie-line) in Fig. 2. The difference in  $\Delta \underline{G}_i^{*sol}$  for the two phases in equilibrium indicates (the negative value of) the difference in the liberation free energy for a solute in the two phases  $[-4.81-(-0.08)=-4.73=\ln(0.41/45.98)]$ .

For mixture fluids, the constants a and b can be determined from using the van der Waals one-fluid mixing rule  $(a = \sum_{i} \sum_{i} x_{i} x_{j} \sqrt{a_{i} a_{j}})$  and  $b = \sum_{i} x_{i} b_{i}$ , and the solvation free

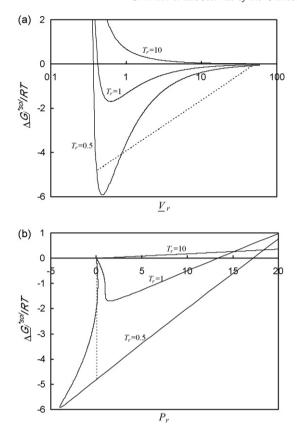


Fig. 2. The solvation free energy as a function of reduced volume (a) or as a function of reduced pressure (b) for a pure van der Waals fluid at reduced temperatures 0.5, 1.0, and 10.

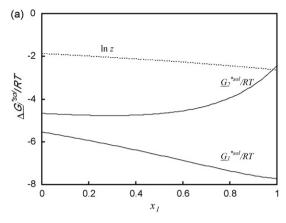
energy becomes:

$$\Delta \underline{G}_{i}^{*\text{sol}} = \frac{\partial N\underline{A}^{\text{CONF}}}{\partial N_{i}} = RT \ln \frac{\underline{V}}{\underline{V} - b} + RT \frac{b_{i}}{\underline{V} - b} - \frac{2\sum_{j} x_{j} a_{ij}}{\underline{V}}$$

$$\tag{40}$$

Fig. 3(a) shows the variation of solvation free energy with composition for a binary mixture (the relative critical properties for the component species are  $T_{\rm c,1}/T_{\rm c,2}=1.5$  and  $P_{\rm c,1}/P_{\rm c,2}=3$ ) at constant temperature ( $T/T_{\rm c,2}=0.5$ ) and pressure ( $P/P_{\rm c,2}=0.5$ ). For comparison, the corresponding activity coefficients are shown in Fig. 3(b). It can be seen that  $\Delta\underline{G}_i^{\rm *sol}$  may vary by a few units of RT (in this case about 2RT) with composition. Furthermore, the variation in  $\Delta\underline{G}_i^{\rm *sol}$  may be nonmonotonic with composition (e.g.,  $\Delta\underline{G}_2^{\rm *sol}$  exhibits a minimum at  $x_1=0.29$ ) even though the behavior in the activity coefficient (degree of non-ideality) is monotonic. Such differences in composition dependences are due to the variation of the compressibility factor (dashed line in Fig. 3(a)) as indicated by Eq. (33). Thus, the change in  $\Delta\underline{G}_i^{\rm *sol}$  may not necessarily infer a corresponding increase/decrease in non-ideality as one perceives it with the activity coefficient.

Using the VDW EOS, it can be shown that all of the 10 relationships presented in Fig. 1 are correct. For example, the total solvation free energy of the mixture fluid determined from



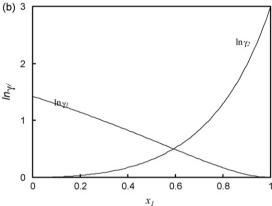


Fig. 3. The solvation free energy (a) and activity coefficient (b) as a function of composition for a binary mixture of van der Waals species at constant temperature and pressure.  $(P/P_{\rm c,2}=0.5,\ T/T_{\rm c,2}=0.5,\ T_{\rm c,1}/T_{\rm c,2}=1.5,\ P_{\rm c,1}/P_{\rm c,2}=3)$  The dashed line in (a) indicates the value of  $\ln z$ .

Eq. (20) is

$$\Delta \underline{G}^{*\text{sol}} = \sum_{i} x_{i} \, \Delta \underline{G}_{i}^{*\text{sol}} = RT \ln \frac{\underline{V}}{\underline{V} - b} + RT \frac{b}{\underline{V} - b} - \frac{2a}{\underline{V}}$$

and the configuration Helmholtz free energy can then the obtained from Eq. (23):

$$\underline{A}^{\text{CONF}} = -\underline{V} \int_{-\infty}^{\underline{V}} \frac{\Delta \underline{G}^{*\text{sol}}}{\underline{V}^{2}} d\underline{V} = RT \ln \frac{\underline{V}}{\underline{V} - b} - \frac{a}{\underline{V}}$$

which is identical to that found in Eq. (38).

### 8. Conclusion

Presented here are several relationships that are useful for connection between classical, statistical and solvation thermodynamics. It has been shown that engineering thermodynamic models can be derived with the knowledge of the configuration Helmholtz free energy, which is the difference in Helmholtz free energy of a real system and an ideal gas having the same temperature, volume and composition. Here, we show that the solvation free energy can also be derived from the configuration Helmholtz free energy simply by taking the partial derivative with respect to the number of moles.

In order to go back and forth between solvation and other thermodynamics models, we found it useful to define a new quantity, the total solvation free energy, which is simply the sum of individual solvation free energies of the constituent compounds in the system. There exist simple relationships between the total solvation free energy, the configuration Helmholtz free energy, and the compressibility factor. Therefore a complete network between these properties can be established, which is presented in Fig. 1. By making the connections clear, we hope to promote the research and utilization of solvation theory in phase equilibrium modeling. Conversely, solvation models, which are, in general, developed for liquids at the limits of pure liquid or infinite dilution, can be possibly extended to condition at all density and concentrations.

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## Appendix A. Expression for the pseudochemical potential

Here, we follow the procedure of Ben-Naim and provide the derivation for obtaining the expression of the pseudochemical potential. The chemical potential  $\mu$  is the incremental change in Helmholtz free energy upon addition of a molecule under condition of constant volume and temperature:

$$\mu = A(N+1) - A(N) = -kT \ln \left[ \frac{Q(N+1)}{Q(N)} \right]$$

$$= -kT \ln \left\{ \frac{q_i}{(N_i+1)\Lambda_i^3} \times \frac{\iint_V \exp[-u(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N)/kT] d\mathbf{r}_0 d\mathbf{r}_1 \cdots d\mathbf{r}_N}{\iint_V \exp[-u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)/kT] d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N} \right\}$$

$$= -kT \ln \left\{ \frac{q_i}{(N_i+1)\Lambda_i^3} \iint_V P(\mathbf{r}_1, \mathbf{r}_2, \dots, d\mathbf{r}_N) \times \exp\left[-\frac{B_0(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N)}{kT}\right] d\mathbf{r}_0 d\mathbf{r}_1 \cdots d\mathbf{r}_N \right\}$$

$$\times \exp\left[-\frac{B_0(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N)}{kT}\right] d\mathbf{r}_0 d\mathbf{r}_1 \cdots d\mathbf{r}_N \right\}$$
(A-1)

where, in the last equality, we have defined the probability density P as

$$P(\mathbf{r}_{1}, \mathbf{r}_{2}, \dots, \mathbf{r}_{N})$$

$$= \frac{\exp[-u(\mathbf{r}_{1}, \mathbf{r}_{2}, \dots, \mathbf{r}_{N})/kT]}{\iint_{V} \exp[-u(\mathbf{r}_{1}, \mathbf{r}_{2}, \dots, \mathbf{r}_{N})/kT] d\mathbf{r}_{1} d\mathbf{r}_{2} \cdots d\mathbf{r}_{N}}$$
(A-2)

and the binding energy between the added molecule and all other molecules in the system  $B_0$ 

$$B_0(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N) = u(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N) - u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$
(A-3)

If we choose the origin of the integration at  $\mathbf{r}_0$ , Eq. (A-1) then simplifies to:

$$\mu = -kT \ln \left\{ \frac{q_i V}{(N_i + 1)\Lambda_i^3} \iint_V P(\mathbf{r}_1, \mathbf{r}_2, \dots, d\mathbf{r}_N) \right.$$

$$\times \exp \left[ -\frac{B_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}{kT} \right] d\mathbf{r}_1 \cdots d\mathbf{r}_N \right\}$$
(A-4)

In the classical limit, the number density  $\rho_i = (N_i + 1)/V \cong N_i/V$ . Using the symbol  $\langle \rangle$  to express the Boltzmann average, Eq. (A-4) can be rewritten in a compact form as follows:

$$\mu = -kT \ln \left[ \frac{q_i}{\rho_i \Lambda_i^3} \left\langle \exp\left(-\frac{B_0}{kT}\right) \right\rangle \right] \tag{A-5}$$

We can now use the same strategy to derive the expression for the pseudochemical potential  $\mu^*$ , which is the chemical potential of a molecule at a fixed point in a fluid. It is apparent that  $\mu^*$  is different from  $\mu$  because the added molecule is now placed at a fixed point. This difference has two important consequences. First, the added molecule does not possess kinetic energy. Therefore, the translational partition function is equivalent to unity. Second, the added molecule is distinguishable from all other molecules. Therefore,

$$\mu^* = A(N+1; r_0) - A(N)$$

$$= kT \ln \left\{ q_i \frac{\iint_V \exp[-u(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N)/kT] \, d\mathbf{r}_1 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N}{\iint_V \exp[-u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)/kT] \, d\mathbf{r}_1 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N} \right\}$$

$$= -kT \ln \left\{ q_i \iint_V P(\mathbf{r}_1, \mathbf{r}_2, \dots, d\mathbf{r}_N) \right\}$$

$$\times \exp \left[ -\frac{B_0(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N)}{kT} \right] d\mathbf{r}_1 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N \right\}$$

$$= -kT \ln \left[ q_i \left\langle \exp\left(-\frac{B_0}{kT}\right) \right\rangle \right] \tag{A-6}$$

# Appendix B. Partial derivative of $A^{CONF}(N_i, V, T)$ with respective to $N_i$

Here, we show that the partial derivative of the configuration Helmholtz free energy with respect to the amount of species i gives the solvation free energy of that species. The  $A^{\rm CONF}$  can be expressed in terms of integrals of molecular interactions as:

$$A^{\text{CONF}}(N_1, N_2, \dots, V, T) = A(N_1, N_2, \dots, V, T) - A^{\text{IG}}(N_1, N_2, \dots, V, T)$$

$$= -kT \ln \left\{ \frac{\prod_i q_i^{N_i} \iint_V \exp[-u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)/kT] d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N}{\prod_i q_i^{\text{IG}^{N_i}} V^N} \right\}$$
(B-1)

Taking the partial derivative of Eq. (B-1) we have:

$$\begin{split} \frac{\partial A^{\text{CONF}}}{\partial N_i} \bigg|_{T,V} &= A^{\text{CONF}}(N+1) - A^{\text{CONF}}(N) \\ &= -kT \ln \frac{q_i V^N}{q_i^{\text{IG}} V^{N+1}} \\ &\times \frac{\iint_V \exp[-u(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N)/kT] \, d\mathbf{r}_0 \, d\mathbf{r}_1 \cdots d\mathbf{r}_N}{\iint_V \exp[-u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)/kT] \, d\mathbf{r}_1 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N} \\ &= -kT \ln \frac{q_i V^{N+1}}{q_i^{\text{IG}} V^{N+1}} \\ &\times \frac{\iint_V \exp[-u(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N)/kT] \, d\mathbf{r}_1 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N}{\iint_V \exp[-u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)/kT] \, d\mathbf{r}_1 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N} \\ &= -kT \ln \frac{q_i V^{N+1}}{q_i^{\text{IG}} V^{N+1}} \\ &\times \iint_V \exp\left(-\frac{B_0}{kT}\right) d\mathbf{r}_1 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N \\ &= -kT \ln \left[\frac{q_i}{q_i^{\text{IG}}} \left\langle \exp\left(-\frac{B_0}{kT}\right) \right\rangle \right] \end{split} \tag{B-2}$$

This is identical to the solvation free energy in Eq. (11).

# Appendix C. Total solvation free energy in terms of $A^{\mathrm{CONF}}$ and z

Substituting Eq. (19) into Eq. (20), we have the total solvation free energy related to the total Gibbs free energy shown as:

$$\Delta G^{*\text{sol}} = G(T, P, x) - G^{\text{IG}}(T, P, x) + NkT \ln z \tag{C-1}$$

Since G = A + PV = A + zNkT, Eq. (C-1) can be rewritten as:

$$\Delta G^{*\text{sol}} = A(T, P, \underline{x}) + zNkT - A^{\text{IG}}(T, P, \underline{x}) - NkT + NkT \ln z$$

$$= A(T, V, \underline{x}) + zNkT - A^{\text{IG}}\left(T, V = \frac{NkT}{P}, \underline{x}\right)$$

$$- NkT + NkT \ln z$$

$$= A(T, V, \underline{x}) - A^{\text{IG}}(T, V, \underline{x}) + (z - 1)NkT$$

$$- NkT \ln z + NkT \ln z = A^{\text{CONF}} + (z - 1)NkT \quad \text{(C-2)}$$

where we have used  $A^{IG}(T,V,N) - A^{IG}(T,NkT/P,N) = -NkT \ln z$  in the above derivation.

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### 溶合與化工熱力學

林祥泰 謝介銘 李旻聰 國立台灣大學化學工程學系

### 摘 要

近年來由於計算化學的理論趨於完備與成熟,透過第一原理量子力學計算溶合自由能,進而求得流體 其他熱力學性質,已成為預測相行為以及相平衡的有效方法之一。然而,除了文獻上少數的例子外,此法 尚未被廣泛地採用。除了歸咎於溶合理論本身的概念十分抽象,缺乏溶合特性與常見熱力學性質間清楚而 明確的關係,也是主因。在此,我們將描述相平衡時常用的熱力學性質與溶合之間的關係,作一清楚且嚴 謹的推演與整理。藉由定義系統之「總溶合自由能」,我們可以很容易地將任何現有的熱力學模型轉變為 溶合自由能模型,反之亦然。因此,在本論文中所推導的關係式廣泛適用於所有系統,可提供透過溶合自 由能的量子力學計算而求得現有熱力學模型內之參數的正確方法,也有助於從溶合理論開發新的熱力學模 型。