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More Than You Ever Cared to Know About Solution Thermodynamics

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I. SYNOPSIS

These readings are a compendium of earlier works put together, and corrected for minor errors (actually some of them weren't so tiny!).

II. INTRODUCTION

Theoretical Chemistry holds out the promise (dangles it before our gluttonous eyes) that the properties of species can be determined solely from fundamental constants such as the charge on the electron, the mass of nuclei, Planck's constant, etc.. All one need know is the identity of the substance in question, and given enough (human) energy and computational effort, one could calculate, say, the vapor pressure of the material at any desired temperature. (Or its color, ductility, melting point, etc..)

This tantalizing promise, in effect, weaves the chemical tapestry using quantum mechanics and statistical thermodynamics as its thread (warp and woof?).

We here offer a part of the puzzle, the non-ideal solution part, in the context of an example which allows us to see where in the partition function the non-ideality comes into play, and how this relates to thermodynamics. We also show how the various classical thermodynamic relations are related to this point of view, offering a reverse viewing of traditional solution thermodynamics.

A. Preliminaries

Before beginning, we offer some preliminary calculus aimed at the two-component solution. We start with the definition of the mole fraction of component A (the other is B),

$$x_A = \frac{n_A}{n_A + n_B} \quad (2.1)$$

where, n refers to number of moles, and x refers to mole fraction.

By partial differentiation we obtain

$$\left(\frac{\partial x_A}{\partial n_A}\right)_{n_B} = \left(\frac{\partial \frac{n_A}{n_A+n_B}}{\partial n_A}\right)_{n_B}$$

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which is

$$\left(\frac{\partial x_A}{\partial n_A}\right)_{n_B} = \frac{1}{n_A + n_B} - \frac{n_A}{(n_A + n_B)^2}$$

which, bringing the r.h.s. to a common denominator simplifies into

$$\left(\frac{\partial x_A}{\partial n_A}\right)_{n_B} = \frac{x_B}{n_A + n_B}$$

It then follows that

$$\left(\frac{\partial x_B}{\partial n_A}\right)_{n_A} = \left(\frac{\partial \left(\frac{n_B}{n_A+n_B}\right)}{\partial n_A}\right)_{n_B} = -\frac{x_B}{n_A + n_B}$$

However,

$$\left(\frac{\partial x_A}{\partial n_A}\right)_{n_A} = -\frac{n_A}{(n_A + n_B)^2} = -\frac{x_A}{n_A + n_B}$$

with the symmetric result

$$\left(\frac{\partial x_B}{\partial n_A}\right)_{n_B} = -\frac{x_B}{n_A + n_B}$$

Great care must be taken when taking these partial derivatives to hold constant the variables demanded by the (perhaps old-fashioned) notation.

We will use these (and similar) results in the subsequent work.

B. An ideal gaseous mixture

The equation of state of an ideal gaseous mixture would be given by

$$V = \frac{(N_A + N_B)kT}{p} + N_A\Sigma_A + N_B\Sigma_B \quad (2.2)$$

where we are using capital letters uniformly to indicate a per atom (or molecule) basis (we will convert to lower case when we go to a molar basis). V is the volume, N_A is the number of molecules of A (and similarly for B), and Σ_A is the effective van der Waals' hard sphere parameter.

The partition function from which this equation of state came is

$$Z = \left(\frac{(V - N_A\Sigma_A - N_B\Sigma_B)^{(N_A+N_B)}}{N_A!N_B!}\right) \left(\frac{2\pi m_A kT}{h^2}\right)^{3N_A/2} \left(\frac{2\pi m_B kT}{h^2}\right)^{3N_B/2} \quad (2.3)$$

where m_A is the mass (per atom or molecule) of substance A. We will (*vide infra*) abbreviate

$$\Lambda_i = \left(\frac{2\pi m_i kT}{h^2} \right)$$

Parenthetically, for future reference, we note the units of this term:

$$\frac{\frac{\text{grams}}{\text{atom}} \frac{\text{ergs}}{\text{K}}}{\text{erg}^2 \text{sec}^2}$$

which is

$$\frac{\frac{\text{grams}}{\text{atom}} \text{erg}}{\text{erg}^2 \text{sec}^2}$$

which is

$$\frac{\frac{\text{grams}}{\text{atom}}}{\frac{g \text{ cm}^2}{\text{sec}^2} \frac{\text{cm}}{\text{s}}} \text{ec}^2$$

After some work, this becomes $\frac{\text{atom}}{\text{cm}^3}$ which offsets the V terms.

The Helmholtz Free Energy is then

$$\begin{aligned} & \frac{A}{kT} = \\ & -(N_A + N_B) \ln(V - N_A \Sigma_A - N_B \Sigma_B) + \ln N_A! + \ln N_B! \\ & \frac{3N_A}{2} \ln \left(\frac{2\pi m_A kT}{h^2} \right) - \frac{3N_B}{2} \ln \left(\frac{2\pi m_B kT}{h^2} \right) \end{aligned} \quad (2.4)$$

since $A = -kT \ln Z$. But $G = A + pV$, and

$$\left(\frac{\partial A}{\partial V} \right)_T = -p$$

so we can re-write Equation 2.2:

$$pV = (N_A + N_B)kT + (N_A \Sigma_A + N_B \Sigma_B)p$$

and adding this to A we obtain G :

$$\frac{G}{kT} = -(N_A + N_B) \ln \frac{(N_A + N_B) kT}{p}$$

i.e.,

$$\begin{aligned} \frac{G}{kT} = & -(N_A + N_B) \ln \frac{(N_A + N_B) kT}{p} \\ & - \frac{3N_A}{2} \ln \Lambda_A - \frac{3N_B}{2} \ln \Lambda_B + \\ & \frac{p}{kT} (N_A \Sigma_A + N_B \Sigma_B) + N_A \ln N_A + N_B \ln N_B \end{aligned} \quad (2.5)$$

where we will, of course, use Stirling's approximation where appropriate. Note that we have explicitly forced V out of this expression, and made sure that only p and T appear. The Legendre Transformations in going from A to G means that this is a necessity!

We can now find the chemical potentials of both A and B . We have, taking the appropriate partial derivative:

$$\begin{aligned} & \left(\frac{\partial G}{\partial N_A} \right)_{p,T,N_B} \equiv \mu_A = \\ & kT \left(-\ln \frac{(N_A + N_B)kT}{p} - \frac{3}{2} \ln \Lambda_A + \frac{p \Sigma_A}{kT} + \ln N_A \right) \end{aligned}$$

where we are using Λ to hide a number of atomic constants. Re-writing in compact notation, we have

$$\frac{\mu_A}{kT} = \ln \left(x_A \frac{p}{kT} e^{p \Sigma_A / kT} \Lambda_A^{-3/2} \right) \quad (2.6)$$

where x_A is the mole fraction (of A, of course).

As $N_B \rightarrow 0$, the mixture approaches pure A ($x_A \rightarrow 1$), and we obtain

$$\frac{\mu_A^{pure}}{kT} = \ln \left(\frac{p}{kT} e^{p \Sigma_A / kT} \Lambda_A^{-3/2} \right) \quad (2.7)$$

which, as $p \rightarrow p_{std}$, the standard pressure become

$$\frac{\mu_A^{std}}{kT} = \ln \left(\frac{p_{std}}{kT} e^{p_{std} \Sigma_A / kT} \Lambda_A^{-3/2} \right) \quad (2.8)$$

Note the difference between being pure, and being at the standard state. (Further, note that the old standard state, 1 atm, has been supplanted by the new standard state, 1 bar, which forces the choice of R 's units.) From Equation 2.8 one has

$$\frac{\mu_A^{std}}{kT} = \ln \left(\frac{p}{kT} \right) + \left(p_K \frac{\Sigma_A}{kT} \right) - \frac{3}{2} \ln \Lambda_A \quad (2.9)$$

and from Equation 2.7 one has

$$\ln \left(\frac{p}{kT} \right) = \left(p_{std} \frac{\Sigma_A}{kT} \right) - \frac{3}{2} \ln \Lambda_A \quad (2.10)$$

so, subtracting, one has

$$\mu_A^{pure} - \mu_A^0 = kT \ln \left(\frac{p}{p_{std}} e^{(p-p_{std}) \Sigma_A / kT} \right)$$

It is interesting to notice how nicely the fugacity emerges in this example, i.e., we define

$$f_A = p e^{p \Sigma_A / kT}$$

which as the pressure goes to zero becomes

$$\lim_{p \rightarrow 0} \frac{f_A}{p} = 1$$

In the standard state ($p \rightarrow p^{std}$, $f_A \rightarrow f_A^0$), one has

$$f_A^0 = p_{std} e^{p_{std} \Sigma_A / kT}$$

so that the equation for the chemical potential of pure A becomes

$$\mu_A^{pure} - \mu_A^0 = kT \ln \frac{p}{p_{std}} e^{(p-p_{std}) \Sigma_A / kT} = kT \ln \frac{f_A}{f_A^0}$$

or, even more familiarly,

$$\mu_A^{pure} = \mu_A^0 + RT \ln \frac{f_A}{f_A^0}$$

(where we have also, quickly, gone to a "pre mole" basis ($N_{Av}k = R$, $N_{Av}\Sigma_A = \sigma_A$)).

Finally, for the solution, we have from Equation 2.6

$$\frac{\mu_A}{kT} = \frac{\mu_A^0}{kT} + \ln \left(x_A \frac{f_A}{f_A^0} \right) \quad (2.11)$$

which can be rewritten as

$$\frac{\mu_A}{kT} = \frac{\mu_A^{pure}}{kT} + \ln x_A \quad (2.12)$$

This last equation says as succinctly as possible, that the original solution is ideal. This is known as Raoult's Law.

The definition of an ideal solution is exactly what this solution has as a property. To obtain the partial molar volume, we take the partial derivative of μ with respect to p , holding T , N_A , and N_B constant. First, we convert finally to a molar basis, so

$$\left(\frac{\partial G}{\partial n_A} \right)_{p,T,n_B} \equiv \mu_A = RT \left(\ln \frac{(n_A + n_B)RT}{p} - \frac{3}{2} \ln \lambda_A + \frac{p\sigma_A}{RT} + \ln n_A \right)$$

so

$$\frac{1}{RT} \left(\frac{\partial \mu_A}{\partial p} \right)_{n_A,n_B,T} = \frac{1}{p} + \frac{\sigma_A}{RT} \equiv \bar{v}_A$$

with an equivalent expression for B, i.e.

$$\frac{1}{RT} \left(\frac{\partial \mu_B}{\partial p} \right)_{n_A,n_B,T} = \frac{1}{p} + \frac{\sigma_B}{RT} \equiv \bar{v}_B$$

From these two, we recover the volume per mole of solution (v)

$$n_A \bar{v}_A + n_B \bar{v}_B = \frac{(n_A + n_B)RT}{p} + n_A \sigma_A + n_B \sigma_B$$

C. The Osmotic Pressure

Assume we have a solution of A and B in equilibrium with pure A (call that the solvent). Assume the two are separated by the mythic semi-permeable membrane, which keeps the B molecules from infecting the pure solvent (A) side. Since there is no possibility of B molecules living in the pure A side, A molecules must migrate across the semi-permeable membrane attempting to dilute the solution infinitely, whereupon "there would be vanishingly small B molecules there also". To prevent this migration one needs to apply an external pressure (π) called the osmotic pressure.

At equilibrium, the chemical potential of A (solvent) must be equal on the two sides of the semipermeable membrane, so

$$\mu_A^{pure} = \mu_A^{in\ solution}$$

which translates into

$$\mu_A^0 + RT \ln \left(\frac{p}{p_{std}} e^{(p-p_{std})\sigma_A/RT} \right) = \mu_A^0 + RT \ln \left(x_A p + \pi e^{(p-p_{std}+\pi)\sigma_A/RT} \right)$$

which simplifies to

$$p = x_A \left(\frac{p + \pi}{p_{std}} \right) e^{\pi\sigma_A/RT}$$

which is, unfortunately, a transcendental equation for the osmotic pressure, π .

III. A NON-IDEAL SOLUTION

The one dimensional hard line model, originally introduced by Rayleigh [1] and extended to hard line mixtures [2], was used to explicitly discuss solution thermodynamics [3]. Unfortunately, the hard line mixture (suitably extended to three dimensions) is an ideal solution, and as a result, part of the value of using it as an example is lost. Here, a non-ideal system is constructed which allows one to follow the thread from the partition function through to thermodynamics. This is a partial example which exemplifies all but the initial step in the schema, i.e., we can not obtain the partition function from an intermolecular potential energy form itself derived from elementary quantum mechanics.

IV. THE PARTITION FUNCTION

Given the partition function:

$$Z \equiv \frac{(V - N_A \Sigma_A - N_B \Sigma_B + x_A x_B (N_A + N_B) \Sigma_{AB})^{N_A + N_B}}{N_A! N_B!} \lambda_A^{3N_A/2} \lambda_B^{3N_B/2}$$

where N_A is the number of moles of A in the system, N_B is the number of moles of B in the system, Σ_A is the molar hard sphere diameter of A molecules, Σ_B is the molar hard sphere diameter of B molecules, and Σ_{AB} is the *non-additive molar repulsive interaction between A and B molecules (approximately)*. We obtain the Helmholtz free energy

$$\frac{A}{RT} = -(N_A + N_B) \ln \{ V - N_A \Sigma_A - N_B \Sigma_B + (N_A + N_B) x_A x_B \Sigma_{AB} \} - \frac{3N_A}{2} \ln \lambda_A - \frac{3N_B}{2} \ln \lambda_B + \ln N_A! + \ln N_B!$$

by following the standard prescription. Taking the partial derivative of A with respect to V we generate the equation of state:

$$V = \frac{(N_A + N_B)kT}{p} + N_A \Sigma_A + N_B \Sigma_B - \frac{N_A N_B}{N_A + N_B} \Sigma_{AB}.$$

Then, since $G = A + pV$ and

$$pV = (N_A + N_B)RT + p(N_A \Sigma_A + N_B \Sigma_B - x_A x_B (N_A + N_B) \Sigma_{AB})$$

we obtain

$$\frac{G}{RT} = -(N_A + N_B) \ell n \frac{(N_A + N_B)RT}{p} - \frac{3N_A}{2} \ell n \lambda_A - \frac{3N_B}{2} \ell n \lambda_B \quad (4.1)$$

i.e.,

$$\begin{aligned} \frac{G}{RT} = & -(N_A + N_B) \ell n \frac{(N_A + N_B)RT}{p} \\ & - \frac{3N_A}{2} \ell n \lambda_A - \frac{3N_B}{2} \ell n \lambda_B \\ & + \frac{p}{RT} \{ N_A \Sigma_A + N_B \Sigma_B - (N_A + N_B) x_A x_B \Sigma_{AB} \} \\ & + N_A \ell n N_A + N_B \ell n N_B \end{aligned}$$

where we have written G as $G(T, p)$ explicitly, i.e., every mention of V has been obliterated! (It may be appropriate to mention here that the Legendre transformations which relate E to H to A to G carry with them definite rules about which variables are appropriate, and which are not.)

V. THE EQUATION OF STATE OF AN ARTIFICIALLY NON IDEAL MIXTURE

Instead of the equation of state for an ideal mixture

$$V = \frac{(N_A + N_B)kT}{p} + N_A \Sigma_A + N_B \Sigma_B$$

where V is the volume, N_A is the number of molecules of A (similarly for B), and σ_A is something like a van der Waals hard sphere volume (with a similar term for B), we are here and now forced to use the aforementioned (now on a atomic basis rather than a molar basis)

$$V = \frac{(N_A + N_B)kT}{p} + N_A \Sigma_A + N_B \Sigma_B - \frac{N_A N_B}{N_A + N_B} \Sigma_{AB} \quad (5.1)$$

where the minus sign before the term $\frac{N_A N_B}{N_A + N_B} \Sigma_{AB}$, is arbitrary (i.e., we can define the constant σ_{AB} as either positive or negative in this, the non-ideal term). Please

note that we are following a convention that lowercase letters refer to molar quantities (and uppercase letters refer to "per particle" properties). Converting Equation 5.3 to a "per mole" basis gives us

$$\begin{aligned} v &= \frac{(n_A + n_B) \frac{n_{Av}}{n_{Av}} RT}{p} + n_A \frac{n_{Av}}{n_{Av}} \sigma_A + \\ & \quad n_B \frac{n_{Av}}{n_{Av}} \sigma_B - \frac{n_A n_B}{n_A + n_B} \frac{n_{Av}}{n_{Av}} \sigma_{AB} \\ v &= \frac{(n_A + n_B)RT}{p} + n_A \sigma_A + n_B \sigma_B - \frac{n_A n_B}{n_A + n_B} \frac{1}{n_{Av}} \sigma_{AB} \\ v &= \frac{(n_A + n_B)RT}{p} + n_A \sigma_A + n_B \sigma_B - x_A x_B (n_A + n_B) \sigma_{AB} \end{aligned} \quad (5.3)$$

from which we obtain the partial molar volumes by explicit partial differentiation. We have (omitting the third term, which vanishes)

$$\begin{aligned} \left(\frac{\partial V}{\partial n_A} \right)_{T,p,n_B} &= \left(\frac{\partial \frac{(n_A + n_B)RT}{p}}{\partial n_A} \right)_{T,p,n_B} \\ & \quad + \left(\frac{\partial n_A \sigma_A}{\partial n_A} \right)_{T,p,n_B} \\ & \quad - \left(\frac{\partial (x_B x_A) (n_A + n_B) \sigma_{AB}}{\partial n_A} \right)_{T,p,n_B} \end{aligned}$$

which is

$$= \frac{RT}{p} + \sigma_A - \sigma_{AB} \left(\frac{\partial (x_B x_A) (n_A + n_B)}{\partial n_A} \right)_{T,p,n_B}$$

i.e.

$$\begin{aligned} &= \frac{RT}{p} + \sigma_A - \sigma_{AB} \left(x_A (n_A + n_B) \left(\frac{\partial x_B}{\partial n_A} \right)_{T,p,n_B} \right. \\ & \quad \left. + x_B (n_A + n_B) \left(\frac{\partial x_A}{\partial n_A} \right)_{T,p,n_B} + x_A x_B \right) \\ &= \frac{RT}{p} + \sigma_A + x_A \sigma_{AB} (n_A + n_B) \left(\frac{x_B}{n_A + n_B} \right)_{T,p,n_B} \\ & \quad - x_B \sigma_{AB} (n_A + n_B) \left(\frac{x_B}{n_A + n_B} \right)_{T,p,n_B} - x_A x_B \sigma_{AB} \end{aligned}$$

which becomes using the preliminary materials (*vide ante*)

$$= \frac{RT}{p} + \sigma_A - x_B^2 \sigma_{AB}$$

or

$$= \frac{RT}{p} + \sigma_A - x_B (1 - x_A) \sigma_{AB}$$

$$= \frac{RT}{p} + \sigma_A + x_B x_A \sigma_{AB} - x_B \sigma_{AB}$$

Our final result then is

$$\left(\frac{\partial V}{\partial n_A} \right)_{T,p,n_B} \equiv \bar{v}_A = \frac{RT}{p} + \sigma_A + x_B x_A \sigma_{AB} - x_B \sigma_{AB} \quad (5.4)$$

with a similar term for \bar{v}_B

$$\left(\frac{\partial V}{\partial n_B} \right)_{T,p,n_A} \equiv \bar{v}_B = \frac{RT}{p} + \sigma_B - x_A \sigma_{AB} + x_A x_B \sigma_{AB}.$$

Later, we show that these expressions can be used to verify that $v = n_A \bar{v}_A + n_B \bar{v}_B$ (Euler's Theorem).

VI. EXPERIMENTAL DETERMINATION OF THE PARTIAL MOLAR VOLUME.

Assume that we have experimental information on the molar volume of a solution as a function of the mole fraction of A (or B). If V is the total volume, and v is the volume per mole of solution, i.e., if

$$v = \frac{V}{n_A + n_B}$$

then since

$$V = (n_A + n_B)v$$

it follows that

$$\left(\frac{\partial V}{\partial n_A} \right)_{n_B} \equiv \bar{v}_A = (n_A + n_B) \frac{\partial v}{\partial n_A} + v$$

and using the chain rule one obtains

$$\left(\frac{\partial V}{\partial n_A} \right)_{n_B} \equiv \bar{v}_A = (n_A + n_B) \frac{\partial v}{\partial x_A} \frac{\partial x_A}{\partial n_A} + v$$

which yields (see footnote for partial derivatives)

$$\bar{v}_A = v + x_B \left(\frac{\partial v}{\partial x_A} \right)_{n_B} \quad (6.1)$$

which phrases the calculation of the partial molar volume of A in terms of the experimental molar volume and mole fraction. This result is a direct recovery of the standard textbook form for graphically obtaining the partial molar volume. We can verify that this form holds in our case. From Equation 5.3 we have:

$$v = \frac{V}{n_A + n_B} = \frac{RT}{p} + x_A \sigma_A + x_B \sigma_B - x_A x_B \sigma_{AB} \quad (6.2)$$

which becomes, upon partial differentiation with respect to x_A :

$$\sigma_A + \left(\frac{\partial x_B}{\partial x_A} \right)_{n_B} \sigma_B - x_B \sigma_{AB} - x_A \left(\frac{\partial x_B}{\partial x_A} \right)_{n_B} \sigma_{AB},$$

$$\left(\frac{\partial v}{\partial x_A} \right)_{n_B} = \sigma_A - \sigma_B - x_B \sigma_{AB} + x_A \sigma_{AB}$$

But, we already had (Equation 6.2):

$$v = \frac{RT}{p} + x_A \sigma_A + x_B \sigma_B - x_A x_B \sigma_{AB}$$

so that (Equation 6.1)

$$\bar{v}_A = v + x_B \left(\frac{\partial v}{\partial x_A} \right)_{n_B} =$$

$$\frac{RT}{p} + x_A \sigma_A + x_B \sigma_B - x_A x_B \sigma_{AB} + x_B (\sigma_A - \sigma_B - x_B \sigma_{AB} + x_A \sigma_{AB})$$

Selectively expanding x_B we obtain:

$$\bar{v}_A = \frac{RT}{p} + x_A \sigma_A + x_B \sigma_B - \sigma_{AB} x_A x_B + x_B \sigma_A - x_B \sigma_B - x_B^2 \sigma_{AB} + x_A x_B \sigma_{AB}$$

which succumbs to impressive cancellation yielding:

$$= \frac{RT}{p} + \sigma_A - x_B \sigma_{AB} + x_A x_B \sigma_{AB}$$

which verifies Equation 5.4.

VII. THE CHEMICAL POTENTIAL

Although interest in partial molar volumes may not be intense, interest in partial molar quantities in the area of the partial molar free energy, nominally, the Chemical Potential, is. The mixture under discussion here lends itself gracefully to exercising one's manipulative skills in this area also. Taking the partial of G (Equation 4.2) with respect to n_A yields,

$$\left(\frac{\partial G}{\partial n_A} \right)_{T,p,n_B} = RT \left\{ -\ln \frac{(n_A + n_B)RT}{p} + \ln n_A - \frac{3}{2} \ln \lambda_A \right\} + p \left(\sigma_A - x_A x_B \sigma_{AB} - (n_A + n_B) \frac{\partial x_A}{\partial n_A} x_B \sigma_{AB} - (n_A + n_B) x_A \frac{\partial x_B}{\partial n_A} \sigma_{AB} \right)$$

Substituting the footnoted equations herein we obtain

$$\frac{\partial G}{\partial n_A} = RT \left\{ -\ln \frac{(n_A + n_B)RT}{p} + \ln n_A - \frac{3}{2} \ln \lambda_A \right\} + p \left(\sigma_A + \left\{ -x_A x_B - x_B^2 + \frac{x_A n_B}{(n_A + n_B)} \right\} \sigma_{AB} \right)$$

which yields

$$\frac{\partial G}{\partial n_A} = RT \left\{ -\ln \frac{(n_A + n_B)RT}{p} + \ln n_A - \frac{3}{2} \ln \lambda_A \right\} + p \{ \sigma_A - x_B^2 \sigma_{AB} \}$$

so we finally obtain

$$\frac{\mu_A}{RT} = \ln \left(x_A \frac{p}{RT} \lambda_A^{-3/2} e^{(\sigma_A - x_B^2 \sigma_{AB})p/RT} \right) \quad (7.1)$$

with an equivalent expression for B

$$\frac{\mu_B}{RT} = \ln \left(x_B \frac{p}{RT} \lambda_B^{-3/2} e^{(\sigma_B - x_A^2 \sigma_{AB})p/RT} \right) \quad (7.2)$$

In the limit of pure A the chemical potentials of A properly approach those of pure A i.e.,

$$\frac{\mu_A^{pure}}{RT} = \ln \left(\frac{p}{RT} \lambda_A^{-3/2} e^{p\sigma_A/RT} \right)$$

with an equivalent expression for pure B

$$\frac{\mu_B^{pure}}{RT} = \ln \left(\frac{p}{RT} \lambda_B^{-3/2} e^{p\sigma_B/RT} \right).$$

At the standard pressure (1 bar), one would have

$$\frac{\mu_B^{pure-std}}{RT} = \ln \left(\frac{1}{RT} \lambda_B^{-3/2} e^{\sigma_B/RT} \right).$$

One can see how one obtains the form:

$$\mu = \mu^{std} + RT \ln f \equiv \mu^0 + RT \ln f$$

(the standard notation has standard states using the zero superscript) from these forms, and why the fugacity is defined as it is.

A. The Gibbs Duhem Equation

One consequence of the chemical potential being a homogenous function of order zero is the Gibbs Duhem equation which allows us to obtain the chemical potential of a solute from that of a solvent. Since the equation

$$n_A \left(\frac{\partial \mu_A / RT}{\partial n_A} \right)_{n_B} + n_B \left(\frac{\partial \mu_A / RT}{\partial n_B} \right)_{n_A} = 0$$

can be rewritten

$$n_A \left(\frac{\partial \mu_A}{\partial n_A} \right)_{n_B} + n_B \left(\frac{\partial \left(\frac{\partial G}{\partial n_A} \right)_{n_B}}{\partial n_B} \right)_{n_A} = 0$$

and since the order of differentiation

$$\frac{\partial^2 G}{\partial n_B \partial n_A} = \left(\frac{\partial \mu_A}{\partial n_B} \right)_{n_A} = \left(\frac{\partial \mu_B}{\partial n_A} \right)_{n_B}$$

is irrelevant, we have

$$n_A \left(\frac{\partial \mu_A}{\partial n_A} \right)_{n_B} + n_B \left(\frac{\partial \mu_A}{\partial n_B} \right)_{n_A} = 0$$

giving us

$$n_A \left(\frac{\partial \mu_A}{\partial n_A} \right)_{n_B} + n_B \left(\frac{\partial \mu_B}{\partial n_A} \right)_{n_B} = 0.$$

Since we have (from Equation 7.1)

$$\frac{1}{RT} \left(\frac{\partial \mu_A}{\partial n_A} \right)_{n_B} = \frac{1}{x_A} \left(\frac{\partial x_A}{\partial n_A} \right)_{n_B} - \frac{2p x_B \sigma_{AB}}{RT} \left(\frac{\partial x_B}{\partial n_A} \right)_{n_B} \quad (7.3)$$

so that, substituting, we obtain

$$\frac{n_A}{RT} \left(\frac{\partial \mu_A}{\partial n_A} \right)_{n_B} = x_B + 2x_A x_B^2 \frac{p\sigma_{AB}}{RT} = -\frac{n_B}{RT} \left(\frac{\partial \mu_B}{\partial n_A} \right)_{n_B}$$

This is almost in integrable form. We rewrite this as

$$\begin{aligned} \frac{N_A}{RT} \frac{\partial \mu_A}{\partial n_A} &= x_B + 2x_A x_B^2 \left(\frac{p\sigma_{AB}}{RT} \right) = \\ &= -\frac{n_B}{RT} \left(\frac{\partial \mu_B}{\partial n_A} \right) = \\ &= -n_B \left(\frac{\partial \mu_B}{\partial x_A} \right) \left(\frac{\partial x_A}{\partial n_A} \right), \end{aligned}$$

having employed the chain rule, to obtain

$$x_B + 2x_A x_B^2 \frac{p\sigma_{AB}}{RT} = -x_B^2 \frac{\partial \mu_B}{\partial x_A}.$$

We finally obtain

$$\frac{\partial \mu_B}{\partial x_A} = -\frac{1}{(1-x_A)} - 2x_A \frac{p\sigma_{AB}}{RT}$$

which allows us to write

$$\int d\mu_B = -\int \frac{1}{1-x_A} dx_A - \frac{2p\sigma_{AB}}{RT} \int x_A dx_A$$

yielding

$$\mu_B = \ln x_B - \frac{p\sigma_{AB}}{RT} x_A^2 + constant$$

which can be rewritten

$$\mu_B = \ln x_B + \ln e^{-x_A^2 p\sigma_{AB}/RT} + \ln C_I.$$

This expression recovers the mole fraction dependence in Equation 7.2. We have therefore obtained the form of the chemical potential of B (solute?) from that of A (solvent?) which is a direct example of how the Gibbs Duhem equation is used in practice. If the chemical potential of one component has been measured, and is therefore known as a function of concentration, then this integration would be performed either graphically or numerically [4] to obtain the chemical potential of the other component.

B. Euler's Theorem holds for V

It is important to show that Euler's theorem holds properly for these partial molar volumes, i.e., that

$$n_A \bar{v}_A + n_B \bar{v}_B = V,$$

by substituting Equation 5.4 (and its analog for \bar{v}_B into Equation 6.2 to obtain

$$V = \frac{(n_A + n_B)RT}{p} + n_A \sigma_A + n_B \sigma_B - n_A x_B \sigma_K$$

$$V = \frac{(n_A + n_B)RT}{p} + n_A \sigma_A + n_B \sigma_B - n_A x_B \sigma_{AB}$$

$$+ n_A x_A x_B \sigma_{AB} - n_B x_A \sigma_{AB} + n_B x_A x_B \sigma_{AB}$$

which simplifies into

$$V = \frac{(n_A + n_B)RT}{p} + n_A \sigma_A + n_B \sigma_B - 2x_A x_B (n_A + n_B) \sigma_{AB} + x_A x_B (n_A + n_B) \sigma_{AB}$$

which is exactly correct (i.e., simplifies into Equation 5.3). In the context of this paper Euler's theorem demands that any valid expression for a partial molar volume must not only be a homogeneous function of the numbers of moles, but that it must be of order zero! This is because the volume itself is homogeneous of order one, so that removing one order of mole number brings the homogeneity to zero.

C. Euler's Theorem holds for G

It is worthwhile verifying that

$$G = n_A \mu_A + n_B \mu_B$$

regenerates Equation 4.2 (Euler's theorem for G), i.e., using equations 7.1 and 7.2 we obtain

$$n_A RT \ln \left(x_A \frac{p}{RT} \lambda_A^{-3/2} e^{p(\sigma_A - 2x_B^2 \sigma_{AB})/RT} \right) + n_B RT \ln \left(x_B \frac{p}{RT} \lambda_B^{-3/2} e^{p(\sigma_B - 2x_A^2 \sigma_{AB})/RT} \right) \stackrel{?}{=} G$$

(where the question marks indicate that we are asking, does the right hand side equal the left hand side?). Focussing our attention solely on the logarithm of the exponential we have

$$p(n_A \sigma_A + n_B \sigma_B - (x_B^2 n_A + x_A^2 n_B) \sigma_{AB})$$

which, upon algebraic manipulation generates the correct value for the Gibbs Free Energy of the mixture (Equation 4.2).

D. Chemical Potential is Homogenous of Order Zero

Since the Chemical Potential is homogeneous of order zero (one less than the Gibbs Free Energy itself), the equation

$$n_A \left(\frac{\partial \mu_A / RT}{\partial n_A} \right)_{n_B} + n_B \left(\frac{\partial \mu_A / RT}{\partial n_B} \right)_{n_A} = 0 \quad (7.4)$$

should hold, which can now be verified. Since

$$\frac{\partial \mu_A}{\partial n_A} = \frac{\partial (\ell n x_A + \frac{p}{RT} (\sigma_A - x_B^2 \sigma_{AB}))}{\partial n_A}$$

and

$$\frac{\partial \mu_A}{\partial n_B} = \frac{\partial (\ell n x_A + \frac{p}{RT} (\sigma_A - x_B^2 \sigma_{AB}))}{\partial n_B}$$

we obtain, substituting Equations 7.1 and its n_B equivalent into Equation 7.4,

$$\frac{n_A}{RT} \left(\frac{1}{x_A} \frac{\partial x_A}{\partial n_A} + \frac{p}{RT} \left(-2x_B \frac{\partial x_B}{\partial n_A} \right) \sigma_{AB} \right) + \frac{n_B}{RT} \left(\frac{1}{x_A} \frac{\partial x_A}{\partial n_B} + \frac{p}{RT} \left(-2x_B \frac{\partial x_B}{\partial n_B} \right) \sigma_{AB} \right) \stackrel{?}{=} 0$$

which is

$$\frac{n_A}{RT} \left(\frac{1}{x_A} \left(\frac{x_B}{n_A + n_B} \right) - 2 \left(\frac{x_B^2}{n_A + n_B} \right) \frac{p \sigma_{AB}}{RT} \right) + \frac{n_B}{RT} \left(\frac{1}{x_A} \left(-\frac{x_A}{n_A + n_B} \right) - 2 \left(-\frac{x_B x_A}{n_A + n_B} \right) \frac{p \sigma_{AB}}{RT} \right) \stackrel{?}{=} 0$$

which finally is

$$\frac{1}{RT} \left(x_B - \frac{2p \sigma_{AB}}{RT} (x_A x_B^2) \right) + \frac{1}{RT} \left(-x_B - \frac{2p \sigma_{AB}}{RT} (-x_A x_B^2) \right) \stackrel{!}{=} 0$$

i.e., we have shown that Equation 7.4 holds in this case.

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