

Non-Ideality Through Fugacity and Activity

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In this discussion, we consider one way to incorporate *non-ideality* into our physical model of fluids and solids. It is to be appreciated that once we leave the realm of ideality, we are relegated to considering models of physical reality. Thus, we need to always be careful of our interpretations arising from such models which, despite our best intentions, are always approximations of actual physical reality. Moreover, we are required to bear in mind the assumptions, approximations, and limitations associated with such models. With this preface we now consider an alternate description of the chemical potential of a pure species and a species in various mixtures (liquids and gases).

A. Pure Gases and Gas Mixtures

1. Pure Gas

The total differential of Gibb's Free energy for a pure fluid is given by:

$$dG = Vdp - SdT + \mu dN \quad (1)$$

Dividing this extensive property by the moles of pure fluid, we have the total differential of the molar Gibb's Free Energy or the chemical potential:

$$d\mu = d\bar{G} = \bar{V}dp - \bar{S}dT \quad (2)$$

For constant temperature, this reduces to:

$$d\mu = d\bar{G} = \bar{V}dp \quad (3)$$

For an **ideal gas**, the molar volume is: $\bar{V} = \frac{RT}{p}$. This leads to:

$$d\mu = d\bar{G} = RT d(\ln p) \quad (4)$$

We now take inspiration from Equation 4 for an ideal gas to introduce a new **function**, the **fugacity of pure species** "i" which will contain all the non-ideality of the fluid.

$$d\mu = d\bar{G} = RT d(\ln f) \quad (5)$$

- Note that fugacity is **not** pressure
- Fugacity is a function of pressure
- Fugacity is a direct measure of the chemical potential of a real, non-ideal fluid! **Fugacity is chemical potential!**
- Equivalence of a species' chemical potentials in various phases at equilibrium coexistence is the same as the equivalence of fugacities in various phases at equilibrium coexistence.
- $\lim_{p \rightarrow 0} f(p) = p$. Thus, $f^{ig} = p$.

Now, for an **ideal gas** the chemical potential at a particular temperature, T, and pressure, p, relative to some reference state chemical potential, $\mu^{ref}(T, p^{ref})$, at a reference state pressure of p^{ref} is:

$$\mu^{ig}(T, p) = \mu^{ig,ref}(T, p^{ref}) + RT \ln \left(\frac{p}{p^{ref}} \right) \quad (6)$$

We can compute the same for the **real gas, rg**:

$$\mu^{rg}(T, p) = \mu^{rg,ref}(T, p^{ref}) + RT \ln \left(\frac{f}{f^{ref}} \right) \quad (7)$$

Taking the difference between Equations 7 and 6 gives:

$$\mu^{rg}(T, p) - \mu^{ig}(T, p) = \mu^{rg,ref}(T, p^{ref}) - \mu^{ig,ref}(T, p^{ref}) + RT \ln \left(\frac{f p^{ref}}{f^{ref} p} \right) \quad (8)$$

If we take the reference state to be an ideal gas state (low pressure reference state), the first two terms on the right hand side of Equation 8 cancel one another, and $p^{ref} = f^{ref}$; this leads to

$$\mu^{rg}(T, p) - \mu^{ig}(T, p) = RT \ln \left(\frac{f}{p} \right) \quad (9)$$

Equation 9 allows us to define the fugacity coefficient for a pure species as:

$$\phi_{pure\ gas}(T, p) = \frac{f}{p} \quad (10)$$

- Fugacity coefficient of a pure species at a temperature, T, and pressure, P is defined as $\phi_{pure\ gas}(T, p) = \frac{f}{p}$

We can thus rewrite Equation 9 as:

$$\mu^{rg}(T, p) = \mu^{ig}(T, p) + RT \ln(\phi_{pure\ gas}) \quad (11)$$

If we now reference the ideal gas chemical potential to a reference state with pressure = 1 bar ($p^0 = 1bar$), we can rewrite the previous equation as :

$$\mu^{rg}(T, p) = \mu^{ig}(T, p^0) + RT \ln\left(\frac{p}{p^0}\right) + RT \ln(\phi_{pure\ gas}) \quad (12)$$

Finally, we can combine the second and third terms on the right-hand side of equation 12 to obtain the following relation which we will return to later in our discussion of activity.

$$\mu^{rg}(T, p) = \mu^{ig}(T, p^0) + RT \ln\left((\phi_{pure\ gas}) \frac{p}{p^0}\right) \quad (13)$$

2. Gas Mixtures

We can follow an analogous route as we did for the pure gas in our treatment of the chemical species of a species "i" in a mixture of real gases.

For an ideal gas species "i" in an ideal gas mixture (mixture of ideal gases) at a temperature, T, and pressure, P, relative to a **pure gas** reference state at p^{ref} and the same temperature, we can write the chemical potential as:

$$\mu_i^{ig}(T, p) = \mu_i^{ig}(T, p^{ref}, pure) + RT \ln\left(\frac{p_i}{p^{ref}}\right) \quad (14)$$

For a real (non-ideal) gas (superscripted as **rg** in the following) species in a non-ideal gas mixture, we can write analogously, making use of our definition of fugacity as presented in the section on pure gases, as:

$$\mu_i^{rg}(T, p) = \mu_i^{rg}(T, p^{ref}, pure) + RT \ln\left(\frac{\hat{f}_i}{f_i^{ref}}\right) \quad (15)$$

Here, \hat{f}_i is the fugacity of species in the non-ideal gas mixture. Again, the reference state is a pure fluid state; thus we omit the hat on the fugacity of species in the denominator of fraction of which we take the natural log.

Taking the difference of Equations 15 and 14, we obtain:

$$\mu_i^{rg}(T, p) - \mu_i^{ig}(T, p) = \mu_i^{rg}(T, p^{ref}, pure) - \mu_i^{ig}(T, p^{ref}, pure) + RT \ln \left(\frac{\hat{f}_i p^{ref}}{f_i^{ref} p_i} \right) \quad (16)$$

Taking the reference state to be an ideal gas state, we can make the simplifications as for the pure gas case to obtain:

$$\mu_i^{rg}(T, p) - \mu_i^{ig}(T, p) = RT \ln \left(\frac{\hat{f}_i}{p_i} \right) \quad (17)$$

Since $p_i = y_i p^{Total} = y_i p$,

$$\mu_i^{rg}(T, p) - \mu_i^{ig}(T, p) = RT \ln \left(\frac{\hat{f}_i}{y_i p} \right) \quad (18)$$

We now define the fugacity coefficient for species "i" in a gas mixture (non-ideal) as $\hat{\phi}_i = \frac{\hat{f}_i}{y_i p}$.

This allows us to write Equation 18 as:

$$\mu_i^{rg}(T, p) = \mu_i^{ig}(T, p) + RT \ln \left(\hat{\phi}_i \right) \quad (19)$$

The chemical potential of the ideal gas species at temperature T and total pressure p can be written in terms of the chemical potential of the pure ideal gas at a reference pressure p^0 as we did before:

$$\mu_i^{rg}(T, p) = \mu_i^{ig}(T, p^0) + RT \ln \left(\frac{p_i}{p^0} \right) + RT \ln \left(\hat{\phi}_i \right) \quad (20)$$

which can be written as:

$$\mu_i^{rg}(T, p) = \mu_i^{ig}(T, p^0) + RT \ln \left(\left(\hat{\phi}_i \right) \frac{p_i}{p^0} \right) \quad (21)$$

Equation 21 is analogous to Equation 13; we will return to Equations 13 and 21 in our discussion of activity.

B. Pure Liquids and Liquid Mixtures

1. Pure Liquid

Unlike the pure ideal gas, there is no liquid analogue, so we define the pure liquid fugacity by analogy to the pure non-ideal gas case:

$$d\mu_i^{pure\ liquid} = RT d \ln (f^{pure\ liquid}) \quad (22)$$

We will not say more about this relation, but will use it later in our discussion of general vapor-liquid equilibria.

2. Real Liquid Mixtures

We have seen that the chemical potential of a species "i" in an ideal mixture at a temperature T and total pressure p is:

$$\mu_i^{is}(T, p) = \mu_i(T, p, pure) + RT \ln(x_i) \quad (23)$$

Using Equation 22, we can write an analogous expression for a real solution as:

$$\mu_i^{rs}(T, p) = \mu_i(T, p, pure) + RT \ln \left(\frac{\hat{f}_i}{f_i} \right) \quad (24)$$

Taking the difference between Equations 24 and 23, we obtain:

$$\mu_i^{rs}(T, p) - \mu_i^{is}(T, p) = RT \ln \left(\frac{\hat{f}_i}{x_i f_i} \right) \quad (25)$$

We define the **activity coefficient** as $\gamma_i = \frac{\hat{f}_i}{x_i f_i}$ to allow us to write Equation 25 as:

$$\mu_i^{rs}(T, p) = \mu_i^{is}(T, p) + RT \ln(\gamma_i) \quad (26)$$

Inserting Equation 23 for $\mu_i^{is}(T, p)$, we obtain:

$$\mu_i^{rs}(T, p) = \mu_i(T, p, pure) + RT \ln(x_i) + RT \ln(\gamma_i) \quad (27)$$

which can also be expressed as:

$$\mu_i^{rs}(T, p) = \mu_i(T, p, pure) + RT \ln(x_i \gamma_i) \quad (28)$$

Equation 28, along with Equations 13 and 21, will be central to our discussion of activity further below. To summarize our discussion up to this point:

- We have defined the fugacity for pure gases and liquids, as well as for species "i" in a gas and liquid mixture.
- Fugacity is a direct measure of the chemical potential of a species in a mixture.
- Fugacity coefficient of a pure gas or liquid: $\phi_{\text{pure gas}}(T, p) = \frac{f}{p}$
- Fugacity coefficient of species "i" in non-ideal gas mixture: $\hat{\phi}_i = \frac{\hat{f}_i}{y_i p}$
- Activity coefficient of species "i" in non-ideal liquid mixture: $\gamma_i = \frac{\hat{f}_i}{x_i f_i}$

II. VAPOR-LIQUID EQUILIBRIA

Using the definitions of the various coefficients in the last section, we can generalize the idea of chemical potential equalization at equilibrium to fugacity equalization at equilibrium. Thus, our expression for vapor-liquid equilibrium using fugacities is:

$$\hat{f}_i^l(T, p, x) = \hat{f}_i^v(T, p, y) \quad (29)$$

In Equation 29, we have included the temperature, pressure, and composition dependence of the fugacities. Using the definitions of activity and fugacity coefficients (for the liquid and vapor fugacities, respectively), we obtain:

$$\gamma_i x_i f_i^l(T, p) = y_i p \hat{\phi}_i(T, p) \quad (30)$$

We now make use of Equation 30 to derive a practical expression for vapor-liquid equilibria at low to moderate pressures which are common for most applications.

To obtain the fugacity of pure liquid "i" at temperature T and pressure p, we use two steps. First, we consider the change from zero pressure to the saturation pressure at the temperature of interest. We then transition from the saturation pressure to the pressure of interest.

For a pure gas, since we can relate the fugacity to the fugacity coefficient, we consider the fugacity coefficient.

$$d(\mu^{rg} - \mu^{ig}) = RT d \ln(\phi) = (\bar{V}^{rg} - \bar{V}^{ig}) dp \quad (31)$$

Recall that the compressibility factor, Z , is $Z = \frac{\bar{V}^{rg}}{\bar{V}^{ig}}$. Thus, Equation 31 becomes:

$$RT d \ln(\phi) = RT (Z - 1) \frac{dp}{p} \quad (32)$$

$$d \ln(\phi) = (Z - 1) \frac{dp}{p} \quad (33)$$

We can use Equation 33 to integrate from $p=0$ to the saturation pressure of the fluid at the desired temperature. At $p=0$, $\phi = 1$ and $\ln(\phi) = 0$. Thus, upon integrating we obtain:

$$\int_0^{p^{sat}} d \ln(\phi) = \int_0^{p^{sat}} (Z - 1) \frac{dp}{p} \quad (34)$$

Thus, the fugacity coefficient at the saturation pressure, p^{sat} is given by:

$$\ln(\phi^{sat}) = \int_0^{p^{sat}} (Z - 1) \frac{dp}{p} \quad (35)$$

Once we know ϕ^{sat} , we know the fugacity of the liquid at the saturation pressure:

$$f^{sat,liquid} = f^{sat,vapor} = \phi^{sat} p^{sat} \quad (36)$$

Now, we can integrate from the saturation pressure to the desired pressure to obtain the liquid fugacity needed in Equation 30.

$$d\mu^{liq} = RT d \ln(f^{liq}) = \bar{V}^{liq} dp \quad (37)$$

$$\ln(f^{liq}) - \ln(f^{sat,liquid}) = \frac{\bar{V}^{liq}}{RT} \int_{p^{sat}}^p dp \quad (38)$$

$$f^{liq} = f^{sat,liquid} \exp\left(\frac{\bar{V}^{liq} (p - p^{sat})}{RT}\right) \quad (39)$$

Using Equation 36, we obtain:

$$f^{liq} = \phi^{sat} p^{sat} \exp\left(\frac{\bar{V}^{liq} (p - p^{sat})}{RT}\right) \quad (40)$$

Equation 30 can now be revisited, using the expression for the pure liquid fugacity at the temperature and pressure of interest given by Equation 40:

$$\gamma_i x_i \phi_i^{sat} p_i^{sat} \exp\left(\frac{\bar{V}^{liq}(p - p^{sat})}{RT}\right) = y_i p \hat{\phi}_i(T, p) \quad (41)$$

Finally, we make two major approximations:

- For low pressures up to 1 bar, the exponential can be taken as unity (equilibrium pressures are not that far from saturation pressures of pure species)
- Taking the vapor to be ideal gas, the fugacity coefficients are unity

This gives finally,

$$\gamma_i x_i p_i^{sat} = y_i p \quad (42)$$

Equation 42 is sometimes referred to as a modified Raoult's Law. The non-ideality of the liquid phase is totally contained in the activity coefficient, while the vapor is considered to be ideal. One can construct T-xy and P-xy phase diagrams using this expression for liquid non-ideality if one is given information about the activity coefficients and their temperature, pressure, and composition dependence.

A. Activity

Returning to Equations 13, 21, and 28, we note a similarity in the form of each of the relations:

$$\mu^{rg}(T, p) = \mu^{ig}(T, p^0) + RT \ln\left(\left(\phi_{pure\ gas}\right) \frac{p}{p^0}\right) \quad (43)$$

$$\mu_i^{rg}(T, p) = \mu_i^{ig}(T, p^0) + RT \ln\left(\left(\hat{\phi}_i\right) \frac{p_i}{p^0}\right) \quad (44)$$

$$\mu_i^{rs}(T, p) = \mu_i(T, p, pure) + RT \ln(x_i \gamma_i) \quad (45)$$

Each of these expression for the chemical potential of a species "i" (Equation 43 for a pure species, and Equations 44 and 45 for species "i" in gas and liquid mixtures, respectively) has the following general form:

$$\mu_i^{real}(T, p) = \mu_i(\text{reference state}) + RT \ln(a_i) \quad (46)$$

This defines the activity of species "i", a_i with respect to some reference, or standard, state. The activity contains the non-ideality of the mixture (enthalpy and entropy of mixing). Since it is usually introduced in the context of liquid mixtures, we first consider the condensed phase (liquid) case.

For a species "i" in a liquid mixture, the activity is defined as:

$$a_i = \gamma_i x_i \quad (47)$$

$$= \frac{x_i \hat{f}_i^{liquid}}{f_i x_i} \quad (48)$$

$$a_i = \frac{\hat{f}_i^{liquid}}{f_i} \quad (49)$$

Equation 49 is a general definition of the activity of a species "i" in a liquid mixture. To generalize to any mixture, we can write

$$a_i = \frac{\hat{f}_i^{mixture}}{f_i} \quad (50)$$

Finally, we allow for the denominator to represent an arbitrary reference, or standard, state to obtain our final expression defining the activity generally in terms of fugacities:

$$a_i = \frac{\hat{f}_i^{mixture}}{f_i^0} \quad (51)$$

where the superscript "0" refers to the standard state. **Equation 51 is our general definition of activity.**

With this definition of activity, we can now quickly write new expressions for the activity coefficients for liquid and gas mixtures:

- Liquid Mixture: $\gamma_i^{liquid} = \frac{a_i}{x_i} = \frac{\hat{f}_i^{liquid}}{x_i f_i^0}$
- Gas Mixture: $\gamma_i^{vapor} = \frac{a_i}{y_i} = \frac{\hat{f}_i^{vapor}}{y_i f_i^0} = \frac{\hat{\phi}_i^{vapor} y_i p}{y_i f_i^0} = \frac{\hat{\phi}_i^{vapor} p}{f_i^0}$
- For the gas mixture introduced in the previous line, we can consider, for the moment, two reference (standard) states.

Pure ideal gas standard state at p^0 : $\gamma_i^{vapor} = \frac{\hat{\phi}_i^{vapor} p}{p^0} = \hat{\phi}_i^{vapor} \frac{p}{p^0}$

Pure ideal gas standard state at the pressure of interest, p :

$$\gamma_i^{vapor} = \frac{\hat{\phi}_i^{vapor} p}{p} = \hat{\phi}_i^{vapor} \frac{p}{p} = \hat{\phi}_i^{vapor}$$

Using the relations for the activity, activity coefficient, and knowledge of the meaning of fugacity (i.e, its relation to chemical potential), we are equipped to handle various cases for treating vapor-liquid equilibria. In effect, this allows us to treat all cases in a general way.

For example, if we have an ideal vapor above a non-ideal liquid mixture, the activity of a species in the liquid mixture is:

$$a_i^{liquid} = \frac{\hat{f}_i^{liquid}}{f_i^0} \quad (52)$$

Here, we make use of the fact that $\hat{f}_i^{liquid} = \hat{f}_i^{vapor}$ and $\hat{f}_i^{vapor} = \hat{\phi}_i^{vapor} y_i p = y_i p$ (recall that $\hat{\phi}_i^{vapor} = 1$ for ideal vapor) to write:

$$a_i^{liquid} = \frac{\hat{f}_i^{liquid}}{f_i^0} = \frac{\hat{f}_i^{vapor}}{f_i^0} = \frac{y_i p}{f_i^0} \quad (53)$$

If we take the standard state for the liquid as being the pure liquid at its saturation (vapor pressure), then we have $f_i^0 = f_i^{sat,liquid} = f_i^{sat,vapor} = \phi_i^{sat,vapor} p_i^{sat} = (1) p_i^{sat}$, the last equality being since the vapor is ideal (for pure "i" and when it is in the ideal gas mixture). This gives us finally for the activity of species "i" in the liquid mixture:

$$a_i^{liquid} = \frac{\hat{f}_i^{liquid}}{f_i^0} = \frac{\hat{f}_i^{vapor}}{f_i^0} = \frac{y_i p}{p_i^{sat}} \quad (54)$$

Making use of the fact that $y_i p$ is the partial pressure of "i" in the ideal gas mixture above the non-ideal solution, we can write:

$$a_i^{liquid} = \frac{\hat{f}_i^{liquid}}{f_i^0} = \frac{\hat{f}_i^{vapor}}{f_i^0} = \frac{p_i}{p_i^{sat}} \quad (55)$$

The last expression is Equation 9.48 in your text book, though in this presentation, we have formally derived it within the rigorous context of fugacities. Note that Equation 9.48 in your text is presented based on the same approximations and standard states we have used in the present discussion, thus both are equivalent.

III. ACKNOWLEDGEMENTS

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