Fugacity, Activity, and Standard States

Fugacity of gases:

Since $dG = VdP - SdT$, for an isothermal process, we have

$$\Delta G = \int_{p_1}^{p_2} Vdp.$$

For ideal gas, we can substitute for V and obtain

$$\Delta G = nRT\ln\left(\frac{p_2}{p_1}\right),$$

or with reference to a standard pressure, $p°$, we may write

$$G - G° = nRT\ln\left(\frac{p}{p°}\right), \text{ or}$$

$$G_m = G_m° + RT\ln\left(\frac{p}{p°}\right).$$

Now, consider a real gas that obeys the equation of state

$$(p + a)(V_m - b) = RT,$$

which would give

$$G_m = G_m° + RT\ln\left(\frac{p+a}{p°+a}\right) - b(p - p°).$$

More complicated equations of state will give rise to more complicated expressions for ΔG.

In order to preserve the simplicity of the expression for ΔG even for real gases, the concept of **fugacity**, f, was introduced by G.N. Lewis so that

$$G_m = G_m° + RT\ln\left(\frac{f}{p°}\right).$$

The defining equation for fugacity is

$$d\mu = RTd\ln f$$

with the condition that

$$\lim_{p\to 0} \frac{f}{p} = 1.$$

A working expression to calculate fugacity:

For a constant temperature process, $dG_m = V_m dp$, or

$$\Delta G_m = G_{2,m} - G_{1,m} = \int_{p_1}^{p_2} V_m dp$$

Let us add and subtract RT/p to the right hand side:

$$\Delta G_m = \int_{p_1}^{p_2} \left[\frac{RT}{P} + \left(V_m - \frac{RT}{p} \right) \right] dp$$

$$= RT\ln\left(\frac{p_2}{p_1}\right) + \int_{P_1}^{P_2} \left(V_m - \frac{RT}{p} \right) dp.$$

Now, *by definition*, for all gases, $\Delta G_m = Rt\ln(f_2/f_1)$. Therefore, we get

$$RT\ln\frac{f_2/p_2}{f_1/p_1} = \int_{P_1}^{P_2} \left(V_m - \frac{RT}{p} \right) dp.$$

We now set $p_1 = 0$ (recall that $f = p$ as $p \to 0$), $f_2 = f$ and $p_2 = p$, where p is the pressure of interest, to get

$$RT\ln\left(\frac{f}{p}\right) = \int_0^p \left(V_m - \frac{RT}{p} \right) dp.$$

The right hand side can be evaluated if V_m can be conveniently expressed as a function of R, T and p. However, this is often very difficult (consider the van der Waals equation of state, for example). An alternative is to express V_m in terms of the compressibility factor Z,

$$V_m = ZRT/p,$$

to get

$$RT\ln\left(\frac{f}{p}\right) = \int_0^p \left(\frac{ZRT}{p} - \frac{RT}{p} \right) dp, \text{ or}$$

$$\ln\left(\frac{f}{p}\right) = \int_0^P \left(\frac{Z-1}{p} \right) dp.$$

The last expression can be conveniently and fairly accurately evaluated in most cases using Virial expansions.

Fugacity of Pure Condensed Phases

The defining equation for fugacity of pure condensed phases is, like that of gases,

$$d\mu_c = RTd\ln f_c$$

with the condition that

$$\operatorname*{Lim}_{p\to 0}\frac{f_c}{p} = 1,$$

where μ_c is the chemical potential of the condensed phase. Applying the criterion for phase equilibrium, $d\mu_c = d\mu_g$ (where g stands for gas phase), we get

$$RTd\ln f_c = RTd\ln f_g,$$

from which we conclude that $f_c = kf_g$.

Now, in theory, any solid or liquid taken to zero pressure would eventually become a gas for which $f = p$, so that $k = 1$. The conclusion is that *fugacity of a condensed phase is the same as the fugacity of the gas phase in equilibrium with it*.

Variation of fugacity with pressure

The above statement (italics) and the relationship

$$\left(\frac{\partial\ln f}{\partial p}\right)_T = \frac{1}{RT}\left(\frac{\partial G_m}{\partial p}\right)_T = \frac{V_m}{RT},$$

is sufficient to derive the **Gibbs equation**

$$\ln\left(\frac{f_2}{f_1}\right) = \frac{V_m}{RT}\left(p_2 - p_1\right),$$

where the left hand side refers to vapor fugacities (which could be replaced with vapor pressures) while the right hand side refers to total pressures acting on the liquid surface. Therefore, this equation provides a way to calculate the variation of vapor pressures with changes in the total pressure.

Activity

The defining equation for fugacity of the i-th component in a mixture is

$$d\mu_i = RTd \ln f_i.$$

This equation can be integrated to give

$$\int_{\mu_i^\circ}^{\mu} d\mu = RT \int_{\ln f_i^\circ}^{\ln f_i} d \ln f_i$$

$$\mu_i = \mu_i^\circ + RT \ln\left(\frac{f_i}{f_i^\circ}\right),$$

where μ_i° and f_i° are the chemical potential and fugacity in a reference or standard state. The ratio f_i/f_i° is defined as the **activity** a_i, so that the above equation becomes

$$\mu = \mu_i^\circ + RT \ln a_i.$$

Standard States

The standard state for a gas

The standard state for a gas is taken to be the "ideal gas at 1 bar (100 kPa or 0.100 Mpa) pressure." For such a gas, we have $f^\circ = p^\circ = 1$ bar. For a real gas, in general, $f^\circ \neq 1$ bar when $p^\circ = 1$ bar but, with the above definition, we can define activity for a gas as $a_i = f_i/p^\circ$, and set $p^\circ = 1$ bar.

Standard states for pure solids and liquids

The pure solid or liquid under 1 bar *external pressure* is taken to be the standard state. With this definition, we have $f^\circ = f^*$ (where f^* is the fugacity at $p = 1$ bar).

Activity is still defined as

$$a = \frac{f}{f^\circ} = \frac{f}{f^*(1\ \text{bar})},$$

which means that for a pure substance at standard pressure, $a = 1$.

Standard state of a solvent in a solution

The convention is the same as above, with $a_i = f_i/f_i^*(1\ \text{bar})$.

Raoult's law (to be covered later) states that for a volatile component of a solution, $f_i = x_i f_i^*$. Therefore, we get $a_i = x_i$ for solutions that obey Raoult's law.

In general, we may write

$$a_i = \gamma_i x_i$$

where γ_i is called the **activity coefficient**. For solutions that obey Raoult's law, obviously, $\gamma_i = 1$. Sometimes, the activity coefficient defined here is given the subscript 'R' to indicate that this refers to a "Raoult's law standard state."

Standard state of solute in a solution

The standard state of a solute in a solution is defined as its activity in a solution whose concentration is 1 molal, i.e., 1 mole of solute in 1 kg of solvent. In general,

$$a_i = \gamma_{H,i} m$$

with the condition that $\gamma_{H,i} \to 1$ as $m \to 0$.