University of Washington
Department of Chemistry
Chemistry 452/456
Summer Quarter 2014

Lecture 18 8/08/14

A. The Gibbs-Duhem Equation

- In Gibbs-Duhem (GD) equation is an extremely important equation in solution thermodynamics. It states that the chemical potentials of the compoenents of a solution are related. If you know a lot about one solution component, i.e. because it is volatile, you can learn a lot about the other solution component using the GD equation. The GD equation is derived using the properties of partial molar quantities.
- The volume is a state function. For a binary mixture we write:

$$\begin{aligned} dV &= \left(\frac{\partial V}{\partial n_A}\right)_{n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{n_A} dn_B \\ &= \bar{V}_A dn_A + \bar{V}_B dn_B \end{aligned} \tag{18.1}$$

- Now let's integrate this equation to get the final volume of the solution. If we change n_A and n_B by just a little, we can treat $\bar{V}_A$ and $\bar{V}_B$ as constants. Then 18.1 integrates to

$$V = \bar{V}_A n_A + \bar{V}_B n_B \tag{18.2}$$

- The same reasoning can be applied to the Gibbs energy which for a binary solution is:

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B \tag{18.3}$$

- Suppose we make a solution at constant T andP. Then dG becomes

$$dG = \mu_A dn_A + \mu_B dn_B \tag{18.4}$$

- Now let's figure out the final Gibbs energy for making this solution using the same reason as with the volume change. We integrate assuming the chemical potentials are constants if n_A and n_B do not change much...

$$G = \mu_A n_A + \mu_B n_B \tag{18.5}$$

- Equation 18.5 was obtained from 18.4 by assuming that n_A and n_B changed so little that the chemical potentials did not change and so were treated as constants. But in general the chemical potentials can change when the composition of the solution changes. So let us take the solution in 18.5 and assume it can change as a result of changes in nA, nB, or the chemical potentials. Let's take the differential of both sides of equation 18.5

$$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B \tag{18.6}$$

- Toi reconcile 18.4 with 18.6 we have to require that
  - $$n_A d\mu_A + n_B d\mu_B = 0 \tag{18.7}$$

- This expression is called the Gibbs-Duhem equation. At constant T and P and for a binary solution the Gibbs-Duhem equation has the form

$$d\mu_A = -\frac{n_B}{n_A} d\mu_B \qquad (18.8)$$

- The equation 18.8 means a change in chemical potential of component B is related to a change in the chemical potential of component A by a simple ratio of the moles present. This equation is important in evaluating activity coefficients of non-volatile solutes.
- For practical calculations the Gibbs-Duhem eqn is commonly expressed in terms of activities and molality is used instead of mole fraction. Using the definition $\mu = \mu^0 + RT \ln a$ it follows that $d\mu = RTd \ln a$
- The G-D eqn now has the equivalent forms

$$d \ln a_A = -\frac{n_B}{n_A} d \ln a_B = -\frac{\chi_B}{\chi_A} d \ln a_B \qquad (18.9)$$

B. Applications: Measuring Solute Activity by Measuring Solvent Activity

- It is common to deal with solutions where there is a dominant volatile solvent like water and a much less abundant solute which may not be volatile. Let us designate all properties associated with solvent with a 1 and all properties associated with the solute with a 2. Let us assume the solvent 1 is water.
- Let us assume we can measure the activity coefficient for water by measuring its vapor pressure as a function of solute concentration. Assuming the water vapor behaves ideally:

$$\frac{P_1}{P_1^0} = a_1 = \gamma_1 \chi_1 \qquad (18.10)$$

- If the solute is non-volatile, we can use the G-D equation to determine the solute activity and its activity coefficient at some solute concentration. First we simplify the G-D equation to get it solely in terms of the solvent and solute activity coefficients
- $$\begin{aligned} d \ln a_2 &= d \ln \gamma_2 + d \ln \chi_2 = -\frac{\chi_1}{\chi_2} d \ln a_1 \\ \therefore \chi_2 d \ln \gamma_2 + d\chi_2 &= -\chi_1 d \ln \gamma_1 - d\chi_1 \end{aligned} \qquad (18.11)$$
- Now because $\chi_1 + \chi_2 = 1$ it is true that $d\chi_1 + d\chi_2 = 0$. Then the G.-D. equation integrates to:

$$\int_1^2 d \ln \gamma_2 = -\int_1^2 \frac{\chi_1}{\chi_2} d \ln \gamma_1 \qquad (18.12)$$

- State 1 is pure solvent. In this limit $\gamma_2(1) \approx 1$. Also for a binary solution $\chi_2 = 1 - \chi_1$. Therefore the G.-D. equation becomes:

$$\int_1^2 d\ln\gamma_2 = \ln\gamma_2(2) - \ln\gamma_2(1) = \ln\gamma_2(2) = -\int_1^2 \frac{\chi_1}{1-\chi_1}\, d\ln\gamma_1 \qquad (18.13)$$

- This equation means if we plot $\frac{\chi_1}{1-\chi_1}$ as a function of $\ln\gamma_1$ (which we obtain for each χ_1 from the equation $\frac{P_1}{P_1^0} = \gamma_1\chi_1$), the area under the curve is $-\ln\gamma_2(2)$.
- Note when you plot the data, the integral will diverge as $\chi_1 \to 1$. Therefore state 1 is defined as $\chi_1 = 1 - c$ where c is a small enough number that $\ln\gamma_2(1) \approx 0$.

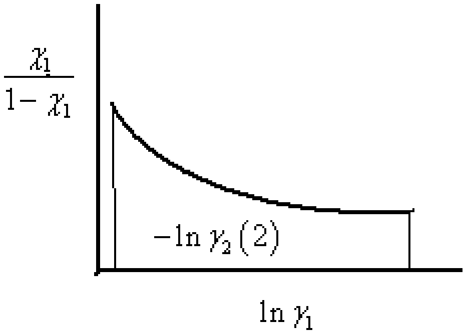

FIGURE 1: The activity coefficient of the a non-volatile solute can be found from the activity coefficient of the solvent obtained as a function of x_1, the solvent mole fraction.

C. Colligative Properties

- A colligative property is a physical property of the solvent that varies as the activity of the solvent. Vapor pressure, freezing point, boiling point, and osmotic pressure are all colligative properties.
- At the normal freezing point, ice is in equilibrium with pure water: $\mu^*_{solid} = \mu^*_{liquid}$. At P=1atm, this temperature is T_f=273.15K. The presence of a solute will affect the freezing point. The condition for equilibrium is now

$$\begin{aligned}
&\mu^*_{solid} = \mu^*_{liquid} + RT_f \ln a_1 \\
&\therefore \ln a_1 = \frac{\mu^*_{solid} - \mu^*_{liquid}}{RT_f} = -\frac{\mu^*_{liquid} - \mu^*_{solid}}{RT_f} = -\frac{\Delta G_{fusion,m}}{RT_f}
\end{aligned} \qquad (18.14)$$

- Now differentiate with respect to Tf:

$$\begin{aligned}
&\frac{\partial \ln a_1}{\partial T_f} = -\frac{\partial}{\partial T_f}\left(\frac{\Delta G_{fusion,m}}{RT_f}\right) = -\left(\frac{1}{RT_f}\frac{\partial \Delta G_{fusion,m}}{\partial T_f} - \frac{\Delta G_{fusion,m}}{RT_f^2}\right) \\
&= \frac{\Delta S_{fusion,m}}{RT_f} + \frac{\Delta G_{fusion,m}}{RT_f^2} = \frac{T_f \Delta S_{fusion,m} + \Delta H_{fusion,m} - T_f \Delta S_{fusion,m}}{RT_f^2} = \frac{\Delta H_{fusion,m}}{RT_f^2} \quad (18.15) \\
&\therefore \frac{\partial \ln a_1}{\partial T_f} = \frac{\Delta H_{fusion,m}}{RT_f^2}
\end{aligned}$$

- The most useful form of this equation is obtained by integrating with respect to T_f from state 1 (pure water0 to state 2 (solution)

$$\int_1^2 d\ln a_1 = \int_{T_f^*}^{T_f} \frac{\Delta H_{fusion,m}}{RT_f^2} dT_f \qquad (18.16)$$

- The activity of pure water (state 1) is 1 so $\ln a_1=0$ for state 1. Therefore:

$$\ln a_1(2) = \frac{\Delta H_{fusion,m}}{R}\left(\frac{1}{T_f^*} - \frac{1}{T_f}\right) = \frac{\Delta H_{fusion,m}}{R}\left(\frac{T_f}{T_f^* T_f} - \frac{T_f^*}{T_f^* T_f}\right) \approx \frac{\Delta H_{fusion,m}}{R}\frac{\Delta T_f}{\left(T_f^*\right)^2}$$

$$\therefore \ln\gamma_1 + \ln\chi_1 = \frac{\Delta H_{fusion,m}}{R}\frac{\Delta T_f}{\left(T_f^*\right)^2}$$

(18.17)

- Equation 18.17 says that by measuring the freezing point depression ΔT for water, the activity coefficient γ_1 for water in an aqueous solution of particular concentration can be found.
- In the dilute solution limits where $\chi_2 << 1$ and $\gamma_1 \approx \gamma_2 \approx 1$ equation 18.17 can be used to determine the solute concentration:

$$\ln\chi_1 = \ln(1-\chi_2) \approx -\chi_2 = \frac{\Delta H_{fusion,m}}{R}\frac{\Delta T_f}{\left(T_f^*\right)^2}$$

$$\therefore \chi_2 = \frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1} = \frac{n_2}{n_1}\frac{M_1}{M_1} = \frac{n_2 M_1}{w_1} = m_2 M_1 = -\frac{\Delta H_{fusion,m}}{R}\frac{\Delta T_f}{\left(T_f^*\right)^2}$$

$$\therefore m_2 = -\frac{\Delta H_{fusion,m}}{M_1 R}\frac{\Delta T_f}{\left(T_f^*\right)^2}$$

- The molality m is a unit of concentration defined as moles solute per kilogram of solvent, which replaces other common concentration units like molarity in colligative calculations. Molarity changes over the range of practical freezing points changes so molality is used because it is invariant to temperature changes.