**University of Washington**
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Lecture 20 8/08/13

## A. The Gibbs-Duhem Equation

- From Lecture 17 and from the discussion in sections A and B of this lecture, it is clear that the activity of each component of a solution can be related to the fugacity of the corresponding vapor component. Solution activity coefficients can be obtained for any volatile solution component from a knowledge of the fugacities of the vapor components.
- However, if a given solute is not volatile, its vapor fugacity cannot be obtained. How then to characterize its solution activity? A relationship between the chemical potentials of the various solution components can be obtained from the Gibbs-Duhem equation. The G.-D. equation relates the activity of volatile solution components to the activities of non-volatile components. The G.-D. equation is the foundation for the theory of so-called colligative properties.
- The Gibbs-Duhem equation is founded on a mathematical property of state functions called homogeneity. Suppose f is a function of N independent variables $x_1$, $x_2$, $x_3$, etc. such that $f = f\left(x_1, x_2 \ldots x_N\right)$. The function f is first order homogeneous if $f\left(\lambda x_1, \lambda x_2 \ldots \lambda x_N\right) = \lambda f\left(x_1, x_2 \ldots x_N\right)$ where λ is a constant.
- Functions that are first order homogeneous have useful relationships with their partial derivatives. Because $f\left(\lambda x_1, \lambda x_2 \ldots \lambda x_N\right) = \lambda f\left(x_1, x_2 \ldots x_N\right)$ it follows that

$$\frac{df\left(\lambda x_1, \lambda x_2 \ldots \lambda x_N\right)}{d\lambda} = \frac{d}{d\lambda}\left(\lambda f\left(x_1, x_2 \ldots x_N\right)\right) = f\left(x_1, x_2 \ldots x_N\right)$$

  - But by the chain rule of calculus

$$\frac{df\left(\lambda x_1, \lambda x_2 \ldots \lambda x_N\right)}{d\lambda} = \sum_i \frac{df}{d\left(\lambda x_i\right)} \frac{d\left(\lambda x_i\right)}{d\lambda} = \sum_i \frac{df}{d\left(\lambda x_i\right)} x_i .$$

  - The preceding equation must be valid for any value of λ. Therefore setting λ=1 we must conclude

$$f\left(x_1, x_2, \ldots x_N\right) = \frac{df\left(\lambda x_1, \lambda x_2 \ldots \lambda x_N\right)}{d\lambda} = \sum_i \frac{df}{d\left(x_i\right)} x_i$$

  - State function are homogenous first order functions. To see how to use this property consider the state function U. The natural variables for U are S, V, and $\{n_i\}$. Therefore, from the discussion above…

$$U = \left(\frac{\partial U}{\partial S}\right)_{V,\{n_j\}} S + \left(\frac{\partial U}{\partial V}\right)_{S,\{n_j\}} V + \sum_{j \neq k} \left(\frac{\partial U}{\partial n_j}\right)_{S,V,\{n_k\}} n_j$$

$$= TS - PV + \sum_{j \neq k} \mu_j n_j$$

- Now we take the differential of U

$$dU = TdS + SdT - PdV - VdP + \sum_{j \neq k} \left( \mu_j dn_j + n_j d\mu_j \right)$$

- However, by definition we also know that

$$dU = TdS - PdV + \sum_{j \neq k} \mu_j dn_j$$

- These two equations can only be reconciled if

$$SdT - VdP + \sum_j n_j d\mu_j = 0$$

- 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

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \Rightarrow d\mu_2 = -\frac{n_1}{n_2} d\mu_1$$

- The equation $d\mu_2 = -\frac{n_1}{n_2} d\mu_1$ means a change in chemical potential of the solvent 1 is related to a change in the chemical potential of the solute 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 termsof 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
- $$d \ln a_2 = -\frac{n_1}{n_2} d \ln a_1 = -\frac{\chi_1}{\chi_2} d \ln a_1 = -\frac{m_1}{m_2} d \ln a_1$$

## B. Applications: Measuring Solute Activity by Measuring Solvent Activity

- 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:

$$\frac{P_1}{P_1^0} = a_1 = \gamma_1 \chi_1$$

- 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 integrate the G.-D. equation:

$$d \ln a_2 = d \ln \gamma_2 + d \ln \chi_2 = -\frac{\chi_1}{\chi_2} d \ln a_1$$

$$\therefore \chi_2 d \ln \gamma_2 + d\chi_2 = -\chi_1 d \ln \gamma_1 - d\chi_1$$

- 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:

$$\int_1^2 d \ln \gamma_2 = -\int_1^2 \frac{\chi_1}{1 - \chi_1} d \ln \gamma_1$$

- State 1 is pure solvent. In this limit $\gamma_2(1) \approx 1$. Therefore the G.-D. equation becomes: $\int_1^2 d\ln\gamma_2 = \ln\gamma_2(2) - \ln\gamma_2(1) = \ln\gamma_2(2) = -\int_1^2 \frac{\chi_1}{1-\chi_1} d\ln\gamma_1$
- This equation means if we plot $\frac{\chi_1}{1-\chi_1}$ as a function of $\ln\gamma_1$ (which we obtain for each $\chi_1$ 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 $\ln\gamma_2(1) \approx 0$.

## 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

$$\mu^*_{solid} = \mu^*_{liquid} + RT_f \ln a_1$$

$$\therefore \ln a_1 = \frac{\mu^*_{solid} - \mu^*_{liquid}}{RT_f} = -\frac{\mu^*_{liquid} - \mu^*_{solid}}{RT_f} = -\frac{\Delta G_{fusion,m}}{RT_f}$$

- Now differentiate with respect to Tf:

$$\frac{\partial \ln a_1}{\partial T_f} = -\frac{\partial}{\partial T_f}\left(\frac{\Delta G_{fusion,m}}{RT_f}\right) = -\left(\frac{1}{RT_f}\frac{\partial \Delta G_{fusion,m}}{\partial T_f} - \frac{\Delta G_{fusion,m}}{RT_f^2}\right)$$

$$= \frac{\Delta S_{fusion,m}}{RT_f} + \frac{\Delta G_{fusion,m}}{RT_f^2} = \frac{T_f\Delta S_{fusion,m} + \Delta H_{fusion,m} - T_f\Delta S_{fusion,m}}{RT_f^2} = \frac{\Delta H_{fusion,m}}{RT_f^2}$$

$$\therefore \frac{\partial \ln a_1}{\partial T_f} = \frac{\Delta H_{fusion,m}}{RT_f^2}$$

- 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)

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

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

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

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

- There are two limits for this equation. In its present form, the activity coefficient of the solvent can be determined as a function of $\chi_1$ from the freezing point depression $\Delta T_f$. Then the activity coefficient for the solute at some value of $\chi_2$ may be determined as described above from the G.-D. equation. But in the dilute limit where $\gamma_1 \approx 1$ we get:

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

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

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

## D. Other Applications of Gibbs-Duhem: The Gibbs Isotherm Equation

- Returning to the thermodynamics of surfaces, we consider the surface tension of a solution:

$$dG = -SdT + VdP + \gamma d\sigma + \sum_i \mu_i dn_i$$

  - We need an equation which describes the relationship between the molar free energy of the surface, and properties of the surface that we can measure (e.g. surface tension). Consider an air-liquid interface where the liquid is a solution. A component i of the solution is distributed between the bulk solution phase $\alpha$, the vapor phase $\beta$, and the surface $\sigma$. If i is in equilibrium between the three phases we have $\mu_i^\alpha = \mu_i^\beta = \mu_i^\sigma = \mu_i$.
  - The total free energy is the sum of the free energies for a componet of the system in the vapor, bulk liquid, and in the surface…

$$G = -ST + \gamma\sigma + \mu_1 n_1 + \mu_2 n_2$$

    where $n_i = n_i^\alpha + n_i^\beta + n_i^\sigma$

- For the bulk solution phase at constant temperature the Gibbs-Duhem equation is:

$$n_1^\alpha d\mu_1 + n_2^\alpha d\mu_2 = 0 \Rightarrow d\mu_1 = -\frac{n_2^\alpha}{n_1^\alpha} d\mu_2$$

- Differentiating $G = -ST + \gamma\sigma + \mu_1 n_1 + \mu_2 n_2$ and applying the Gibbs-Duhem equation we get a useful equation for the surface tension and how it depends on solution composition:

$$\sigma d\gamma + n_1 d\mu_1 + n_2 d\mu_2 = \sigma d\gamma + \left(n_1^\alpha + n_1^\beta + n_1^\sigma\right) d\mu_1 + \left(n_2^\alpha + n_2^\beta + n_2^\sigma\right) d\mu_2 =$$

$$= \sigma d\gamma + n_1^\sigma d\mu_1 + n_2^\sigma d\mu_2 = 0$$

$$\therefore d\gamma = -\frac{1}{\sigma}\left(n_1^\sigma d\mu_1 + n_2^\sigma d\mu_2\right) = -\frac{d\mu_2}{\sigma}\left(n_2^\sigma - n_1^\sigma \frac{n_2^\alpha}{n_1^\alpha}\right)$$

$$= -d\mu_2\left(\Gamma_2 - \Gamma_1 \frac{n_2}{n_1}\right)$$

where $\Gamma_i = \frac{n_i^\sigma}{\sigma}$ is the surface adsorption of species i and has units of moles per $m^2$.

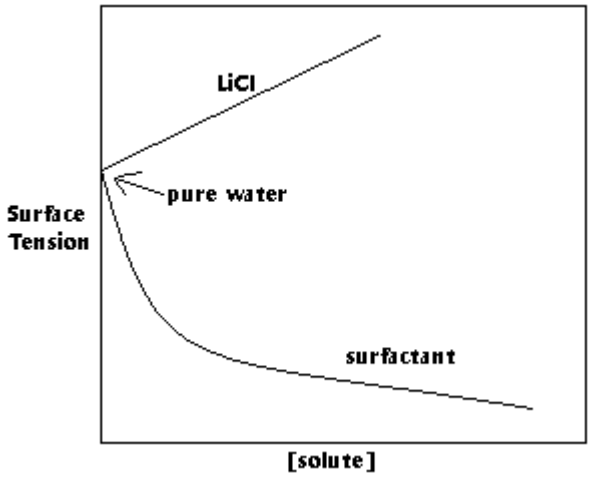
- For dilute solutions $\frac{n_2^\alpha}{n_1^\alpha} << 1$ and the equation can be rearranged to:

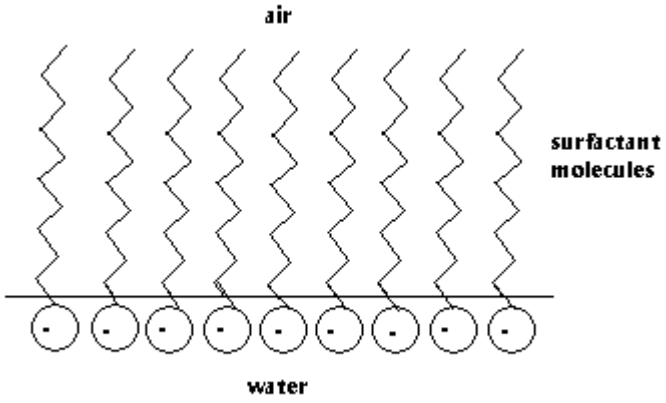
  $d\gamma \approx= -\Gamma_2 d\mu_2$
- Use the definition of the chemical potential for a dilute solution
- $d\mu_2 = RTd\ln a_2 = RTd\ln \gamma_2 C_2 \approx RTd\ln C_2$
- The relationship between surface tension and surface adsorption (i.e. surface concentration) is given by

  $$\Gamma_2 = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln C_2}\right)_T = -\frac{C_i}{RT}\left(\frac{\partial\gamma}{\partial C_2}\right)_T$$
- This means that a graph of the surface tension of a solution versus logarithm of the bulk concentration of a given component gives the surface adsorption. This is called the Gibbs Isotherm Equation.

## E. Surfactants

The surface tension of a pure liquid can be raised or lowered by the presence of certain solutes. The graph below shows typical behavior for some solutes.



- Inorganic salts generally raise the surface tension when they are added to water.
- Certain molecules drastically lower the surface tension when they are added to water. Such molecules frequently amphiphilic in the sense that they are linear molecules composed of a charged end that is attracted to water and a hydrophobic end that is repelled by water. Examples include organic acids like butanoic acid. $CH_3CH_2CH_2COO^-$ adsorbs to the surface of the water with the $COO^-$ group solvated and the aliphatic chain directed away from the water surface (see diagram above, right). Such molecules are called surface-active molecules or surfactants. Other examples include lipids and detergents.
- The total concentration of the surfactant $c_2$ and the change in surface tension of the solvent $\gamma_0 - \gamma$ where $\gamma_0$ is the surface tension of the pure solvent. For aliphatic acids this relationship is $\gamma_0 - \gamma = a\log(1+bc_2)$. The constants a and b are determined by the acid.

| Acid | a (N/m) | b (L/mole) |
|---|---|---|
| Propanoic acid | 0.0298 | 6.07 |
| Butanoic acid | 0.0298 | 19.64 |
| Caproic acid | 0.0298 | 232.70 |

Example: What is the surface tension of a 0.1M solution of caproic acid?
Solution:

$$\gamma_0 - \gamma = a\log(1+bc_2) \Rightarrow \gamma = \gamma_0 - a\log(1+bc_2)$$

$$\gamma = 0.07275N/m - (0.0298N/m)\log(1+232.70\cdot 0.1)$$

$$= 0.07275N/m - (0.0298N/m)(1.385) = 0.03147N/m$$

- The relationship between the concentration of surfactant molecules at the surface, called the surface adsorption Γ, and the change in surface tension per unit change in total concentration of surfactant $c_2$ is given by the Gibbs Isotherm Equation

$$\Gamma = -\frac{c_2}{RT}\left(\frac{d\gamma}{dc_2}\right)_{P,T}$$

  - Example: Calculate the surface adsorption Γ for a 0.1M solution of caproic acid.
    - $\gamma = \gamma_0 - a\log(1+bc_2) = \gamma_0 - \frac{a}{2.303}\ln(1+bc_2)$

$$\Gamma = -\frac{c_2}{RT}\left(\frac{d\gamma}{dc_2}\right)_{P,T} = -\frac{c_2}{RT}\frac{d}{dc_2}\left(\gamma_0 - \frac{a}{2.303}\ln(1+bc_2)\right)$$

$$= \frac{c_2}{RT}\frac{ab}{2.303(1+bc_2)} = \frac{(0.1M)(0.0298J/m^2)(232.70M^{-1})}{(8.31J/mole\cdot K)(298K)(1+(232.70M^{-1})(0.1M))}$$

$$= \frac{0.693}{6.01\times 10^4}moles/m^2 = 1.15\times 10^{-5}moles/m^2$$