Lecture 2: Simple Mixtures 14-09-2010

- Aim of the lecture: Express chemical potential of the mixture in terms of its composition (molar fraction)
- Lecture:
 - partial molar quantities
 - thermodynamics of mixing
 - ideal solutions
 - colligative properties
 - activities
 - Debye-Hückel limiting law
 - problems

Partial molar quantities

- we know how to describe phase equilibrium in the case of a single substance.
 <u>How it can be done in the case of mixtures?</u>
- partial molar quantities: contribution of each component to the properties of mixtures *our final goal is chemical potential, but let's start with some simpler ones...*
- <u>Example:</u> partial gas pressures (Dalton's Law): The pressure exerted by mixture of gases if the sum of partial pressures of the gases.

 $p = p_A + p_B + \dots$, where $p_i = x_i p$ and $x_i = n_i / n$

Partial molar volume

- How the total volume changes when we change the amount of one of the components
- Observation: If we add say 18 cm³ of water to water the total volume increase will be exactly 18cm³, but if we add it to ethanol the increase would be just 14 cm³.
 Partial molar volume depends on composition.
- Partial molar volume:

$$V_{j} = \left(\frac{\partial V}{\partial n_{j}}\right)_{p,T,n'}$$

K
Everything else is constant!





How we can calculate the total volume at a given concentration?

- Let's follow a path of constant cocentration:

$$V = V_A n_A + V_B n_B$$



Partial molar Gibbs energy

The concept of partial molar quantity can be extended to any extensive state function:



Fixing the composition the same we can prove that:

 $G = n_A \mu_A + n_B \mu_B$

Fundamental equation of chemical thermodynamics:

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \dots$$

• At p, T=const

$$dG = \mu_A dn_A + \mu_B dn_B + \dots$$
$$dw_{add, \max} = \mu_A dn_A + \mu_B dn_B + \dots$$

Differential form of thermodynamic functions



Partial molar quantities

The Gibbs-Duhem equation

Let's find change in Gibbs energy with infinitesimally change in composition: $G = \mu_A n_A + \mu_B n_B \implies dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$ At P, T=const $dG = \mu_A dn_A + \mu_B dn_B$

Thus, as G is state function:
$$n_A d\mu_A + n_B d\mu_B = 0 \implies d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

Gibbs-Duhem equation:

$$\sum_{J} n_{J} d \mu_{J} = 0$$

The same is true for all partial molar quantities

Gibbs-Duhem equation shows that chemical potential of one compound cannot be changed indepentently of the other chemical potentials.

Thermodynamics of mixing

The Gibbs energy of mixing

Let's consider mixing of 2 perfect gases at constant pressure p:

For each of them:
$$\mu = \mu^{\theta} + RT \ln \frac{p}{p^{\theta}}$$

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

After mixing the energy difference:

$$\Delta_{mix}G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

Using Dalton's law:

$$\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B)$$

as $x_{A,B} < 1$, $\Delta_{mix}G < 0$



 Δ_{mix} G/nRT

Thermodynamics of mixing

entropy of mixing

$$\Delta_{mix}S = -\left(\frac{\partial \Delta_{mix}G}{\partial T}\right)_{p,n_A,n_B} = -nR(x_A \ln x_A + x_B \ln x_B)_{0.8}$$

enthalpy of mixing

$$\Delta_{mix}H = \Delta_{mix}G + TdS = 0$$

The driving force of mixing is a purely entropic one!



Ideal solutions

Let's consider vapour (treated as perfect gas) above the solution. At equilibrium the chemical potential of a substance in vapour phase must be equal to its potential in the liquid phase

For pure substance:

$$\mu_A^* = \mu_A^0 + RT \ln p_A^*$$

In solution:

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p}$$

 $\mu_{A} = \mu_{A}^{\theta} + RT \ln p_{A}$

Francouis Raoult experimentally found that:

$$p_A = x_A p_A^*$$
 Raoult's law:
 $\mu_A = \mu_A^* + RT \ln x_A$

Mixtures obeying Raoult's law called ideal solutions



Molecular interpretation of Raoult's law

of condensation

$$k' p_A = k x_A$$

rate of evaporation

$$p_A = \frac{k}{k'} x_A$$

rate

and in case of pure liquid $(x_A = 1)$:

$$p_A^* = \frac{k}{k'}$$







Ideal-dilute solutions: Henry's law

In a dilute solution the molecule of solvent are in an environment similar to a pure liquid while molecules of solute are not!





• Using Henry's law

Example: Estimate molar solubility of oxygen in water at 25 °C at a partial pressure of 21 kPa.

$$p_{A} = x_{A}K_{A}$$

$$x_{A} = \frac{p_{A}}{K_{A}} = \frac{21 \text{kPa}}{7.9 \times 10^{4} \text{ kPa kg mol}^{-1}} = 2.9 \times 10^{-4} \text{ mol kg}^{-1}$$

$$[O_{2}] = x_{A}\rho_{H_{2}O} = 0.29mM$$

Synoptic Table 5.1*	Henry's law
constants for gases in w	ater at 298 K

	$K/(\mathrm{kPa}\ \mathrm{kg}\ \mathrm{mol}^{-1})$	
CO ₂	3.01×10^{3}	
H_2	1.28×10^5	
N ₂	1.56×10^{5}	
O ₂	7.92×10^4	

* More values are given in the *Data section*.

- Elevation of boiling point
- Depression of freezing point
- Osmotic pressure phenomenon

All stem from lowering of the chemical potential of the solvent due to presence of solute (even in ideal solution!)



• Elevation of boiling point

if liquid (solution) and vapour of pure A are in equilibrium:

$$\mu_{A}^{*}(g) = \mu_{A}^{*}(l) + RT \ln x_{A}$$
$$\ln(1 - x_{B}) = \frac{\mu_{A}^{*}(l) - \mu_{A}^{*}(g)}{RT} = \frac{\Delta G_{vap}}{RT}$$

Let's take derivative of both sides and apply Gibbs-Helmholtz equation:

$$\partial \left(\frac{\Delta G}{T}\right) / \partial T = \frac{\Delta H_{vap}}{RT^2}$$



boiling constant

$$\ln(1-x_B) = \frac{\Delta H_{vap}}{RT^*} (\frac{1}{T} - \frac{1}{T^*}) \implies x_B \approx \frac{\Delta H_{vap}}{R} (\frac{1}{T^*} - \frac{1}{T}) \approx \frac{\Delta H_{vap}}{R} \frac{\Delta T}{T^{*2}}$$
$$\Delta T = \frac{RT^{*2}}{\Delta H_{vap}} x_B \qquad \square \qquad \Delta T = K_b b \qquad \text{molality [mol/(kg solvent)]}$$

• Depression of freezing point

 $\mu_{A}^{*}(s) = \mu_{A}^{*}(l) + RT \ln x_{A}$

$$\Delta T = \frac{RT^{*2}}{\Delta H_{vap}} x_B$$

$$\Delta T = K_f b$$
Cryoscopic constant

Can be used to measure molar mass of a solute



• Dealing with boiling and cryoscopic constants

	$K_{\rm f}/({\rm Kkgmol^{-1}})$	$K_{\rm b}/({\rm K~kg~mol^{-1}})$
Acetic acid	3.90	3.07
Benzene	5.12	2.53
Camphor	40	
Carbon disulfide	3.8	2.37
Carbon tetrachloride	30	4.95
Naphthalene	6.94	5.8
Phenol	7.27	3.04
Water	1.86	0.51

Table 5.2 Freezing-point and boiling-point constants

if we need to find boiling/freezing temperature change

- Calculate the molality of **solute**
- Multiply by the relevant constant of **solvent**

can be also used to calculate molar mass

• Solubility

$$\mu_B^*(s) = \mu_B^*(l) + RT \ln x_B$$
$$\ln \kappa_B = \frac{\mu_B^*(s) - \mu_B^*(l)}{RT} = \frac{-\Delta G_{fus}}{RT}$$
$$\Delta G_{fus} = \Delta H_{fus} - T\Delta S_{fus}$$
$$\Delta G_{fus}(T^*) = \Delta H_{fus} - T * \Delta S_{fus} = 0$$
$$\ln x_B = \frac{\Delta H_{fus}}{R} (\frac{1}{T} - \frac{1}{T^*})$$



Colligative properties: Osmosis

 Osmosis – spontaneous passage of pure solvent into solution separated by semipermeable membrane



Osmosis

$$\mu_{A}^{*}(p) = \mu_{A}^{*}(p+\Pi) + RT \ln \kappa_{A}$$

$$dG = -SdT + Vdp$$

$$\mu_{A}^{*}(p+\Pi) = \mu_{A}^{*}(p) + \int_{p}^{p+\Pi} V_{m}dp$$
For dilute solution:
$$RTx_{B} = \Pi V_{m} + V/n_{A}$$



Van't Hoff equation: $\Pi = [B]RT$, $[B] = n_B / V$

More generally:
$$\Pi = [B]RT(1 + b[B] + ...)$$

Somotic virial coefficients

Osmosis: Examples

 Calculate osmotic pressure exhibited by 0.1M solutions of mannitol and NaCl.

 $\Pi = [B]RT, \quad [B] = n_B / V$



Osmosis: Examples



Internal osmotic pressure keeps the cell "inflated"

Application of Osmosis

• Using osmometry to determine molar mass of a macromolecule

Osmotic pressure is measured at a series of mass concentrations c and a plot of Π/c vs. c is used to determine molar mass.



Membrane potential

• Electrochemical potential

$$\overline{\mu}_{j} = \mu_{j} + z_{j} N_{A} e \Phi = \mu_{j}^{\theta} + RT \ln[j] + z_{j} F \Phi$$

• Example: membrane potential

Na⁺ salt of a protein-

$$\mu_{Na^{+}}^{\theta} + RT \ln[Na^{+}_{in}] + z_{Na^{+}}F\Phi_{in} = \mu_{Na^{+}}^{\theta} + RT \ln[Na^{+}_{out}] + z_{Na^{+}}F\Phi_{out}$$
$$\Delta \Phi = \frac{RT}{F} \ln\left(\frac{[Na^{+}_{out}]}{[Na^{+}_{in}]}\right)$$





Activities

• the aim: to modify the equations to make them applicable to real solutions

Generally:

$$\mu_{A}^{*} = \mu_{A}^{*} + RT \ln \frac{p_{A}}{p_{A}^{*}}$$
vapour pressure of A above solution
vapour pressure of A above pure A

For ideal solution

$$\mu_A^* = \mu_A^* + RT \ln x_A \qquad \text{(Raoult's law)}$$

For real solution

$$\mu_A^* = \mu_A^* + RT \ln a_A \quad \text{activity of A} \quad a_A = \frac{p_A}{p_A^*}; \quad a_A \to x_A \text{ as } x_A \to 1$$

$$\mu_{A}^{*} = \mu_{A}^{*} + RT \ln x_{A} + RT \ln \gamma_{A}$$
activity coefficient of A

Activities

• Ideal-dilute solution: Henry's law $p_B = K_B \kappa_B$

$$\mu_{B}^{*} = \mu_{B}^{*} + RT \ln \frac{p_{B}}{p_{B}^{*}} = \mu_{B}^{*} + RT \ln \frac{K_{B}}{p_{B}^{*}} + RT \ln x_{B}$$

$$\mu_{B}^{*} = \mu_{B}^{0} + RT \ln x_{B}$$

• Real solutes

$$\mu_B^* = \mu_B^{\theta} + RT \ln a_B \qquad a_B = \frac{p_B}{K_B}$$

Example: Biological standard state

• Biological standard state: let's define chemical potential of hydrogen at pH=7

$$\mu_{H^+} = \mu_{H^+}^{0} + RT \ln a_{H^+}$$

$$\mu_{H^+} = \mu_{H^+}^{\theta} - 7RT \ln(10) = \mu_{H^+}^{\theta} - 40kJ / mol$$

$$\mu = \mu^{\theta} + RT \ln a$$

$$a = \gamma \frac{b}{b^{\theta}}$$
standard state: ideal solution at molality b⁰=1mol/kg

Alternatively:

$$\mu = \mu^{\Theta} + RT \ln b + RT \ln \gamma = \mu^{ideal} + RT \ln \gamma$$
ideal solution of the same molality b

In ionic solution there is no experimental way to separate contribution of cations and anions

$$G_{m} = \mu_{+} + \mu_{-} = \mu_{+}^{ideal} + \mu_{-}^{ideal} + RT \ln \gamma_{+} \gamma_{-} \gamma_{\pm} \gamma_{\pm}^{2}$$
$$\mu_{+} = \mu_{+}^{ideal} + RT \ln \gamma_{\pm}; \ \mu_{-} = \mu_{-}^{ideal} + RT \ln \gamma_{\pm}$$

In case of compound $M_p X_q$: $G_m = p \mu_+ + q \mu_- = G_m^{ideal} + RT \ln \gamma_+^p \gamma_-^q$

Debye-Hückel limiting law

- Coulomb interaction is the main reason for departing from ideality
- Oppositely charged ions attract each other and will form shells (*ionic atmosphere*) screening each other charge
- The energy of the screened ion is lowered as a result of interaction with its atmosphere



Debye-Hückel limiting law

In a limit of low concentration the activity coefficient can be calculated as:

$$\log \gamma_{\pm} = -|z_{\pm}z_{-}| AI^{\frac{1}{2}}, \quad A = -0.509 \text{ for water}$$

where: $I = \frac{1}{2} \sum_{i} z_{i}^{2} (b_{i}/b^{\theta})$ lonic strength of the solution

Example: calculate mean activity coefficient of 5 mM solution of KCL at 25C.

$$I = \frac{1}{2} (b_{+} + b_{-}) / b^{\theta} = b / b^{\theta} = 5 \cdot 10^{-3}$$
$$\log \gamma_{\pm} = -|z_{+} z_{-}| A I^{\frac{1}{2}} = -0.509 * (5 \cdot 10^{-3})^{1/2} = -0.036$$
$$\gamma_{\pm} = 0.92$$

Debye-Hückel limiting law





Problems (to solve in class)

- 5.2a At 25°C, the density of a 50 per cent by mass ethanol water solution is 0.914 g cm⁻³. Given that the partial molar volume of water in the solution is 17.4 cm³ mol⁻¹, calculate the partial molar volume of the ethanol
- 5.6a The addition of 100 g of a compound to 750 g of CCl₄ lowered the freezing point of the solvent by 10.5 K. Calculate the molar mass of the compound.
- 5.14a The osmotic pressure of solution of polystyrene in toluene were measured at 25 °C and the pressure was expressed in terms of the height of the solvent of density 1.004g/cm³. Calculate the molar mass of polystyrene: c [g/dm3] 2.042 6.613 9.521 12.602 h [cm] 0.592 1.910 2.750 3.600
- 5.20(a) Estimate the mean ionic activity coefficient and activity of a solution that is 0.010 mol kg⁻¹ CaCl₂(aq) and 0.030 mol kg⁻¹ NaF(aq).