

### 3 CHEMICAL THERMODYNAMICS

#### 3.1 Definitions: (From Smith, 1982, and Anderson and Crerar, 1994)

1. **Thermodynamics:** Energy differences and transfers between systems.
2. **Systems:**
  - *Isolated system:* “have walls or boundaries that are rigid, do not permit transfer of mechanical energy, perfectly insulating, and impermeable. They have a constant energy and mass content.
  - *Adiabatic systems:* Perfectly insulated systems.
  - *Closed systems:* have walls that allow transfer of energy in or out of the system but are impervious to matter. They contain a fixed mass and composition, but variable energy.
  - *Open Systems:* have walls that allow transfer of both energy and matter to and from the system.
  - *Simple Systems:* Contain no interior walls.
  - *Composite system:* Two or more simple systems, and thus contain internal walls.
3. **Equilibrium:**
  - “A system at equilibrium has none of its properties changing with time”. A system at equilibrium will return to that state after being disturbed.
4. **State Variables:**
  - Variables that define the state of a system. *Extensive* variables are proportional to the quantity of matter being considered (V, total Cp). *Intensive* variables are independent of quantity (concentration, viscosity, density, molar Cp)
5. **Work (w):** “The transfer of energy from one mechanical system to another. It is always completely convertible to the lifting of a weight”. “The energy that flows across a system boundary in response to a force moving through a distance (such as happens when a system changes volume”.
6. **Heat (q):** “The transfer of energy that results from temperature differences”. “The energy that flows across a system boundary in response to a temperature gradient.” “that part of any energy transfer that is not accounted for by mechanical work (FxD).”  $q = \Delta U - w$
7. **Heat Capacity:** The relation between heat transferred to a body and the change in T.
8. **Enthalpy:** The increase in enthalpy of a system is equal to the heat absorbed at constant pressure, assuming the system does only PV work.
9. **Entropy:** A measure of the loss of capacity of the system to do work.
10. **ZEROth LAW:** “Two bodies in thermal equilibrium with a third are in thermal equilibrium with each other” (Basis of the concept of temperature)
11. **FIRST LAW:** “The algebraic sum of all energy changes in an isolated system is zero” (Conservation of energy). Energy can be converted from one form to another but cannot be created or destroyed.  $\Delta U = q + w$ . This is based only on observation
12. **SECOND LAW:** “Spontaneous changes are those which, if carried out under the proper conditions, can be made to do work. If carried out reversibly they yield a maximum amount of work. In natural processes, maximum work is never obtained.

### 3.2 Basic Principles

Thermodynamics is the study of energy in systems, and the distribution of energy among components. In chemical systems, it is the study of chemical potential, reaction potential, reaction direction, and reaction extent

#### 3.2.1 First Law of Thermodynamics:

$$dU = dq + dw$$

where U is the internal energy, q is the heat transferred to a system from the surroundings, and w is the work done on a system by the surroundings.

- “The change in the internal energy,  $dE$ , is the sum of the heat transferred *to* the system,  $dq$ , and the work done *on* the system,  $dw$ . This is the energy conservation principle for a system” (Stumm and Morgan, 1981, p. 17). For a finite change:

$$\Delta U = q + w$$

#### 3.2.2 Work and Reversible reactions.:

- “**Work** is the transfer of energy from one mechanical system to another. *It is always completely convertible to the lifting of a weight.*
- Work done **on** a system is positive, and work done **by** the system as negative. An example of work by the system is the expansion of a cylinder against the atmosphere.

$$w_{rev} = - \int_{v1}^{v2} P dV$$

- For a system doing only PV work:

$$dU = dq + dw$$

$$dU = dq - PdV$$

where  $PdV$  is the reversible expansion work done on the system by the surroundings.

- An analog of **a system doing no work** would be a sled going down a hill. The reaction is spontaneous, and potential energy is eventually converted to heat due to friction ( $\mathbf{w}=\mathbf{0}$ ,  $\mathbf{dU} = \mathbf{dq}$ ). The reaction proceeds until the potential energy minima is reached, i.e., the bottom of the hill. The reverse reaction is not spontaneous.
- An analog for a **system doing work** would be if one attached an object to the sled over a pulley, where the mass of the object  $M_2 < M_1$ , the mass of the sled and driver. As the sled goes down hill, the object is pulled upward, and work is done ( $\mathbf{dU} = \mathbf{dq} + \mathbf{w}$ ;  $\mathbf{w} = M_2 g dh$ ).
- As the mass of the object  $M_2$  increases, more work is accomplished, until  $M_1$  is only infinitesimally greater than  $M_2$ , and the maximum amount of work can be accomplished as the sled moves infinitely slowly, and only an infinitesimal amount of energy is required to reverse the process.

### 3.2.3 Second Law of Thermodynamics

The second law is concerned with *entropy* ( $S$ ), which is that part of the total energy of the system that is not available to do useful work.

**Statement One:** “The total entropy change of the closed system is  $dS_{\text{sys}}$  and is the sum of changes inside the system,  $dS_{\text{int}}$ , and entropy transferred to the system from its surroundings,  $dS_{\text{sur}}$ .

$$dS_{\text{sys}} = dS_{\text{int}} + dS_{\text{sur}}$$

$$dS_{\text{sur}} = dq/T$$

For a reversible process or *equilibrium* state of the system, the second law states that the internal entropy change is zero:

$$dS_{\text{int}} = 0$$

For a spontaneous or natural process in the system

$$dS_{\text{int}} > 0$$

So for any spontaneous natural process

$$dS_{\text{sys}} > dq/T$$

*The internal entropy change for a closed system is zero at equilibrium and positive for a spontaneous process. The heat transferred to a closed system, divided by  $T$ , is equal to or less than the entropy increase for any possible process. The entropy of an isolated system increases in any spontaneous process and attains a maximum for any reversible process. (Stumm and Morgan, p. 19).*

### 3.3 Free Energy

The Gibbs Free energy is that portion of the total system energy that is available for useful work.

- For most cases in water chemistry, the system is closed to the addition and removal of matter, but open to the transfer of energy.
- The system is at constant temperature and pressure, does only PV work, with P constant, so only expansion work is done:

$$dw = -PdV$$

At equilibrium, and with fixed composition (no addition of material):

$$dq = TdS(\text{sys})$$

so

$$dU = TdS - PdV$$

So the internal energy is a function of entropy and volume. Another expression for total system energy is Enthalpy (H):

$$H = U + PV$$

$$dH = dU + PdV$$

When T and P are constant, we can use Gibbs expression for free energy

$$dG = dU + PdV - TdS$$

$$dG = dH - T^{\circ}dS$$

Where:

G = Gibbs free energy, kcal/mol

T = absolute temperature, °K

S = entropy, cal/°K

H = enthalpy, kcal/mol

This equation tells us if a reaction will happen, and in what direction.

- Enthalpy:** the total energy content of a compound ( $dH = dU + PdV$ ) in kJ/mol; .
- Free Energy:** That part of the total energy that is available to perform "useful work", that is, other than **PV** work, such as electrical work, in kJ/mol.
- Entropy:** the degree of disorder of a system. The product TS is that part of the free energy which is NOT available for useful work, in joules/°K.

### 3.3.1 Heat Capacity:

Heat capacity is defined as the change in temperature of a system with a change of heat transferred to the system:

$$C = \frac{dq}{dT}$$
$$C_v = \left( \frac{\partial U}{\partial T} \right)_v \sim C_p = \left( \frac{\partial H}{\partial T} \right)_p$$

Heat capacity can be measured directly by calorimetry (at constant pressure), and can provide information on enthalpy for a closed-system process.

### 3.3.2 Law of Mass Action:

The driving force of a reaction is related to the concentrations of reactants and products.



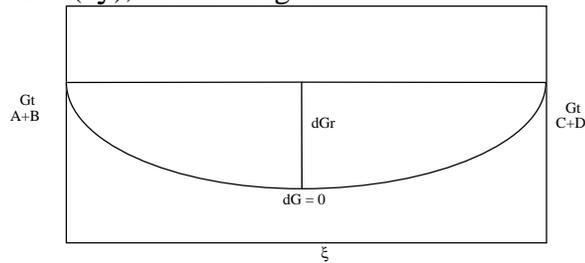
- The ratio of products to reactants is expressed by the equation:

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = Q$$

At equilibrium this ratio is equal to the equilibrium constant, **K**.

### 3.3.3 Equilibrium

- For a closed system at constant pressure and constant temperature, the criterion for equilibrium is that **the total free energy of the system ( $G_T$ ) is a minimum**.
- If we were to add A and B to a reaction vessel and calculate total free energy as a function of *reaction extent* ( $\xi$ ), we would get:



The TOTAL FREE ENERGY is the sum of the free energies of each component.

$$G_T = n_A G_A + n_B G_B + n_C G_C + n_D G_D$$

Where  $G_i$  = Free energy / mole of  $i$   
 $n_i$  = number of moles of  $i$

- For a reaction proceeding in incremental amounts toward equilibrium, the change in  $G_T$  is proportional to  $dG$ , where**

$$\Delta G = (\sum \nu_i G_i)_{\text{products}} - (\sum \nu_i G_i)_{\text{reactants}}$$

Where:  $\nu_i$  = the stoichiometric coefficient  
 $G_i$  = the free energy per mole

- Applying to our base equation:  $\Delta G = \Delta H - T^\circ \Delta S$  (at constant T,P)
  - $\Delta G < 0$ , and  $G_T$  decreases as the reaction proceeds, the reaction is spontaneous.
  - $\Delta G = 0$ , the reaction is at equilibrium, and  $G_T$  is at a minimum
  - $dG > 0$ , the reaction is not spontaneous as written, but proceeds in the opposite direction.

- Values of  $\Delta G$  for a reaction can predict whether or not reactions are possible. To calculate  $\Delta G$  for the general mass reaction we use the relationship:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Where:  $\Delta G^\circ = (\sum \nu_i G^\circ_{f,i})_{\text{products}} - (\sum \nu_i G^\circ_{f,i})_{\text{reactants}}$

$G^\circ_{f,i}$  = free energy per mole at standard state.

### 3.3.4 Free energy of formation:

- To calculate the equilibrium state before the reactions occurs, it is necessary to calculate the chemical potential of each component, but it is only possible to measure *change* in free energy.
- Therefore, the **standard free energy of formation** is defined as *the change in free energy to form the compound from its constituent elements*, which are arbitrarily assigned a value of 0.
- This can be used to determine the overall standard free energy change for the reaction,  $\Delta G_r^\circ$  from the free energies of formation:

### 3.3.5 Free Energy of Reaction:

- The free energy of the reaction is equal to the sum of the free energies of formation of the products minus the sum of the free energies of the reactants *at standard state*:

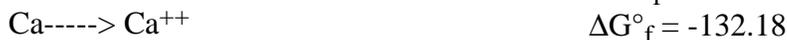
$$\Delta G^\circ = (\sum \nu_i G^\circ_{f,i})_{\text{products}} - (\sum \nu_i G^\circ_{f,i})_{\text{reactants}}$$

- Further, we can relate the free energy of a single substance at a state other than standard to its free energy of formation at standard state by the expression:

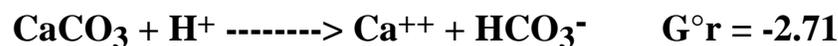
$$G_i = \Delta G^\circ_{f,i} + RT \ln \{i\}$$

Where  $\{i\}$  is the *effective concentration* or **activity** of species I

#### 3.3.5.1 Example Calcium carbonate:



$$\Delta G^\circ = (\sum \nu_i G^\circ_{f,i})_{\text{products}} - (\sum \nu_i G^\circ_{f,i})_{\text{reactants}}$$



Reacting 1 mole of acid with one mole of calcite releases free energy, so the reaction is spontaneous.

### 3.4 Activity vs. Concentration

The value of the **activity** of a substance is dependent on the choice of standard state conditions, or the conditions that result in unit activity.

1. For **ions and molecules in solution**, (i) is related to the molar concentration [i], by (i) =  $\gamma_i[i]$ , where  $\gamma$  is the activity coefficient. As the solution becomes dilute  $\gamma_i$  approaches 1.
2. For the **solvent in a solution** (i) =  $\gamma_i X_i$ , where  $X_i$  is the mole fraction. As the solution becomes more dilute,  $\gamma_i$  approaches 1. The activity generally is assumed to be 1 for the dilute solutions of concern here.
3. For **pure solids** or liquids in equilibrium with a solution, (i) = 1.
4. For **gases** in equilibrium with a solution, (i) =  $\gamma_i P_i$  where  $P_i$  = is the partial pressure of the gas in atmospheres. As the total pressure decreases,  $\gamma_i$  approaches 1. When reactions take place at atmospheric pressure, the activity of a gas can be approximated closely by its partial pressure.
- 6 For mixtures of liquids, (i) =  $X_i$

Returning to the example:

$$\Delta G = [\Delta G_{f, \text{HCO}_3^-}^\circ + RT \ln \{ \text{HCO}_3^- \} + \Delta G_{f, \text{Ca}^{++}}^\circ + RT \ln \{ \text{Ca}^{++} \}] -$$

Collecting Terms:

$$- [\Delta G_{f, \text{H}^+}^\circ + RT \ln \{ \text{H}^+ \} + \Delta G_{f, \text{CaCO}_3}^\circ + RT \ln (\text{CaCO}_3)]$$

We can state

$$\Delta G = \Delta G^\circ + RT \ln \frac{\{ \text{HCO}_3^- \} \{ \text{Ca}^{2+} \}}{\{ \text{H}^+ \} \{ \text{CaCO}_{3(s)} \}}$$

and since the activity of a solid is unity:  $\Delta G = \Delta G^\circ + RT \ln \frac{\{ \text{HCO}_3^- \} \{ \text{Ca}^{2+} \}}{\{ \text{H}^+ \}}$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

When the value of Q is identical to that of the equilibrium constant K, and  $\Delta G = 0$ ,

$$0 = \Delta G^\circ + RT \ln K; \quad \Delta G^\circ = -RT \ln K$$

When not at equilibrium, substituting we can get

$$\Delta G = -RT \ln K + RT \ln Q$$

$$= +RT \ln Q/K$$

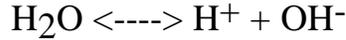
when  $Q/K > 1$ , not spontaneous

$Q/K = 1$ , equilibrium

$Q/K < 1$ , spontaneous

### 3.4.1 Example 3-1, S&J

Determine the equilibrium constant for the dissociation of water at 25°C:



1. Find the  $\Delta G_f^\circ$  of the reactants and products:

Species	$\Delta G_f^\circ$
H <sub>2</sub> O	-56.69
H <sup>+</sup>	0
OH <sup>-</sup>	-37.60

2. Sum the energies of formation to get a standard free energy of reaction

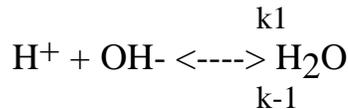
$$\Delta G^\circ = (1)(0) + (1)(-37.6) - (1)(-56.69) = 19.09 \text{ kcal}$$

$$19.09 = -RT \ln K$$

$$\frac{-19.09}{(1.987)(10^{-1})(298)} = \ln K = -32.24$$

$$K = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

3. Use reaction rates to find equilibrium:



with  $k_1 = 1.4 \times 10^{11}$  liter/mole sec

$$k_2 = 2.5 \times 10^{-5} / \text{sec}$$

- These are the fastest rates known in aqueous solutions, where the reaction is essentially instantaneous, with the overall rate limited by the rate of diffusion of reactants.
- Since the reaction is elementary, we can write:  
Forward rate =  $k_1[\text{H}^+][\text{OH}^-]$   
Reverse rate =  $k_2[\text{H}_2\text{O}]$
- Since at equilibrium, the forward rate = reverse rate:

$$k_1[\text{H}^+][\text{OH}^-] = k_2[\text{H}_2\text{O}]$$

$$k_2[\text{H}_2\text{O}]/k_1 = [\text{H}^+][\text{OH}^-] \text{ (mole}^2\text{/liter}^2\text{)}$$

- Substituting for k's, and using 55.5 moles/l for water concentration:

$$\frac{(2.5 \times 10^{-5} / \text{sec})(55.5 \text{ moles} / \text{l})}{1.4 \times 10^{11} \text{ liter} / \text{mole} - \text{sec}} = 0.99 \times 10^{-14}$$

### 3.5 Temperature And Pressure Dependence OF K, G, H

The driving force of a reaction is  $\Delta G$ , as an expression of useful work (non-PV work). This is comprised of 2 components, enthalpy and entropy. At equilibrium:

$$\Delta G = \Delta H - T^\circ \Delta S$$

So the magnitude and direction of the driving force depends on the magnitude and direction of H and S. Neither by themselves controls the reaction.

### 3.6 Enthalpy And The Temperature Dependence Of K

- The enthalpy change of a chemical reaction ( $\Delta H$ ) is the amount of heat that is released or taken up during the course of the reaction.
  - a) Endothermic = positive  $\Delta H$
  - b) Exothermic = negative  $\Delta H$

$\Delta H$  can be expressed in terms of G, S, and T as:  $\Delta H^\circ = \Delta G^\circ + T^\circ \Delta S^\circ$  and represents the TOTAL energy of the system, both usable and unusable. At equilibrium,  $\Delta H = +T^\circ \Delta S$

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- Similarly to  $\Delta G^\circ$ ,  $\Delta H^\circ$  for a reaction can be calculated by:

$$\Delta H^\circ = \Sigma (\Delta H^\circ_{\text{products}}) - \Sigma (\Delta H^\circ_{\text{reactants}})$$

- Also similarly to  $\Delta G^\circ$ , the absolute value of  $\Delta H^\circ$  cannot be directly measured, and so the elements are assigned a value of 0, and then calculating the enthalpy of formation.
- The standard enthalpy change  $\Delta H^\circ$  is used to determine the effect of temperature on the position of equilibrium. The basic equation is:

$$dG = -SdT + VdP$$

Which at **constant pressure** can be written as

$$dG = -SdT,$$
$$\left( \frac{\partial G}{\partial T} \right)_p = -S$$

so the change in free energy with temperature is related to entropy. For a finite change in state:

$$\Delta G = -S\Delta T,$$
$$\left( \frac{\partial \Delta G}{\partial T} \right)_p = -\Delta S$$

$$\Delta G = \Delta H + T \left( \frac{\partial \Delta G}{\partial T} \right)_p$$

divide through by  $T^2$ :

$$-\frac{\Delta G}{T^2} + \frac{1}{T} \left( \frac{\partial \Delta G}{\partial T} \right)_p = -\frac{\Delta H}{T^2}$$

and

$$-\frac{\Delta G}{T^2} + \frac{1}{T} \left( \frac{\partial \Delta G}{\partial T} \right)_p = \left[ \frac{\partial \left( \frac{\Delta G}{T} \right)}{\partial T} \right]_p = -\frac{\Delta H}{T^2}$$

giving the **Gibbs-Helmholtz equations**

By differentiating the equation:  $\Delta G^\circ = -RT \ln K$ , we obtain

$$\left( \frac{\partial \ln K_p}{\partial T} \right)_p = -\frac{1}{R} \left[ \frac{\partial \left( \frac{\Delta G^\circ}{T} \right)}{\partial T} \right]_p = \frac{\Delta H^\circ}{RT^2}$$

Since by definition the standard system is at 1 atm, and  $\Delta G^\circ$  and  $\Delta H^\circ$  are not function of pressure, we can write the full differential thus:

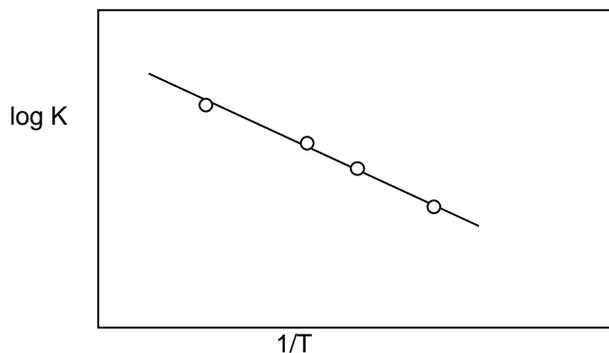
$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2} \text{ called the } \mathbf{Van't Hoff Isochore}$$

So the equilibrium constant varies with temperature as a function of the **Enthalpy** of the system (Assuming  $dH$  does not vary with temperature.).

- If we assume that  $-\Delta H^\circ$  is independent of temperature, integration of the equation yields:

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Plotting  $\log K$  against  $1/T$  results in a line whose slope is  $-\Delta H^\circ/2.3R$



a) For an exothermic reaction,  $K$  must decrease as the temperature increases....

### 3.7 Ideal And Non Ideal Solutions

#### 3.7.1 Chemical Potentials In Phases:

Chemical Potential:  $G = \bar{\mu} = \mu(T,P)$

- For pure solids and pure liquids the chemical potential is the molar free energy  $G$  bar, and is a function of  $T$  and  $P$  only.

- by convention we refer to the chemical potential of a component at 1 atm as  $\mu^\circ$ , so

$$\mu = \mu^\circ(T)$$

#### 3.7.2 2. Chemical potential of an ideal gas.

- For  $n$  moles of pure gas at constant temperature

$$dG = VdP$$

- From the ideal gas law:

$$V = nRT/P$$

$$\text{So: } dG = nRT \frac{dP}{P} \quad \text{or} \quad dG = nRT d \ln P$$

- Integrating from a standard pressure  $P^\circ$  to a pressure  $P$  yields

$$G - G^\circ = nRT \ln \frac{P}{P^\circ}$$

Dividing by  $n$

$$G/n - G^\circ/n = RT \ln \frac{P}{P^\circ}$$

- Since the chemical potential for a one-component phase is  $G/n$ :

$$\mu(g) - \mu^\circ(g) = RT \ln P/P^\circ$$

When  $P = P^\circ$ ,  $\mu(g) = \mu^\circ(g)$ , or

$$\mu_{i(g)} = \mu^\circ_{i(g)} + RT \ln P/P^\circ$$

If  $P^\circ = 1$

$$\mu_{i(g)} = \mu^\circ_{i(g)} + RT \ln P$$

and in an ideal gas **mixture**:

$$\mu_{i(g)} = \mu^\circ_{i(g)} + RT \ln P_i$$

- where the value of  $\mu$  at 1 atm is  $\mu^\circ$  standard state, and  $P_i$  is the partial pressure of component  $i$ . If  $x_i$  is the mole fraction of component  $i$ :  $P_i = X_i P$ , leading to:

$$\mu_{i(g)} = \mu^\circ_{i(g)} + RT \ln P + RT \ln X_i$$

### 3.7.3 Chemical potentials in ideal solutions:

This closely follows ideal gas mixtures:  $\mu_{i(sol)} = \mu^\circ_{i(sol)} + RT \ln X_i$

Where:  $X_i$  = the mole fraction of  $i$  in solution

- For a solution of component  $i$  in equilibrium with a vapor phase, the general criterion of equilibrium  $dG = 0$ , yields as the condition of 2-phase equilibrium

$$\mu_{i(sol)} = \mu_{i(g)}$$

- Assuming the vapor phase is an ideal gas mixture, we get:

$$\mu_{i(sol)} + RT \ln X_i = \mu^\circ_{i(g)} + RT \ln P_i$$

Rearranging

$$\frac{P_i}{X_i} = \exp \left[ \frac{\mu^\circ_{i(sol)} - \mu^\circ_{i(g)}}{RT} \right]$$

- 1) This equation states that *the vapor pressure of component  $i$  is proportional to its mole fraction in a solution behaving ideally*. This is the base equation for **Raoult's** and **Henry's** law.:

### 3.7.4 Raoult's Law:

*The ideal gas vapor pressure of an ideal solution component is equal to the vapor pressure of the pure liquid component multiplied by the mole fraction of the component in the solution, or:*

$$P_i = X_i P_i^\circ$$

where  $P_i$  is the partial pressure,  
 $X_i$  is the mole fraction, and  
 $P_i^\circ$  is the partial pressure of pure component  $i$ .

$$P_i = \exp\left[\frac{\mu_{i(sol)}^\circ - \mu_{i(g)}^\circ}{RT}\right]$$

and when  $X_i = 1$ :

$$\mu_{i(sol)}^\circ = \mu_{i(g)}^\circ + RT \ln P_i^\circ$$

Thus the standard state chemical potential for the ideal solution component depends on the ideal gas state and the convention that  $X_i = 1$  is the standard state for the component in solution.

**--For real solutions, Raoult's law behavior is approached as  $X_i \rightarrow 1$ .**

### 3.7.5 Henry's Law:

*For a dilute solution the ideal gas vapor pressure of a volatile solute is proportional to its mole fraction in the solution; that is, escaping tendency of the solute molecule is proportional to their mole fraction, ie:*

$$P_i = K_i X_i$$

This means that  $K_i$  is the *slope* of the plot of  $P_i$  vs  $X_i$  for sufficiently dilute solutions, or where solute-solute interactions are negligible.. So:

$$K_i = \exp\left[\frac{\mu_{i(sol)}^\circ - \mu_{i(g)}^\circ}{RT}\right]$$

**For real solutions, Henry's law behavior is approached as  $X_i$  approaches 0.**

**Important:**  $\mu_{i(sol)}^\circ$  for a Henry's law solute reflects the properties of a dilute solution, and for a Raoult's law component it reflects the properties of a pure component, in other words, the solvent.

### 3.8 Nonideal Behavior Of Ions And Molecules In Solutions:

#### 3.8.1 For Real Solutions:

1) The term activity is used for *idealized* concentration, vs actual concentration:

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

and

$$a_i = \gamma_i X_i$$

giving the chemical potential in a real solution:

$$\mu_i = \mu_i^\circ + RT \ln \gamma_i X_i; \quad \mu_i = \mu_i^\circ + RT \ln \gamma_i + RT \ln X_i$$

Where the expression  $RT \ln \gamma_i$  is *the partial molar free energy of the interactions that occur in nonideal mixtures.*

#### 3.9 Ionic Strength Effects On Equilibrium:

- In very dilute aqueous solutions, ions behave independently of one another and we assume that activity coefficients of ions are unity.
- However, as the concentration of ions in solution increases, electrostatic interactions between the ions also increase, and the activity of ions becomes somewhat less than their measured or analytical concentration:

$$a_i = \gamma_i X_i \text{ or } \{i\} = \gamma[i]$$

--The activity coefficient becomes less than one and the chemical equilibrium is affected, forcing the rewriting of the mass action equation to:

$$K = \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b} = \frac{(\gamma_c [C])^c (\gamma_d [D])^d}{(\gamma_a [A])^a (\gamma_b [B])^b}$$

- But from a purely thermodynamic point of view there is no way in which the activity of a single ion can be measured without introducing non thermodynamic assumptions, i.e. Single ion activity coefficients
- To calculate the activity coefficients of solutes in real solutions, the effects of actual solute mixture must be taken into account, ie, non-infinite dilution.
- The generalized expression of these effects is the ionic strength, defined as:

$$I = \frac{1}{2} \sum_i (C_i Z_i^2)$$

### 3.9.1 Debye-Huckel limiting law:

$$-\log \gamma_i = 0.5 Z_i^2 I^{\frac{1}{2}}$$

This is the simplest equation, and is good up only up to  $I = 0.005$

- Based on the effect ionic interactions should have on free energy. In an ionic solution, positive ions will tend to have a cloud of negative ions around them, and negative ions a cloud of positive ions.

### 3.9.2 Extended Debye-Huckel approximation of the Debye-Huckel limiting law,

- applicable for ionic strength  $I < 0.1M$

$$-\log \gamma_i = \frac{AZ_i^2 I^{\frac{1}{2}}}{1 + Ba_i I^{\frac{1}{2}}}$$

Where:

**A** = a constant that relates to the solvent, and varies with temperature. ( $A = 1.82 \times 10^6 (\epsilon T)^{-3/2}$ ,  $\epsilon$  = dielectric constant.)

$A = 0.5$  at  $15^\circ C$ ;  $0.509$  at  $25^\circ C$

**B** = a constant that relates to the solvent and varies with temperature.  $B = 50.3 (\epsilon T)^{-1/2}$

$B = 0.326 \times 10^8$  at  $15^\circ C$ ; and  $0.328 \times 10^8$  at  $25^\circ C$ .

**$a_i$**  = a constant that relates to the diameter of the hydrated ion. For monovalent ions except  $H^+$  this is about  $3-4 \times 10^{-8}$

**$Z_i$**  = the charge of the ion

### 3.9.3 The Guntelberg approximation

- plugs in the monovalent coefficients at  $15^\circ C$ :

$$-\log \gamma_i = \frac{0.5 Z_i^2 I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}}$$

This approximation is useful in solutions of mixed ions with varying charges, since the limiting law is not satisfactory with mixed charge types, and is useful up to  $I = 0.1$ .

### 3.9.4 Davies equation

$$\text{For } I = 0.5m; \quad -\log \gamma_i = AZ_i^2 \left( \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.2(0.3)I \right)$$

### 3.9.5 Electroneutrality:

- All solutions are charge balanced, with the meq of anions exactly balanced by the meq of cations. The standard equation is:

$$CB = \frac{\sum meq(anions) - \sum meq(cations)}{\sum meq(anions) + \sum meq(cations)} \times 100$$

The usual QA cutoff is +/- 5% on the CB, or with the alternative equation, 10%. This is often exceeded with very dilute waters and brines.

### 3.9.6 Relation of ionic strength to TDS

$$\mu = 2.5 \times 10^{-5} \times \text{TDS}$$

$$\mu = 1.6 \times 10^{-5} \times \text{specific conductance } (\mu\text{mho/cm})$$

### 3.9.7 Activity coefficients of nonelectrolytes in aqueous solutions:

This is not as well developed as for electrolytes, and is based on empirical equations such as

$$\log \gamma = k_s \mu$$

- For this equation, the salting-out coefficient  $k_s$  must be experimentally determined, and is generally in the range of 0.01 - 0.15
- nonionic solutes have activity coefficient of nearly 1 for  $I < 0.1$

#### 3.9.7.1 Example: dissolved oxygen in NaCl:

$$\begin{aligned} k_s &= 0.132 \\ \mu &= 0.05 \\ \log \gamma &= 0.132 \times 0.05 = 0.0066 \\ \gamma &= 1.02 \end{aligned}$$

so as the ionic strength increases, the activity coefficient increases.