CHEM 2880 - Kinetics

Thermodynamics IV - Free Energy and Chemical Equilibria

Tinoco Chapter 4

Chemical Potential

(Partial Molar Gibbs Free Energy)

The chemical potential (μ) of the *i*th component in a system is the partial molar Gibbs free energy of that component and is given by:

$$\mu_i = \overline{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

where n_j represents the number of moles of all the other components of the system.

The partial molar Gibbs free energy can be thought of as the increase in the Gibbs free energy of the system when 1 mole of *i* is added to a large amount of the system at constant T and P.

Any extensive property of a system can be determined by summing the partial molar quantities across all of the components of the system.

For a two component system the total Gibbs free energy (G) is:

$$G = n_1\mu_1 + n_2\mu_2$$

For a change in a system from an initial state A to a final state B, where dn_1 moles of component i are changing:

The initial chemical potential for i is μ_i^A
The final chemical potential for i is μ_i^B

The change in the Gibbs free energy for this process is:

$$dG = \mu_i^B dn_1 - \mu_i^A dn_1 = (\mu_i^B - \mu_i^A)\, dn_1$$

If $(\mu_i^B - \mu_i^A) < 0$ then $dG < 0$ and the change from state A to state B will be spontaneous.

If $(\mu_i^B - \mu_i^A) > 0$ then $dG > 0$ and the change from state A to state B will be non-spontaneous. The change from B to A will be spontaneous.

If $(\mu_i^B - \mu_i^A) = 0$ then $dG = 0$, the system is at equilibrium and no net change will occur.

Thus spontaneous processes always proceed from a state of high chemical potential to one of lower chemical potential.

This applies to both physical and chemical processes including transfers between phases and transfers between chemical states.

i.e. diffusion, evaporation, sublimation, condensation, crystallization, solution formation or chemical reaction

For the reaction:

$$aA + bB \rightarrow cC + dD$$

$$\Delta G = (d\mu_D + c\mu_{C)} - (a\mu_A + b\mu_B)$$

Reactions of Gases - Dependence of μ on P

At constant T, the change in G with a change in P for an ideal gas is calculated as:

$$G(P_2) - G(P_1) = nRT \ln\left(\frac{P_2}{P_1}\right)$$

If P_1 is taken as standard state, then this becomes:

$$G - G^\circ = nRT \ln\left(\frac{P}{1\,atm}\right)$$

$$\frac{G}{n} - \frac{G^\circ}{n} = RT \ln\left(\frac{P}{1\,atm}\right)$$

$$\mu = \mu^\circ + RT \ln\left(\frac{P}{1\,atm}\right)$$

where μ is the chemical potential at any pressure
and μ° is the chemical potential at standard state

In a mixture of ideal gases, partial pressures are used and:

$$\mu_A = \mu_A{}^\circ + RT \ln\left(\frac{P_A}{1\,atm}\right)$$

Equilibrium Constant

Consider the Gibbs free energy for a reaction involving only gases:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

The Gibbs free energy for the reaction is:

$$\Delta G = 2\mu_{NH_3} - \mu_{N_2} - 3\mu_{H_2}$$

$$\Delta G = 2\left[\mu^\circ_{NH_3} + RT\ln\left(\frac{P_{NH_3}}{1atm}\right)\right] - \left[\mu^\circ_{N_2} + RT\ln\left(\frac{P_{N_2}}{1atm}\right)\right]$$

$$-3\left[\mu^\circ_{H_2} + RT\ln\left(\frac{P_{H_2}}{1atm}\right)\right]$$

$$\Delta G = \left(2\mu^\circ_{NH_3} - \mu^\circ_{N_2} - 3\mu^\circ_{H_2}\right)$$

$$+RT\left(2\ln\left(\frac{P_{NH_3}}{1atm}\right) - \ln\left(\frac{P_{N_2}}{1atm}\right) - 3\ln\left(\frac{P_{H_2}}{1atm}\right)\right)$$

$$\Delta G = \Delta G^\circ + RT\ln\left(\frac{P^2_{NH_3}}{P_{N_2}P^3_{H_2}}\right)$$

$$\Delta G = \Delta G^\circ + RT\ln\left(\frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3}\right)$$

Note that the ‘1 atm’ terms have been removed in this equation. This implies that all the pressures have been divided by 1 atm and are thus unitless quantities. They represent the ratio between the measured pressure and the standard state and are numerically equal to the pressures measured in atm.

This equation relates the Gibbs free energy of a process, ΔG, to the Gibbs free energy at standard state, ΔG°. The Gibbs free energy at standard state implies all species present at standard state (1atm partial pressure for gases). ΔG is used for any set of conditions other than standard state and these conditions must be specified.

When the system is at equilibrium, ΔG = 0. Thus

$$\Delta G = 0 = \Delta G^\circ + RT\ln\left(\frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3}\right)$$

$$\Delta G^\circ = -RT\ln\left(\frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3}\right)$$

$\Delta G°$ is a state function with the specific conditions of standard state. At any given T, $\Delta G°$ for a reaction is a constant.

Therefore the ratio $\dfrac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$ must also be constant at any specified T and total P. This ratio is denoted K and is called the equilibrium constant of the reaction. Thus:

$$\Delta G° = RT\ln K$$

Note that the equilibrium constant, K, relates to $\Delta G°$ which relates to standard state concentrations, and not to ΔG(at equilibrium) which is 0.

The general form of this equation which relates to any reaction involving gases with near ideal behaviour is for:

$$aA + bB \rightarrow cC + dD$$

$$\Delta G = \Delta G° + RT\ln Q$$

where

$$Q = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

Again, P_A, P_B, P_C and P_D are the partial pressures of each component, measured in atm and divided by 1 atm. Q is unitless.

If the number of moles involved in the reaction is doubled, Q is squared.

If Q is large (>1), there is more product / less reagent and an unfavourable (positive) contribution to ΔG.

If Q is small (<1), there is less product / more reagent and a favourable (negative) contribution to ΔG.

Another form of this equation is:

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

$$\Delta G = RT \ln \frac{Q}{K}$$

If Q > K then ΔG will be > 0 and the reaction will be non-spontaneous as written.

If Q < K then ΔG will be < 0 and the reaction will be spontaneous as written.

Non-ideal Systems

The equations on the previous pages apply to systems of ideal gases. It would be useful to apply them to solids, liquids and solutions as well. This is done using activities.

Activity

For substance A, its activity a_A is related to its chemical potential by:

$$\mu_A = \mu_A^\circ + RT\ln a_A$$

So the activity for an ideal gas would be equal to its partial pressure divided by 1 atm. For a real gas, the activity is a function of its partial pressure.

Activity can be viewed as an effective pressure (or in the case of solutions, an effective concentration) which corrects the measured concentration for the non-ideal behaviour observed in real, complex systems.

For the reaction:

$$aA + bB \rightarrow cC + dD$$

the Gibbs free energy is:

$$\Delta G = \Delta G° + RT\ln Q$$

where

$$Q = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

The equilibrium constant is

$$K = \frac{\left(a_C^{eq}\right)^c \left(a_D^{eq}\right)^d}{\left(a_A^{eq}\right)^a \left(a_B^{eq}\right)^b}$$

where a_A^{eq} is the equilibrium activity of A.

Equilibrium constants are calculated using the activities of all the species involved in the reaction.

Like Q and K, activities are unitless.

Activities are defined with respect to a standard state.

$$\mu_A - \mu_A^\circ = RT\ln a_A$$

This standard state must be specified. Then the activity at any other state can be determined by measuring the chemical potential at that state, and comparing it to the chemical potential at standard state. When A is at standard state, a_A is 1.

Activities can be related to more widely used measurements such as partial pressures for non-ideal gases, and concentrations for solutions by using various standard states.

Standard States

Standard states are chosen out of convenience to relate activities to commonly used experimental parameters.

For gases, activities relate to partial pressures, and for solutions to concentration.

Ideal Gases

The standard state for an ideal gas is the gas with a partial pressure of 1 atm. The activity of an ideal gas is its partial pressure (in atm) divided by 1 atm.

$$a_A = \frac{P_A}{1 atm}$$

Real Gases

The activity of a real gas is a function of its partial pressure

$$a_A = \frac{\gamma_A P_A}{1 atm}$$

where γ_A is the activity coefficient. Activity coefficients range from 0 to 1 in value. Thus the effective pressure of a real gas is always equal to or less than its measured pressure.

At low pressures all gases show ideal behaviour, so $\gamma_A \rightarrow 1$ as $P \rightarrow 0$. At atmospheric pressures, the activity coefficients for gases are close to 1and they can be treated as ideal gases.

For ideal gases:

$$\mu_A - \mu_A^\circ = RT\ln P_A$$

A plot of $\mu_A - \mu_A^\circ$ vs $\ln P_A$ for an ideal gas would have a slope of RT and go through the origin: when P=1, ln P=0, $\mu_A = \mu_A^\circ$ and $\mu_A - \mu_A^\circ = 0$.

The same equation for non-ideal gases is:

$$\mu_A - \mu_A^\circ = RT\ln\gamma_A P_A = RT\ln\gamma_A + RT\ln P_A$$

As pressure increases, activity coefficients for real gases decrease below 1. The same plot for a non-ideal gas would follow the same straight line at low pressures (as all gases show ideal behaviour at low pressures and $\ln\gamma_A=0$) but would drop below the ideal line at higher pressures as the activity coefficient started to drop below 1 and $\ln\gamma_A<0$.

The standard state for real gases is the extrapolated state where P_A is 1 atm, but the properties are extrapolated from low pressures where the behaviour is ideal. This is a strictly hypothetical state.

Solids/Liquids

The standard state for a pure solid or liquid is the pure substance at 1 atm pressure. The activity for a pure solid or liquid is equal to 1 at 1 atm pressure. G for solids and liquids does not vary significantly with changes in pressure, so the activity for solids and liquids can be taken as 1 at any pressure

$$a_A = 1$$

Solutions

- a mixture of two or more substances
- can be solid, liquid, or more complicated
- activity of each component depends on the concentrations of every other species in the solution

$$a_A = \gamma_A \text{concentration}_A$$

- γ_A, the activity coefficient for component A, depends on the activity of all the other components of the solution
- the concentration of A, can be expressed in a number of different units including: mole fraction, ,molarity and molality
- different units of concentration result in different values for activity of the same component in the same system

Solvent Standard State

- the solvent standard state is defined as the pure component
- this standard state is often used for a solvent and uses mole fraction for the unit of concentration

$$X_A = \frac{n_A}{n_T}$$

$$a_A = \gamma_A X_A$$

- the standard state is defined such that as X_A approaches 1, γ_A approaches 1, and a_A approaches X_A
- in very dilute solutions, $X_{\text{solvent}} \approx 1$and $a_{\text{solvent}} \approx 1$
  - thus for very dilute solutions we can ignore the solvent when writing equilibrium constants as its activity is 1
- for:

Very dilute solutions	$a_{\text{solvent}} \approx 1$
Dilute or ideal solutions	$a_{\text{solvent}} \approx X_{\text{solvent}}$
(if $a_{\text{solvent}} \approx X_{\text{solvent}}$, then the solution is ideal)	
Real solutions	$a_{\text{solvent}} \approx \gamma X_{\text{solvent}}$

- activity coefficients for solvents in real solutions can be determined by measuring the free energy of the solvent using methods such as measurement of vapour pressure, freezing-point depression, boiling point elevation and measurement of osmotic pressure

Solute Standard States

- used for components whose concentrations are never very high
- defined as the extrapolated state where concentration is 1 M or 1 m but the properties are those extrapolated from very dilute solution
- hypothetical state which corresponds to a 1 M or 1 m ideal solution

Molarity

- units of moles of solute per litre of solution ($\mathrm{mol\ L^{-1}}$ or M), symbol is c

$$a_A = \gamma_A c_A$$

- as the molarity goes to zero (more and more dilute solution), the activity goes to 1 and the activity coefficient goes to 1
- for:

Dilute or ideal solutions $a_A = c_A$
Real solutions $a_A = \gamma_{AcA}$

- activity coefficients for solutes in real solutions can be determined by measuring the free energy of the solute using vapour pressure for volatile solutes and electrochemical cells for electrolytes

- to measure the (hypothetical) standard state, a series of measurements at low concentration must be made to determine μ_A as a function of c_A, and a plot of μ_A vs $\ln c_A$ is extrapolated to $\ln c_A = 0$ ($c_A = 1$) (see Tinoco Figs 4.1 and 4.2)

- when a strong electrolyte dissolves in solution, dissociation occurs, and multiple charged species are produced in solution
- in the case of NaCl, the chemical potential of the solute can be expressed as the sum of the potentials of the two ions:

$$\mu_{NaCl} \equiv \mu_{Na^+} + \mu_{Cl^-}$$

$$\mu_{NaCl} \equiv \mu^0_{Na^+} + \mu^0_{Cl^-} + RT\ln a_{Na^+} + RT\ln a_{Cl^-}$$

$$\mu_{NaCl} \equiv \mu^0_{Na^+} + \mu^0_{Cl^-} + RT\left(\ln a_{Na^+} \cdot a_{Cl^-}\right)$$

$$Also: \quad \mu_{NaCl} \equiv \mu^0_{NaCl} + RT\ln a_{NaCl}$$

$$Therefore: \quad a_{NaCl} = a_{Na^+} \cdot a_{Cl^-}$$

$$Similarly: \quad a_{Na_2SO_4} = a^2_{Na^+} \cdot a_{SO_4{}^{2-}}$$

Molality

- units of moles of solute per kilogram of solvent (mol kg^{-1}), symbol is m

$$a_A = \gamma_A m_A$$

- as the molality goes to zero (more and more dilute solution), the activity goes to 1 and the activity coefficient goes to 1
- for:

Dilute or ideal solutions	$a_A = m_A$
Real solutions	$a_A = \gamma_A m_A$

- the (hypothetical) standard state is measured by extrapolation in the same way as described for molarity
- molality measurements are more accurate than molarity measurements as the mass of solvent can be more accurately measured than the volume and the mass is not dependant on temperature
- in dilute aqueous solution, 1 L of water contains ~1 kg of water and numerically molarity≈ molality

Biochemists

- the above solute standard states assume the concentration of all species in solution are known. When the species include weak acids and bases, this can get complicated as one solute may produce multiple species in solution, and their concentrations are pH dependent

  eg. dissolution of Na_2HPO_4 produces 5 different species in solution: Na^+, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}

- biochemists have simplified this situation by defining a biochemical standard state
- the biochemical standard state for H^+ is $a_{H^+} = 1$ when the concentration of $H^+ = 10^{-7}$ M or pH = 7.0 (near physiological pH)
- the activity of the other species in solution are set equal to the sum of all the concentrations of all the species of that molecule at pH 7.0 (the activity is equal to the analytical concentration) eg. for Na_2HPO_4:

$$a_{H_2PO_4^-} = c_{H_3PO_4} + c_{H_2PO_4^-} + c_{HPO_4^{2-}} + c_{PO_4^{3-}}$$

- using this standard states means that the ionization constants and concentrations of the individual species do not need to be known
- the biochemical standard state Gibbs free energy is indicated as $\Delta G^{0'}$ - this specifies reactions run at pH 7 with all other reactants and products at 1 M concentration
- as with other solutions, the standard state is strictly hypothetical, extrapolated from dilute solutions
- note that $\Delta G^{0'}$ calculated from tabulated values and the corresponding K’ values only apply at pH at or near 7.0. If the reaction is run at a different pH, the equilibrium constant must be measured, or calculated using known ionization constants

Example: Hydrolysis of ethyl acetate to produce acetic acid and ethanol:

$$EtOAc + H_2O \rightleftharpoons HOAc + EtOH$$

$$K = \frac{(a_{HOAc})(a_{EtOH})}{(a_{EtOAc})(a_{H_2O})}$$

Using the dilute standard state for EtOAc, HOAc and EtOH, the activities are replaced by molarities. Using the solvent standard state the activity of water is 1. K becomes:

$$K = \frac{[HOAc][EtOH]}{[EtOAc]}$$

Using the biochemical standard state, one must consider that HOAc is a weak acid and can dissociate to H^+ and OAc^-.

$$EtOAc + H_2O \rightleftharpoons OAc^- + H^+ + EtOH$$

$$K' = \frac{(a_{OAc^-})(a_{H^+})(a_{EtOH})}{(a_{EtOAc})(a_{H_2O})}$$

The major differences are that the activity of H^+ is 1 and the activity of OAc^- is the sum of the concentrations of HOAc and OAc^-

$$K' = \frac{([HOAc]+[OAc^-])[EtOH]}{[EtOAc]}$$

Activity Coefficients of Ions

- activity coefficients are often set to 1 to simplify calculations
- this is a good approximation for small, uncharged species, and singly-charged ions at low c. However for multiply- charged species and higher c, activity coefficients may vary significantly from 1
- charge balance in solution means there are always as many positive charges as negative, and the activity coefficients for cations and anions cannot be measured separately, only a mean activity coefficient for an ion-counterion pair can be determined
- for a 1:1 electrolyte such as HCl or $ZnSO_4$ the mean ionic activity coefficient is

  $$\gamma_{\pm} = (\gamma_{+}\gamma_{-})^{1/2}$$
- for a 1:2 electrolyte such as H_2SO_4

  $$\gamma_{\pm} = (\gamma_{+}^{2}\gamma_{-})^{1/3}$$
- for a 1:3 electrolyte such as $LaCl_3$

  $$\gamma_{\pm} = (\gamma_{+}\gamma_{-}^{3})^{1/4}$$
- the effect of concentration on $\gamma_{\pm}$ is illustrated in Tinoco figure 4.3
  - as concentration increases to 0.1 M and higher, the mean activity coefficient drops below 1 with the decrease much more significant for multiply charged species

  - if we set the standard for a dilute solution where a = c at $\gamma \geq 0.9$, then for a 1:1 electrolyte the concentration could not be higher than 0.01 M. For the more highly charged electrolytes, the cutoff would be at least an order of magnitude lower.

- the Debye-Hückel equation allows for calculation of individual activity coefficients in very dilute solutions
$$\log\gamma_i = 0.509 Z_i^2 I^{½}$$
where Z_i is the charge on the ion, I is the ionic strength of the solution ($I = ½\sum_i c_i Z_i^2$) and the value 0.509 depends on the temperature and dielectric constant of the solvent
- the ionic strength is summed over all the charged species in the solution, not just the salt in question, and therefore a species not directly involved in a reaction can have a significant effect
- calculate the ionic strength of the following solutions: 0.01 M NaCl, 0.033 M $MgCl_2$ and 0.0025 M $MgSO_4$

K and ΔG°

- the equation:

  $$\Delta G° = RT\ln K$$

  relates the Gibbs free energy at standard state to the equilibrium constant for the reaction
- if the change in Gibbs free energy is determined, the equilibrium can be calculated, and vice versa

- the change in Gibbs free energy under any conditions is:

  $$\Delta G = \Delta G° + RT\ln Q$$
- if the reaction is at equilibrium:

  $$\Delta G = 0 \quad \text{and} \quad \Delta G° = RT\ln Q_{eq} = RT\ln K$$
- if the reaction is at standard state:

  $$Q = 1 \quad \text{and} \quad \Delta G = \Delta G°$$

- the values for ΔG° and K will depend on the standard states used

Example 1: The dissociation of acetic acid in aqueous solution.

$$\mathrm{HOAc\ (aq)} \rightleftarrows \mathrm{H^+\ (aq)} + \mathrm{OAc^-\ (aq)}$$

$$K = \frac{\left(a_{H^+}\right)\left(a_{OAc^-}\right)}{\left(a_{HOAc}\right)}$$

Using the molarity solute standard state, $a = \gamma c$

$$K = \frac{\left(c_{H^+}\right)\left(c_{OAc^-}\right)}{\left(c_{HOAc}\right)} \frac{\gamma_+ \gamma_-}{\gamma_{HOAc}} = K_c \frac{\gamma_\pm^2}{\gamma_{HOAc}}$$

$$K_c = \frac{\left(c_{H^+}\right)\left(c_{OAc^-}\right)}{\left(c_{HOAc}\right)}$$

In dilute, aqueous solutions, the activity coefficients are ~1 and

$$K = K_c.$$

Note: K is unitless. K_c is also unitless as each concentration is actually the concentration divided by the standard state of 1M. However, K_c values are sometimes expressed with units (in this case M). Units expressed with equilibrium constants should be viewed as a reminder as to which standard state was used to determine K. All equilibrium constants are unitless.

For the reaction:

$$\mathrm{HOAc\ (aq)} \rightleftarrows \mathrm{H^+\ (aq)} + \mathrm{OAc^-\ (aq)}$$

The standard Gibbs free energy of reaction would be

$$\Delta G^\circ = \mu^0_{H^+} + \mu^0_{OAc^-} - \mu^0_{HOAc}$$

where the standard states for all the species are the hypothetical 1 M standard states extrapolated from dilute solution.

If the reaction conditions are specified:

$$\mathrm{HOAc\ (10^{-4}\ M, aq)} \rightleftarrows \mathrm{H^+\ (10^{-4}\ M, aq)} + \mathrm{OAc^-\ (10^{-4}\ M, aq)}$$

then

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

$$\Delta G = \Delta G^\circ + RT \ln \frac{(10^{-4})(10^{-4})}{(10^{-4})}$$

$$\Delta G = \Delta G^\circ + RT \ln 10^{-4}$$

$$\Delta G = \Delta G^\circ - 22820\ Jmol^{-1}$$

The dilution decrease the ΔG by 22.8 $kJmol^{-1}$ and thus favours the dissociation. This is in keeping with Le Châtelier’s principle.

Example 2: Hydrolysis of ethylacetate.

$$\mathrm{EtOAc} + H_2O \rightleftharpoons \mathrm{HOAc} + \mathrm{EtOH}$$

$$K = \frac{\left(a_{HOAc}\right)\left(a_{EtOH}\right)}{\left(a_{H_2O}\right)\left(a_{EtOAc}\right)}$$

Using the solute standard state as in the last example for all the species in this reaction is problematic, specifically for the water. The concentration of water in dilute solution is ~55.5 M and its activity coefficient would not be 1. In this case it is better to use the solvent standard state, $a = \gamma X$, for the water and the molarity solute standard state for the rest of the species in the reaction.

$$K = \frac{\left(c_{HOAc}\right)\left(c_{EtOH}\right)}{\left(X_{H_2O}\right)\left(c_{EtOAc}\right)} \cdot \frac{\left(\gamma_{HOAc}\right)\left(\gamma_{EtOH}\right)}{\left(\gamma_{H_2O}\right)\left(\gamma_{EtOAc}\right)}$$

In dilute solution, the mole fraction of water approaches 1 as do all of the activity coefficients and again, $K = K_c$.

The value for K (and the corresponding value for ΔG°) depends on which standard states are chosen for each reagent and product. Using the solvent standard state for water gives its activity as 1. Using the solute standard state, its activity would be near 55.5.

Because one of the species involved in this reaction is ionizable, this problem could also be viewed using the biochemists standard state.

Which standard state is employed is largely a matter of convenience. In dilute solutions, it is easiest to choose the standard states such that all the activity coefficients are 1and $K = K_c$. In concentrated solutions, this calculation may be off by a factor of 2 or more.

We must also keep in mind that it is not just the concentration of the species reacting that are relevant. For reactions involving ions, the ionic strength has a significant effect, and this is dependent on all the ions in solution not just those involved in the reaction.

Calculation of Equilibrium Concentrations

- the goal here is to calculate the concentrations of all species in solution
- some situations are very complex and require the use of a computer, some are simpler and can be solved using the method described below

- this method assumes that all of the relevant equilibrium constants are known, and that the solution is ideal so all activity coefficients are 1
- problem is algebraic, you must have as many equations as there are unknown species
- equations include: mass balance, charge balance, and equilibrium expressions
- assumptions and simplifications can be made based on past experience and knowledge of the system

Example: A solution is prepared by adding c_A mol of acetic acid and c_S mol of sodium acetate to form 1 L of aqueous solution at 298 K.

Species: Na^+, HOAc, OAc^-, H^+ and OH^-

Mass balance: $c_S = [Na^+]$

$c_A + c_S = [HOAc] + [OAc^-]$

Charge balance: $[Na^+] + [H^+] = [OAc^-] + [OH^-]$

Equilibria:

$$K_{HOAc} = \frac{[OAc^-][H^+]}{[HOAc]} = 1.8 \times 10^{-5}$$

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14}$$

Note: square brackets [ ] indicate molarity. We are using the mole fraction solvent standard state for water and the molarity solute standard for everything else.

Ex 4.5 What are the concentrations of all species in pure water?

Species: H^+ and OH^-

Charge balance: $[H^+] = [OH^-]$

Equilibria: $K_W = [H^+][OH^-] = [H^+]^2 = 1.0\text{x}10^{-14}$

$[H^+] = [OH^-] = 1.0\text{x}10^{-7}$

Ex 4.6 What are the concentrations of all species in a 0.100 M HOAc solution?

Species: $HOAc$, OAc^-, H^+ and OH^-

Mass balance: $0.100\ M = [HOAc] + [OAc^-]$

Charge balance: $[H^+] = [OAc^-] + [OH^-]$

Equilibria:

$$K_{HOAc} = \frac{[OAc^-][H^+]}{[HOAc]} = 1.8 \times 10^{-5}$$

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14}$$

Assumption:

Except for pure water or solutions close to pH 7, either $[H^+]$ or $[OH^-]$ will be negligible in the charge balance equation. The solution is either acidic or basic. Even at pH 6.5, $[H^+] > 10x[OH^-]$.

Remember that we can sometimes ignore terms in a sum, but never in a multiplication.

Assuming acidic solution:

$[H^+] >> [OH^-]$ and $[OAc^-] >> [OH^-]$

Charge balance: $[H^+] = [OAc^-] = x$

Mass balance: $[HOAc] = 0.100\ M - x$

Equilibria (solve using quadratic equation):

$$K_{HOAc} = \frac{x^2}{0.100 - x} = 1.8 \times 10^{-5}$$

$$x^2 + 1.8 \times 10^{-5} x - 1.8 \times 10^{-6} = 0$$

$$x = \frac{-1.8 \times 10^{-5} + \sqrt{3.24 \times 10^{-10} + 7.2 \times 10^{-6}}}{2}$$

$$x = 1.33 \times 10^{-3}$$

$[H^+] = 1.33\text{x}10^{-3}$ M
$[OAc^-] = 1.33\text{x}10^{-3}$ M
[HOAc] = 0.100 M - x = $9.9\text{x}10^{-2}$ M
$[OH^-] = K_W / [H^+] = 7.5\text{x}10^{-12}$ M

Assumption that $[OAc^-] >> [OH^-]$ is verified.

Alternately, we can use successive approximations:

Set x equal to one of the concentrations that is not expected to be the largest one. In this case, expect HOAc to be the largest, so set x = $[H^+] = [OAc^-]$, and assume $x << 0.100$. Equilibria now becomes:

$$K_{HOAc} = \frac{x^2}{0.100 - x} = \frac{x^2}{0.100} = 1.8 \times 10^{-5}$$

$$x \cong 1.34 \times 10^{-3}$$

This is pretty close, but we can use our first approximation to generate a second approximation:

$$K_{HOAc} = \frac{x^2}{0.100 - 1.34 \times 10^{-3}} = 1.8 \times 10^{-5}$$

$$x = 1.33 \times 10^{-3}$$

Which is the same as the result using the quadratic equation.

Ex 4.7 What are the concentrations of all species in a 0.200 M NaOAc solution?

Species: Na^+, HOAc, OAc^-, H^+ and OH^-
Mass balance: 0.200 M = $[Na^+]$
0.200 M = [HOAc] + $[OAc^-]$
Charge balance: $[Na^+] + [H^+] = [OAc^-] + [OH^-]$
Equilibria:

$$K_{HOAc} = \frac{[OAc^-][H^+]}{[HOAc]} = 1.8 \times 10^{-5}$$

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14}$$

Assuming basic solution: $[OH^-] >> [H^+]$
Charge balance: $0.200 = [OAc^-] + [OH^-]$
$[OAc^-] = 0.200 - [OH^-]$
Sub into mass balance:
0.200 M = [HOAc] + 0.200 - $[OH^-]$
$[HOAc] = [OH^-] = x$
Mass balance: $[OAc^-] = 0.200 - x$
Equilibria: $[H^+] = 10^{-14}/x$

$$K_{HOAc} = \frac{(0.200 - x)\left(\frac{10^{-14}}{x}\right)}{x} = 1.8 \times 10^{-5}$$

$$K_{HOAc} = \frac{(0.200 - x)\left(10^{-14}\right)}{x^2} = 1.8 \times 10^{-5}$$

$$\frac{(0.200 - x)}{x^2} = 1.8 \times 10^{9}$$

$$x = 1.05 \times 10^{-5}$$

$[HOAc] = 1.05 \times 10^{-5}$ M
$[OH^-] = 1.05 \times 10^{-5}$ M
$[OAc^-] = 0.200 - x = 0.200$ M
$[H^+] = 10^{-14}/x = 9.5 \times 10^{-10}$ M

For this example, we could have used K_B instead of K_A which would have looked like:

$$K_{Ac^-} = \frac{[HOAc][OH^-]}{[OAc^-]} = \frac{K_W}{1.8 \times 10^{-5}}$$

$$K_{Ac^-} = \frac{x^2}{0.200 - x}$$

For buffers which contain both the acid and its conjugate base (or base and its conjugate acid) in appreciable amounts the solution is simpler.

Species: Na^+, HOAc, OAc^-, H^+ and OH^-

Mass balance: $c_S = [Na^+]$

$c_A + c_S = [HOAc] + [OAc^-]$

Charge balance: $[Na^+] + [H^+] = [OAc^-] + [OH^-]$

Equilibria:

$$K_{HOAc} = \frac{[OAc^-][H^+]}{[HOAc]} = 1.8 \times 10^{-5}$$

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14}$$

Assumptions: $[Na^+] >> [H^+]$ and $[OAc^-] >> [OH^-]$

Charge balance: $[Na^+] = [OAc^-] = c_S$

Mass balance: $c_A = [HOAc]$

Equilibria:

$$K_{HOAc} = \frac{[OAc^-][H^+]}{[HOAc]} = \frac{c_S[H^+]}{c_A} = 1.8 \times 10^{-5}$$

This yields the Henderson-Hasselbach equation:

$$pH = pKa + \log \frac{c_S}{c_A}$$

See Tinococ Ex 4.8

All of the preceding examples have assumed ideal behaviour with all activity coefficients equal to 1, so lets look at a non-ideal situation.

Ex 4.9 What are the concentrations of all species in a 0.200 M NaOAc solution if we take into account the mean ionic activity coefficients for the ions in solution? The mean ionic activity coefficient for 1:1 electrolytes in this solution is $\gamma_{\pm} = 0.592$; we assume the activity coefficient of the HOAc is 1.

Species: Na^+, HOAc, OAc^-, H^+ and OH^-
Mass balance: $0.200\ M = [Na^+]$
$0.200\ M = [HOAc] + [OAc^-]$
Charge balance: $[Na^+] + [H^+] = [OAc^-] + [OH^-]$
No changes so far.
Equilibria:

$$K_{HOAc} = \frac{[OAc^-][H^+]}{[HOAc]} \cdot \frac{\gamma_+ \gamma_-}{\gamma_{HOAc}}$$

$$K_{HOAc} = \frac{[OAc^-][H^+]}{[HOAc]} \cdot \frac{\gamma_{\pm}^2}{\gamma_{HOAc}} = 1.8 \times 10^{-5}$$

$$K_W = [H^+][OH^-] \cdot \gamma_{\pm}^2 = 1.0 \times 10^{-14}$$

Substituting in for the activity coefficients yields:

$$\frac{[OAc^-][H^+]}{[HOAc]} = \frac{1.8\times10^{-5}}{(0.755)^2} = 3.16\times10^{-5}$$

$$[H^+][OH^-] = \frac{1.\times10^{-14}}{(0.755)^2} = 1.75\times10^{-14}$$

Using the same steps as previously:

$[Na^+] = 0.200$ M
$[OAc^-] = 0.200$ M
$[OH^-] = [HOAc] = 1.05\times10^{-5}$ M
$[H^+] = 1.67\times10^{-9}$ M

The only change is in $[H^+]$, compare to 9.5×10^{-10} M without using activity coefficients.

Effect of T on K

- the effect of temperature on an equilibrium constant depends on the whether the reaction is exothermic or endothermic
- Le Châtelier’s principle says that for an exothermic reaction, increasing the temperature should shift the reaction to the reagent side, and for an endothermic reaction it should shift to the product side
- the thermodynamic equation that describes this behaviour is the van’t Hoff equation

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

- this equation holds over small ranges of T (~50 K) where ΔH° is constant
- if K is known at one temperature, it can be calculated at a second temperature using this equation

- measuring equilibrium constants at different temperatures is one way to determine ΔH° and ΔS° values for a reaction

$$\ln K = -\frac{\Delta G^\circ}{RT}$$

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

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

- a plot of lnK versus 1/T has a slope of -ΔH°/R and a y-intercept of ΔS°/R. This is a van't Hoff plot
- if the van't Hoff plot is not linear, that ΔH° is not independent at temperature, and the slope of the tangent at anyone point is equal to -ΔH°/R at that temperature

Effect of P on K

- for ideal gases, K is independent of pressure
- this does not mean that the partial pressures of all the species involved does not change with pressure

Consider: $A\ (g) \rightleftarrows 2B\ (g)$
$n(1-\alpha) \quad 2n\alpha$

n is the total number of moles of A at the start of reaction (no B present) and α is the fraction of A reacted. The total moles present at equilibrium is $n(1+\alpha)$

The mole fractions of A and B are:

$$X_A = \frac{n(1-\alpha)}{n(1+\alpha)} = \frac{(1-\alpha)}{(1+\alpha)}$$

$$X_B = \frac{2n\alpha}{n(1+\alpha)} = \frac{2\alpha}{(1+\alpha)}$$

The partial pressures of A and B are:

$$P_A = \frac{(1-\alpha)}{(1+\alpha)} P \quad and \quad P_B = \frac{2\alpha}{(1+\alpha)} P$$

The equilibrium constant is:

$$K = \frac{P_B^2}{P_A} = \frac{\left(\frac{2\alpha}{(1+\alpha)} P\right)^2}{\frac{(1-\alpha)}{(1+\alpha)} P} = \frac{4\alpha^2}{\left(1-\alpha^2\right)} P$$

$$\alpha = \sqrt{\frac{K}{K+4P}}$$

- K is constant , so α depends only on P
- if P is large, α is small and if P is small, α is large
- again, this is in keeping with Le Châtelier’s principle

Effect of a Catalyst on K

- catalysts speed up both the forward and reverse reactions
- the equilibrium constant is not effected by the catalyst
- equilibrium will be achieved more quickly if a catalyst is present, but the position of the equilibrium will not change

Thermodynamics of Metabolism

Reading Assignment: Tinoco pp 165-170

- the example discussed in detail is glycolysis, the multi-step conversion of glucose to pyruvate
- some of these steps are thermodynamically favoured, others are not, but the whole process is very important to metabolism
- read and understand why, how and under what conditions thermodynamically unfavoured reactions can and do occur

ΔG and Electrochemistry

- the use of galvanic cells allows for the direct measurement of the free energy of the reversible reaction occurring in the cell
- these methods can be used to measure many chemical and biochemical reactions as well as dissolution of salts and differences across osmotically active membranes

The relation between Gibbs free energy and cell voltage is:

$$\Delta G = -nF\mathscr{E}$$

where F = Faraday's constant = 96 485 C mol^{-1}

- for a spontaneous reaction, ΔG is -ve, so $\mathscr{E}$ is +ve

Example: Tinoco Fig 4.5

$$H_2\ (g) + \tfrac{1}{2}O_2\ (g) \rightarrow H_2O\ (l)$$

- inert Pt electrodes are used to make electrical contact
- an electrolyte must already be present in the cell to carry charge
- the gases are bubbled over the electrodes
- a salt bridge or porous membrane connects the two sides of the cell - prevents mixing of two sides, but allows ions to pass

Oxidation reaction:

$$H_2\ (g, P_{H_2}) \rightarrow 2H^+\ (aq, c_{H^+}) + 2e^-$$

- this occurs at the negatively charged anode

Reduction reaction:

$$\tfrac{1}{2}O_2\ (g, P_{O_2}) + 2H^+\ (aq, c_{H^+}) + 2e^- \rightarrow H_2O\ (l)$$

- this occurs at the positively charged cathode

Cell Notation:

$$\mathrm{Pt}|H_2(g, P_{H_2})|H^+(aq, c_{H^+})||H^+(aq, c_{H^+})|O_2(g, P_{O_2})|\mathrm{Pt}$$

- anode first, then cathode
- vertical line indicates phase change
- double vertical line indicates salt bridge

Overall reaction is:

$$H_2\ (g) + \tfrac{1}{2}O_2\ (g) \rightarrow H_2O\ (l)$$

- note that H^+ does not appear in the overall reaction
- by measuring the change in voltage and ΔG with changes in the partial pressures of the two gases, ΔG° can be determined by extrapolating to standard state conditions

Standard Reduction Potentials

- potentials can only be measured for a cell, and not for individual oxidation or reduction half-cell reactions
- a zero point was set and all other half-cell potentials are measured relative to that point
- the reference half-cell is:
  H^+ (aq, a=1) + e^- → ½H_2 (g, P=1 atm) $\mathscr{E}°$=0.000 V
- the standard half-cell potentials for many reactions have been tabulated; they are always written as reductions (standard reduction potential) and must be reversed for oxidations
- to calculate the $\mathscr{E}°$ for a cell, it is necessary to know the standard potentials for the two half-cells

$$\mathscr{E}^{\circ}_{\text{cell}} = \mathscr{E}^{\circ}_{\text{cathode}} - \mathscr{E}^{\circ}_{\text{anode}}$$

- note that the standard potentials are not multiplied by any stoichiometric coefficients - the voltage is independent of the number of electrons involved, it is an intensive property
- ΔG is an extensive property and does depend on the number of electrons involved. Therefore the standard potential must be multiplied by the number of electrons to calculate the free energy.

Concentration Dependence of $\mathscr{E}$

Like G, $\mathscr{E}$ is also dependent on concentration

$$\Delta G = \Delta G° + RT\ln Q$$

$$\Delta G = -nF\,\mathscr{E}$$

thus, the Nernst Equation:

$$\mathscr{E} = \mathscr{E}° - RT/nF \ln Q$$

or at 25°C:

$$\mathscr{E} = \mathscr{E}° - 0.0591/n \log Q$$

When $\Delta G = 0$, $\mathscr{E}=0$ and

$$\mathscr{E}° = RT/nF \ln K$$

Biological Redox Reactions

Reading Assignment: Tinoco pp 170-172

- oxidative phosphorylation which occurs in mitochondria
- oxidation of NADH to NAD^+
- involves three membrane-associated enzymes