

# General Chemistry II

## Chapter 14 Lecture Notes

### Chemical Equilibrium

#### THE CONCEPT OF EQUILIBRIUM

Few physical and chemical changes proceed only in one direction. Fire is one chemical change that does. Once burned, a piece of paper cannot be restored.

The evaporation of water in a *closed* system is a *reversible* physical change that establishes a *dynamic equilibrium*. At equilibrium, when water seems to cease evaporating, water is still evaporating but recondensing at the same rate. There is no net change, (therefore equilibrium) but molecules are continually shuttling between the liquid and vapor state (dynamic). Many chemical systems act in this manner where product is continually being formed and then back-reacting to form the reactants again.

#### THE EQUILIBRIUM CONSTANT

Weak acid dissociation in water is an example of a dynamic equilibrium. Acid molecules dissociate to anion and hydrogen ion, but the molecular acid reforms, keeping the acid concentration relatively high.



A value called the equilibrium constant can be assigned to the chemical system by measuring, at equilibrium, the concentrations of all the species.

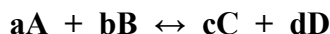
The equilibrium constant,  $K$  can be taken as the product of the product molar concentrations divided by the reactant molar concentration.

$$K_{\text{eq}} = \frac{[\text{H}^{+1}] \cdot [\text{A}^{-1}]}{[\text{HA}]}$$

The usefulness of  $K_{\text{eq}}$  is that it remains *constant* for the system at one particular temperature. Its value does not change when any of the reactant or product concentrations are altered. The other concentrations adjust so that  $K_{\text{eq}}$  remains the same.

Ex: What happens to the system if  $[\text{H}^{+1}]$  is changed? What happens if  $[\text{HA}]$  is changed? What happens if the temperature is changed?

In general, all chemical equilibrium systems obey the law of mass action. For the general equilibrium equation

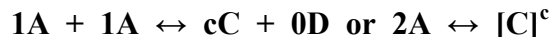


the equilibrium constant will be given by

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

The law of mass action can be extended to systems of any number of reactants and products. If  $K$  is much larger than unity, the reaction is said to lie on the right. If  $K$  is much smaller than one, then the equilibrium lies to the left.

As an example of the use of the exponents, note that if  $A$  is the same species as  $B$  and if  $D$  is not formed, in other words



then the equilibrium expression becomes

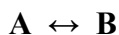
$$K = [C]^c [D]^0/[A]^{-1} [A]^{-1} = [C]^c/[A]^2$$

### EQUILIBRIUM CONSTANT EXPRESSIONS

Substances in solution will have their concentrations expressed in moles/liter or  $M$ . Gases require an expression to convert between  $M$  and pressure. Solids and liquids in heterogeneous systems will have their concentration expressed simply as unity, since their effective concentration will not change as long as some condensed phase remains.

### HOMOGENEOUS EQUILIBRIA

All reactants and products are in the same liquid or gas phase.



$A$  can be (g) or (l) and  $B$  can be (g) or (l)

Concepts of  $K_c$  based on molar concentrations in gas or in solution and  $K_p$ , based on partial pressures of gaseous species.

$$K_c = [B]/[A]$$

whether  $A$  and  $B$  are in solution or in gas phase

$$K_p = P_B/P_A$$

In general  $K_c \neq K_p$  unless the number of moles of gas does not change during the reaction.

If the equilibrium expression does not contain different powers of  $[A]$  or  $[B]$  in the numerator or denominator, the ratio of  $[B]/[A]$  is the same as that of  $P_B/P_A$ . If there are different powers of  $[B]$  or  $[A]$  in the expression, then the ratio changes.

Text example of derivation of equation

$K_p = K_c (RT)^{\Delta n}$  calculation of the value of  $K_p$  requires the absolute temperature.

Ex: Write  $K_p$  and  $K_c$  for the decomposition of hydrogen peroxide.

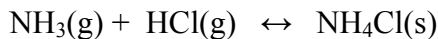
Ex: Write  $K_p$  and  $K_c$  for the reaction of carbon dioxide gas with NaOH solution

Derivation of  $K_a$  equation from  $K_c$  for the dissociation of a weak acid.

Write  $K_c$  for the reaction of ammonia with water.

### HETEROGENEOUS EQUILIBRIA

If a solid or liquid is part of a chemical equilibrium, its "concentration" is taken as unity and may be eliminated from the equilibrium expression.



$$K_{\text{eq}} = [\text{NH}_4\text{Cl}] / [\text{NH}_3] \cdot [\text{HCl}]$$

Since  $\text{NH}_4\text{Cl}$  is a solid, its effective concentration in the reaction does not change as long as some solid is present. Since  $[\text{NH}_4\text{Cl}]$  is constant, it can be eliminated from the right side of the equation and incorporated into the  $K_{\text{eq}}$  constant, which then becomes

$$K_{\text{eq}} = 1/[\text{NH}_3] \cdot [\text{HCl}] \text{ if the molar concentrations of the gases will be expressed, or}$$

$$K_p = 1/P_{\text{NH}_3} \cdot P_{\text{HCl}} \text{ if the gas pressures will be expressed.}$$

Ex: How will  $[\text{NH}_3]$  vary in the system as  $[\text{HCl}]$  increases or decreases?

### MULTIPLE EQUILIBRIA

The  $K_{\text{eq}}$  values from two or more successive reactions are simply multiplied together if the reactions can be added together to make one net reaction.

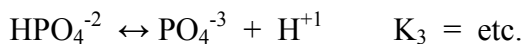
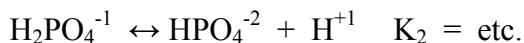
$$\text{For } A \rightarrow B \quad K_{\text{eq}} = [A]/[B] \text{ and}$$

$$\text{For } B \rightarrow C, \quad K_{\text{eq}} = [B]/[C]$$

Adding the two equations together gives  $A \rightarrow C$  with  $K_{\text{eq}} = [A]/[C]$

The same  $K_{\text{eq}}$  expression would have been obtained by multiplying together the two first  $K$  values.

Applications include stepwise dissociation of polyprotic acids such as  $\text{H}_3\text{PO}_4$



The overall  $K = K_1 \cdot K_2 \cdot K_3$  for the equation  $\text{H}_3\text{PO}_4 \rightarrow \text{PO}_4^{-3} + 3\text{H}^{+1}$

## THE FORM OF K AND THE EQUILIBRIUM CONSTANT

The K for an equilibrium reaction is the reciprocal of the K for the reverse reaction. Therefore it is important to specify what reaction the K meant to represent.

For  $A \leftrightarrow B + C$ ,  $K_f = [B][C]/[A]$

For  $B + C \leftrightarrow A$ ,  $K_r = [A]/[B][C]$

Therefore  $K_f \times K_r = [A][B][C]/[A][B][C] = 1$

Remember that the reactant and product concentrations in the  $K_{eq}$  expression are raised to the power equal to their coefficients. What happens if the equation is written in more than one way?

$H_2(g) + I_2(g) \leftrightarrow 2HI(g)$       $K_1 = [H_2][I_2]/[HI]^2$

$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \leftrightarrow HI(g)$       $K_2 = [H_2]^{1/2}[I_2]^{1/2}/[HI]$

Will the  $K_{eq}$  values be different or the same for the two ways of writing the same equation?

Consider both as representing the same system. Set  $[H_2] = 0.020M$ ,  $[I_2] = 0.030M$  and  $[HI] = 0.010M$ . Calculate both  $K_{eq}$  values.

$$K_1 = [H_2][I_2]/[HI]^2 = (0.020M)(0.030M)/(0.010M)^2 = 6.0$$

$$K_2 = [H_2]^{1/2}[I_2]^{1/2}/[HI] = (0.020M)^{1/2}(0.030M)^{1/2}/(0.010M)^1 = 2.4 \text{ (or } 6^{1/2}\text{)}$$

$$K_1 = (K_2)^2$$

Both  $K_{eq}$  values will give the *same* reactant and product concentrations when applied to the corresponding equations.

## RELATION BETWEEN CHEMICAL KINETICS AND CHEMICAL EQUILIBRIUM

There is a direct relationship between the rate constant for the forward and reverse directions of a chemical reaction and the equilibrium constant for that reaction. That stands to reason because a large forward rate constant will lead to a larger K. A large backward rate constant will lead to a small K. for a first order chemical reaction,

$A \leftrightarrow B$ ,  $rate_f = k_f[A]$  and  $K_f = [B]/[A]$

For the reverse reaction,  $B \leftrightarrow A$ ,  $rate_r = k_r[B]$   $K_r = [A]/[B]$

By definition, at equilibrium the two rates, but not the  $k_f$  and the  $k_r$ , are the same.

(Remember that the rates depend on the k values *and* on the A and B concentrations.)

If  $rate_f = rate_r$ , then  $k_f[A] = k_r[B]$

$k_f/k_r = [A]/[B]$  which is equal to the equilibrium constant,  $K_f$ . A large forward rate constant leads to a high rate of formation of B and a large value of  $K_f$ .

Similarly,  $k_r/k_f = [B]/[A] = K_r$ .

## PREDICTING THE DIRECTION OF A REACTION

The reaction quotient,  $Q_c$  can help keep track of reaction direction on changing some concentrations.

$K_c$  is the constant at equilibrium;  $Q_c$  is the value obtained with the nonequilibrium initial or forced values given by the problem. If  $K_c$  and  $Q_c$  are equal, then the system is already at equilibrium. If  $Q_c > K_c$ , then the reaction must shift to the left before equilibrium is reached (products must back react to become reactants). If  $Q_c < K_c$ , then the system must shift to the right for the system to attain equilibrium (reactants must turn into products).

Ex: The  $K_a$  for the dissociation of acetic acid is  $1.8 \times 10^{-5}$ .  $\text{HA}(\text{aq}) \leftrightarrow \text{A}^{-1}(\text{aq}) + \text{H}^{+1}(\text{aq})$   
 If a system contains  $[\text{A}^{-1}] = 2.0 \times 10^{-4}\text{M}$ ,  $[\text{H}^{+1}] = 1.5 \times 10^{-5}\text{M}$  and  $[\text{HA}] = 0.55\text{M}$ , determine whether the system is in equilibrium or not and in what direction it must shift to put it into equilibrium.  $Q_c = 5.5 \times 10^{-9}$  (compared to  $K_a = 1.8 \times 10^{-5}$ ) so the system must shift to the right (more product) to attain equilibrium.

## CALCULATING EQUILIBRIUM CONCENTRATIONS

Use the Law of Mass action equation

$$K = [\text{C}]^c [\text{D}]^d / [\text{A}]^a [\text{B}]^b$$

If all the reactant and product concentrations are known and the balanced equation is known, then a value for  $K$  can be easily calculated.

When  $K$  is known, the *equilibrium* concentration values can be calculated knowing one or more *initial* concentration values. Use the balanced equation to relate initial and equilibrium values. The resulting equation may involve the quadratic formula.

Ex: For the dissociation of any weak acid,  $\text{HA}(\text{aq}) \leftrightarrow \text{H}^{+1}(\text{aq}) + \text{A}^{-1}(\text{aq})$

$K = [\text{H}^{+1}] \cdot [\text{A}^{-1}] / [\text{HA}]$  Suppose  $K = 4.2 \times 10^{-7}$  and imagine a system where the initial  $\text{HA}$  concentration is  $0.100\text{M}$ . What are the equilibrium concentrations of  $\text{HA}$ ,  $\text{H}^{+1}$  and  $\text{A}^{-1}$ ?

At equilibrium, let  $[\text{A}^{-1}] = [\text{H}^{+1}] = X$ . Let  $[\text{HA}] = 0.100 - X$

(Sometimes,  $X$  is so small that the  $[\text{HA}]$  change can be ignored and equilibrium  $[\text{HA}] = 0.100\text{M}$  also. See if this is true in this case.)

$$4.2 \times 10^{-7} = X^2 / (0.100) \quad X^2 = 4.2 \times 10^{-8} \quad X = 2.1 \times 10^{-4}\text{M} = [\text{A}^{-1}] = [\text{H}^{+1}]$$

$$[\text{HA}] = (0.100 - X) = 0.100 - 0.00021 \approx 0.100\text{M} \quad (\text{The assumption holds.})$$

To check the answer, plug the numbers into the  $K$  expression to see if the original  $K$  value is obtained.

Other calculations may be more difficult and require use of the quadratic formula.

Ex:  $\text{Ca}^{+2} + \text{EDTA}^{-2} \leftrightarrow \text{CaEDTA} \quad K = 4.80$

Suppose initial  $[\text{Ca}^{+2}] = 0.1000\text{M}$  and initial  $[\text{EDTA}^{-2}] = 0.0500\text{M}$ , what are the equilibrium concentrations of  $\text{Ca}^{+2}$ ,  $\text{EDTA}^{-2}$  and  $\text{CaEDTA}$ ?

Let  $X = [\text{CaEDTA}]$ ,  $0.0100 - X = [\text{Ca}^{+2}]$  and  $0.0500 - X = [\text{EDTA}^{-2}]$ .

$$K = [\text{CaEDTA}] / [\text{Ca}^{+2}] \cdot [\text{EDTA}^{-2}] = 9.80 = X / (0.0100 - X)(0.0500 - X)$$

$$X = 9.80(5.00 \times 10^{-4} - 0.0600X + X^2)$$

$$X = 4.90 \times 10^{-3} - 0.588X + 9.80X^2$$

$$9.80X^2 - 1.588X + 4.90 \times 10^{-3}$$

Using the quadratic equation,  $X = -0.159$  (physically impossible) and  $X = 0.0032$  (a plausible value)

$[\text{CaEDTA}] = 0.0032\text{M}$ ,  $[\text{Ca}^{+2}] = 0.0068\text{M}$  and  $[\text{EDTA}^{-2}] = 0.0468\text{M}$

## **FACTORS THAT AFFECT CHEMICAL EQUILIBRIUM**

### **LE CHATELIER'S PRINCIPLE**

Le Chatelier's principle states that any stress on the system ( $\Delta P$ ,  $\Delta T$ , change in reactant or product concentration) causes the system to adjust so as to *partially* offset the change and establish a new equilibrium.

### **CHANGES IN CONCENTRATION**

The effect of concentration changes can be understood by considering the effect of changes in reactant and product molecule collisions or by solving the Law of Mass Action.

The effects of concentration changes can be determined qualitatively by inspection of the equilibrium expression or by calculating  $Q_c$  values for initial reactant and product concentration in the equilibrium expression.

### **CHANGES IN VOLUME AND PRESSURE**

Pressure has a small and generally negligible effect on equilibria in the liquid or solid state reactions. (An exception is the huge pressures involved in the graphite-diamond transition.)

In gas phase reactions, pressure changes affect the equilibrium *if the reaction produces a change in the number of moles of gas*. Pressure change can be brought about by changing the volume of the system or by adding or removing one of the reaction components.

Example: If a gas reaction causes the number of moles of gas to double, the system pressure at constant volume will double. According to Le Chatelier's principle, an imposed increase in the system pressure will drive the reaction to the left (restoring the system equilibrium). This pressure change can be created by a piston that changes the system volume.

The  $\text{CaCO}_3(\text{s}) \leftrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  equilibrium will shift left with a pressure increase

The  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2\text{HI}$  equilibrium is unaffected by pressure changes.

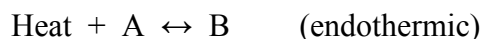
The  $\text{CH}_3\text{COOH}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{CH}_3\text{COONa}(\text{aq}) + \text{H}_2\text{O}(\text{l})$  equilibrium is unaffected by pressure.

The  $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g})$  equilibrium shifts right with a pressure increase.

What happens to the same reactions when the pressure change is caused by adding or removing one of the reaction components?

### **CHANGES IN TEMPERATURE**

Equilibrium constants change with changes in temperature. (K is only constant for constant T.) In general, a temperature increase favors an endothermic reaction and a temperature decrease favors an exothermic reaction. To remember this, think of heat as a reactant or product in a reaction and think how its addition or removal from a system will affect the outcome.



Increasing temperature causes the equilibrium to shift to the right since heat is needed to force the reaction.

### **THE EFFECT OF A CATALYST**

A catalyst affects only the *speed* of a reaction. A catalyst has no effect on the position of equilibrium. A catalyst has an equal effect on lowering the  $E_{\text{act}}$  of the forward and the backward reaction.