

# Section 13.1

## Chemical Equilibria



Michael Stogsdill

Mott Community College

# Learning Objectives



- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

# Writing Reversible Reactions



- When you begin studying chemical reactions it's easiest to talk about chemical reactions that proceed completely from the reactants to products.



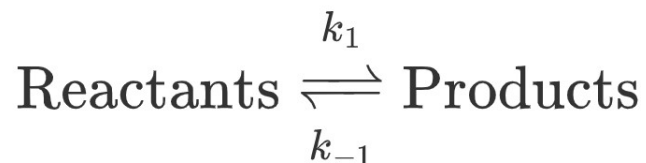
- In actuality, most reactions are **reversible** to some extent. Reactants can be converted to products and products can be converted to reactants.



# Reversible Rates



- When a reaction is reversible, there is a forward rate ( $k_1$ ) and a reverse rate ( $k_{-1}$ ).

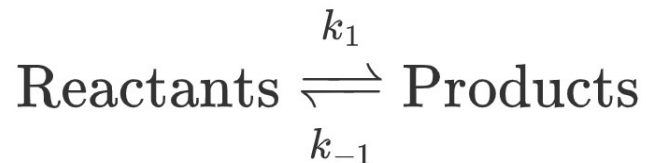


- When forward rate is faster than the reverse rate,  $k_1 > k_{-1}$ , the reaction will proceed towards the products.
- When the reverse rate is faster than the forward rate,  $k_1 < k_{-1}$ , the reaction will proceed towards the reactants.

# Chemical Equilibrium

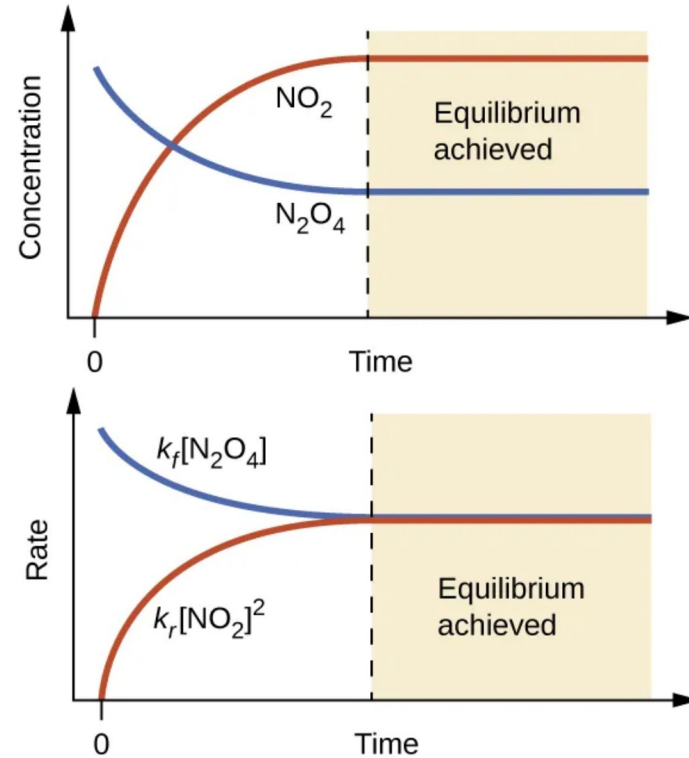
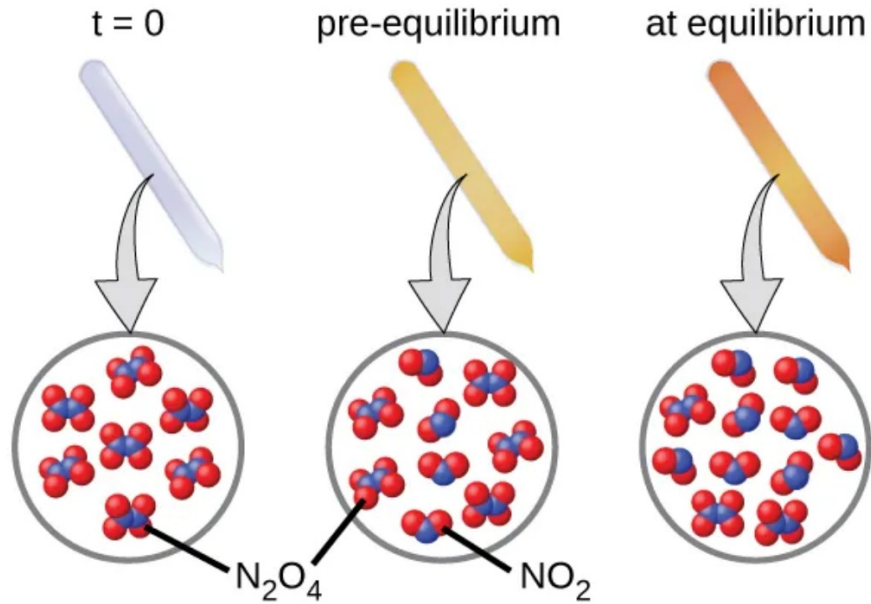
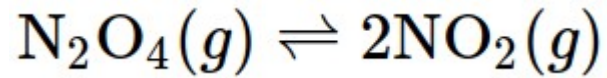


- When the two rates are equal,  $k_1 = k_{-1}$ , **equilibrium** has been reached. The concentrations of the reactants and products remains constant.



- The relative concentrations of reactants and products in equilibrium systems vary greatly.
  - Some systems contain mostly products at equilibrium
  - Some contain mostly reactants
  - Some contain appreciable amounts of both

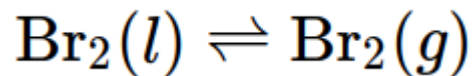
# Equilibrium Example



# Physical Equilibrium



- Physical processes can also reach equilibrium.
  - We saw an example of this with vapor pressure in the previous chapter.



# Section 13.2

## Equilibrium Constants



Michael Stogsdill

Mott Community College



# Learning Objectives

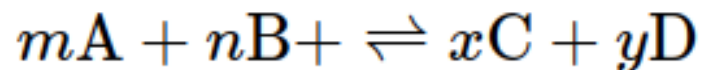


- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants, using concentrations and pressures
- Relate the magnitude of an equilibrium constant to properties of the chemical system

# Reaction Quotient



- The status of a reversible reaction is conveniently assessed by evaluating its **reaction quotient** (Q).
- It can be derived directly from the stoichiometry of the reaction and **either** the concentration or partial pressure of the reactants and products.



$$Q_c = \frac{[\text{C}]^x [\text{D}]^y}{[\text{A}]^m [\text{B}]^n}$$

$$Q_p = \frac{P_{\text{C}}^x P_{\text{D}}^y}{P_{\text{A}}^m P_{\text{B}}^n}$$

# Units of Reaction Quotients

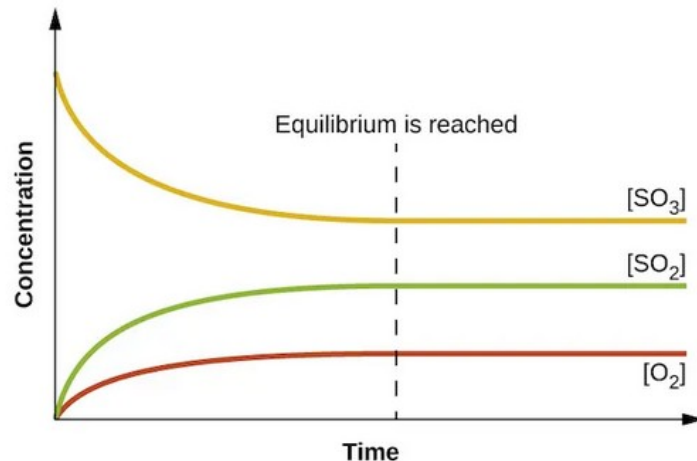
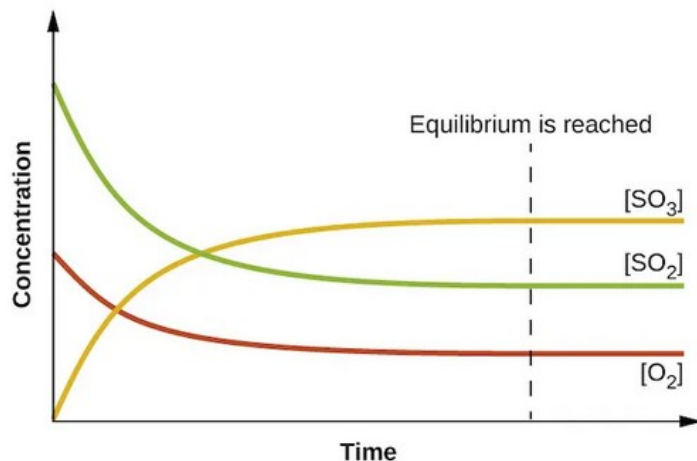
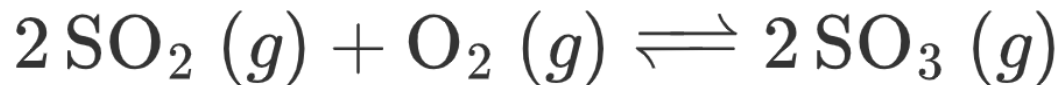


- Reaction quotient equations in our text are a simplification of more rigorous expressions that use *relative values* for concentrations and pressures rather than *absolute values*.
- These relative concentration and pressure values are dimensionless (they have no units); consequently, so are the reaction quotients.
- We will use the simplified equations and disregard units when computing  $Q$ .

# Directional Equilibrium



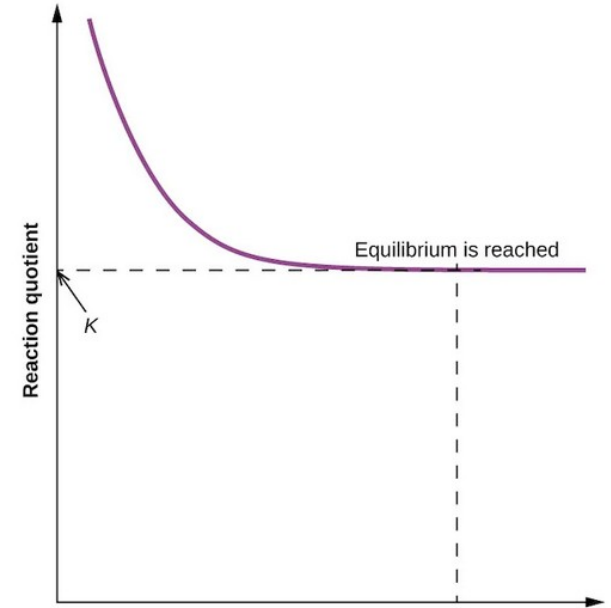
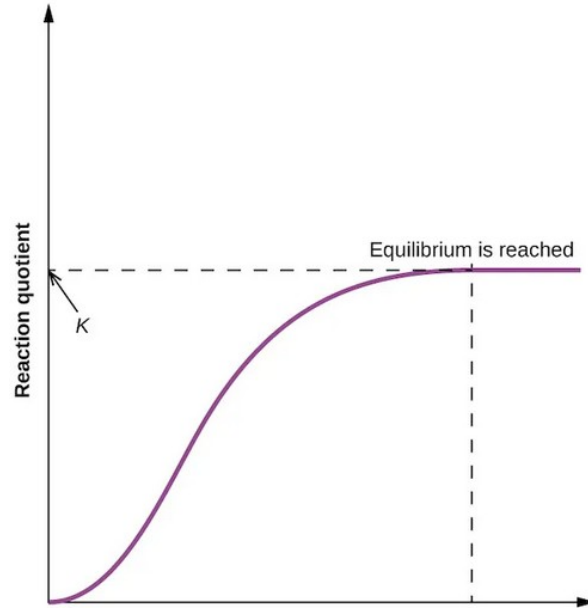
- A reversible reaction can start with an excess of reactants or products and proceed in either direction.
- This means equilibrium can be reached from two directions.



# Directional Reaction Quotient



- Reaction Quotients will change as the reaction proceeds to equilibrium.
- But it always converges to the same value once equilibrium is reached.



# Equilibrium Constant



- The value that  $Q$  takes on at equilibrium is called the **equilibrium constant**,  $K$ .

$$K \equiv Q \text{ at equilibrium}$$

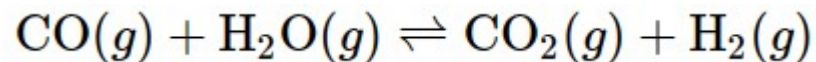
- **Law of Mass Action:** At a given temperature, the reaction quotient for a system at equilibrium is constant.
- When  $K$  is known for a reaction and temperature,  $Q$  can be used to predict the direction of the reaction.
- $K$  has nothing to do with the speed of the reaction.

# Predicting Direction



- When  $Q < K$ , there is an excess of reactants and the reaction will proceed in the forward direction towards the products.
- When  $Q > K$ , there is an excess of products and the reaction will proceed in the reverse direction towards the reactants.
- When  $Q = K$ , equilibrium has been reached.
  - The forward rate is equal to the reverse rate.
  - The concentration of products and reactants remains constant.

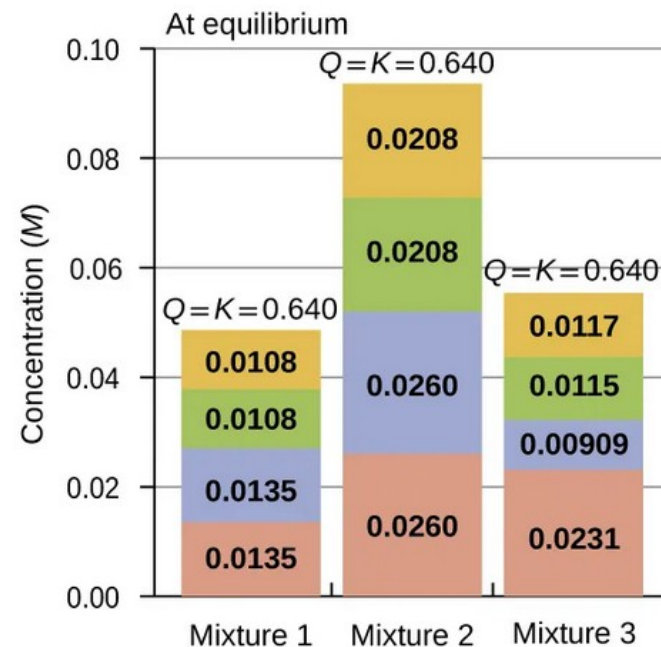
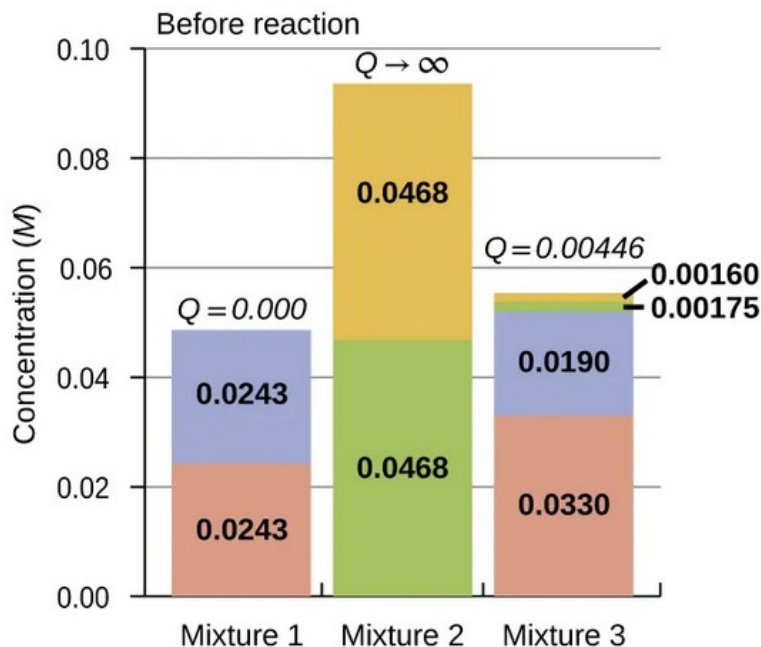
# Reaction Quotient Example



$$K_c = 0.640$$

$$T = 800\text{ }^\circ\text{C}$$

■ [CO]   
 ■ [H<sub>2</sub>O]   
 ■ [CO<sub>2</sub>]   
 ■ [H<sub>2</sub>]





# Homogeneous Equilibria

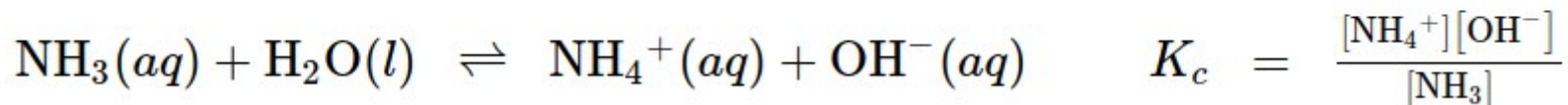
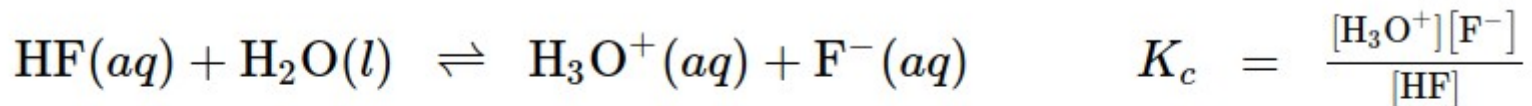
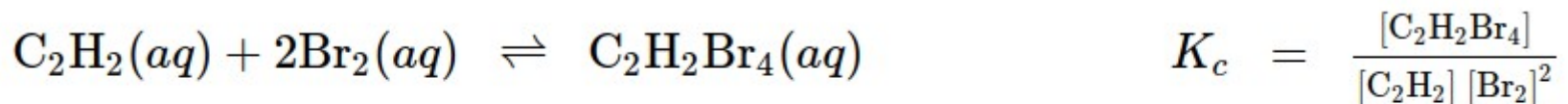


- A **homogeneous equilibrium** is one in which all reactants, products, and any catalysts are present in the same phase.
- Homogeneous equilibria take place in *solutions*
- These solutions are most commonly either liquid or gaseous phases

## Omitting Solids and Liquids



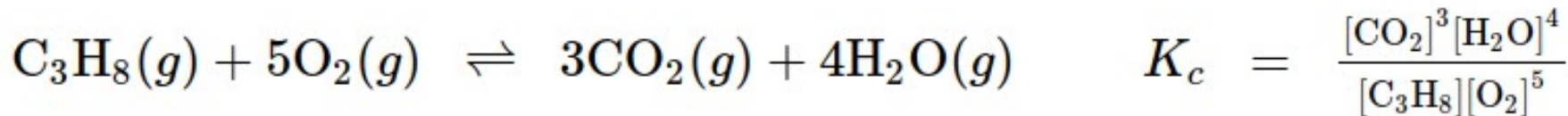
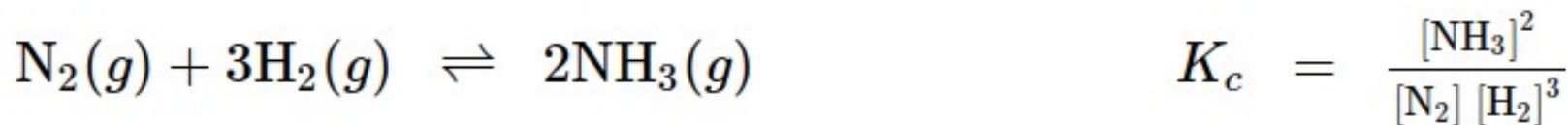
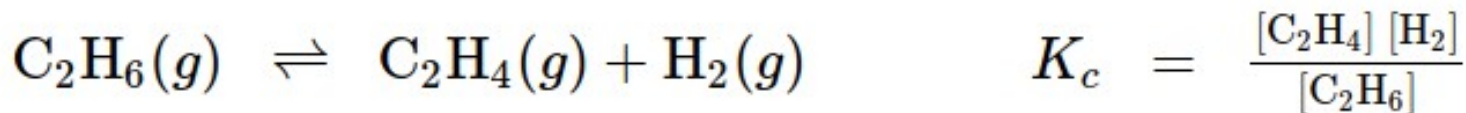
- When pure solids and liquids are present in a chemical equation, they are omitted from  $Q$  and  $K$ .
- The reason for this omission is related to the more rigorous form of the  $Q$  (or  $K$ ) expression.



## Gas Phase Components



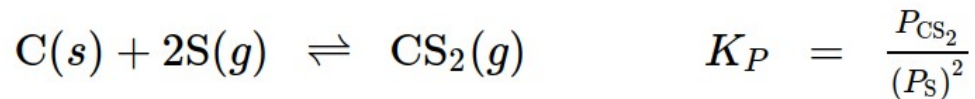
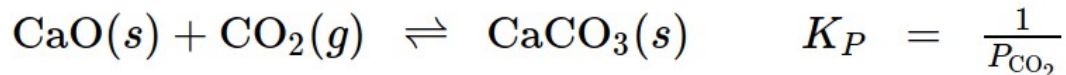
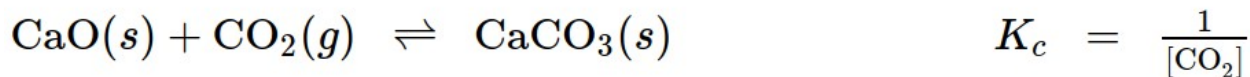
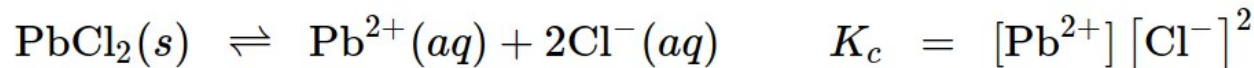
- Be careful, gas phase species are always included in  $Q$  and  $K$ , even when they are often seen as liquids or solids.



# Heterogeneous Equilibria



- A **heterogeneous equilibrium** involves reactants and products in two or more different phases
  - The same rules about solids and liquids apply



## Relationship Between $K_p$ and $K_c$



- To derive a relationship between  $K_c$  and  $K_p$ , we will begin by considering the Ideal Gas Law.

$$PV = nRT$$

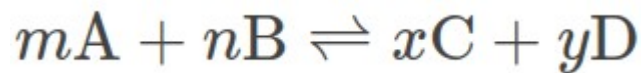
$$P = \left( \frac{n}{V} \right) RT$$

$$= MRT$$

## Relationship Between $K_p$ and $K_c$



- We can now substitute this result into a generic  $K_p$  expression.



$$K_c = \frac{[\text{C}]^x [\text{D}]^y}{[\text{A}]^m [\text{B}]^n}$$

$$\begin{aligned} K_P &= \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \\ &= \frac{([\text{C}] \times RT)^x ([\text{D}] \times RT)^y}{([\text{A}] \times RT)^m ([\text{B}] \times RT)^n} \\ &= \frac{[\text{C}]^x [\text{D}]^y}{[\text{A}]^m [\text{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \\ &= K_c (RT)^{(x+y)-(m+n)} \end{aligned}$$

## Relationship Between $K_p$ and $K_c$



- We now have a relationship between  $K_p$  and  $K_c$ .

$$K_P = K_c(RT)^{\Delta n} \quad K_c = \frac{K_P}{(RT)^{\Delta n}} = K_P(RT)^{-\Delta n}$$

$$\Delta n = (x+y) - (m+n)$$

# Coupled Equilibria



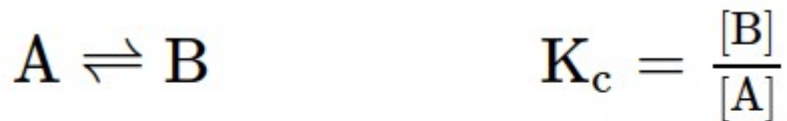
- Many systems involve two or more **coupled equilibrium reactions**, which have one or more reactant or product species in common.
- The  $K$  value for a system involving coupled equilibria can be related to the  $K$  values of the individual reactions.
- There are three basic manipulations we can do.



## Rule One



- 1) Changing the direction of a chemical equation essentially swaps the identities of “reactants” and “products,” and so the equilibrium constant for the reversed equation is simply the reciprocal of that for the forward equation.



$$K_{c'} = \frac{1}{K_c}$$

## Rule Two



- 2) Changing the stoichiometric coefficients in an equation by some factor  $x$  results in an exponential change in the equilibrium constant by that same factor:

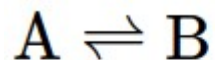


$$K_{c'} = K_c^x$$

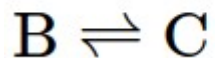
## Rule Three



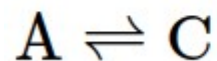
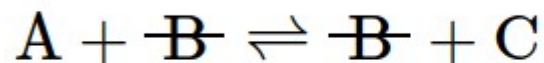
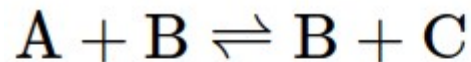
- 3) Adding two or more equilibrium equations together yields an overall equation whose equilibrium constant is the mathematical product of the individual reaction's  $K$  values:



$$K_{c1} = \frac{[B]}{[A]}$$



$$K_{c2} = \frac{[C]}{[B]}$$



$$K_{c'} = \frac{[C]}{[A]}$$

## Proof of Rule Three



- Comparing the equilibrium constant for the net reaction to those for the two coupled equilibrium reactions we can prove that the product of  $K_{c1}$  and  $K_{c2}$  is  $K_c$

$$K_{c1} K_{c2} = \frac{[B]}{[A]} \times \frac{[C]}{[B]} = \frac{\cancel{[B]}[C]}{[A]\cancel{[B]}} = \frac{[C]}{[A]} = K_c$$

$$K_c = K_{c1} K_{c2}$$

# Section 13.3

## Shifting Equilibria: Le Châtelier's Principle



Michael Stogsdill

Mott Community College

# Learning Objectives



- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Châtelier's principle

# Le Châtelier's principle



- We've learned that equilibrium is a dynamic balance where the forward and reverse rates are equal.
- When subjected to a change in conditions that affects these reaction rates differently (a stress), then the equilibrium is disturbed.
- The system will undergo a net reaction in the direction of greater rate (a shift) that will re-establish the equilibrium.
- **Le Châtelier's principle:** *If an equilibrium system is stressed, the system will experience a shift in response to the stress that re-establishes equilibrium.*

# Stressors



- Reaction rates are affected primarily by concentration (reaction's rate law) and temperature (Arrhenius equation).
- An equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the equilibrium constant,  $K$ .
- An equilibrium stressed by a temperature change, is re-established with a different composition and a new  $K$  value.



# Effect of Concentration



- When this system is at equilibrium, the forward and reverse reaction rates are equal.

$$\text{rate}_f = \text{rate}_r$$

- If the system is stressed by adding reactant or removing product the rate of the forward reaction exceeds the reverse.

$$\text{rate}_f > \text{rate}_r$$

- Removing reactant or adding product to an equilibrium system results in an increased rate for the reverse reaction.

$$\text{rate}_f < \text{rate}_r$$

## Q Logic



- You can also rationalize the effect of concentration by considering the reaction quotient.
- When the concentration of a reactant or product in a system at equilibrium is changed the reaction quotient will no longer equal the equilibrium constant.
- The reaction will proceed in the forward or reverse direction until equilibrium is reestablished.

# Effect of Volume on Gas Phase Reactions



- If the total molar amounts of reactants and products are equal a change in volume does not shift the equilibrium.
- If the molar amounts of reactants and products are different, a change in volume will shift the equilibrium in a direction that better “accommodates” the volume change.

## Volume Change Example



- At equilibrium, the reaction  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$  is described by the reaction quotient

$$Q_P = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}} = K_p$$

- If the volume is decreased by a factor of 3, the partial pressures of all three species will be increased by a factor of 3:

$$Q_{p'} = \frac{(3P_{\text{HI}})^2}{3P_{\text{H}_2} 3P_{\text{I}_2}} = \frac{9P_{\text{HI}}^2}{9P_{\text{H}_2} P_{\text{I}_2}} = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}} = Q_P = K_P$$

$$Q_{P'} = Q_P = K_P$$

## Volume Change Example



- A similar treatment to a different system,  $2\text{NO}_2(g) \rightleftharpoons 2\text{NO}(g) + \text{O}_2(g)$  yields a different result:

$$Q_P = \frac{P_{\text{NO}}^2 P_{\text{O}_2}}{P_{\text{NO}_2}^2}$$

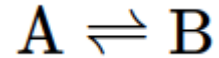
$$Q_{P'} = \frac{(3P_{\text{NO}})^2 3P_{\text{O}_2}}{(3P_{\text{NO}_2})^2} = \frac{9P_{\text{NO}}^2 3P_{\text{O}_2}}{9P_{\text{NO}_2}^2} = \frac{27P_{\text{NO}}^2 P_{\text{O}_2}}{9P_{\text{NO}_2}^2} = 3Q_P > K_P$$

$$Q_{P'} = 3Q_P > K_P$$

# Effect of Temperature



- Consider the elementary reaction



- Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation's stoichiometry:

$$\text{rate}_f = k_f[A]$$

$$\text{rate}_r = k_r[B]$$

# Effect of Temperature



- When the system is at equilibrium,

$$\text{rate}_r = \text{rate}_f$$

- Substituting the rate laws into this equality and rearranging gives

$$k_f[A] = k_r[B]$$
$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_c$$

- Since the rate constants vary with temperature as described by the Arrhenius equation, it stands to reason that the equilibrium constant will likewise vary with temperature

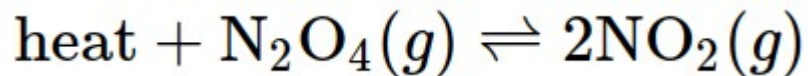
## Heat as a Reagent



- Predicting the shift an equilibrium will experience in response to a change in temperature is most conveniently accomplished by considering the enthalpy change of the reaction.



- For purposes of applying Le Chatelier's principle, heat (q) may be viewed as a reactant:

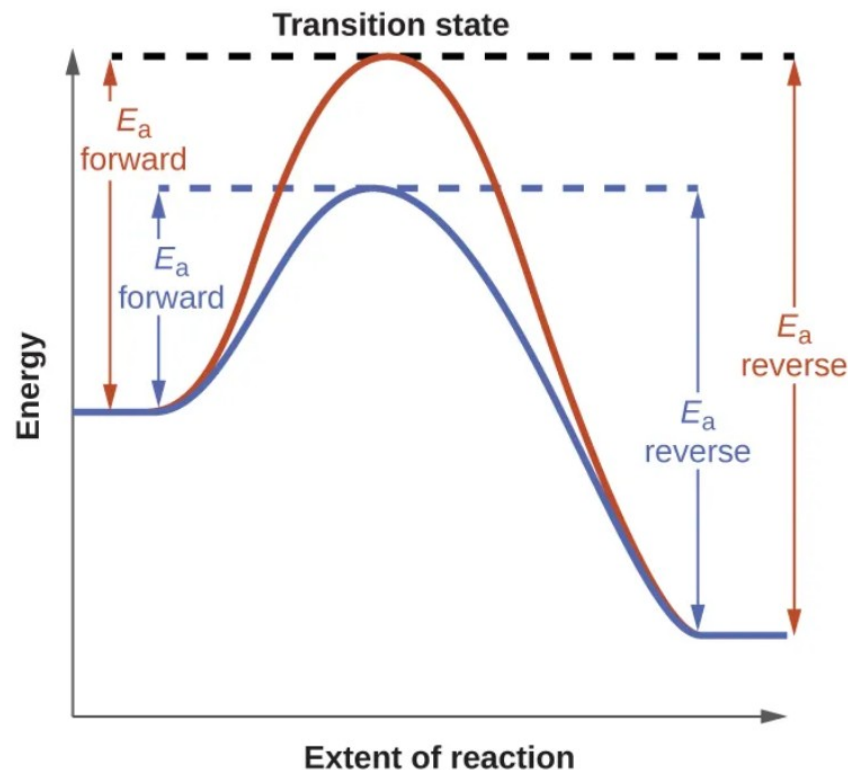




# Effect of a Catalyst



- The lowered transition state energy of the catalyzed reaction results in lowered activation energies for both the forward and the reverse reactions.
- Both forward and reverse reactions are accelerated, and equilibrium is achieved faster *without a change in the equilibrium constant*.



# Section 13.4

## Equilibrium Calculations



Michael Stogsdill

Mott Community College

# Learning Objectives



- Identify the changes in concentration or pressure that occur for chemical species in equilibrium systems
- Calculate equilibrium concentrations or pressures and equilibrium constants, using various algebraic approaches

# Calculating Equilibrium Constant

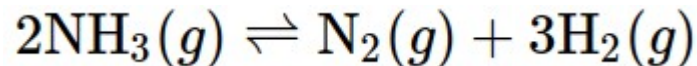


- Equilibrium constants are calculated from the equilibrium concentrations of reactants and products.
- If equilibrium concentrations are known, they can simply be substituted into the  $K$  expression
- If less information is available, you may need to make an ICE table to calculate the equilibrium concentration.

# Representing Changes in Concentration



- Representing changes in concentration can be done using an ICE table.

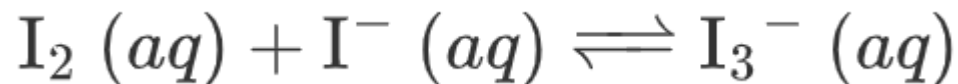


	$[\text{NH}_3]$	$[\text{N}_2]$	$[\text{H}_2]$
Initial Concentration	$[\text{NH}_3]_i$	$[\text{N}_2]_i$	$[\text{H}_2]_i$
Change	$-2x$	$+x$	$+3x$
Equilibrium Concentration	$[\text{NH}_3]_i - 2x$	$[\text{N}_2]_i + x$	$[\text{H}_2]_i + 3x$

## $K_c$ Calculation Example



- Iodine molecules react reversibly with iodide ions to produce triiodide ions.



If a solution with the concentrations of  $\text{I}_2$  and  $\text{I}^-$  both equal to  $1.000 \times 10^{-3} \text{ M}$  before reaction gives an equilibrium concentration of  $\text{I}_2$  of  $6.61 \times 10^{-4} \text{ M}$ , what is the equilibrium constant for the reaction?

## $K_c$ Calculation Example



	$I_2$	+	$I^-$	$\rightleftharpoons$	$I_3^-$
Initial concentration (M)	$1.000 \times 10^{-3}$		$1.000 \times 10^{-3}$		0
Change (M)	$-x$		$-x$		$+x$
Equilibrium concentration (M)	$1.000 \times 10^{-3} - x$		$1.000 \times 10^{-3} - x$		$x$

- At equilibrium the concentration of  $I_2$  is  $6.61 \times 10^{-4}$  M so

$$1.000 \times 10^{-3} \text{ M} - x = 6.61 \times 10^{-4} \text{ M}$$

$$x = 3.39 \times 10^{-4} \text{ M}$$

## $K_c$ Calculation Example



- The ICE table may now be updated with numerical values for all its concentrations

	$I_2$	+	$I^-$	$\rightleftharpoons$	$I_3^-$
Initial concentration (M)	$1.000 \times 10^{-3}$		$1.000 \times 10^{-3}$		0
Change (M)	$-3.39 \times 10^{-4}$		$-3.39 \times 10^{-4}$		$+3.39 \times 10^{-4}$
Equilibrium concentration (M)	$6.61 \times 10^{-4}$		$6.61 \times 10^{-4}$		$3.39 \times 10^{-4}$



## $K_c$ Calculation Example



- Finally, substitute the equilibrium concentrations into the  $K$  expression and solve

$$K_c = \frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]}$$
$$= \frac{3.39 \times 10^{-4} \text{ M}}{(6.61 \times 10^{-4} \text{ M})(6.61 \times 10^{-4} \text{ M})} = 776$$

## Missing Equilibrium Concentration Example



Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the  $K_c$  for the reaction,  $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$ , is  $4.1 \times 10^{-4}$ . Calculate the equilibrium concentration of  $\text{NO}(g)$  in air at 1 atm pressure and 2000 °C. The equilibrium concentrations of  $\text{N}_2$  and  $\text{O}_2$  at this pressure and temperature are 0.036 M and 0.0089 M, respectively.

# Missing Equilibrium Concentration Example



$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$[\text{NO}]^2 = K_c[\text{N}_2][\text{O}_2]$$

$$[\text{NO}] = \sqrt{K_c[\text{N}_2][\text{O}_2]}$$

$$= \sqrt{(4.1 \times 10^{-4})(0.036 \text{ M})(0.0089 \text{ M})} = 3.6 \times 10^{-4} \text{ M}$$

# Equilibrium Concentrations from Initial Concentrations



- The most challenging type of equilibrium calculation can be one in which equilibrium concentrations are derived from initial concentrations and an equilibrium constant.
- For these calculations, a four-step approach is used
  - 1) Identify the direction in which the reaction will proceed to reach equilibrium.
  - 2) Develop an ICE table.
  - 3) Calculate the concentration changes and, subsequently, the equilibrium concentrations.
  - 4) Confirm the calculated equilibrium concentrations.

## Equilibrium Concentration Example



- Under certain conditions, the equilibrium constant  $K_c$  for the decomposition of  $\text{PCl}_5(g)$  into  $\text{PCl}_3(g)$  and  $\text{Cl}_2(g)$  is 0.0211. What are the equilibrium concentrations of  $\text{PCl}_5$ ,  $\text{PCl}_3$ , and  $\text{Cl}_2$  in a mixture that initially contained only  $\text{PCl}_5$  at a concentration of 1.00 M?

## Step One



- Determine the direction the reaction proceeds.



- Because only the reactant is present initially  $Q_c = 0$ , which is less than  $K_c$ . Therefore the reaction will proceed to the right.

## Step Two



- Develop an ICE table.

	$\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$		
Initial concentration (M)	1.00	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$1.00 - x$	$x$	$x$

## Step Three



- Substituting the equilibrium concentrations into the equilibrium constant equation gives

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

$$= \frac{(x)(x)}{(1.00 - x)} = \frac{x^2}{(1.00 - x)} = 0.0211$$

$$x^2 = 0.0211(1.00 - x) = 0.0211 - 0.0211x$$

$$x^2 + 0.0211x - 0.0211 = 0$$

$$x = 0.135 \quad \text{or} \quad -0.156$$



## Step Three Continued



- We can now substitute  $x$  into our concentration expressions.

$$[\text{PCl}_5] = 1.00 - x = 1.00 - 0.135 = 0.87 \text{ M}$$

$$[\text{PCl}_3] = x = 0.135 \text{ M}$$

$$[\text{Cl}_2] = x = 0.135 \text{ M}$$

## Step Four



- To check the calculation, substitution the concentrations expression for  $K_c$ .

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

# Approximations

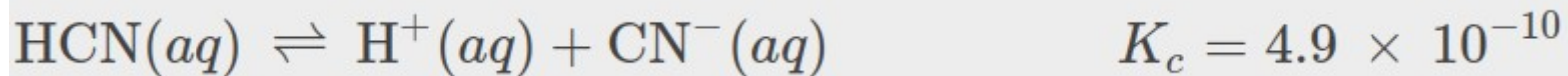


- When the change in concentration ( $x$ ) is significantly less than the initial concentration the initial concentration experiences a negligible change.
  - This is a consequence of the small  $K$  value
- When these conditions are met, a clever approximation can be used.

## Approximation Example



- What are the concentrations at equilibrium of a 0.15 M solution of HCN?



	$\text{HCN}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CN}^-(aq)$		
Initial concentration (M)	0.15	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$0.15 - x$	$x$	$x$

## Approximation Example



$$K_c = \frac{(x)(x)}{0.150 - x} \approx \frac{x^2}{0.150}$$

$$x = \sqrt{0.150K_c} = \sqrt{(0.150)(4.9 \times 10^{-10})} = 8.6 \times 10^{-6} \text{ M}$$

$$[\text{HCN}] = 0.150 - x = 0.150 - (8.6 \times 10^{-6}) = 0.14999 \text{ M} \approx 0.150 \text{ M}$$

$$[\text{H}^+] = [\text{CN}^-] = x = 8.6 \times 10^{-6} \text{ M}$$