

# Equilibria

- Law of Chemical Equilibrium (Law of Mass Action)
  - At a given temperature, a chemical system reaches a state in which a particular ratio of reactant and product concentrations has a constant value
- For a particular system and temperature, the same equilibrium state is attained regardless of how the reaction is run – any combination of reactants & products & catalysts will result in the same equilibrium mixture of reactants & products
- As the reaction proceeds toward equilibrium, there is a continually smooth change in the concentrations of reactants and products
- The ratio of reactants and products is continually changing until equilibrium is reached

# Equilibria

- The ratio of concentration terms for a given reaction at a given time during the reaction is called the “**Reaction Quotient (Q)**”
- The expression for this is referred to as a:  
**Mass-Action Expression**
- The reaction quotient is written directly from the balanced equation and is made up of product concentration terms multiplied together and divided by the reactant concentration terms multiplied together
- Each concentration term is raised to the power of the stoichiometric coefficient
- For reactions involving gaseous reactants & products, the concentration units are expressed as pressure units



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

# Equilibria

- All chemical systems (reactions) reach a point where the concentrations of the reactants & products  
    “no longer change”
- All chemical reactions are reversible and reach a state of “Equilibrium”
  - Reactant & Product concentrations stop changing
  - The forward and reverse reaction rates have become equal
  - The rate of reactant decomposition or combination to form one or more products is balanced by the rate of product decomposition or combination to form the original reactants
  - At equilibrium:

$$\text{rate}_{(\text{fwd})} = \text{rate}_{(\text{rev})}$$

# Equilibria

## ■ Example:



- $\text{N}_2\text{O}_4(l)$  vaporizes at  $21^\circ\text{C}$
- $\text{N}_2\text{O}_4(g)$  begins to turn brown decomposing to ( $\text{NO}_2$ )
- Initially the color darkens (forward reaction)
- After a few moments, the **color stops changing** as the reaction reaches equilibrium
- The rate of  $\text{N}_2\text{O}_4$  decomposition decreases with time
- The rate of  $\text{NO}_2$  formation increases with time
- $\text{NO}_2$  molecules also begin to collide and reform  $\text{N}_2\text{O}_4$
- Eventually,  $\text{N}_2\text{O}_4$  decomposes into  $\text{NO}_2$  molecules as fast as  $\text{NO}_2$  molecules combine into  $\text{N}_2\text{O}_4$  molecules, i.e., the reaction reaches equilibrium

# Equilibrium Constant

$$\text{rate}_{(fwd)} = \text{rate}_{(rev)}$$

$$k_{fwd} [\text{N}_2\text{O}_4]_{eq} = k_{rev} [\text{NO}_2]_{eq}^2$$

$$\frac{k_{fwd}}{k_{rev}} = \frac{[\text{NO}_2]_{eq}^2}{[\text{N}_2\text{O}_4]_{eq}}$$

$$K = \frac{k_{fwd}}{k_{rev}} = \frac{[\text{NO}_2]_{eq}^2}{[\text{N}_2\text{O}_4]_{eq}}$$

$K_{fwd}$  &  $K_{rev}$  – rate constants

**Note: Both the forward and reverse reactions are “elementary” steps (no intermediate products); thus, the rate law can be written directly from the stoichiometric balanced equation, i.e., reaction orders not involved**

## **K = Equilibrium Constant**

- The Equilibrium Constant, **K**, is a number equal to a particular ratio of product concentration terms and reactant concentration terms at a particular temperature when the reaction has reached equilibrium, i.e., the forward reaction rate equals the reverse reaction rate

# Equilibria

## ■ Reaction Coefficient & Equilibrium Constant

- The Reaction Coefficient,  $Q$ , is defined at any time during the reaction, i.e., not at equilibrium
- The Equilibrium Constant,  $K$ , is defined at the point in the reaction when the rate of the forward reaction equals the rate of the reverse reaction and there is no net change in the product and reactant concentrations
- At equilibrium:  $Q$  becomes  $K$



$$Q \text{ (reaction at any time)} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = K \text{ (reaction at equilibrium)}$$

# Practice Problem

Write the Equilibrium Constant for the combustion of Propane gas



Balance the Equation



$$K_c = \frac{[\text{CO}_2]^3[\text{H}_2\text{O}]^4}{[\text{C}_3\text{H}_8]^1[\text{O}_2]^5}$$

The subscript "c" in  $K_c$  indicates the equilibrium constant is based on reactant and product concentrations

The value of "K" is usually shown as a unitless number,

BUT IT ACTUALLY DOES HAVE A UNIT EXPRESSION

# Equilibria

- The **magnitude** of the Equilibrium Constant,  $K$ , is an indication of **how far** the reaction proceeds toward a product at a **given temperature**

Note: the reaction rates are equal at equilibrium, not necessarily the *concentrations*

- Small  $K$  ( $< 0.001$ ) – The reaction forms very little Product
- Large  $K$  ( $> 1000$ ) – Reaction has gone to completion, with **very little reactant** remaining
- Intermediate  $K$  – Significant amounts of reactant remain and significant amounts of product have formed



# Equilibria

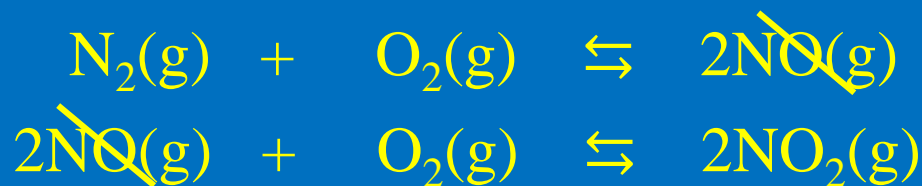
## ■ Form of the Equilibrium Constant

- A reaction can be an individual reaction step or a multistep reaction
- If the overall reaction is the sum of two or more reactions, the overall reaction Equilibrium Constant (or Reaction Quotient), is the product of the Equilibrium Constants (Reaction Coefficients) for the steps

$$\mathbf{K_{overall} = K_1 \times K_2 \times K_3 \times \dots}$$

# Practice Problem

Determine the overall equilibrium constant for the reaction between Nitrogen & Oxygen to form the toxic gas Nitrogen Dioxide – a component of atmospheric smog



$$K_{c1} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$K_{c2} = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

$$K_{c_{\text{overall}}} = K_{c1} \times K_{c2} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} = \frac{[\text{NO}_2]^2}{[\text{N}_2][\text{O}_2]^2}$$

$$K_{c_{\text{overall}}} = K_{c1} \times K_{c2} = (4.3 \times 10^{-25})(6.4 \times 10^9) = 2.4 \times 10^{-15}$$

# Equilibrium

- Equilibrium Constant – Forward & Reverse reactions
  - The Equilibrium Constant (Reaction Quotient) for a forward reaction is the Reciprocal of the reverse reaction



$$K_{\text{c forward}} = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \quad K_{\text{c reverse}} = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{1}{K_{\text{c forward}}}$$

$$K_{\text{c forward}} = \frac{1}{K_{\text{c reverse}}} \quad K_{\text{c reverse}} = \frac{1}{K_{\text{c forward}}}$$

# Equilibrium

## ■ Equilibrium Constant - Multiplication Factor

- If all the coefficients of the balanced equation are multiplied by some factor (n), that factor becomes the exponent for relating the equilibrium constants (reaction coefficients)



$$K = \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$



$$K' = \left( \frac{[C]^{nc} [D]^{nd}}{[A]^{na} [B]^{nb}} \right) = \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)^n$$

$$K' = K^n$$

### (Math Review)

$$\text{Let } x = 2 \quad a = 2 \quad n = 2$$

$$x^a = 2^2 = 4$$

$$x^{na} = x^{2 \times 2} = 2^4 = 16$$

$$x^{a^n} = (x^2)^2 = (2^2)^2 = 4^2 = 16$$

$$\therefore x^{n \times a} = (x^a)^n$$

# Equilibrium

## ■ Reactions involving Pure Liquids and Solids

- If the components of the reactions involve different phases (solids, liquids, gases), the system reaches heterogeneous equilibrium



- Reaction Quotient

$$Q'_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$$

- Pure solids, such as  $\text{CaCO}_3(\text{s})$  &  $\text{CaO}(\text{s})$ , always have the same concentration at a given temperature
- Thus, Concentration terms for solid reactants in an Equilibrium expression are "Eliminated"

$$Q'_c = \frac{\cancel{[\text{CaO}]}[\text{CO}_2]}{\cancel{[\text{CaCO}_3]}} = [\text{CO}_2] = Q_c$$

# Equilibrium

## ■ Summary of ways of Expressing Equilibrium Expressions

Form of Chemical Equation	Form of $Q$	Value of $K$
Reference reaction: $A \rightleftharpoons B$	$Q_{(\text{ref})} = \frac{[B]}{[A]}$	$K_{(\text{ref})} = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}}$
Reverse reaction: $B \rightleftharpoons A$	$Q = \frac{1}{Q_{(\text{ref})}} = \frac{[A]}{[B]}$	$K = \frac{1}{K_{(\text{ref})}}$
Reaction as sum of two steps: (1) $A \rightleftharpoons C$ (2) $C \rightleftharpoons B$	$Q_1 = \frac{[C]}{[A]}$ ; $Q_2 = \frac{[B]}{[C]}$ $Q_{\text{overall}} = Q_1 \times Q_2 = Q_{(\text{ref})}$ $= \frac{\cancel{[C]}}{[A]} \times \frac{[B]}{\cancel{[C]}} = \frac{[B]}{[A]}$	$K_{\text{overall}} = K_1 \times K_2$ $= K_{(\text{ref})}$
Coefficients multiplied by $n$	$Q = Q_{(\text{ref})}^n$	$K = K_{(\text{ref})}^n$
Reaction with pure solid or liquid component, such as $A(s)$	$Q = Q_{(\text{ref})}[A] = [B]$	$K = K_{(\text{ref})}[A] = [B]$

# Equilibrium

- Expressing Equilibria with Pressure Terms
- Recall Combined Gas Law:

$$PV = nRT \quad \text{or} \quad \frac{n}{V} = M = \frac{P}{RT}$$

- "P" is the pressure of the gas (atmospheres, pascals, or torr), "n/V" is its molar concentration - Molarity (moles per liter, M),  $R = 0.0821 \text{ L} \cdot \text{atm} / (\text{mol} \cdot \text{K})$
- When Temperature is kept constant,  
pressure is directly proportional to the concentration
- When all reactants and products are gases, the reaction coefficient (and equilibrium constant) can be expressed in terms of "Partial Pressures" instead of concentrations



$$Q_p = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \times P_{\text{O}_2}} = K_p \quad (\text{at equilibrium})$$

$P_{\text{NO}_2}$  – Partial Press Product  $\text{NO}_2$   
 $P_{\text{NO}}$  – Partial Press Reactant  $\text{NO}$   
 $P_{\text{O}_2}$  – Partial Press Reactant  $\text{O}_2$

# Equilibrium

- In many cases  $Q_c$  and  $Q_p$  ( $K_c$  &  $K_p$ ) do not have the same value
- The Gas Law can be rearranged as concentration terms and converted to partial pressures

$$Q_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} \quad Q_p = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \times P_{\text{O}_2}} \quad \frac{n}{V} = \frac{P}{RT}$$

$$[\text{NO}_2]^2 = \frac{n_{\text{NO}_2}^2}{V^2} = \frac{P_{\text{NO}_2}^2}{(\text{RT})^2} \quad [\text{NO}]^2 = \frac{n_{\text{NO}}^2}{V^2} = \frac{P_{\text{NO}}^2}{(\text{RT})^2} \quad [\text{O}_2] = \frac{n_{\text{O}_2}}{V} = \frac{P_{\text{O}_2}}{(\text{RT})}$$

$$Q_c = \frac{\frac{n_{\text{NO}_2}^2}{V^2}}{\frac{n_{\text{NO}}^2}{V^2} \times \frac{n_{\text{O}_2}}{V}} = \frac{\frac{P_{\text{NO}_2}^2}{(\text{RT})^2}}{\frac{P_{\text{NO}}^2}{(\text{RT})^2} \times \frac{P_{\text{O}_2}}{(\text{RT})}} = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \times P_{\text{O}_2}} \times \frac{1}{\frac{1}{(\text{RT})^2} \times \frac{1}{(\text{RT})}}$$

$$Q_c = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 \times P_{\text{O}_2}} \times \text{RT} = Q_p (\text{RT}) \quad \text{At equilibrium } K_c = K_p (\text{RT})$$



# Equilibrium

- The actual form of the equilibrium expression developed on the previous slide takes the following rearranged form:

$$K_p = K_c (RT)^{\Delta n_{\text{gas}}}$$

- The exponent of the "RT" term ( $\Delta n_{\text{gas}}$ ) equals the change in the amount (moles) of gas from the "balanced" equation

$\Delta n_{\text{gas}} = \text{moles gaseous product} - \text{moles gaseous reactant}$

Note:  $\Delta n_{\text{gas}}$  can be positive (+) or negative (-)

- From previous example:



$$\Delta n_{\text{gas}} = (2) - (2 + 1) = 2 - 3 = -1$$

- Thus, for the above reaction:

$$K_p = K_c (RT)^{-1} \quad K_p = \frac{K_c}{RT} \quad K_c = K_p (RT)$$

# Practice Problem

A chemical engineer injects limestone ( $\text{CaCO}_3$ ) into the hot flue gas of a coal-burning power plant to form Lime ( $\text{CaO}$ ), which scrubs  $\text{SO}_2$  from the gas. Find  $K_c$  for the reaction at  $1000^\circ\text{K}$ , if  $\text{CO}_2$  is in atmospheres



$$\Delta n_{\text{gas}}: (0 + 1) - 0 = 1$$

$$K_c = K_p (\text{RT})^{-\Delta n_{\text{gas}}}$$

Rearranged from previous slide

$$K_c = 2.1 \times 10^{-4} \left( 0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times (1000^\circ \text{K}) \right)^{-1}$$

$$K_c = 2.6 \times 10^{-6}$$

# Practice Problem

At 100°C,  $K_p = 60.6$  atm for the reaction



In a given experiment, 0.10 atm of each component is placed in a container

Is the system at equilibrium?

If not, in which direction will the reaction proceed?

$$Q_p = \frac{P_{\text{NO}}^2 P_{\text{Br}_2}}{P_{\text{NOBr}}^2} = \frac{(0.10)^2 (0.10)}{(0.10)^2} = 0.10 < K_p = 60.6$$

$Q_p < K_p$  Thus, the reaction is not at equilibrium

The products, relative to the reactants, must increase until  $Q_p = K_p$

Thus, the reaction will proceed to the right (towards the formation of products)

# Equilibrium – Reaction Direction

- Has the Reaction Reached Equilibrium?
  - Compare the value of “Q” at a particular time with the value of Q at equilibrium ( $Q = K$ )

$$Q = \text{reaction at any time} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = K = \text{reaction at equilibrium}$$

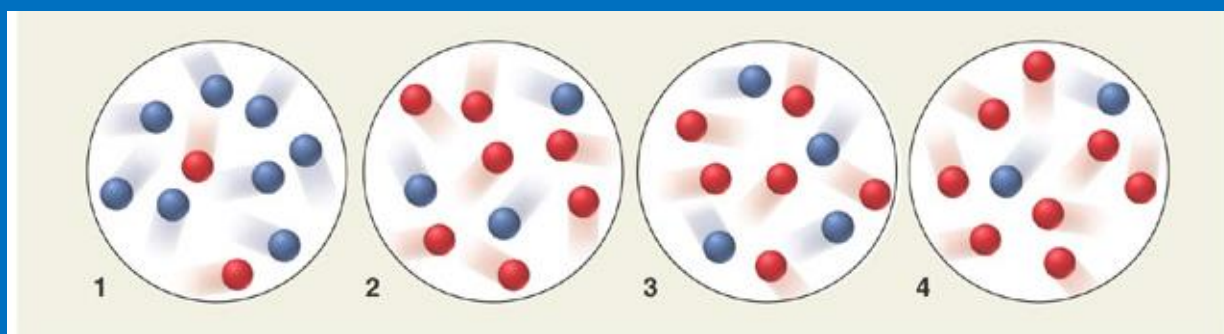
- $Q < K$  - The “Q” product term (numerator) is smaller than the reactant term (denominator)  
The net formation of product will continue until the numerator and denominator are equal and equilibrium has been reached, i.e., reaction moves to the “right”
- $Q > K$  - The “Q” product term (numerator) is larger than the reactant term (denominator)  
Product formation will decrease and the reactant formation will increase until equilibrium is reached – reaction moves “left”
- $Q = K$  - Equilibrium, product term equals reactant term

# Practice Problem

The reaction of  $A(g) \rightleftharpoons B(g)$  at  $175^\circ\text{C}$  is composed of

$[A] = 2.8 \times 10^{-4} \text{ M}$  and  $[B] = 1.2 \times 10^{-4} \text{ M}$  at equilibrium

Which direction does the reaction shift in each of these molecular scenes (A is red; B is blue)?



Calculate  $K_c$  from the actual reaction data. Use number of spheres from depiction to calculate  $Q_c$  and compare to  $K_c$  to determine direction.

$$Q_c = \frac{[B]}{[A]} = \frac{1.2 \times 10^{-4}}{2.8 \times 10^{-4}} = 0.43 = K_c$$

1.  $Q_c = 8/2 = 4.0$     2.  $Q_c = 3/7 = 0.43$     3.  $Q_c = 4/6 = 0.67$     4.  $Q_c = 2/8 = 0.25$

1.  $Q_c > K_c$ ; Left    2.  $Q_c = K_c$ ; Equilibrium    3.  $Q_c > K_c$ ; Left    4.  $Q_c < K_c$ ; Right

# Practice Problem

For the reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ ,  $K_c = 0.21$  at  $100^\circ\text{C}$

At a point during the reaction, the concentrations were:

$$[\text{N}_2\text{O}_4] = 0.12 \text{ M} \quad \text{and} \quad [\text{NO}_2] = 0.55 \text{ M}$$

Is the reaction at equilibrium?

If not, in which direction is it progressing?

Write an expression for  $Q_c$ , substitute with the values given, and compare the  $Q_c$  with the given  $K_c$

$$Q_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{[0.55]^2}{0.12} = 2.5$$

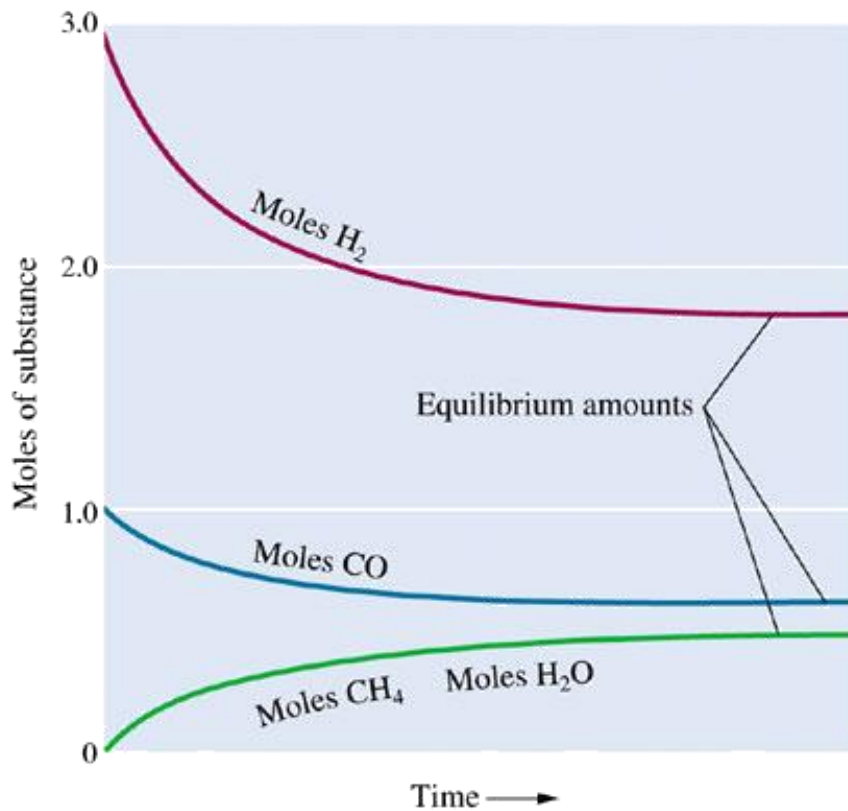
$Q_c > K_c$  ( $2.5 > 0.21$ )      Reaction is not at equilibrium

Product formation (numerator) must decrease reforming reactants until equilibrium is reestablished ( $Q_c = K_c$ )

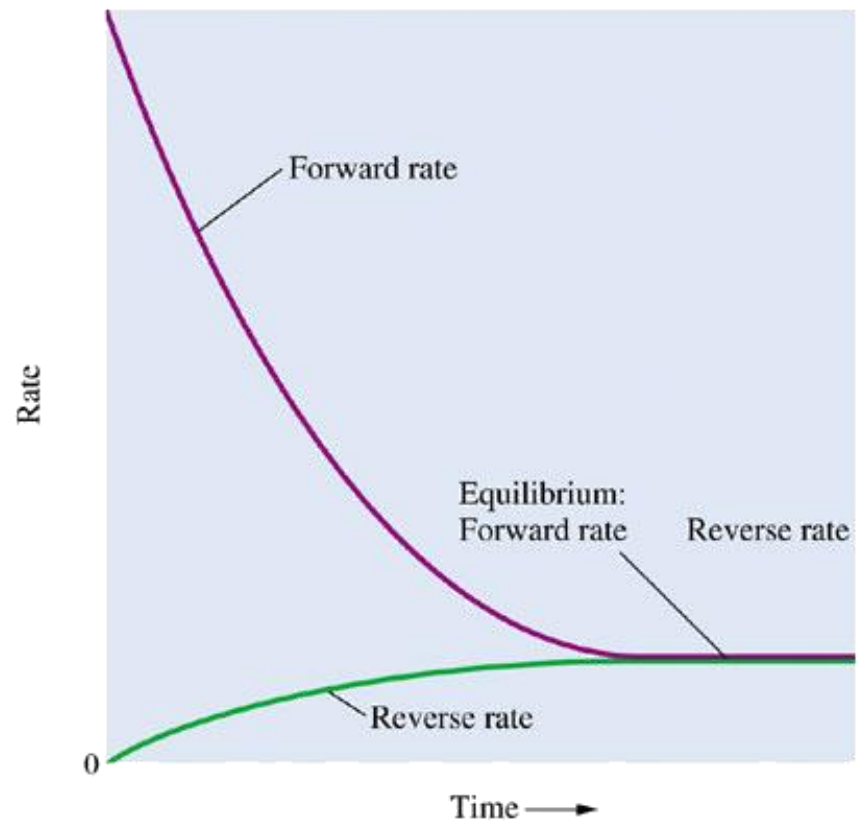
Thus, reaction moves to the left

# Equilibrium

Summary - Changes in concentration and Reaction Rate



A



B

# Heterogeneous Equilibria

- Equilibrium constants for **heterogeneous** equilibria



- Reaction includes multiple phases
- Equilibrium expression,  $K_c$ , does not include concentration terms for pure liquids or solids

Pure Liquids:  $\text{H}_2\text{O}$

Solids:  $\text{Fe}_2\text{O}_3$

$$K_c = [\text{H}_2]^3$$

- Concentrations of pure liquids and solids remain constant throughout a reaction
- The concentrations of the liquids and solids are actually incorporated into the constant  $K_c$  or  $K_p$



# Equilibrium Problems

## ■ The Reaction Table

- Equilibrium problems can be stated with insufficient information to set up the computational form of the equilibrium expression
- Missing concentration terms can be determined by first solving a "stoichiometric" problem and then substituting the values into the equilibrium expression
- A reaction table has the general form:

Balanced Equation	aA	bB	↔	cC
Initial $C_i$	$[A]_i$	$[B]_i$		$[C]_i$
Conc Change( $\Delta$ )	$\pm aX$	$\pm bX$		$\pm cX$
Final $C_f$	$[A]_i \pm aX$	$[B]_i \pm bX$		$[C] \pm cX$

- The initial values of  $[A]$  &  $[B]$  may or may not be zero
- The initial value of  $[C]$  may or may not be zero
- Calculation of "X" allows for the computation of the equilibrium values of A, B, C; then solve for  $K_c$  or  $K_p$

# Equilibrium Problems

## ■ The Quadratic Equation

➤ The computation of the "X" term often results in a quadratic equation:  $aX^2 + bX + c = 0$

➤ The formula for the solution of a quadratic equation is:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

➤ The  $\pm$  sign means that there are two possible values for x

➤ Ex.  $0.56x^2 - 4.68x + 3.12 = 0$

$$x = \frac{-(-4.68) \pm \sqrt{(-4.68)^2 - 4(0.56)(3.12)}}{2(0.56)}$$

$$x = 7.6M \quad \text{and} \quad x = 0.73M$$

The correct answer is  $x = 0.73 M$ ; the larger value ( $x = 7.6M$ ) would produce "negative" concentrations, which have no meaning

# Equilibrium Problems

- Avoiding the Quadratic Equation Using Simplifying Assumption
- Assumption: If a reaction has a relatively small  $K$  and a relatively large initial reactant concentration, the change in concentration ( $x$ ) can often be neglected without introducing significant error

$$[\text{reactant}]_{\text{init}} - x = [\text{reactant}]_{\text{eq}} \approx [\text{reactant}]_{\text{init}}$$

- Assumption Criteria:

If the assumption results in a change that is less than 5% of the initial concentration, the error is not significant and the assumption is justified

# Practice Problem

Decomposition of Phosgene (warfare agent)



$$K_c = 8.3 \times 10^{-4} \quad (\text{at } 360^\circ\text{C})$$

Calculate  $[\text{CO}]$ ,  $[\text{Cl}_2]$ , and  $[\text{COCl}_2]$  when 5.00 mol of  $\text{COCl}_2$  decomposes and reaches equilibrium in a 10.0 L flask

$$Q_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}$$

**Calculating initial  $[\text{COCl}_2]$**

$$[\text{COCl}_2] = \frac{5.00 \text{ mol}}{10.0 \text{ L}} = 0.500 \text{ M}$$

	$\text{COCl}_2(\text{g})$	$\rightleftharpoons$	$\text{CO}(\text{g})$	$\text{Cl}_2(\text{g})$
Initial $C_i$	0.500		0.000	0.000
Conc Change( $\Delta$ )	-X		+X	+X
Equilibrium Values	0.5 - X		X	X

Con't on next Slide

# Practice Problem (con't)

Substitute Values into  $Q_c$

$$Q_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = \frac{x \times x}{0.500 - x} = \frac{x^2}{0.500 - x} = K_c = 8.3 \times 10^{-4}$$

Because  $K_c$  is small, the reaction does not proceed very far to the right (few products formed). i.e., the amount of  $\text{COCl}_2$  reacting is very small

Thus, the equilibrium concentration of  $\text{COCl}_2$  is nearly equal to the initial concentration, and the  $(0.500 - x)$  term can be reduced to 0.500 M

Substituting and solving for  $x$

$$K_c = 8.3 \times 10^{-4} \approx \frac{x^2}{0.500} \quad x^2 \approx (8.3 \times 10^{-4})(0.500) \quad x \approx 2.0 \times 10^{-2}$$

Check Assumption

$$\frac{[\text{Change}]}{[\text{Initial}]} = \frac{2.0 \times 10^{-2}}{0.500} \times 100 = 4\% \quad (\text{less than } 5\% - \text{assumption is justified})$$

# Le Chatelier's Principle

- When a chemical system at equilibrium is disturbed, it reattains equilibrium by undergoing a net reaction that reduces the effect of the disturbance
- Disturbing a System
  - When a disturbance occurs, the equilibrium position shifts
  - Concentrations (or pressures) change in a way that reduces the disturbance
  - The system attains a new equilibrium position where again  $Q = K$
  - 3 Kinds of Disturbance
    - Changes in Concentration
    - Changes in Pressure (Volume)
    - Changes in Temperature

# Le Chatelier's Principle

- The Effect of a Change in Concentration
  - When a system at Equilibrium is disturbed by a change in concentration of one of the components, the system reacts in the "direction" that reduces the change.
    - If the component concentration increases, the system reacts to **consume** some of it
    - reactant side: Equilibrium shifts to the right as reactants combine to form more product
    - product side: Equilibrium shifts to the left as products are decomposed to reform reactants

# Practice Problem

Given initial conditions of the following reaction at equilibrium :



$$[\text{PCl}_3]_i = 0.200 \text{ M}, \quad [\text{Cl}_2]_i = 0.125 \text{ M}, \quad [\text{PCl}_5]_i = 0.600 \text{ M}$$

$$Q_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{0.600}{(0.200)(0.125)} = 24.0 = K_c$$

Disturb the system by increasing the  $\text{Cl}_2$  concentration by 0.075 M

Experiment shows the new  $[\text{PCl}_5]$  at equilibrium is 0.637 M

	$\text{PCl}_3$	$\text{Cl}_2$	$\rightleftharpoons$	$\text{PCl}_5$
Initial $C_i$	$[\text{PCl}_3]_i = 0.200$	$[\text{Cl}_2]_i = 0.125$		$[\text{PCl}_5]_i = 0.600$
Disturbance		+0.075		
New Initial	0.200	0.200		0.600
Conc Change( $\Delta$ )	-X	-X		+X
Equilibrium Values	$0.200 - X$	$0.200 - X$		$0.600 + X = 0.637 \text{ M}$

Con't on next Slide



# Practice Problem (Con't)

Compute X, original K<sub>c</sub> and new K<sub>c</sub>

$$[\text{PCl}_5] = 0.600 \text{ M} + X = 0.637 \text{ M}$$

$$X = 0.637 - 0.600 = 0.037 \text{ M}$$

$$[\text{PCl}_3] = [\text{Cl}_2] = 0.200 \text{ M} - X = 0.200 \text{ M} - 0.037 = 0.163 \text{ M}$$

$$K_{c(\text{orig})} = \frac{0.600}{(0.200)(0.125)} = 24.0$$

$$K_{c(\text{new})} = \frac{0.637}{(0.163)(0.163)} = 24.0$$

- $[\text{PCl}_5]$  (0.637 M) is higher than its original conc (0.600 M)
- $[\text{Cl}_2]$  (0.163 M) is higher than its original equilibrium concentration (0.125 M), but lower than its new initial conc (0.200 M)
- $[\text{PCl}_3]$  (0.163 M) is lower than its original concentration (0.200 M) because some reacted with the added  $\text{Cl}_2$
- Equilibrium has shifted to the right, but K<sub>c</sub> remains the same

# Le Chatelier's Principle

## ■ Effect of Pressure Change

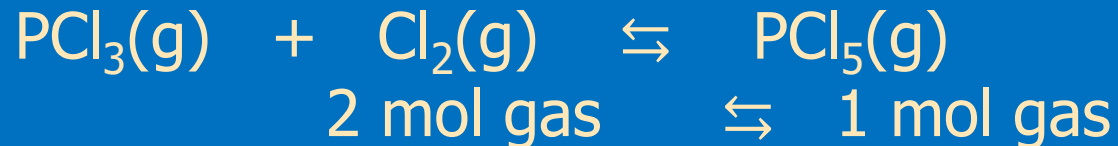
- Changes in pressure have significant effects only on equilibrium systems with gaseous components
- Pressure changes occur in 3 ways:
  - Adding an inert gas
  - Changing the volume of the reaction vessel
  - Changing concentration of gaseous component
- Inert Gas
  - Inert gas does not change volume; thus, the reactant & product concentrations (and their partial pressures) do not change
  - Inert gas does not appear in the  $Q$  ( $K$ ) term

# Le Chatelier's Principle

## ■ Effect of Pressure Change

### ➤ Changing the Volume

- Consider the reaction:



- If the volume is halved, doubling the pressure, the system reacts to reduce this increase in pressure by moving the equilibrium to the side of the reaction with fewer moles of gas, in this case toward the product side,  $\text{PCl}_5$
- At equilibrium, the 1 mol of  $\text{PCl}_5$ , in half the volume, exerts the same pressure as the two moles of combined  $\text{PCl}_3$  &  $\text{Cl}_2$  in the original volume

# Le Chatelier's Principle

## ■ Effect of Pressure Change (con't)

- A change in volume results in a change in concentration
  - Decrease Volume - Increase Concentration
  - Increase Volume - Decrease Concentration
- The value of  $Q_c$  will be changed according to the new values of the numerator and denominator in the  $Q_c$  expression

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

- The equilibrium position will move to the left or right until  $Q_c = K_c$  Note:  $K_c$  does not change
- If there is no change in the number of moles between reactants and products, i.e.,  $\Delta n_{\text{gas}} = 0$ , a change in pressure (volume) has no effect on  $Q_c$  or the equilibrium position

# Le Chatelier's Principle

## ■ Effect of Pressure Change (con't)

### ➤ Example #1

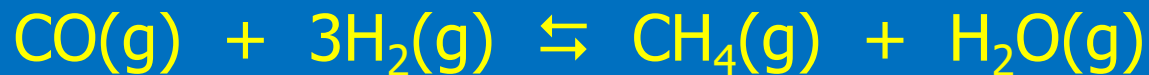


- When the volume is halved, the concentrations double, but the denominator of  $Q_c$  ( $[\text{PCl}_3][\text{Cl}_2]$ ) is the product of two concentrations, so the value of the product quadruples, while the numerator value just doubles
- Thus,  $Q_c$  becomes less than  $K_c$ , forcing the reaction to move to the right, establishing a new equilibrium position, forming more product until  $Q_c$  again equals  $K_c$
- If there is no change in  $\Delta n_{\text{gas}}$ ,  $\Delta n_{\text{gas}} = 0$ , a change in pressure (volume) has no effect on  $Q_c$  or the equilibrium position

# Le Chatelier's Principle

## ■ Effect of Pressure Change (con't)

### Example #2



When the reaction goes forward (formation of  $\text{CH}_4$ ), four moles of reactant gas ( $1 + 3 = 4$ ) becomes 2 moles of product ( $1+1=2$ ); thus  $\Delta n = 2 - 4 = -2$

When the volume of gas is, for example, halved, the partial pressures and concentrations are doubled, changing the values of the numerator to a lesser degree than the value of the denominator term in the  $Q_c$  term

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3}$$

$$Q_c = \frac{(2[\text{CH}_4])(2[\text{H}_2\text{O}])}{(2[\text{CO}])^2(2[\text{H}_2])^3} = \frac{2 \times 2}{2 \times 2^3} \times K_c = \frac{4}{2 \times 8} \times K_c = \frac{1}{4} \times K_c$$

# Le Chatelier's Principle

## ■ Change in Temperature

- Unlike changes in Concentration and Pressure,

Only Changes in Temperature Affect the Value of  $K$

- Changes in temperature require that the **Heat of Reaction** ( $\Delta^{\circ}H_{\text{rxn}}$ ) be considered
- Increase Temperature: The addition of heat shifts the reaction in a direction in which the heat is absorbed

Endothermic reaction,  $\Delta^{\circ}H_{\text{rxn}} > 0$

- Decrease Temperature: Removing heat shifts the reaction in a direction in which heat is released

Exothermic reaction,  $\Delta^{\circ}H_{\text{rxn}} < 0$

# Le Chatelier's Principle

## ■ Change in Temperature (con't)

Example

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



At standard temperature the net reaction is "Exothermic"

Since the forward reaction ( $\rightarrow$  Right) is "Exothermic" (releases heat), the reverse reaction is "Endothermic" (absorbs any added heat)

If heat is added to this reaction, an Endothermic reaction occurs and the system shifts to the left decomposing  $\text{PCl}_5$  to form  $\text{PCl}_3$  &  $\text{Cl}_2$ , which requires absorption of heat

The denominator of  $Q_c$  (reactants) becomes larger and the numerator (products) becomes smaller, resulting in a smaller  $Q_c$

The system reaches a new equilibrium position at a smaller ratio of the concentration terms, i.e., smaller  $K_c$



# Le Chatelier's Principle

Example (Con't)

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



- The system would respond to a **drop** in temperature (**heat removal**) by forming more  $\text{PCl}_5$  releasing heat from the combination of  $\text{PCl}_3$  &  $\text{Cl}_2$
- The reduced concentrations of  $\text{PCl}_3$  &  $\text{Cl}_2$  (reactants) result in a smaller value of the denominator term in the  $Q_c$  expression
- The increased value of the numerator term (products) results in a higher value of  $Q_c$  as the reaction moves to the right
- At equilibrium a new lower value of  $K_c$  has been established

# Van't Hoff Equation

- Each of the concentration-related terms below ( $K$ ,  $k$ ,  $P$ ) is dependent on Temperature ( $T$ ) through an Energy term ( $\Delta H_{\text{rxn}}$ ,  $\Delta E_a$ ,  $\Delta H_{\text{vap}}$ ) divided by "R"

- Effect of Temperature on the Equilibrium Constant ( $k$ )

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_{\text{rxn}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad K = \text{ratio of rate constants } (K = k_2/k_1)$$

- Effect of Temperature on the rate Constant ( $k$ )

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{Arrhenius Equation for Activation Energy, } E_a$$
$$\Delta E_{a(\text{fwd})} - \Delta E_{a(\text{rev})} = \Delta H_{\text{rxn}}^{\circ}$$

- Effect of Temperature on the Equilibrium Vapor Pressure

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{Clausius-Clapeyron Equation}$$
$$\Delta H_{\text{vap}} = \Delta H_{\text{rxn}}^{\circ} \quad \text{where } A_{(l)} \leftrightarrow A_{(g)}$$

Also:  $K_p = P_A$  (Vapor Pressure)

# Van't Hoff Equation

- If  $\Delta H_{\text{rxn}}$  and  $K$  are known at one temperature, then the Van't Hoff equation can be used to determine  $K$  at any other temperature.

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_{\text{rxn}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

- For a Temperature rise

$$T_2 > T_1 \quad \frac{1}{T_2} < \frac{1}{T_1} \quad \left( \frac{1}{T_2} - \frac{1}{T_1} \right) < 0$$

- For an Endothermic reaction ( $\Delta H_{\text{rxn}} > 0$ ), heat is added to system. The solution is warmer after reaction attains equilibrium

$$-\frac{\Delta H_{\text{rxn}}}{R} < 0$$

The overall term is "negative"  
(neg term \* pos term)

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_{\text{rxn}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) > 0$$

The overall term is "positive"  
(neg term \* neg term)

$$\ln \frac{K_2}{K_1} > 0; \text{ thus, } K_2 > K_1$$

Increasing the temperature increases the equilibrium constant,  $K$

# Van't Hoff Equation

- For an Exothermic reaction ( $\Delta H_{\text{rxn}} < 0$ ), The reaction releases heat while attaining equilibrium, warming the solution; thus same temperature conditions as in Endothermic reaction

$$T_2 > T_1 \quad \frac{1}{T_2} < \frac{1}{T_1} \quad \left( \frac{1}{T_2} - \frac{1}{T_1} \right) < 0$$

$$- \frac{\Delta H_{\text{rxn}}}{R} > 0$$

The overall term is "positive"  
(neg term \* neg term)

$$\ln \frac{K_2}{K_1} = - \frac{\Delta H_{\text{rxn}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) < 0$$

The overall term is "negative"  
(pos term \* neg term)

$$\ln \frac{K_2}{K_1} < 0; \text{ thus, } K_2 < K_1$$

Decreasing the temperature decreases the equilibrium constant, K

# Practice Problem

How does an increase in temperature affect the equilibrium concentration of the underlined substance and  $K$  for each of the following reactions?



Adding more heat to Exothermic reaction increases temperature, causing  $\text{Ca(OH)}_2$  to decompose forming  $\text{CaO}$  &  $\text{H}_2\text{O}$

System absorbs the additional heat, shifting reaction to left, decreasing  $[\text{Ca(OH)}_2]$  and decreasing the value of  $K$



Since the net reaction is "Endothermic", i.e.,  $\text{Ca(CO}_3\text{)}$  requires heat to decompose into  $\text{CaO}$  &  $\text{CO}_2$ , any heat added to the system forces the reaction even further to the right producing more  $\text{CO}_2$ ; increasing the value of  $K$



Adding heat to an Endothermic reaction shifts reaction to the right decreasing the  $[\text{SO}_2]$ ; increasing the value of  $K$

# Le Chatelier's Principle

## Effects of Various Disturbances on a System at Equilibrium

Disturbance	Net Direction of Reaction	Effect on Value of $K$
Concentration		
Increase [reactant]	Toward formation of product	None
Decrease [reactant]	Toward formation of reactant	None
Increase [product]	Toward formation of reactant	None
Decrease [product]	Toward formation of product	None
Pressure		
Increase $P$ (decrease $V$ )	Toward formation of fewer moles of gas	None
Decrease $P$ (increase $V$ )	Toward formation of more moles of gas	None
Increase $P$ (add inert gas, no change in $V$ )	None; concentrations unchanged	None
Temperature		
Increase $T$	Toward absorption of heat	Increases if $\Delta H_{\text{rxn}}^{\circ} > 0$ Decreases if $\Delta H_{\text{rxn}}^{\circ} < 0$
Decrease $T$	Toward release of heat	Increases if $\Delta H_{\text{rxn}}^{\circ} < 0$ Decreases if $\Delta H_{\text{rxn}}^{\circ} > 0$
Catalyst added	None; forward and reverse equilibrium attained sooner; rates increase equally	None

# Practice Problem

A 1.500 L reaction vessel was filled with 1.50 mol of  $\text{PCl}_5$  at  $100\text{ }^\circ\text{C}$ . If, at equilibrium, the vessel contains 0.33 mol of  $\text{PCl}_5$ , what is the equilibrium constant of the following reaction at this temperature?



Initial  $[\text{PCl}_5] = 1.50 \text{ mol} / 1.500 \text{ L} = 1.00 \text{ mol/L}$  (1.00 M)

$[\text{PCl}_5]$  at Equilibrium =  $0.33 \text{ mol} / 1.500 \text{ L} = 0.22 \text{ M} = 1.00 - X$

$X = 1.00 - 0.22 = 0.78 \text{ mol/L}$

	$\text{PCl}_3$	$\text{Cl}_2$	$\text{PCl}_5$
Initial $C_i$	$[\text{PCl}_3]_i = 0.0$	$[\text{Cl}_2]_i = 0.0$	$[\text{PCl}_5]_i = 1.00$
Conc Change( $\Delta$ )	+X	+X	-X
Final $C_f$	X	X	$1.00 - X$
Equilibrium Values	$[\text{PCl}_3] = 0.78$	$[\text{Cl}_2] = 0.78$	$[\text{PCl}_5] = 0.22$

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{0.22}{0.78 \times 0.78} = 0.36$$

# Practice Problem

If the initial concentrations of  $\text{PCl}_3$  and  $\text{Cl}_2$  in the previous reaction are 0.10 M, what are the expected equilibrium concentrations of all species at 100 °C?



$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{X}{(0.1 - X) \times (0.1 - X)} = .36$$

$$X = 0.36 \times (0.1 - X)^2$$

$$X = 0.36 \times (0.01 - 0.2X + X^2)$$

$$X = 0.0036 - 0.072X + 0.36X^2$$

$$0.0 = 0.0036 - 1.072X + 0.36X^2 \quad (\text{Quadratic Equation})$$

$$X_1 = 2.97744; \quad X_2 = 0.003362 \quad (\text{Eliminate } X_1 - \text{can't be } > 0.1)$$

	$\text{PCl}_3$	$\text{Cl}_2$	$\text{PCl}_5$
Initial $C_i$	$[\text{PCl}_3]_i = 0.10$	$[\text{Cl}_2]_i = 0.10$	$[\text{PCl}_5]_i = 0.0$
Conc Change ( $\Delta$ )	- X	- X	+ X
Final $C_f$	0.10 - X	0.10 - X	X
Equilibrium Values	$[\text{PCl}_3]_f = 0.097 \text{ M}$	$[\text{Cl}_2]_f = 0.097 \text{ M}$	$[\text{PCl}_5]_f = 0.0034 \text{ M}$



# Practice Problem

The value of  $K_c$  for the following reaction at  $900\text{ }^\circ\text{C}$  is 0.28. What is  $K_p$  at this temperature?



**Determining  $\Delta n_{\text{gas}}$**   $(1 + 2) - (1 + 4) = 3 - 5 = -2$

$$K_p = K_c (RT)^{\Delta n_{\text{gas}}} = K_c (RT)^{-2}$$

$$K_p = 0.28 \times \left( 0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times (900^\circ\text{C} + 273.15)^\circ\text{K} \right)^{-2}$$

$$K_p = 0.28 \times (96.3156)^{-2}$$

$$K_p = 0.28 \times 9.8141$$

$$K_p = 2.75$$

# Practice Problem

The equilibrium constant for the following reaction at 450 °C is 0.159. If at some point in the reaction, the concentrations of N<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub> are found to be 0.062 M, 0.045 M and 0.011 M, respectively, in what direction is the reaction proceeding?



$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$Q_c = \frac{(0.011\text{M})^2}{(0.062\text{M}) \times (0.045\text{M})^3} = \frac{1.21 \times 10^{-4}}{6.2 \times 10^{-2} \times 9.113 \times 10^{-5}}$$

$$Q_c = 21$$

$$Q(21) \gg K(0.159)$$

**The numerator (products) must decrease with the subsequent reformation of reactants, until  $Q_c = K_c$**

**Thus, the reaction proceeds to the left (toward the reactants)**

# Practice Problem

The initial concentrations of  $\text{PCl}_3$  and  $\text{Cl}_2$  in a 2.50 L reaction vessel at 100 °C are 0.67 M. At equilibrium 0.900 mol of  $\text{PCl}_5$  is present. What is the equilibrium constant ( $K_c$ ) for the reaction at 100 °C?



$$[\text{PCl}_5]_f = \frac{0.9 \text{ mol}}{2.5 \text{ L}} = 0.36 \text{ mol / L(M)} = X$$

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{X}{(0.67 - X)(0.67 - X)} = \frac{0.36}{(0.67 - 0.36)(0.67 - 0.36)} = \frac{0.36}{0.0961}$$

$$K_c = 3.75$$

	$\text{PCl}_3$	$\text{Cl}_2$	$\text{PCl}_5$
Initial $C_i$	$[\text{PCl}_3]_i = .67\text{M}$	$[\text{Cl}_2]_i = 0.67\text{M}$	$[\text{PCl}_5]_i = 0.0$
Conc Change ( $\Delta$ )	- X	- X	+ X
Final $C_f$	$0.67 - X$	$0.67 - X$	$0.9/2.5 \text{ M} = 0.36\text{M} = X$
Equilibrium Values	$[\text{PCl}_3]_f = 0.31\text{M}$	$[\text{Cl}_2]_f = 0.31\text{M}$	$[\text{PCl}_5]_f = 0.36\text{M}$

# Practice Problem

A 1.00 L reaction vessel at 70° C was initially filled with 0.20 M SO<sub>2</sub> and 0.010 M O<sub>2</sub>. At equilibrium, 0.0145 mol of SO<sub>3</sub> is present. What is the equilibrium constant for the reaction at 70° C?



$$[\text{SO}_3] = 0.0145 \text{ mol} / 1.0\text{L} = 0.0145 \text{ M} = 2X$$

	SO <sub>2</sub>	O <sub>2</sub>	SO <sub>3</sub>
Initial C <sub>i</sub>	[SO <sub>2</sub> ] <sub>i</sub> = 0.20M	[O <sub>2</sub> ] <sub>i</sub> = 0.01M	[SO <sub>3</sub> ] <sub>i</sub> = 0.0
Δ	- 2X	- X	+ 2X
Final C <sub>f</sub>	0.20 - 2X	0.01 - X	0.0145/1.0 = 0.0145 M = 2X
	0.20-0.0145	0.01 - 0.00725	X = 0.00725
Equilibrium Values	[SO <sub>2</sub> ] <sub>f</sub> =0.1855 M	[O <sub>2</sub> ] <sub>f</sub> = 0.00275M	[SO <sub>3</sub> ] <sub>f</sub> = 0.0145 M

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(0.0145)^2}{(0.1855)^2 \times (0.00275)} = \frac{0.00021025}{(0.03441) \times (0.00275)}$$

$$K_c = 2.2$$

# Practice Problem

If the initial concentration of  $\text{N}_2\text{O}_4$  in a reaction vessel is 0.030 M, what is the percent dissociation of  $\text{N}_2\text{O}_4$  at equilibrium at 25 °C?



$$K_c = 0.125 = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(2X)^2}{0.030 - X}$$

$$(2X)^2 = (0.125) \times (0.030 - X)$$

$$4X^2 + 0.125X - 0.00375 = 0$$

$$X_1 = 0.01875$$

$$X_2 = -0.05 \text{ (neg; conc not valid)}$$

$$[\text{N}_2\text{O}_4]_i = 0.030$$

$$[\text{N}_2\text{O}_4]_f = 0.01125$$

	$\text{N}_2\text{O}_4$	$\text{NO}_2$
Initial $C_i$	$[\text{N}_2\text{O}_4]_i = 0.030\text{M}$	$[\text{NO}_2]_i = 0.0$
$\Delta$	- X	+2X
Final $C_f$	0.030 - X	2X
	0.030 - 0.01875	2 x 0.01875
Equilibrium Values	$[\text{N}_2\text{O}_4]_f = 0.01125 \text{ M}$	$[\text{NO}_2]_f = 0.0375 \text{ M}$

$$\% \text{ Dissociation} = \left( 1 - \frac{0.01125}{0.030} \right) \times 100 = 62.5\%$$

# Practice Problem

For the reaction below, the initial partial pressures of  $\text{H}_2$ ,  $\text{I}_2$  and  $\text{HI}$  were 0.20 atm, 0.20 atm, and 0.50 atm, respectively.

If the equilibrium constant,  $K_p$ , for the reaction is 129 at 500 K, what are the equilibrium partial pressures of all chemical species in the reaction at 500 K?



$$K_p = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$129 = \frac{(0.5 + 2X)^2}{(0.2 - X)(0.2 - X)} = \frac{(0.5 + 2X)^2}{(0.2 - X)^2} = \frac{(0.5 + 2X)}{(0.2 - X)}$$

$$129 \times (0.2 - X) = 0.5 + 2X$$

$$25.80 - 129X = 0.5 + 2X$$

$$131X = 25.3$$

$$X = 0.193$$

	$\text{H}_2$	$\text{I}_2$	$\text{HI}$
Initial $C_i$	$[\text{H}_2]_i = 0.20 \text{ atm}$	$[\text{I}_2]_i = 0.20 \text{ atm}$	$[\text{HI}]_i = 0.50 \text{ atm}$
$\Delta$	- X	- X	+ 2X
Final $C_f$	$0.20 - X$	$0.2 - X$	$0.5 + 2X$
	$0.20 - 0.193$	$0.2 - 0.193$	$0.5 + 2 \times 0.193$
Equilibrium Values	$[\text{H}_2]_f = 0.0070 \text{ atm}$	$[\text{I}_2]_f = 0.0070 \text{ atm}$	$[\text{HI}]_f = 0.88 \text{ atm}$

# Practice Problem

What would  $Q_c$  be if the pressure of the container increased by a factor of 1.791 for the following reaction?



$$K_c = \frac{[\text{H}_2\text{S}]_e^2 [\text{CH}_4]_e}{[\text{CO}]_e [\text{H}_2]_e^3} \quad (\text{Equilibrium})$$

$$Q_c = \frac{(1.791 \times [\text{H}_2\text{S}]_e)^2 (1.791 \times [\text{CH}_4]_e)}{(1.791 [\text{CO}]_e) (1.791 [\text{H}_2]_e)^3}$$

$$Q_c = \frac{(1.791)^3}{(1.791)^4} \times K_c$$

$$Q_c = \frac{1}{(1.791)} \times 13.29$$

$$Q_c = 7.420 \quad (\text{More Product must be formed until } Q_c = K_c)$$

The equilibrium state is disturbed by the pressure increase, which decreases volume and increases the concentration of reactants

Each equilibrium concentration is altered by the “1.791 factor” resulting in new initial concentrations used to define  $Q_c$

# Equation Summary

“Reaction Quotient”



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

At equilibrium:  $\text{rate}_{(\text{fwd})} = \text{rate}_{(\text{rev})}$

$$Q = \text{reaction at any time} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = K = \text{reaction at equilibrium}$$

Multi-Step Reaction  $K_{\text{overall}} = K_1 \times K_2 \times K_3 \times \dots$

$$K_p = K_c (RT)^{\Delta n_{\text{gas}}}$$

$\Delta n_{\text{gas}} = \text{moles gaseous product} - \text{moles gaseous reactant}$

$$Q_c = \frac{P_C^2}{P_A^2 \times P_B} \times RT = Q_p (RT)$$

$P_C$  – Partial Press Product C  
 $P_A$  – Partial Press Reactant A  
 $P_B$  – Partial Press Reactant B



# Summary Equations

- Small  $K$  ( $< 0.001$ ) – The reaction forms very little Product
- Large  $K$  ( $> 1000$ ) – Reaction has gone to completion, with very little reactant remaining
- Intermediate  $K$  ( $\approx 0$ ) – Significant amounts of reactant remain and significant amounts of product have formed

- $Q < K$  – The denominator (reactants) is larger than the numerator (products)

The reaction will continue to the product side until the numerator and denominator are equal (equilibrium has been reached) and  $Q = K$

- $Q > K$  – The products will decrease and the reactants will increase until equilibrium is reached
- $Q = K$  – The reactant and product concentrations have reached equilibrium values. The forward and reverse reactions will continue, but at the same rate

# Summary Equations

- Effect of Temperature on the Equilibrium Constant ( $K$ )

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_{\text{rxn}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

- Effect of Temperature on the rate Constant ( $k$ )

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad \Delta E_{a(\text{fwd})} - \Delta E_{a(\text{rev})} = \Delta H^\circ_{\text{rxn}}$$

- Effect of Temperature on the Equilibrium Vapor Pressure

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad \Delta H_{\text{vap}} = \Delta H^\circ_{\text{rxn}} \quad \text{where } A_{(l)} \rightleftharpoons A_{(g)}$$