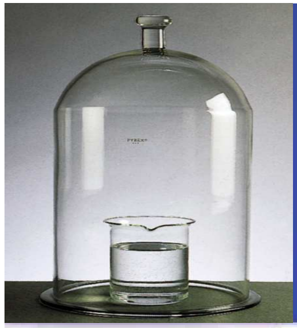
Chapter 13

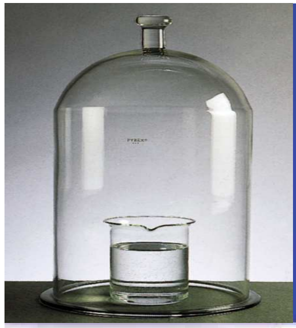
Chemical Equilibrium



Chapter 13 Preview

Chemical Equilibrium

- The Equilibrium condition and constant
  - Chemical equilibrium, reactions, constant expression
- Equilibrium involving Pressure
  - Chemical expressions involving gases
- Heterogeneous Equilibria
  - Application of equilibrium constant and its calculations for pressure and concentrations
- Le Châtellier's Principle
  - Effect of a change of concentration, pressure, and temperature on the reaction equilibrium



Introduction

Reactions that stop far short from completion and have concentrations of reactants and products remain constant with time has reached ***Chemical equilibrium.***

Equilibrium is a state in which there are no observable changes as time goes by.

Chemical equilibrium is achieved when:

- reaction is carried out in a closed vessel
- the concentrations of the reactants and products remain constant

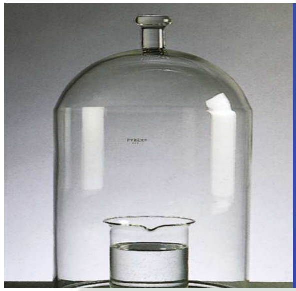
Types of Equilibria:

Physical equilibrium

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

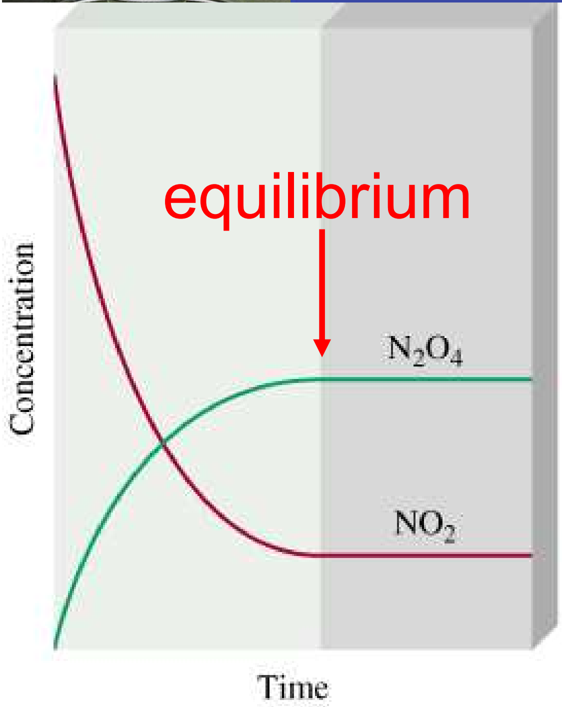
Chemical equilibrium

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

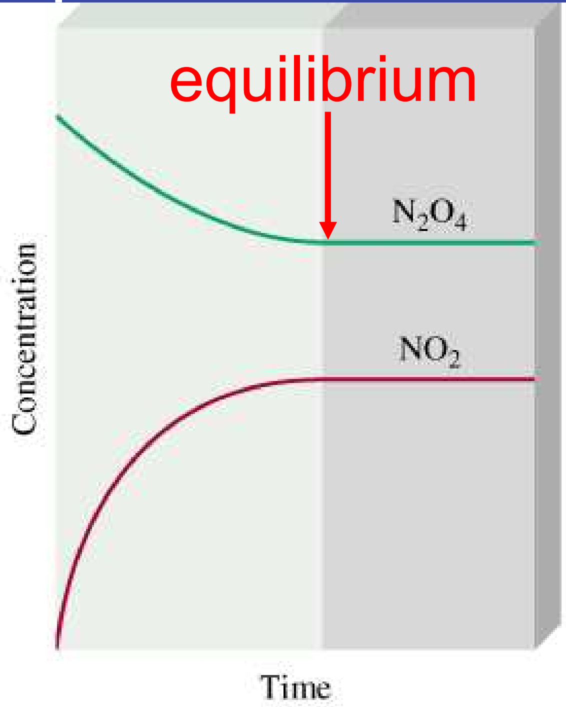


13.1 Equilibrium conditions and constant

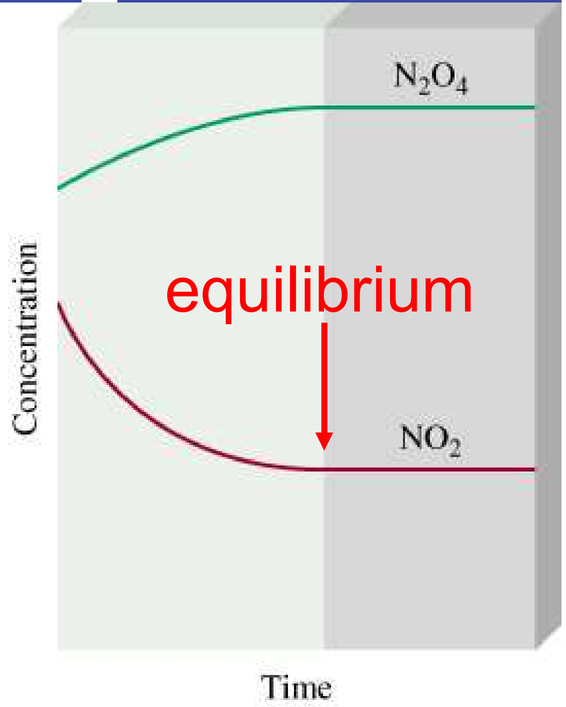
$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$



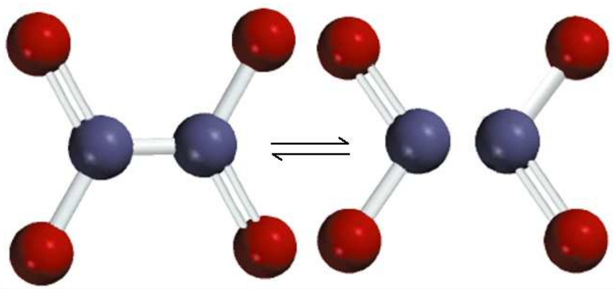
Start with NO_2

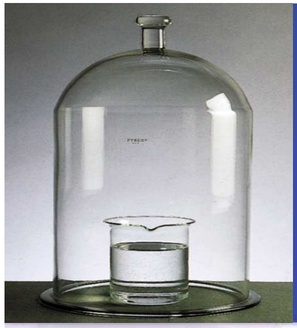


Start with N_2O_4



Start with NO_2 & N_2O_4





13.2 The Equilibrium constant

constant

The NO_2–N_2O_4 System at 25°C

Initial Concentrations (*M*)		Equilibrium Concentrations (*M*)		Ratio of Concentrations at Equilibrium	
$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

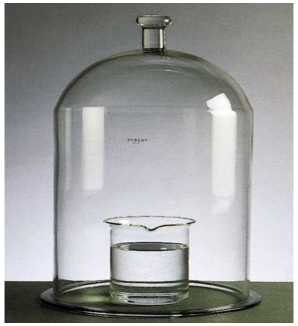
$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$$aA + bB \rightleftharpoons cC + dD$$

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

$$\boxed{\textbf{\textit{Law of Mass Action}}}$$

If $K >> 1$	Equilibrium Will	Lie to the right	Favor products
$K << 1$		Lie to the left	Favor reactants



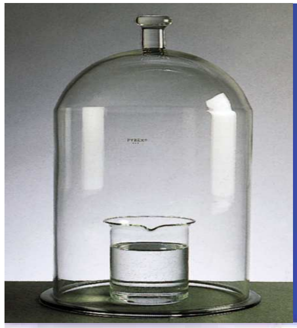
Homogenous equilibrium applies to reactions in which all reacting species **are in the same phase.**

$$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COO^-\ (aq) + H_3O^+\ (aq)$$

$$K'_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]} \qquad [H_2O] = \text{constant}$$

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = K'_c\,[H_2O]$$

General practice **not** to include units for the equilibrium constant.



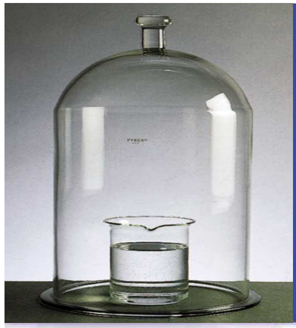
Review Question 1

Consider the chemical system

$$CO + Cl_2 \rightleftharpoons COCl_2;\ K = 4.6 \times 10^9\ \text{L/mol}.$$

How do the equilibrium concentrations of the reactants compare to the equilibrium concentration of the product?

1) They are much smaller.
2) They are much bigger.
3) They are about the same.
4) They have to be exactly equal.
5) You can't tell from the information given.



Review Question 2

Determine the equilibrium constant for the system $N_2O_4 \rightleftharpoons 2NO_2$ at 25°C. The concentrations are shown here:

$[N_2O_4] = 9.43 \times 10^{-2}$ M, $[NO_2] = 1.41 \times 10^{-2}$ M

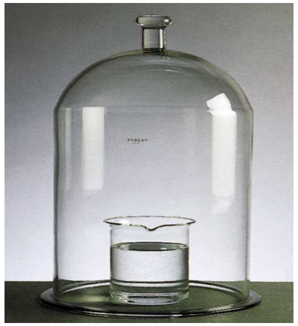
a) 0.150

b) 6.69

c) 474

d) 0.0224

e) 0.00211



13.3 The Equilibrium expression Involving Pressures

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$PV = nRT$$
$$P = (n/V)RT$$
$$P = CRT$$

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

In most cases

$$K_c \neq K_p$$

$$a\text{A}\,(g) + b\text{B}\,(g) \rightleftharpoons c\text{C}\,(g) + d\text{D}\,(g)$$

$$K_p = K_c(RT)^{\Delta n}$$

Δn = moles of gaseous products – moles of gaseous reactants

= $(c + d) - (a + b)$

The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $COCl_2$ (*g*) at 74^0C are [CO] = 0.012 *M*, [Cl_2] = 0.054 *M*, and [$COCl_2$] = 0.14 *M*. Calculate the equilibrium constants K_c and K_p.

$$CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g)$$

$$K_c = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.14}{0.012 \times 0.054} = 220$$

$$K_p = K_c(RT)^{\Delta n}$$

$\Delta n = 1 - 2 = -1$ $\quad$ $R = 0.0821$ $\quad$ $T = 273 + 74 = 347$ K

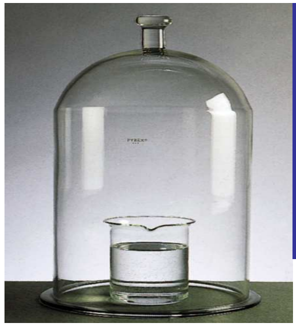
$$K_p = 220 \times (0.0821 \times 347)^{-1} = 7.7$$

The equilibrium constant K_p for the reaction

$$2NO_2\,(g) \rightleftharpoons 2NO\,(g) + O_2\,(g)$$

is 158 at 1000K. What is the equilibrium pressure of O_2 if the P_{NO} = 0.400 atm and P_{NO} = 0.270 atm?

$$K_p = \frac{P^2_{NO}\,P_{O_2}}{P^2_{NO_2}} \qquad P_{O_2} = K_p\frac{P^2_{NO_2}}{P^2_{NO}} \qquad P_{O_2} = 347 \text{ atm}$$



13.4 Heterogeneous Equilibria

Heterogenous equilibrium applies to reactions in which reactants and products **are in different phases.**

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K'_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

$[CaCO_3]$ = constant
$[CaO]$ = constant

$$K_c = [CO_2] = K'_c \times \frac{[CaCO_3]}{[CaO]}$$

$$K_p = P_{CO_2}$$

The concentration of **solids** and **pure liquids** are not included in the expression for the equilibrium constant.

Consider the following equilibrium at 295 K:

$$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$$

The partial pressure of each gas is 0.265 atm. Calculate K_p and K_c for the reaction?

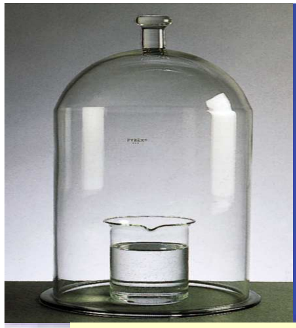
$$K_p = P_{NH_3} P_{H_2S} = 0.265 \times 0.265 = 0.0702$$

$$K_p = K_c(RT)^{\Delta n}$$

$$K_c = K_p(RT)^{-\Delta n}$$

$$\Delta n = 2 - 0 = 2 \qquad T = 295\ \text{K}$$

$$K_c = 0.0702 \times (0.0821 \times 295)^{-2} = 1.20 \times 10^{-4}$$



General Relations

Chemical Kinetics and Chemical Equilibrium

$$A + 2B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} AB_2$$

$\text{rate}_f = k_f\,[A][B]^2$

$\text{rate}_r = k_r\,[AB_2]$

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

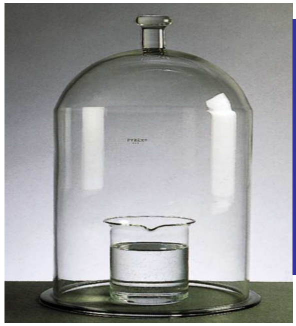
$$k_f\,[A][B]^2 = k_r\,[AB_2]$$

$$\frac{k_f}{k_r} = K_c = \frac{[AB_2]}{[A][B]^2}$$

The equilibrium constant of reversible reaction is the reciprocal of the original equilibrium constant.

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g) \qquad 2NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3} \qquad K' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K} = 216$$



General Relations

The equilibrium constant of the sum of two or more reactions is given by the product of the equilibrium constants of the individual reactions.

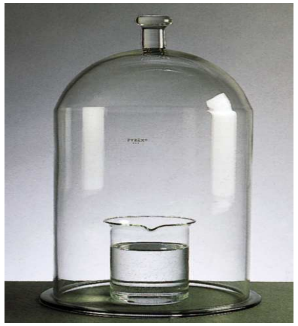
$$A + B \rightleftharpoons \cancel{C} + \cancel{D} \qquad K_c^{\prime}$$

$$\cancel{C} + \cancel{D} \rightleftharpoons E + F \qquad K_c^{\prime\prime}$$

$$A + B \rightleftharpoons E + F \qquad K_c$$

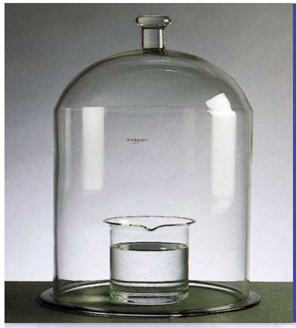
$$K_c^{\prime} = \frac{[C][D]}{[A][B]} \qquad K_c^{\prime\prime} = \frac{[E][F]}{[C][D]}$$

$$K_c = \frac{[E][F]}{[A][B]} \qquad K_c = K_c^{\prime} \times K_c^{\prime\prime}$$



Writing Equilibrium Constant Expressions

- The concentrations of the reacting species in the condensed phase are expressed in *M*. In the gaseous phase, the concentrations can be expressed in *M* or in atm.
- The concentrations of pure solids, pure liquids and solvents do not appear in the equilibrium constant expressions.
- The equilibrium constant is a dimensionless quantity.
- In quoting a value for the equilibrium constant, you must specify the balanced equation and the temperature.
- If a reaction can be expressed as a sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.



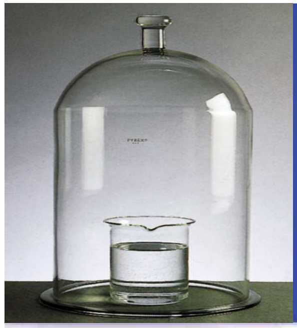
13.5 Application of the Equilibrium Constant

For ***nonequilibrium*** conditions, the expression having the same form as K_c or K_p is called the **reaction quotient**, $\boldsymbol{Q_c}$ or $\boldsymbol{Q_p}$

$$aA + bB + \cdots \rightarrow gG + hH + \cdots$$

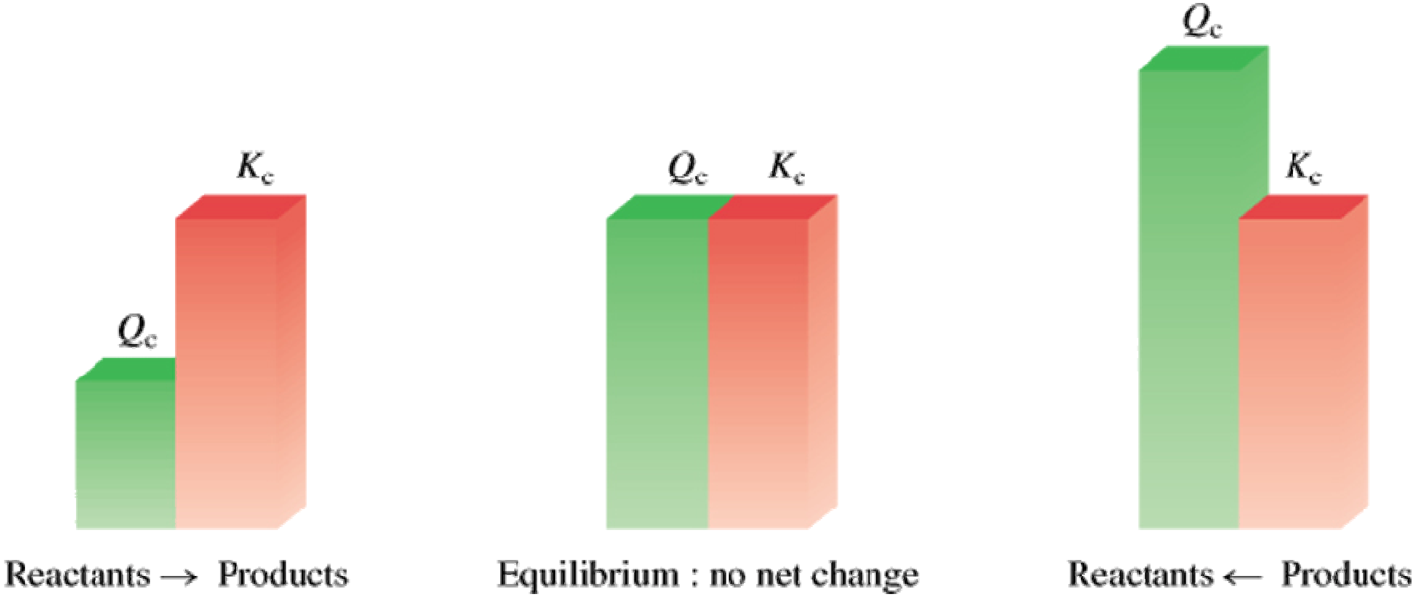
$$Q_c = \frac{[C]^c[D]^d}{[G]^g[H]^h}$$

The reaction quotient is useful for predicting the *direction in which a net change must occur* to establish equilibrium



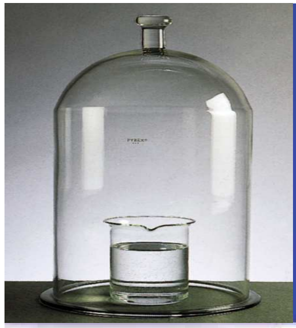
13.5 Application of the Equilibrium Constant

The ***reaction quotient (Q_c)*** is calculated by substituting the initial concentrations of the reactants and products into the equilibrium constant expression.



IF

- $Q_c = K_c$ the system is at equilibrium
- $Q_c < K_c$ system proceeds from left to right to reach equilibrium
- $Q_c > K_c$ system proceeds from right to left to reach equilibrium

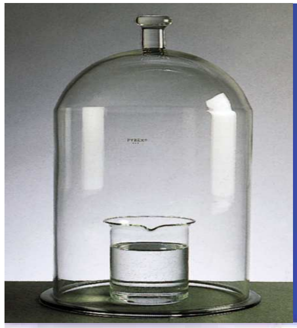


Question

The reaction quotient for a system is 7.2×10^2. If the equilibrium constant for the system is 36, what will happen as equilibrium is approached?

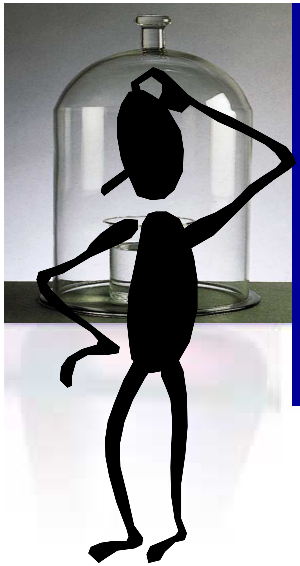
a) **There will be a net gain in product.**
b) **There will be a net gain in reactant.**
c) **There will be a net gain in both product and reactant.**
d) **There will be no net gain in either product or reactant.**
e) **The equilibrium constant will decrease until it equals the reaction quotient.**

ANS: b) **SECTION:** 13.5 **LEVEL:** medium



Calculating Equilibrium Concentrations and Pressure

1. Calculating Q will help in determining the direction of change (x) to establish the equilibrium
2. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown *x*, which represents the change in concentration.
3. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for *x*.
4. Having solved for *x*, calculate the equilibrium concentrations of all species.



At 1280^0C the equilibrium constant (K_c) for the reaction

$$Br_2\,(g) \rightleftharpoons 2Br\,(g)$$

is 1.1×10^{-3}. If the initial concentrations are $[Br_2] = 0.063\ M$ and $[Br] = 0.012\ M$, calculate the concentrations of these species at equilibrium.

$$Q = \frac{[Br^-]^2}{[Br_2]} = \frac{0.012^2}{0.063} = 2.3\times 10^{-3} > K_c$$

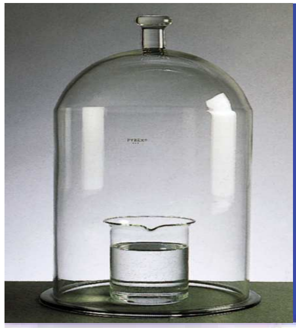
Q>K the system will shift to the left,
using "x" as the change in concentration of Br^-

ICE

	$Br_2\,(g) \rightleftharpoons$	$2Br\,(g)$
Initial (M)	0.063	0.012
Change (M)	$+x$	$-2x$
Equilibrium (M)	$0.063 + x$	$0.012 - 2x$

$$K_c = \frac{[Br]^2}{[Br_2]} \qquad K_c = \frac{(0.012 - 2x)^2}{0.063 + x} = 1.1 \times 10^{-3}$$

Solve for x



$$K_c = \frac{(0.012 - 2x)^2}{0.063 + x} = 1.1 \times 10^{-3}$$

$$4x^2 - 0.048x + 0.000144 = 0.0000693 + 0.0011x$$

$$4x^2 + 0.0469x + 0.0001044 = 0$$

$$ax^2 + bx + c = 0 \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

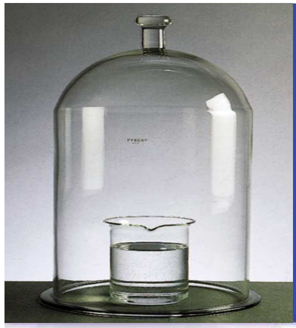
$$x = 8.74 \times 10^{-3} \qquad x = 2.98 \times 10^{-3}$$

$$Br_2\,(g) \rightleftharpoons 2Br\,(g)$$

	$Br_2\,(g)$	$2Br\,(g)$
Initial (M)	0.063	0.012
Change (M)	$+x$	$-2x$
Equilibrium (M)	$0.063 + x$	$0.012 - 2x$

At equilibrium, [Br] = $0.012 + 2x = \cancel{-5.48 \times 10^{-3}}\ M$ or $6.025 \times 10^{-3}\ M$

At equilibrium, [Br_2] = $0.063 + x = 0.066\ M$



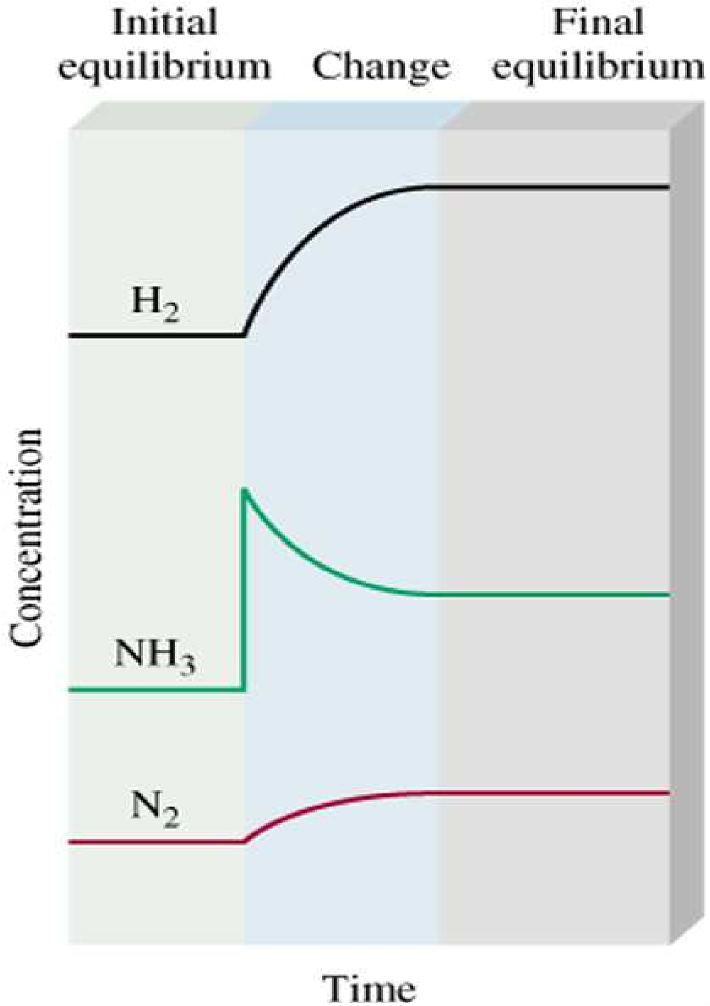
13.7 Le Châtelier's Principle

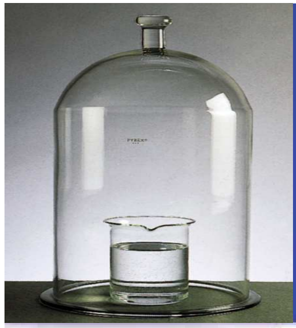
If an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.

- Changes in Concentration

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

Equilibrium shifts left to offset stress ← Add NH_3





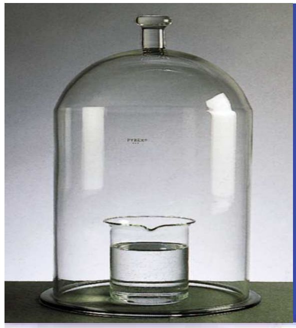
13.7 Le Châtelier's Principle

- Changes in Concentration continued

Remove Add   Remove Add

$$aA + bB \rightleftharpoons cC + dD$$

<u>**Change**</u>	<u>**Shifts the Equilibrium**</u>
Increase concentration of product(s)	left
Decrease concentration of product(s)	right
Increase concentration of reactant(s)	right
Decrease concentration of reactant(s)	left

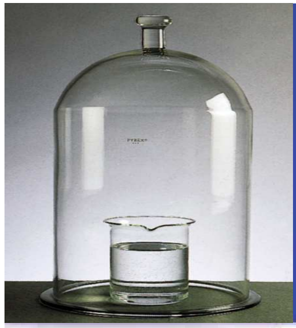


13.7 Le Châtelier’s Principle

- Changes in Volume and Pressure

$$A\ (g) + B\ (g) \rightleftharpoons C\ (g)$$

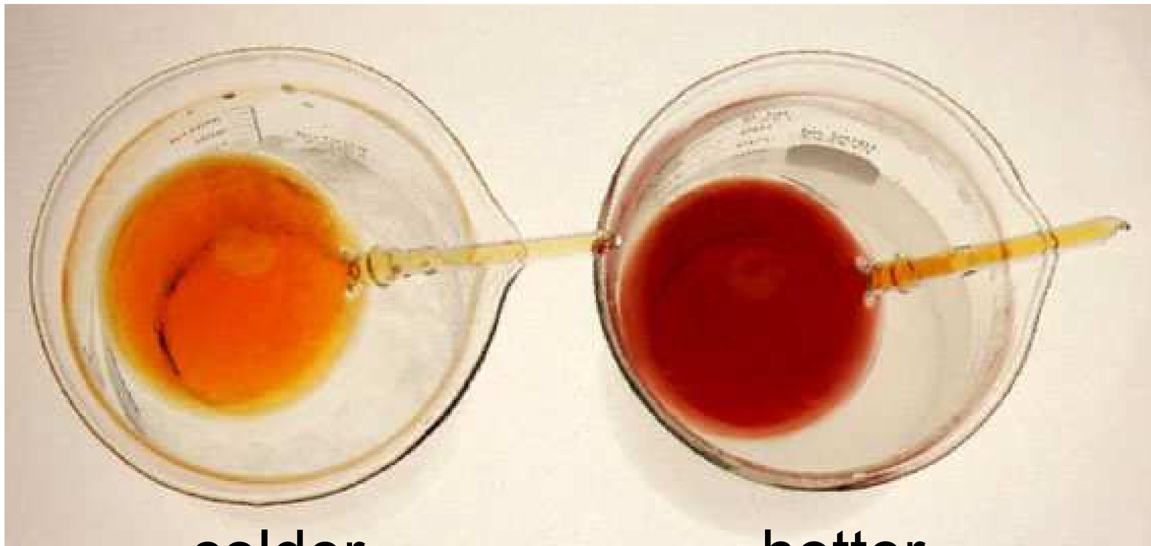
Change	Shifts the Equilibrium
Increase pressure	Side with fewest moles of gas
Decrease pressure	Side with most moles of gas
Increase volume	Side with most moles of gas
Decrease volume	Side with fewest moles of gas



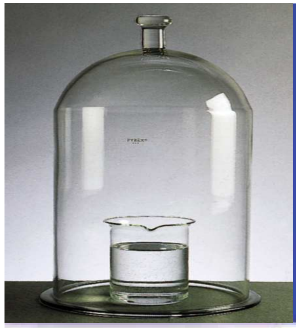
13.7 Le Châtelier's Principle

- Changes in Temperature

Change	Exothermic Rx	Endothermic Rx
Increase temperature	*K* decreases	*K* increases
Decrease temperature	*K* increases	*K* decreases

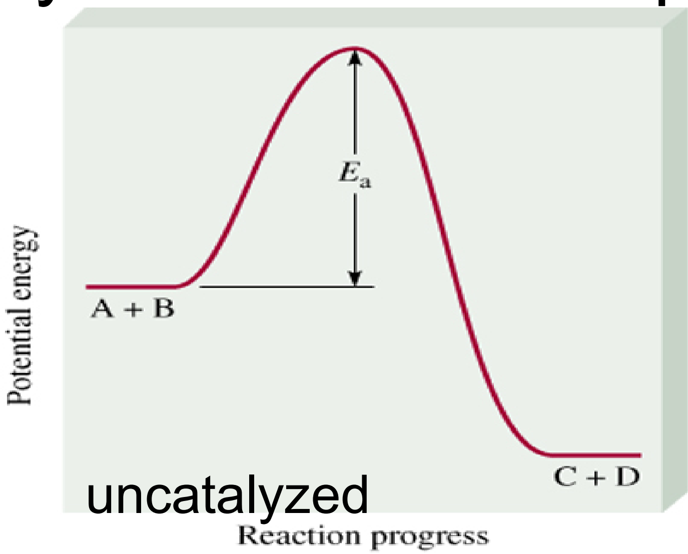


colder hotter

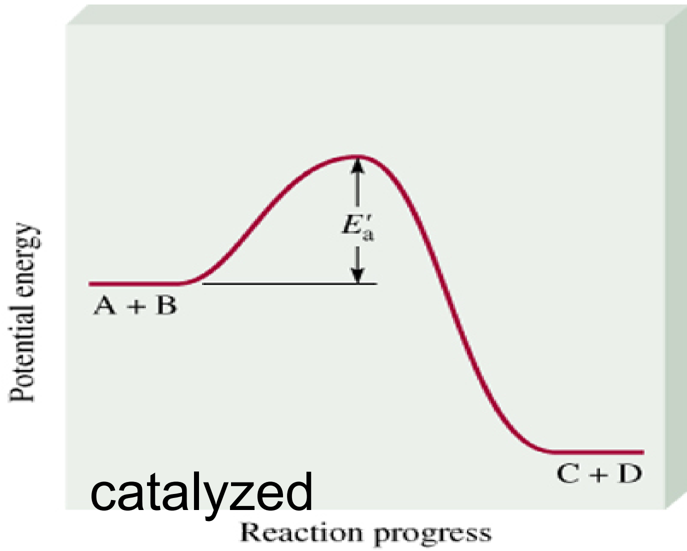


13.7 Le Châtelier's Principle

- Adding a Catalyst
  - does not change K
  - does not shift the position of an equilibrium system
  - system will reach equilibrium sooner



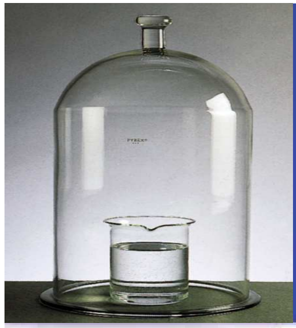
uncatalyzed



catalyzed

Catalyst lowers E_a for **both** forward and reverse reactions.

Catalyst does not change equilibrium constant or shift equilibrium.



13.7 Le Châtelier's Principle

Change	Shift Equilibrium	Change Equilibrium Constant
Concentration	yes	no
Pressure	yes	no
Volume	yes	no
Temperature	yes	yes
Catalyst	no	no

Chemistry In Action

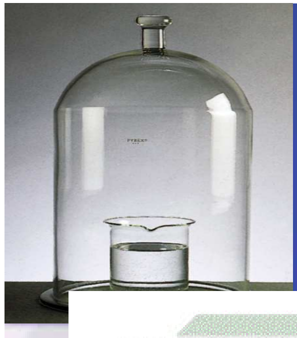
Life at High Altitudes and Hemoglobin Production

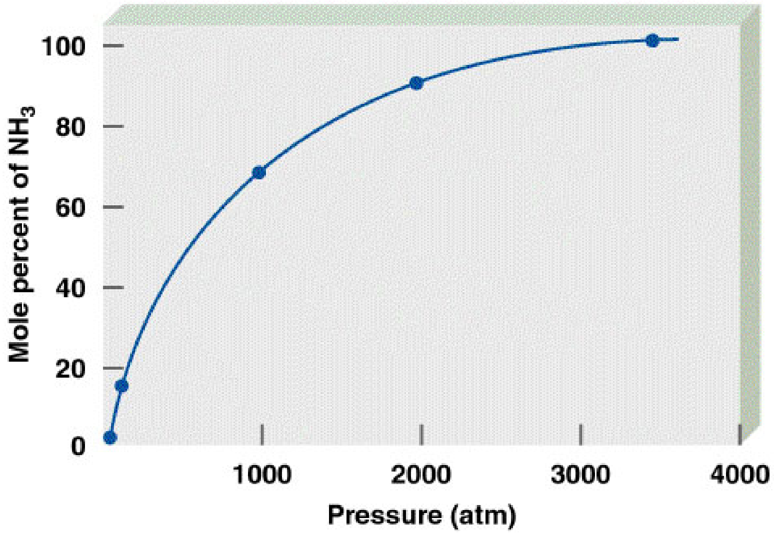
$$Hb\ (aq) + O_2\ (aq) \rightleftharpoons HbO_2\ (aq)$$

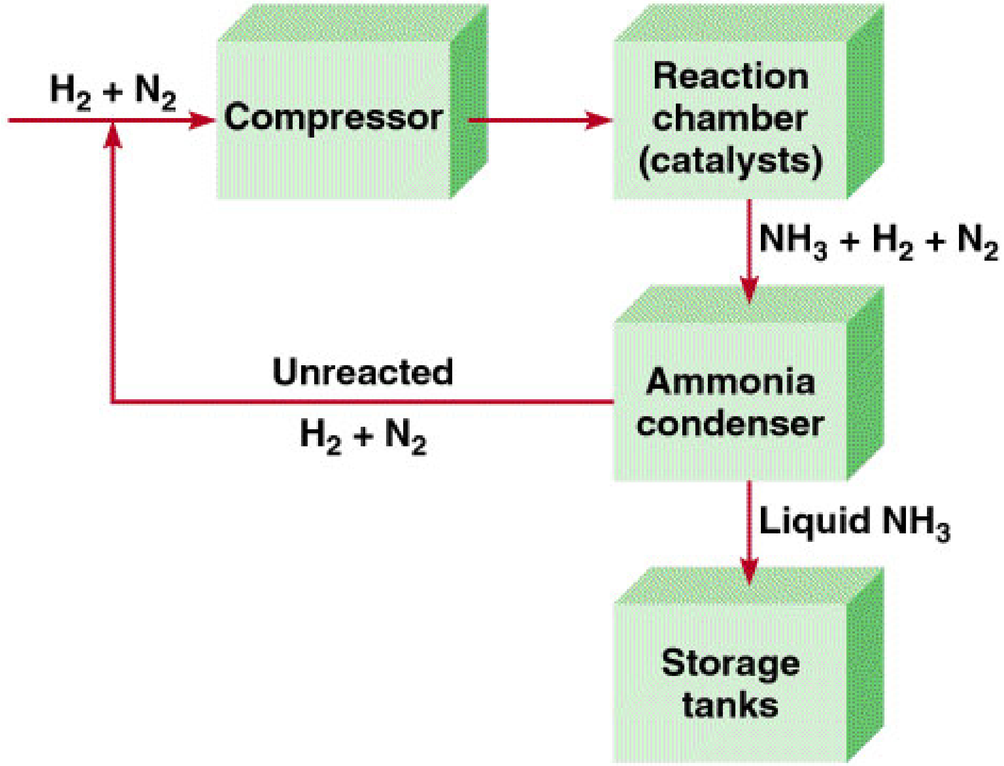
$$K_c = \frac{[HbO_2]}{[Hb][O_2]}$$

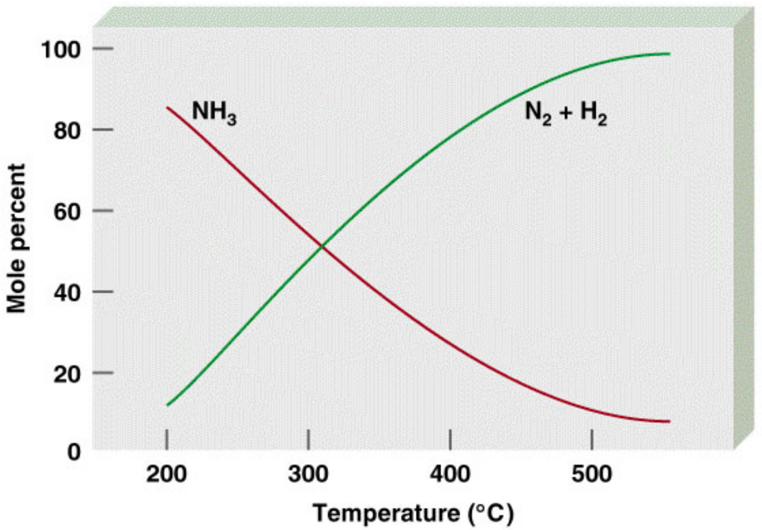
Chemistry In Action: The Haber Process

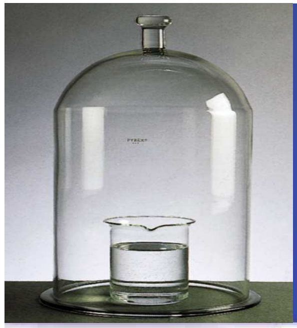
$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) \quad \Delta H^0 = -92.6\ \text{kJ/mol}$$











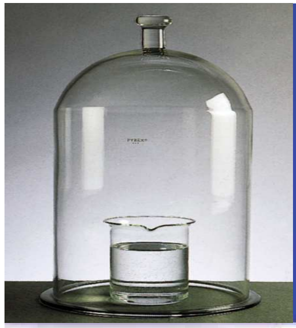
QUESTION

Consider the following equilibrium:

$$4NH_3(g) + 50_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$$

What would happen to the system if oxygen were added?

1) More ammonia would be produced.
2) More oxygen would be produced.
3) The equilibrium would shift to the right.
4) The equilibrium would shift to the left.
5) Nothing would happen.



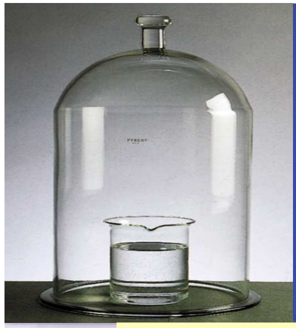
QUESTION

Consider the following system at equilibrium:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92.94 \text{ kJ}$$

Which of the following changes will shift the equilibrium to the right?

a. Increasing the temperature
b. Decreasing the temperature
c. Increasing the volume
d. Decreasing the volume
e. Removing some NH_3
f. Adding some NH_3
g. Removing some N_2
h. Adding some N_2



Review Questions

The equilibrium constant of the following reaction is 2.18 x 106

$$H_2 + Br_2 \rightleftharpoons 2HBr$$

What are the equilibrium concentrations of all the species if the starting concentration of HBr was 0.267 M.

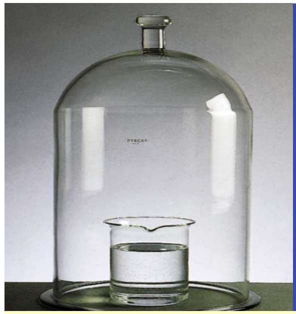
	H_2	Br_2	$2HBr$
Initial (M):	0	0	0.267
Change (M):	$+x$	$+x$	$-2x$
Equilibrium (M):	x	x	$(0.267 - 2x)$

$$K_c = \frac{(0.267 - 2x)^2}{x^2} = 2.18 \times 10^6 \Rightarrow \frac{0.267 - 2x}{x} = 1.48 \times 10^3 \Rightarrow x = 1.80 \times 10^{-4}$$

The equilibrium concentrations are:

$$\mathbf{[H_2] = [Br_2] = 1.80 \times 10^{-4}\ \mathit{M}}$$

$$\mathbf{[HBr] = 0.267 - 2(1.80 \times 10^{-4}) = 0.267\ \mathit{M}}$$



Problem # 42 (or 44 Ed.6)

Starting with 4.0 mole of NH3 in 2.0 L container. After dissociation as given below, 2.0 mole remains. What is the K for this reaction

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \qquad K = \frac{[N_2]^2[H_2]^3}{[NH_3]^2}$$

	$2\,NH_3(g)$		$N_2(g)$	$3\,H_2(g)$
Initial	4.0 mol/2.0 L		0	0

Let $2x$ mol/L of NH_3 react to reach equilibrium

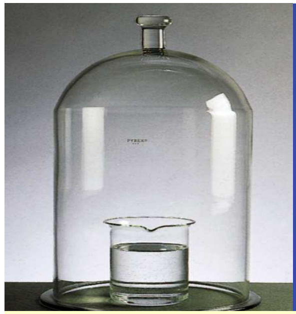
Change	$-2x$	$\rightarrow$	$+x$	$+3x$
Equil.	$2.0 - 2x$		x	$3x$

From the problem:

$$[NH_3]_e = 2.0\text{ mol}/2.0\text{ L} = 1.0\,M = 2.0 - 2x,\quad x = 0.50\,M$$

$$[N_2] = x = 0.50\,M;\quad [H_2] = 3x = 3(0.50\,M) = 1.5\,M$$

$$K = \frac{[N_2]^2[H_2]^3}{[NH_3]^2} = \frac{(0.50)(1.5)^3}{(1.0)^2} = 1.7$$



Problem # 51

At 35 °C, K = 1.6 x 10^{-5} for the following reaction. Calculate the concentration of all the species, if 1.0 mol of NOCl and 1.0 mole of NO are mixed in 1.0 L flask.

	$2\,NOCl(g)$	$\rightleftharpoons$	$2\,NO(g)$ +	$Cl_2(g)$
Initial	1.0 M		1.0 M	0
	$2x$ mol/L of NOCl reacts to reach equilibrium			
Change	$-2x$	$\rightarrow$	$+2x$	$+x$
Equil.	$1.0 - 2x$		$1.0 + 2x$	x

$$1.6 \times 10^{-5} = \frac{(1.0+2x)^2(x)}{(1.0-2x)^2} = \frac{(1.0)^2(x)}{(1.0)^2} \quad \text{(assuming } 2x << 1.0)$$

$x = 1.6 \times 10^{-5}$; Assumptions are great ($2x$ is 3.2×10^{-3} % of 1.0).

$[Cl_2] = 1.6 \times 10^{-5}$ M and $[NOCl] = [NO] = 1.0$ M