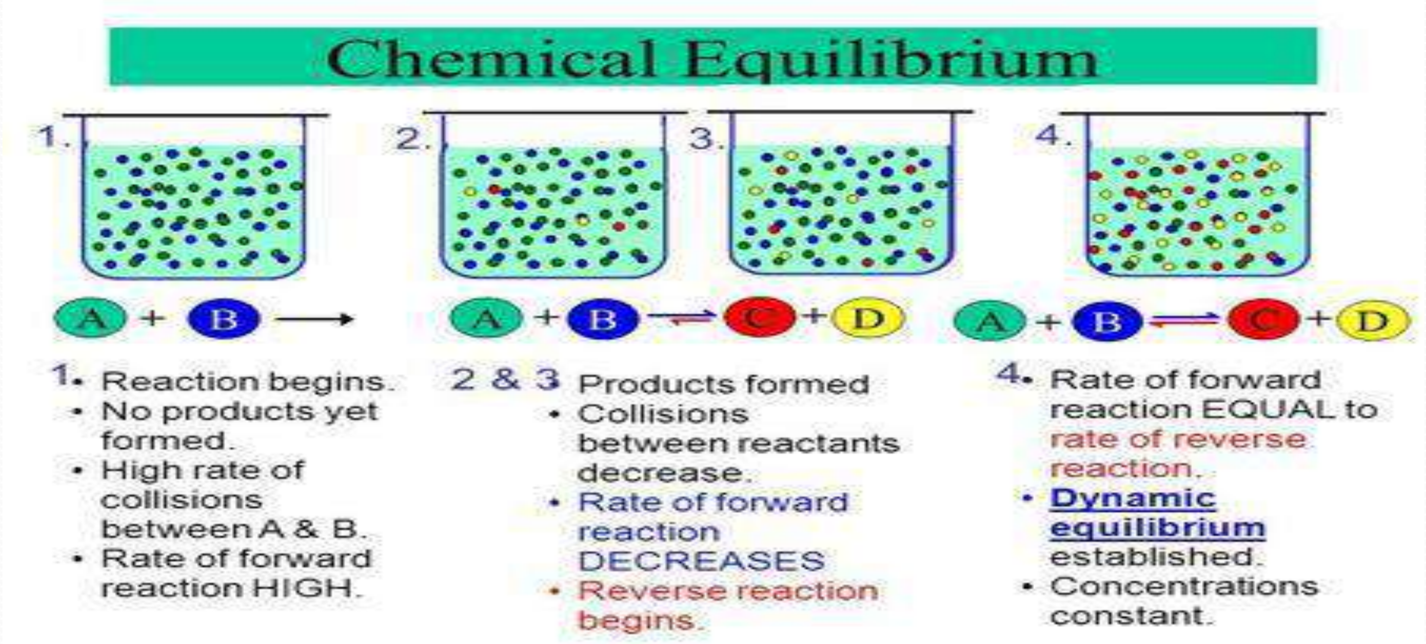
Chapter 11

Chemical equilibrium

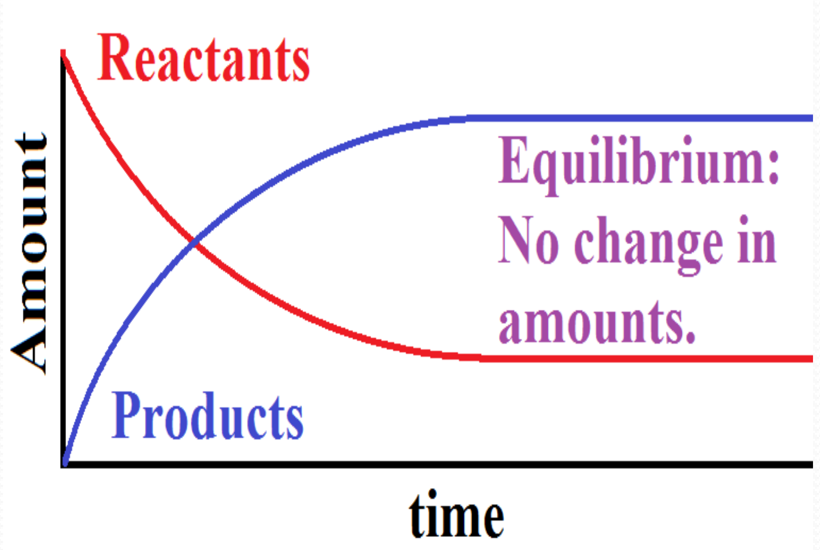
Chemical Equilibrium

- Chemical Equilibrium describes the state in which the rates of forward and reverse reactions are equal and the concentrations of the reactants and products remain unchanged with time.
- Note that a chemical equilibrium reaction involves different substances as reactants and products.



Chemical Equilibrium

- Most chemical reactions are, at least to some extent, reversible.
- At the start of a reversible process, the reaction proceeds toward the formation of products. As soon as some product molecules are formed, the reverse process—that is, the formation of reactant molecules from product molecules—begins to take place.
- When the concentrations of the reactants and products no longer change with time, **chemical equilibrium** is reached. Here the rates of the forward and reverse reactions are equal.



Equilibrium constant

- This state of dynamic equilibrium is characterized by an equilibrium constant.
- By considering the following reversible reaction:

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

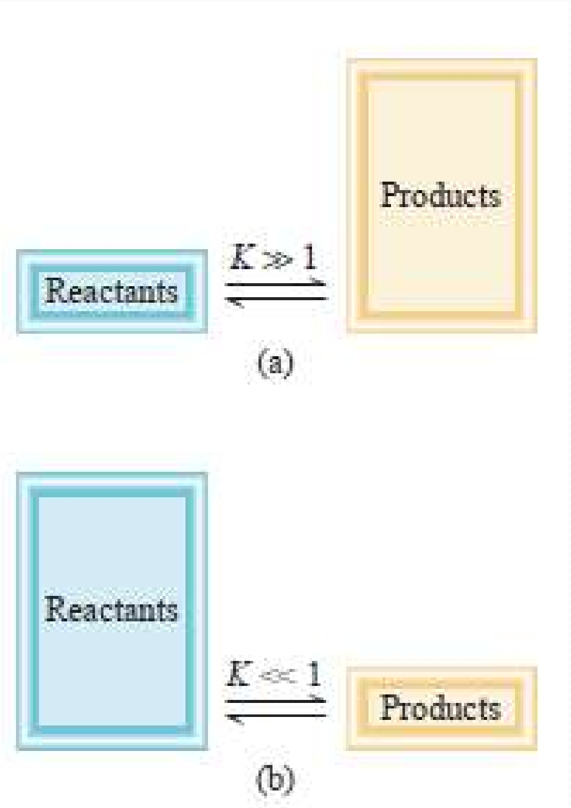
- The equilibrium constant for the reaction at a particular temperature is

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

- *K* is a constant regardless of the equilibrium concentrations of the reacting species at a given temperature.
- The equilibrium constant also change with temperature.

Equilibrium constant

- Finally, we note that if the equilibrium constant is much greater than 1 (that is, $K >> 1$), the equilibrium will lie to the right of the reaction arrows and favor the products.
- Conversely, if the equilibrium constant is much smaller than 1 (that is, $K << 1$), the equilibrium will lie to the left and favor the reactants



Ways of Expressing Equilibrium Constants

- Depending on the nature of reacting species, the equilibrium constant can be expressed in terms of molarities (Kc) or partial pressures (Kp).
- The concentrations of pure solids, pure liquids and solvents do not appear in the equilibrium constant expressions.
- The relationship between Kp and Kc as

$$K_P = K_c(0.0821T)^{\Delta n}$$

Δn = moles of gaseous products - moles of gaseous reactants.

T= temperature in K° .

- Kp = Kc when Δn = 0 as in the following reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Homogeneous Equilibrium

- It refer to reactions in which all reacting species are in the same phase. An example of homogeneous gas-phase equilibrium is the dissociation of N2O4.

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

- The equilibrium constant is

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

- As another example of homogeneous equilibrium, the dissociation of acetic acid (CH3COOH) in water:

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

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

Heterogeneous Equilibrium

- A reversible reaction involving reactants and products that are in different phases leads to a **heterogeneous equilibrium.**
- Calcium carbonate is heated in a closed vessel, this equilibrium is attained:

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

- The equilibrium constant is

$$K_c = [CO_2] \qquad K_P = P_{CO_2} \qquad \Delta n = 1$$

- $2NaHCO_{3(s)} \rightleftharpoons Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$

$$K_c = [H_2O][CO_2] \qquad k_p = P_{H_2O} . P_{CO_2} \qquad \Delta n = 2$$

Write expressions for K_c, and K_P if applicable, for the following reversible reactions at equilibrium:

(a) $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

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

(c) $CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l)$

$$K_c = \frac{[H_3O^+][F^-]}{[HF]}$$

$$K_c = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_P = \frac{P_{NO_2}^2}{P_{NO}^2 P_{O_2}}$$

$$K_c = \frac{[CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]}$$

Example

- Methanol (CH3OH) is manufactured industrially by the reaction

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

- The equilibrium constant (K_c) for the reaction is 10.5 at 220C°. What is the value of K_P at this temperature?

$$K_P = K_c(0.0821T)^{\Delta n}$$

$T = 273 + 220 = 493\ K$

$\Delta n = 1 - 3 = -2.$

$$K_P = (10.5)(0.0821 \times 493)^{-2}$$
$$= 6.41 \times 10^{-3}$$

Consider the following heterogeneous equilibrium:

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

At 800°C, the pressure of CO_2 is 0.236 atm. Calculate (a) K_P and (b) K_c for the reaction at this temperature.

$$K_P = P_{CO_2}$$
$$= 0.236$$

$$K_P = K_c(0.0821T)^{\Delta n}$$

In this case, $T = 800 + 273 = 1073$ K and $\Delta n = 1$, so we substitute these values in the equation and obtain

$$0.236 = K_c(0.0821 \times 1073)$$
$$K_c = 2.68 \times 10^{-3}$$

The Form of *K* and the Equilibrium Equation

When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

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

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

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

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

- A reaction vessel contains NH_3, N_2, and H_2 at equilibrium at a certain temperature. The equilibrium concentrations are $[NH_3] = 0.25$ M, $[N_2] = 0.11$ M, and $[H_2] = 1.91$ M.
- **A) Calculate the equilibrium constant Kc for the synthesis of ammonia if the reaction is represented as-**

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

$$K_c = \frac{[NH_3]^2}{[N_2]\cdot[H_2]^3}$$

$$= \frac{(0.25)^2}{(0.11)\cdot(1.91)^3} = 0.0815$$

- **B) Calculate the equilibrium constant Kc' for the reverse reaction:**

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

$$K_c' = 1/K_c$$

$$= 1/0.0815 = 12.27$$

Calculating Equilibrium Concentrations from Kc

- If we know the equilibrium constant for a particular reaction, we can calculate the concentrations in the equilibrium mixture from a knowledge of the initial concentrations.
- We summarize our approach to solving equilibrium constant problems as

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown quantity x, which represents the change in concentration.

2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for x.

3. Having solved for x, calculate the equilibrium concentrations of all species.

A mixture of 0.500 mol H_2 and 0.500 mol I_2 was placed in a 1.00-L stainless-steel flask at 430°C. The equilibrium constant K_c for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.3 at this temperature. Calculate the concentrations of H_2, I_2, and HI at equilibrium.

Step 1: The stoichiometry of the reaction is 1 mol H_2 reacting with 1 mol I_2 to yield 2 mol HI. Let x be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. It follows that the equilibrium concentration of HI must be $2x$. We summarize the changes in concentrations as follows:

	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial (M):	0.500		0.500		0.000
Change (M):	$-x$		$-x$		$+2x$
Equilibrium (M):	$(0.500 - x)$		$(0.500 - x)$		$2x$

Step 2: The equilibrium constant is given by

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Substituting, we get

$$54.3 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)}$$

Taking the square root of both sides, we get

$$7.37 = \frac{2x}{0.500 - x}$$

$$x = 0.393\ M$$

Step 3: At equilibrium, the concentrations are

$$[H_2] = (0.500 - 0.393)\ M = 0.107\ M$$

$$[I_2] = (0.500 - 0.393)\ M = 0.107\ M$$

$$[HI] = 2 \times 0.393\ M = 0.786\ M$$

The equilibrium constant K_c for the reaction

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

is 4.2 at 1650°C. Initially 0.80 mol H_2 and 0.80 mol CO_2 are injected into a 5.0-L flask. Calculate the concentration of each species at equilibrium.

$$[H_2] = [CO_2] = \frac{0.8}{5} = 0.16\,M$$

	H_2	+ CO_2	$\rightleftharpoons$ H_2O	+ CO
I	0.16 M	0.16 M	0	0
C	−x	−x	+x	+x
E	0.16−x	0.16−x	x	x

$$k_c = \frac{[H_2O]\cdot[CO]}{[H_2]\cdot[CO_2]} = \frac{x^2}{(0.16-x)^2}$$

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$$\sqrt{K_c} = \frac{x}{0.16-x} = \sqrt{4.2} = 2.05$$

$$x = 2.05(0.16-x) \Rightarrow x = 0.1075$$

$$[H_2] = [CO_2] = 0.16 - 0.1075 = 0.0525\,M$$

$$[H_2O] = [CO] = 0.1075$$

Factors That Affect Chemical Equilibrium

- Change in concentration, pressure, or volume may alter the equilibrium position, but it does not change the value of the equilibrium constant. Only a change in temperature can alter the equilibrium constant.
- The rule, known as **Le Châtelier's** principle, states that 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 it tries to reestablish equilibrium.

- **Changes in Concentrations**

At equilibrium all reactants and products are present in the reacting system. Increasing the concentrations of the products shifts the equilibrium to the left, and decreasing the concentration of the products shifts the equilibrium to the right.

For reactants, the opposite is true.

- **Changes in Pressure and Volume**

Changes in pressure affect the concentrations of gases.

The greater the pressure, the smaller the volume, and vice versa. The increase in pressure increases concentration of gases, but the increase will be larger at the site of the reaction with more number of moles, so the reaction will proceed to the opposite site to decrease the effect of the stress.

For pressure decrease, the opposite is true

Consider the following equilibrium systems:

(a) $2PbS(s) + 3O_2(g) \rightleftharpoons 2PbO(s) + 2SO_2(g)$

(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(c) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

Predict the direction of the net reaction in each case as a result of increasing the pressure (decreasing the volume) on the system at constant temperature.

(a) to the right

(b) to the left

(c) no effect

- **Changes in Temperature**
- If forward reaction is endothermic (absorbs heat, $\Delta H^\circ > 0$):

$$\text{heat} + N_2O_4(g) \longrightarrow 2NO_2(g) \qquad \Delta H^\circ = 58.0\ \text{kJ/mol}$$

- A rise in temperature favors the endothermic direction (from left to right of the equilibrium equation).
- A temperature decrease favors the reverse direction (from right to left of the equilibrium equation).
- For the exothermic reaction, the opposite is true.
- **The Effect of a Catalyst**
- A catalyst enhances the rate of a reaction but does not alter the equilibrium constant, nor does it shift the position of an equilibrium system.

- **Consider the following equilibrium process:**

$$N_2F_4(g) \rightleftharpoons 2NF_2(g) \qquad \Delta H^\circ = 38.5 \text{ kJ/mol}$$

- **Predict the changes in the equilibrium if**

(a) The reacting mixture is heated at constant volume;

The system will go from left to right and the equilibrium constant will increase from left to right

(b) Some N2F4 gas is removed from the reacting mixture at constant temperature and volume;

The system will go from right to left

(c) The pressure on the reacting mixture is decreased at constant temperature;

The system will go from left to right

(d) A catalyst is added to the reacting mixture.

A catalyst will not affect either the concentrations or the equilibrium constant.

Consider thermal decomposition of calcium carbonate at equilibrium in a closed container:

Consider this reaction at equilibrium in a closed container:

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

What would happen if (a) the volume is increased, (b) some CaO is added to the mixture, (c) some $CaCO_3$ is removed, (d) some CO_2 is added to the mixture, (e) a few drops of an NaOH solution are added to the mixture, (f) the temperature increased?

$K_c = [CO_2]$

(a) Shift to the right. (b) No effect. (c) No effect. (d) Shift to the left. (e) Shift to the right. (f) Shift to the right.