Chem12 Equilibrium-10

Some reactions are irreversible. Cooking an egg is an example of an irreversible endothermic reaction. Other reactions are reversible. The discharging and recharging of a lead-acid car battery is an example.

If we have a **reversible** reaction where the forward reaction occurs at the same rate as the reverse reaction, we say that the reaction is at **equilibrium**.

The following are necessary conditions for equilibrium :

- The system is closed (matter doesn't enter or leave)
- The forward and reverse reactions occur at the same rate
- Constant macroscopic conditions (T, P, concentrations are constant)
- Equilibrium can be reached from either direction

A reaction will be at equilibrium if the tendency toward lower enthalpy favors one direction and the tendency toward higher entropy favors the opposite direction.

e.g. $N_2O_4(g) + 52kJ \leftrightarrow 2NO_2(g)$

colorless gas brown gas

The chemical equation above is a reversible reaction. It is reversible because increased entropy (S) favors the forward reaction but decreased enthalpy (H) favors the reverse reaction. The double arrow indicates that equilibrium exists, and that the forward and reverse reactions occur at the same rate. The reaction takes place in a closed container. If equilibrium exists, the pressure, temperature and concentrations of the two gases are constant. If there is an increase in temperature there is a shift in the equilibrium to the right. In a closed system the concentration of $NO_2(g)$ will increase and the concentration of $N_2O_4(g)$ will decrease and the color of the gas will become darker as a new equilibrium is reached.

Exercise 1) Decide whether reactants, products or neither have the greater entropy.

a) $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$

b) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
c) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
d) $H_2(g) + I_2(g) \rightarrow 2HI(g)$
e) $I_2(s) \rightarrow I_2$(alcohol solution)
f) $H_2O(l) \rightarrow H_2O(s)$

Exercise 2) Will any of the following reactions reach equilibrium ? For reactions that don't reach equilibrium, state whether reactants or products are favored.

a) $Cl_2(g) \rightarrow Cl_2(aq) + 25kJ$
b) $2Na(s) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g)$ + heat
c) $N_2(g) + 2O_2(g)$ + heat $\rightarrow 2NO_2(g)$
d) $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$ +heat

The Equilibrium Expression

For any equilibrium expression we can define a <u>constant</u> : $\mathbf{K_{eq}}$.

For the reaction : $2HI(g) \leftrightarrow H_2(g) + I_2(g)$ $\quad K_{eq} = \dfrac{[H_2][I_2]}{[HI]^2}$

For the reaction : $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$ $\quad K_{eq} = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

In general for : $wA + xB \rightarrow yC + zD$ $\quad K_{eq} = \dfrac{[D]^z[C]^y}{[B]^x[A]^w}$

The square brackets indicate the concentration of the species inside in Moles/L . For the equilibrium expression we consider only gases and ions. Liquid H_2O and solids are not included in the expression.

Exercise 3) Give the equilibrium expression for the following reactions.

a) $AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$
b) $NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+(aq) + OH^-(aq)$
c) $2S(s) + 3O_2(g) \leftrightarrow 2SO_3(g)$
d) $2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g)$
e) $2NOCl(g) \leftrightarrow 2NO(g) + Cl_2(g)$
f) $2NO_2(g) \leftrightarrow N_2O_4(g)$
g) $SiO_2(s) + 3C(s) \leftrightarrow SiC(s) + 2CO(g)$
h) $H_2(g) + S(s) \leftrightarrow H_2S(g)$

i) $3O_2(g)$ <-> $2O_3(g)$

Answers : 1)a) p, b) p, c) r, d) n, e) p, f) r, 2)a) eq, b) p, c) r, d) p, 3)a) $[Ag^+][Cl^-]$, b) $\{[NH_4^+][OH^-]\}/[NH_3]$, c) $[SO_3]^2/[O_2]^3$, d) $[H_2O]^2/\{[O_2][H_2]^2\}$, e) $\{[Cl_2][NO]^2\}/[NOCl]^2$, f) $[N_2O_4]/[NO_2]^2$, g) $[CO]^2$, h) $[H_2S]/[H_2]$, i) $[O_3]^2/[O_2]^3$.