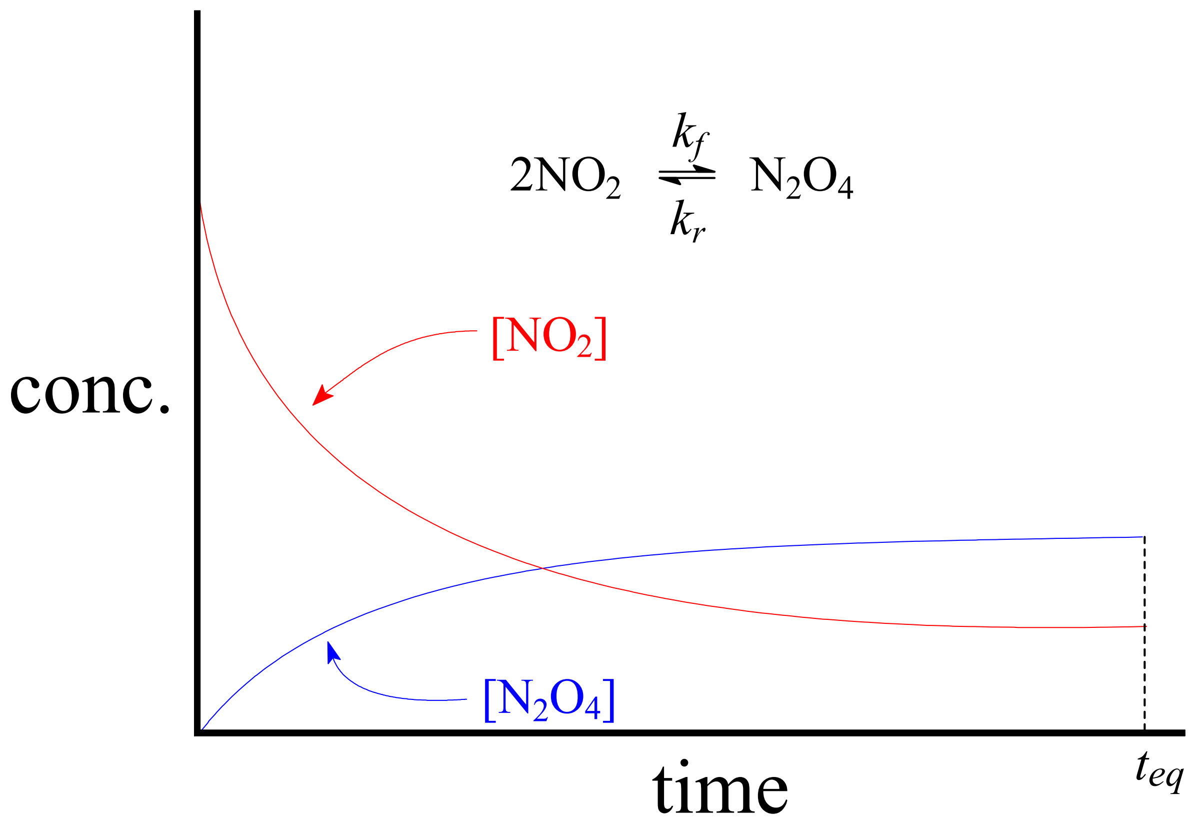
Concentration Change with Time for a Reversible Reaction

(One-Step Mechanism in Both Directions)



L At t_{eq}, when equilibrium is established,

$$Rate = \frac{-1}{2}\frac{d[NO_2]}{dt} = \frac{d[N_2O_4]}{dt} = 0$$

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

- From the Law of Mass Action, for the forward reaction

$$rate_f = k_f[NO_2]^2$$

and for the reverse reaction

$$rate_r = k_r[N_2O_4]$$

- At any point in the reaction, the overall rate, *Rate*, is

$$Rate = rate_f - rate_r = k_f[NO_2]^2 - k_r[N_2O_4]$$

- At equilibrium,

$$Rate = k_f[NO_2]^2 - k_r[N_2O_4] = 0$$

which means

$$k_f[NO_2]^2 = k_r[N_2O_4]$$

or $$rate_f = rate_r$$

L This defines a state of ***dynamic equilibrium***.

Defining the Equilibrium Constant for $2NO_2(g) \rightleftharpoons N_2O_4(g)$

- At equilibrium

$$k_f[NO_2]^2 = k_r[N_2O_4]$$

- Rearranging to put the constants on one side

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

- Defining $K_c = k_f / k_r$

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

L K_c is the **equilibrium constant**, defined as the ratio of product *equilibrium* concentration raised to its stoichiometric power over reactant *equilibrium* concentration raised to its stoichiometric power.

L K_c is a constant for the reaction at a particular temperature, regardless of the starting concentrations.

K_c for a Multi-Step Mechanism

$2NO_2Cl(g) \rightleftharpoons 2NO_2(g) + Cl_2(g)$ $\qquad\qquad$ $Rate = k[NO_2Cl]$

- This is believed to proceed by the following two-step mechanism:

$$\begin{array}{l} NO_2Cl \rightleftharpoons NO_2 + Cl \\ NO_2Cl + Cl \rightleftharpoons NO_2 + Cl_2 \\ \hline 2NO_2Cl \rightleftharpoons 2NO_2 + Cl_2 \end{array}$$

- ***Principle of Microscopic Reversibility***: If the reaction is at equilibrium overall, each elementary step and its reverse in the mechanism must also be at equilibrium.

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[NO_2][Cl]}{[NO_2Cl]}$$

$$K_2 = \frac{k_2}{k_{-2}} = \frac{[NO_2][Cl_2]}{[NO_2Cl][Cl]}$$

- Multiplying $K_1 \times K_2$:

$$K_1 \times K_2 = \frac{k_1 k_2}{k_{-1} k_{-2}} = \frac{[NO_2][Cl]}{[NO_2Cl]} \frac{[NO_2][Cl_2]}{[NO_2Cl][Cl]} = \frac{[NO_2]^2[Cl_2]}{[NO_2Cl]^2}$$

$$= K_c$$

General Form of the Equilibrium Constant, K_c

L For a general reaction of the form

$$aA + bB \; 6 \; cC + dD$$

regardless of the number of steps in the mechanism, at equilibrium the concentrations of all species will have specific values that define a constant of the form

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

Rules for Writing K_c Expressions

1. For K_c, all concentrations are the values *at equilibrium* in mol/L.

2. All solids and neat liquids (not solutions) behave as if they have unit concentration and do not appear in the expression for K_c.

3. For solutions, solutes appear in the expression for K_c, but solvents are usually omitted unless active participants in the reaction.

4. Non-reactive species, such as spectator ions, are omitted from K_c.

5. K_c is defined for the reaction proceeding in the usual left-to-right manner, as written. The value of K_c for the reverse reaction is the inverse of that for the forward reaction.

Examples of K_c

$$N_2(g) + 3H_2(g) \text{ o } 2NH_3(g)$$

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

$$Cu(NO_3)_2(aq) + Zn(s) \text{ o } Cu(s) + Zn(NO_3)_2(aq)$$

$$\text{Y} \quad Cu^{2+}(aq) + Zn(s) \text{ o } Cu(s) + Zn^{2+}(aq)$$

$$K_c = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$CaO(s) + CO_2(g) \text{ o } CaCO_3(s)$$

$$K_c = \frac{1}{[CO_2]}$$

$$HF(aq) + H_2O(l) \text{ o } H_3O^+(aq) + F^-(aq)$$

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