The Concept of Equilibrium

$$\rightleftarrows$$

Reversible reactions

As the concentrations of the reactants decrease the rate of reaction in the forward direction decreases.

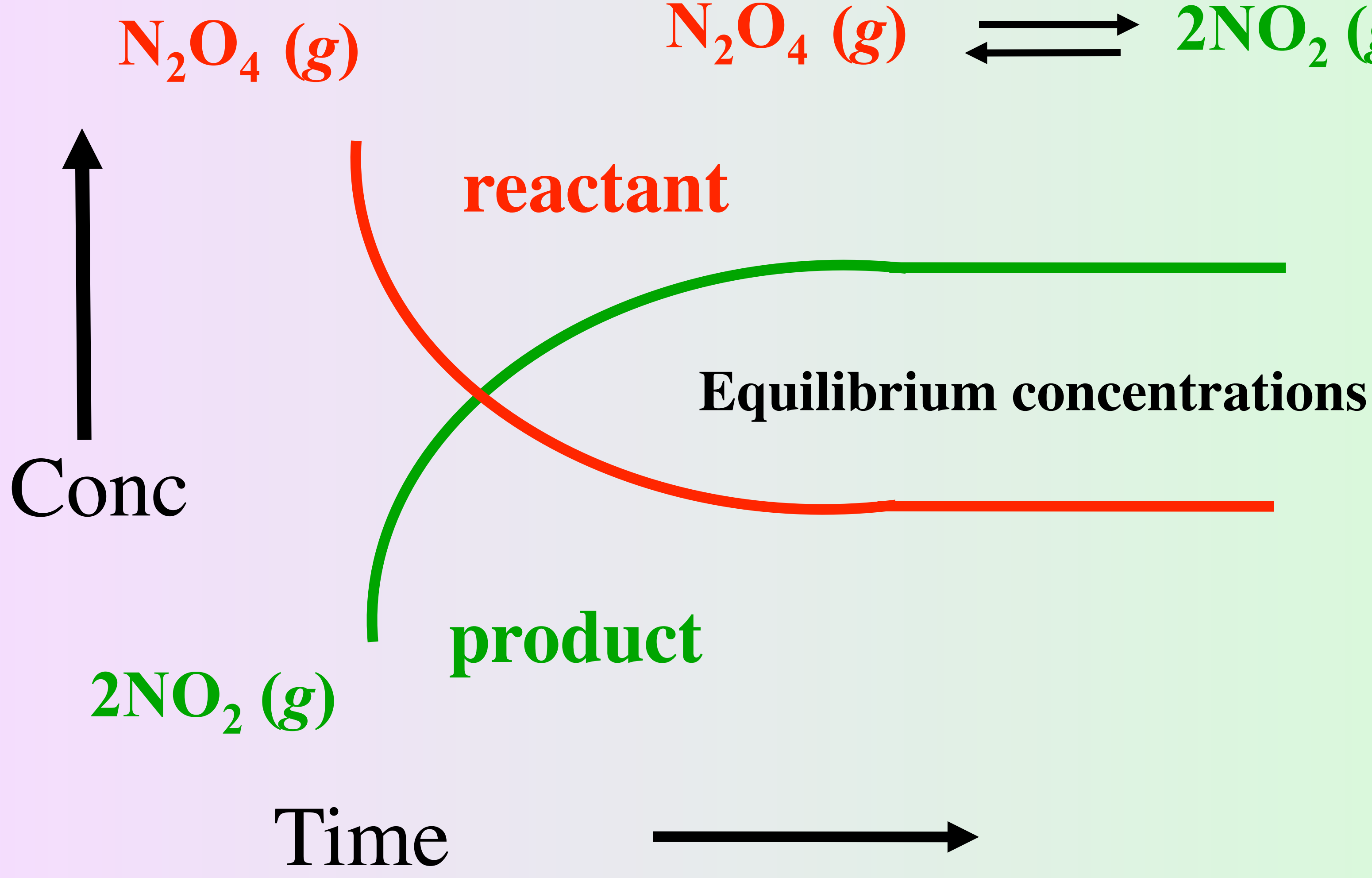
$$\rightleftarrows$$

As the concentrations of the products increase the rate of reaction in the reverse direction increases.

Change in concentrations

Initially only N_2O_4 is present

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



Chemical Equilibrium

reached when rates of the forward and reverse reactions are equal and the concentrations of the reactants and products no longer change with time

Chemical equilibrium is dynamic: chemical reactions take place ,but concentrations of reactants and products remain unchanged

Consider a simple case:

$$A \underset{k'}{\overset{k}{\rightleftharpoons}} B$$

(assume single unimolecular elementary step for forward and reverse processes)

Rate of forward reaction = k [A]

Rate of backward reaction = k' [B]

At equilibrium: k [A] = k' [B]

$$\frac{[B]}{[A]} = \frac{k}{k'} = K_{eq}$$

equilibrium constant

The Law of Mass Action

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D}$$

equilibrium constant

$$k_{eq} = \frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b}$$

$$k_{eq} = \frac{\text{products}}{\text{reactants}}$$

The NO_2 - N_2O_4 system at 25 ° C

Init:	0.670 *M*		0.000 *M*
	$N_2O_4\ (g)$	$\rightleftharpoons$	$2NO_2\ (g)$
equil:	0.643 *M*		0.0547 *M*

$$\frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0547)^2}{0.643} = 4.65 \times 10^{-3}$$

The NO_2 - N_2O_4 system at 25 ° C

Init: 0.500 *M* 0.0300 *M*

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

equil: 0. 491 *M* 0.0475 *M*

$$\frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0475\ M)^2}{0.491\ M} = 4.60 \times 10^{-3}$$

The NO_2 - N_2O_4 system at 25 ° C

Init: $0.000\ M$ $0.200\ M$

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

equil: $0.0898\ M$ $0.0204\ M$

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

The magnitude of the equilibrium constant

depends on temperature

depends on reaction

$$2O_3\,(g) \xrightleftharpoons{2300°C} 3O_2\,(g) \qquad K = 2.5 \times 10^{12}$$

$$Cl_2\,(g) \xrightleftharpoons{25°C} 2Cl\,(g) \qquad K = 1.4 \times 10^{-38}$$

$$CO(g) + H_2O\,(g) \xrightleftharpoons{830°C} H_2\,(g) + CO_2\,(g)$$

$$K = 5.1$$

Ways of Expressing Equilibrium Constants

Homogeneous equilibria

Heterogeneous equilibria

Homogeneous Equilibria

all reacting species are in the same phase

gas phase /solution phase

equilibrium constant can be expressed in terms of concentration

Example: homogeneous gas-phase

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

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

Where K_{eq} is the equilibrium constant when concentrations are expressed in moles/liter

Practice Exercise

The equilibrium concentrations for the reaction

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

Are $[CO] = 1.2 \times 10^{-2}\ M$, $[Cl_2] = 0.054\ M$ and $[COCl_2] = 0.14\ M$. Calculate the equilibrium constant (K_{eq}).

$$K_{eq} = \frac{[COCl_2]}{[CO]\ [Cl_2]} = \frac{0.14}{(1.2 \times 10^{-2})\ (0.054)} = 2.2 \times 10^{2}$$

Homogeneous Equilibria

all reacting species are in the same phase

gas phase / solution phase

equilibrium constant can be expressed in terms of concentration

solution phase

concentration term for the solvent does not appear in the expression for the equilibrium constant

Example: homogeneous aqueous-phase reaction

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}OH\ (\boldsymbol{aq}) \ + \ H_2O(\,\boldsymbol{l}\,)$$

$$\rightleftharpoons$$

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}O^-\ (\boldsymbol{aq}) \ + \ H_3O^+\ (\,\boldsymbol{aq})$$

Example: homogeneous aqueous-phase reaction

$$\mathrm{HOAc}\ (\boldsymbol{aq}) \quad + \quad \mathrm{H_2O}(\ \boldsymbol{l}\ )$$

$$\rightleftharpoons \qquad \mathbf{K'} = \frac{[^{-}\mathrm{OAc}\ ]\ [\mathrm{H_3O^+}\ ]}{[\mathrm{HOAc}]\ [\mathrm{H_2O}]}$$

$$^{-}\mathrm{OAc}\ (\boldsymbol{aq}) \quad + \quad \mathrm{H_3O^+}\ (\ \boldsymbol{aq})$$

Example: homogeneous aqueous-phase reaction

$$\mathrm{HOAc}\ (\boldsymbol{aq}) \quad + \quad \mathrm{H_2O}(\,\boldsymbol{l}\,)$$

$$\rightleftharpoons \quad \mathbf{K}'\,[\mathrm{H_2O}] = \frac{[^{-}\mathrm{OAc}\,]\,[\mathrm{H_3O^+}\,]}{[\mathrm{HOAc}]}$$

$$^{-}\mathrm{OAc}\ (\boldsymbol{aq}) \quad + \quad \mathrm{H_3O^+}\ (\,\boldsymbol{aq})$$

Example: homogeneous aqueous-phase reaction

$$\mathrm{HOAc}\,(\boldsymbol{aq}) \quad + \quad \mathrm{H_2O}(\,\boldsymbol{l}\,)$$

$$\rightleftharpoons \qquad \mathbf{K_{eq}} = \frac{[^{-}\mathrm{OAc}\,]\,[\mathrm{H_3O^+}\,]}{[\mathrm{HOAc}]}$$

$$^{-}\mathrm{OAc}\,(\boldsymbol{aq}) \quad + \quad \mathrm{H_3O^+}\,(\,\boldsymbol{aq})$$

Heterogeneous Equilibria

all reacting species are not in the same phase

concentration term for solid or liquid does not appear in the expression for the equilibrium constant

Example

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

$$K_{eq} = [CO_2]$$

Practice Exercise

$$Ni_{(s)} + 4CO_{(g)} \rightleftharpoons Ni(CO)_{4\,(g)}$$

$$K_{eq} = \frac{[Ni(CO)_4]}{[CO]^4}$$

Practice Exercise

What is the value for K_{eq} for the equilibrium shown at 295 K?

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

0.011 mol/L   0.011 mol/L

$$K_{eq} = [NH_3][H_2S]$$

$$K_{eq} = (0.011)(0.011)$$

$$K_{eq} = (0.011)^2$$

$$K_{eq} = 0.00012$$