Equilibrium

K – Equilibrium Constant (Capitalized!)

Equilibrium Constant

Even though the concentrations of reactants and products are not equal at equilibrium, there is a relationship between them.

Law of Mass Action or also **Equilibrium Expression –** The relationship between the chemical equation and the concentrations of reactants and products is called the

Equilibrium Constant

- For the general equation ***a*A + *b*B → *c*C + *d*D,**
- **The law of mass action** gives the relationship below.
  - The lowercase letters represent the coefficients of the balanced chemical equation.
  - Always products over reactants

K is called the **equilibrium constant.**

  - Unitless

Law of Mass Action

$$K = \frac{\overbrace{[C]^c[D]^d}^{\text{Products}}}{\underbrace{[A]^a[B]^b}_{\text{Reactants}}}$$

Writing Equilibrium Constant Expressions

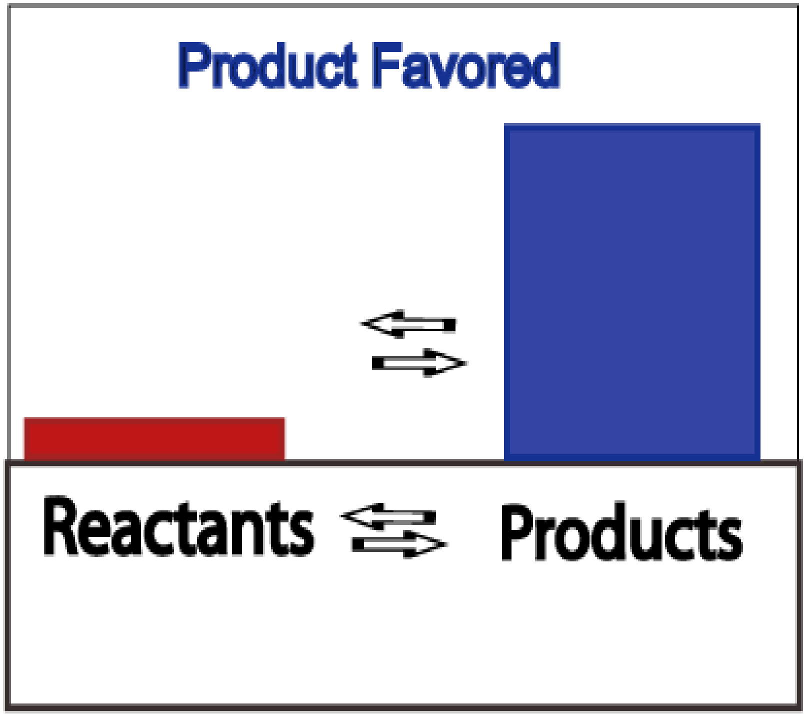
$$2\ N_2O_{5(g)} \Leftrightarrow 4\ NO_{2(g)} + O_{2(g)}$$

The equilibrium constant expression is:

$$K = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$$

Product Favored Equilibrium

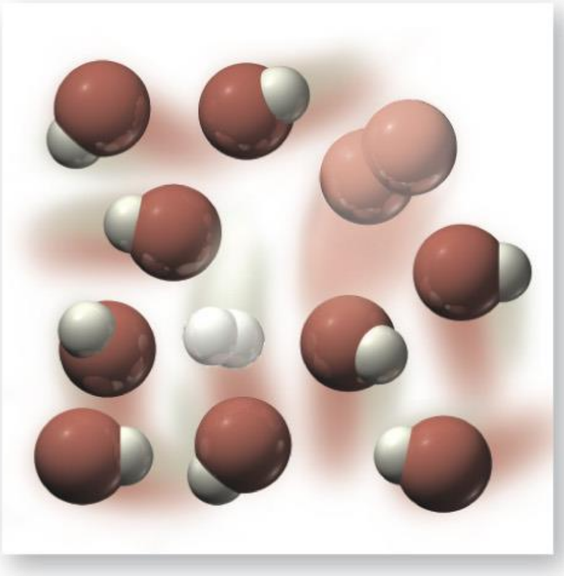
Large values for *K* signify the reaction is **product favored**



When equilibrium is achieved, <u>most reactant</u> has been <u>converted to product</u>

A Large Equilibrium Constant

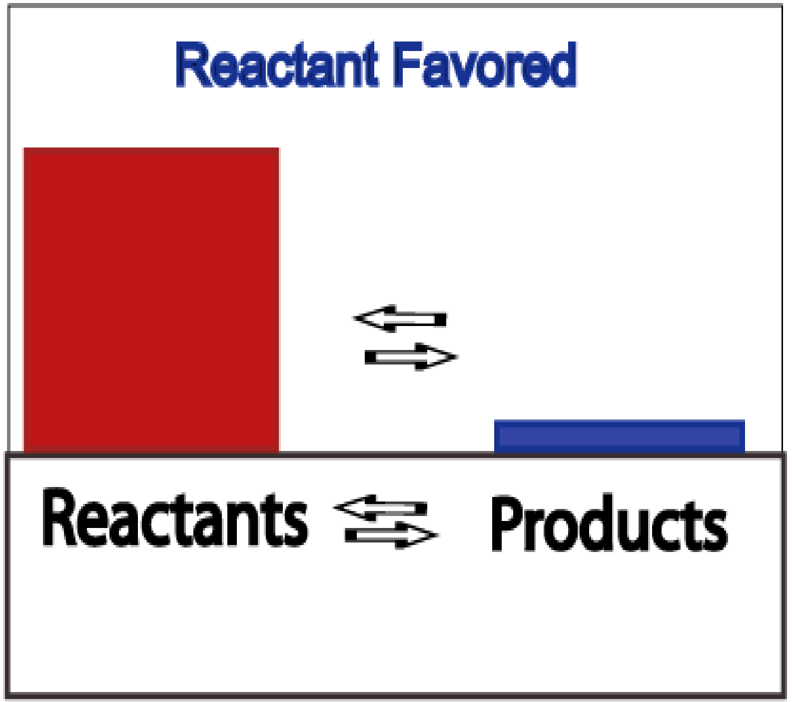
$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$$



$$K = \frac{[HBr]^2}{[H_2][Br_2]} = \text{large number}$$

<u>Reactant Favored Equilibrium</u>

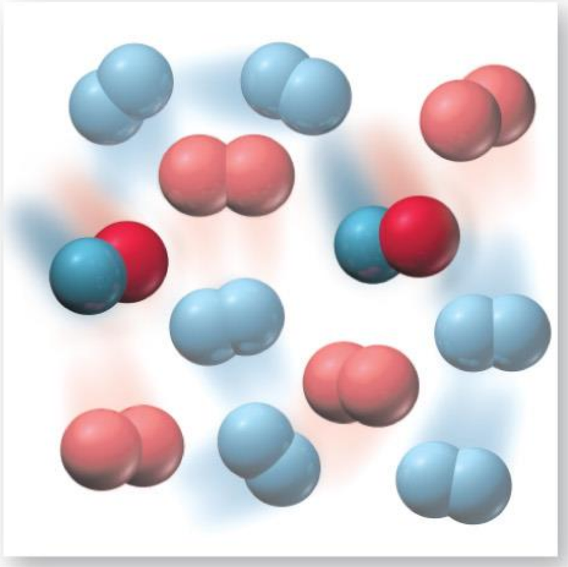
Small values for *K* signify the reaction is **reactant favored**



When equilibrium is achieved, <u>very little reactant</u> has been <u>converted to product</u>

A Small Equilibrium Constant

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$



$$K = \frac{[NO]^2}{[N_2][O_2]} = \text{small number}$$

Relationships between *K* and Chemical Equations

- When the reaction is **written backward**, the equilibrium constant is **inverted.**

aA + bB → cC + dD

the equilibrium constant expression is:

$$K_{\text{forward}} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

cC + dD → aA + bB

the equilibrium constant expression is:

$$K_{\text{backward}} = \frac{[A]^a \times [B]^b}{[C]^c \times [D]^d}$$

$$\boxed{\therefore \quad K_{\text{backward}} = \frac{1}{K_{\text{forward}}}}$$

Relationships between *K* and Chemical Equations

- When the coefficients of an equation are **multiplied** by a factor, the equilibrium constant is **raised to that factor.**

$$aA + bB \Leftrightarrow cC$$

the equilibrium constant expression is:

$$K_{original} = \frac{[C]^c}{[A]^a \times [B]^b}$$

$$2aA + 2bB \Leftrightarrow 2cC$$

the equilibrium constant expression is:

$$K_{new} = \frac{[C]^{2c}}{[A]^{2a} \times [B]^{2b}}$$

$$= \left(\frac{[C]^c}{[A]^a \times [B]^b}\right)^2$$

$$\boxed{\therefore \quad K_{new} = K_{original}^{n}}$$

Relationships between *K* and Chemical Equations

- When you **add equations** to get a new equation, the equilibrium constant of the new equation is the **product** of the equilibrium constants of the old equations.

1) $a\mathrm{A} \Leftrightarrow b\mathrm{B}$
2) $b\mathrm{B} \Leftrightarrow c\mathrm{C}$

the equilibrium constant expressions are:

$$K_1 = \frac{[\mathrm{B}]^b}{[\mathrm{A}]^a} \qquad K_2 = \frac{[\mathrm{C}]^c}{[\mathrm{B}]^b}$$

$a\mathrm{A} \Leftrightarrow c\mathrm{C}$

the equilibrium constant is:

$$K_{new} = \frac{[\mathrm{C}]^c}{[\mathrm{A}]^a}$$

$$= \frac{\cancel{[\mathrm{B}]^b}}{[\mathrm{A}]^a} \times \frac{[\mathrm{C}]^c}{\cancel{[\mathrm{B}]^b}}$$

$$\boxed{\therefore \quad K_{new} = K_1 \times K_2}$$

Equilibrium Constants for Rxns Involving Gases

- The [   ]s of a gas in a mixture is proportional to its partial pressure.

- Therefore, K can be expressed as the ratio of the partial pressures of the gases.

$$\boldsymbol{a\mathrm{A}(g) + b\mathrm{B}(g) \Leftrightarrow c\mathrm{C}(g) + d\mathrm{D}(g)}$$

the equilibrium constant expressions are:

$$K_c = \frac{[\mathrm{C}]^c \times [\mathrm{D}]^d}{[\mathrm{A}]^a \times [\mathrm{B}]^b} \qquad K_p = \frac{P_\mathrm{C}{}^c \times P_\mathrm{D}{}^d}{P_\mathrm{A}{}^a \times P_\mathrm{B}{}^b}$$

Kc and Kp

- K_p, the partial pressures are always in atm.

- K_p and K_c are not necessarily the same because of the difference in units.
  - $K_p = K_c$ when $\Delta n = 0$

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

Δ*n* is the difference between the number of moles of reactants and moles of products.

Deriving the Relationship Between Kc and Kp

$$[\mathrm{A}] = \frac{n_\mathrm{A}}{V}, n_\mathrm{A} = \text{moles of A}, V = \text{volume of gas}$$

$$P_A V = n_\mathrm{A} RT, \text{ from the Ideal Gas Law}$$

$$\textit{substituting} \quad P_A = \frac{n_A}{V} RT = [A]RT$$

$$\boxed{\therefore \quad [A] = \frac{P_A}{RT}}$$

Deriving the Relationship Between Kc and Kp

$$[X] = \frac{P_X}{RT}$$

***a*A(*g*) + *b*B(*g*) ⇔ *c*C(*g*) + *d*D(*g*)**

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

substituting

$$K_p = \frac{P_C{}^c \times P_D{}^d}{P_A{}^a \times P_B{}^b}$$

$$K_c = \frac{\left(\frac{P_C}{RT}\right)^c \times \left(\frac{P_D}{RT}\right)^d}{\left(\frac{P_A}{RT}\right)^a \times \left(\frac{P_B}{RT}\right)^b} = \frac{P_C{}^c P_D{}^d \left(\frac{1}{RT}\right)^{c+d}}{P_A{}^a P_B{}^b \left(\frac{1}{RT}\right)^{a+b}} = K_p \left(\frac{1}{RT}\right)^{(c+d)-(a+b)}$$

rearranging $K_p = K_c(RT)^{(c+d)-(a+b)} = K_c(RT)^{\Delta n}$

Heterogeneous Equilibria

- [   ]s of pure solids and pure liquids do not change during the course of a reaction.

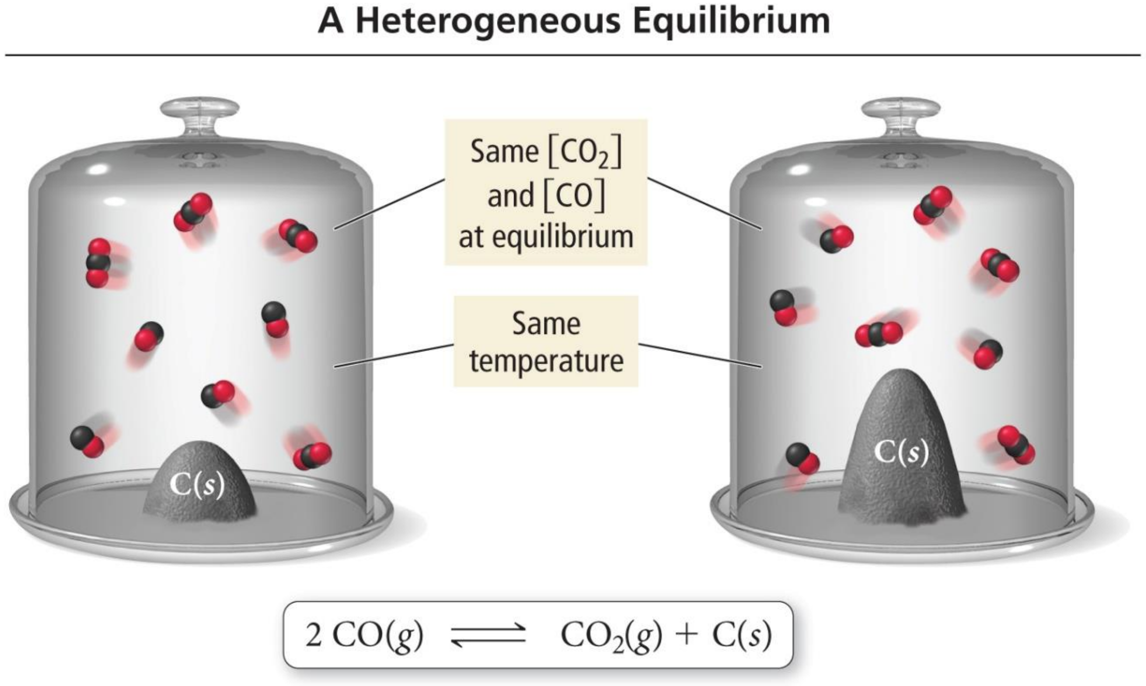
- Because their [ ]s don’t change, solids and liquids are not included in the equilibrium constant expression.

$$CO_2(g) + H_2O(\ell) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

the equilibrium constant expression is as follows:

$$K_c = \frac{[H^+][HCO_3^-]}{[CO_2]}$$

Heterogeneous Equilibria



The amount of C is different, but the amounts of CO and CO_2 remain the same. Therefore, the amount of C has no effect on the position of equilibrium.