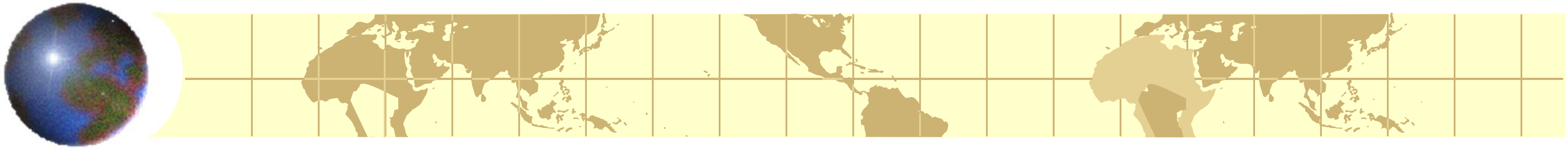
## Chemical Equilibrium

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

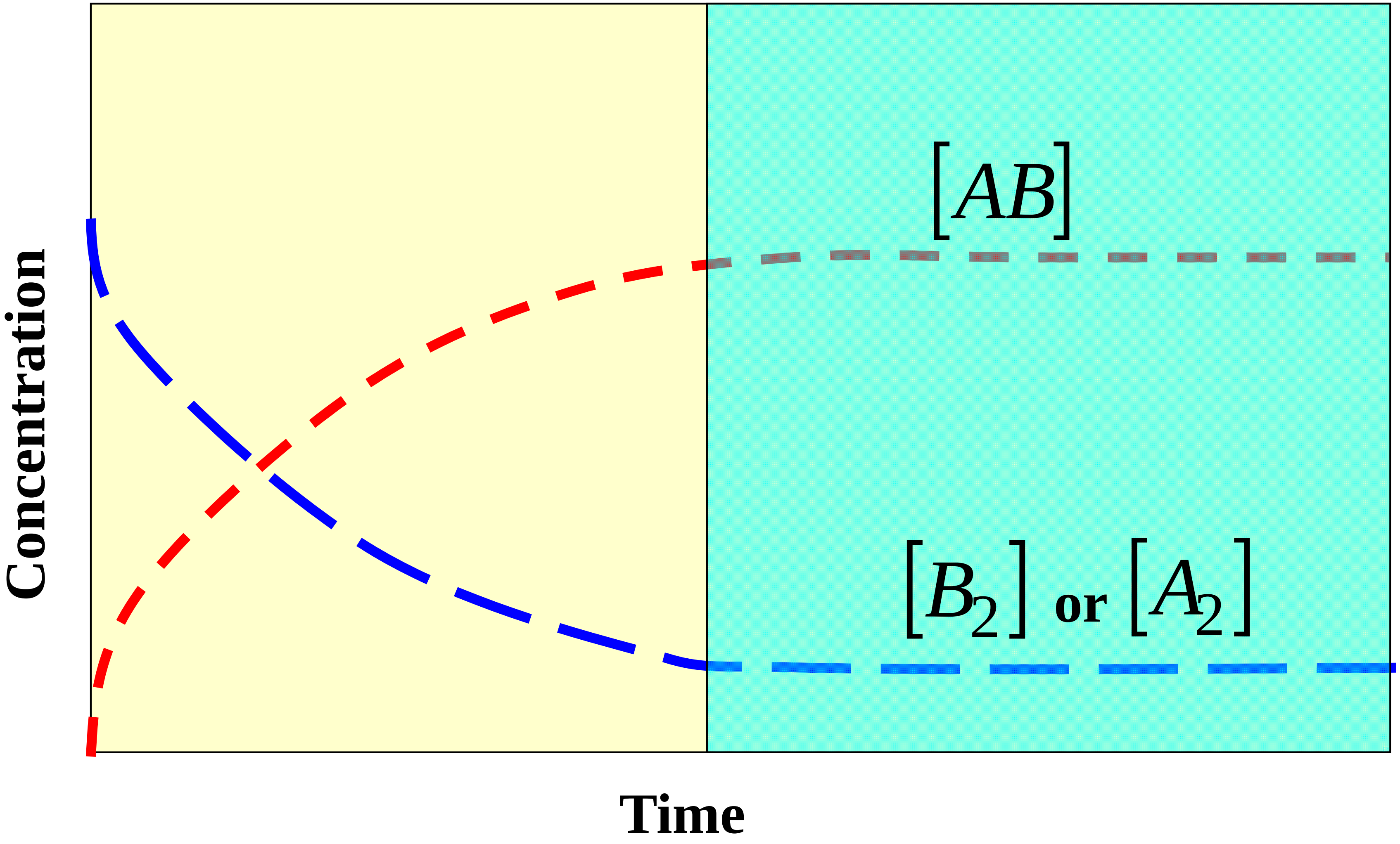
$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$$

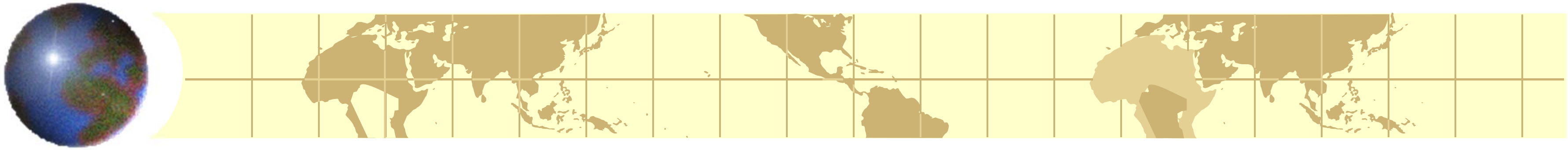
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$\rightleftharpoons$ **: the equation can be read in either direction**



$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$





$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$

$K_f$ **: forward reaction rate constant**

$K_r$ **: reverse reaction rate constant**

$$rate_f = k_f[A_2][B_2]$$

$$rate_r = k_r[AB]^2$$

**At equilibrium** $rate_f = rate_r$

$$k_f [A_2][B_2] = k_r [AB]^2$$

$$\frac{k_f}{k_r} = \frac{[AB]^2}{[A_2][B_2]}$$

$$K_c = \frac{[AB]^2}{[A_2][B_2]}$$

**$K_c$ : equilibrium constant**

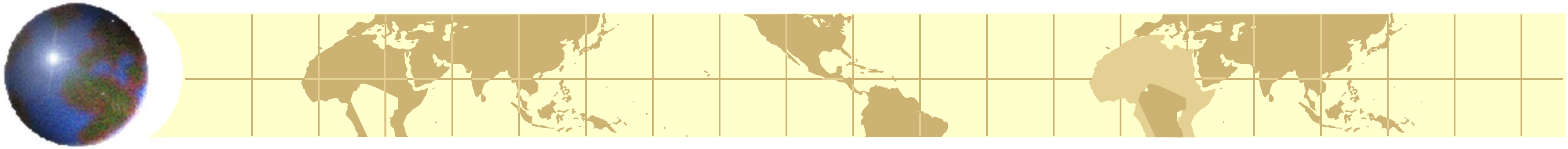
# Heterogeneous equilibria

**Equilibria involving substances in more than one phase are called heterogeneous equilibria**

**The concentration of a pure solid or liquid are constant when temperature and pressure are constant**

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

$$K_c = \left[CO_2\right]$$



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

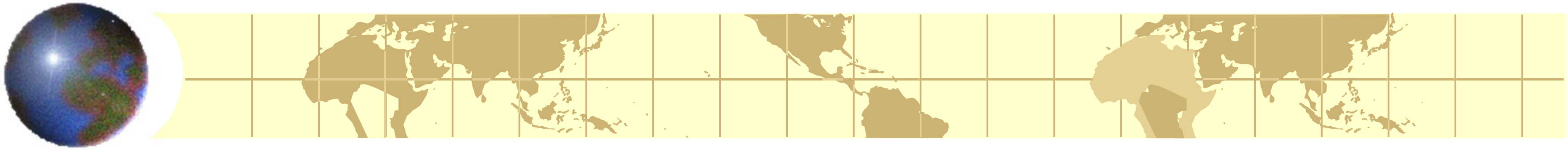
**Equilibrium concentrations:**

$$\left[N_2O_4\right] = 4.27 \times 10^{-2}\, mol\,/\,L$$

$$\left[NO_2\right] = 1.41 \times 10^{-2}\, mol\,/\,L$$

$$K_c = \frac{\left[NO_2\right]^2}{\left[N_2O_4\right]} = \frac{\left(1.41 \times 10^{-2}\, mol/L\right)^2}{\left(4.27 \times 10^{-2}\, mol/L\right)}$$

$$K_c = 4.66 \times 10^{-3}\, mol/L$$



**For a general reaction**

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

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

**Equilibrium constant can be expressed in pressures**

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

$$K_P = P_{CO_2}$$

**For a general reaction**

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

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

***The relation between $K_c$ and $K_P$ :***

**Assuming ideal gas behavior**

**PV = nRT ⇒ P = (n/V) RT**

**n/V = concentration**

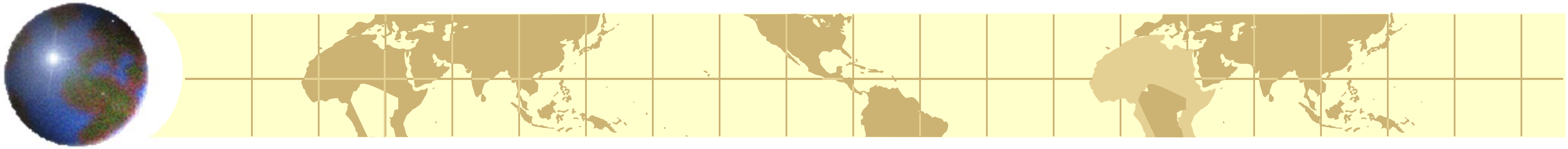
$$P_A = [A]RT$$

$$P_A^a = [A]^a (RT)^a$$

$$P_B^b = [B]^b (RT)^b$$

$$P_C^c = [C]^c (RT)^c$$

$$P_D^d = [D]^d (RT)^d$$



$$K_P = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b}$$

$$K_P = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{c+d-a-b}$$

$$K_P = K_c (RT)^{c+d-a-b}$$

$$K_P = K_c (RT)^{(c+d)-(a+b)}$$

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

$$\Delta n = (c + d) - (a + b)$$

**c + d = total moles of the products**

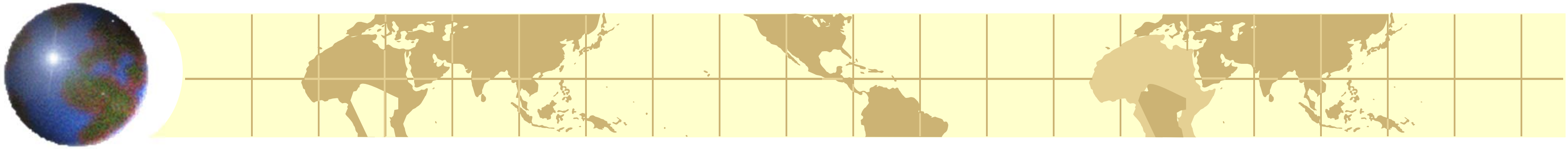
**a + b = total moles of the reactants**

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

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

$$\Delta n = 1 + 1 - 1 = 1$$

$$K_P = K_c(RT)$$



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

$$\Delta n = 1 - (1 + 1) = -1$$

$$K_P = K_c(RT)^{-1}$$

$$K_P = \frac{K_c}{RT}$$

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

$$\Delta n = 2 - (1 + 1) = 0$$

$$K_P = K_c (RT)^0$$

$$K_P = K_c$$

# Direction of the reaction

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

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

**At the beginning of the reaction A and B are present and the forward reaction occurs, the direction is towards the products**

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

**Using initial concentratins**

1. $Q < K_C$

**Reaction direction: left → right** **(forward reaction)**

**A and B decrease until equilibrium is reached**

2. $Q > K_C$

**Reaction direction: right → left** **(reverse reaction)**

**C and D decrease until equilibrium is reached**

## What is the direction of the the following reaction?

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

**Given $K_c$ = 0.36 and the initial concentrations**

**$N_2O_4$ = 0.20 mol/4L**

**$NO_2$ = 0.20 mol/4L**

**In units of mol/L**

**$N_2O_4$ = 0.20/4 = 0.05 mol/L**

**$NO_2$ = 0.20/4=0.05 mol/L**

$$Q = \frac{0.05^{2}}{0.05^{2}} = 0.05$$

$$Q \langle K_{c}$$

**Reaction direction: left → right**

# Le Chatelier’s principle

**A system in equilibrium reacts to a stress in a way that counteracts the stress and establishes a new equilibrium state**

**Stress:**

- **Change in concentration**
- **Change in pressure**
- **Change in temperature**
- **Addition of a catalyst**

# ➢Change in concentration

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

**If hydrogen is added the equilibrium will shift to decrease the effect of the concentration change**

**Reaction direction: left → right**

**If HI is added the equilibrium will shift to decrease the effect of the concentration change**

**Reaction direction: right → left**

**Removal of one of the substances from an equilibrium system will also cause the position of the equilibrium to shift**

## ➢Change in pressure

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

**Pressure increase:**
**Reactants: 4 moles**
**Products: 2moles**

**The equilibrium shifts to the right**

**(direction: towards side with smaller # moles**

**If $\Delta$n =0**
**no effect of pressure change on the equilibrium**

## ➢Change in temperature

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta\text{H} = \text{-}92.4\text{kJ}$$

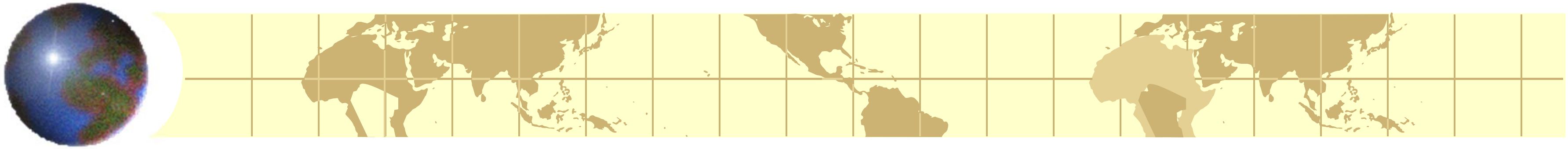
**Since ΔH is negative, the reaction to the right evolves heat**

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92.4\text{kJ}$$

**The forward reaction is *exothermic***

**The reverse reaction is *endothermic***

**If heat is added, the position of the equilibrium shifts to the left**



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

**$\Delta$H = +41kJ**

$$CO_2(g) + H_2(g) + 41kJ \rightleftharpoons CO(g) + H_2O(g)$$

**If heat is added the position of the equilibrium shifts to the right**

**The numerical value of the equilibrium constant changes when the temperature is changed**

**Increasing the temperature always favors the endothermic change**

**Decreasing the temperature always favors the exothermic change**

# ➢Addition of a catalyst

**Addition of a catalyst has no effect on the position of the equilibrium**

**A catalyst would affect both, forward and reverse, reactions equally**

**A catalyst will cause a system to attain equilibrium more rapidly than it otherwise would**

# Adding chemical equations

$$SO_2(g)+\frac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \quad K_{c_1}=\frac{[SO_3]}{[SO_2][O_2]^{\frac{1}{2}}}$$

$$NO_2(g) \rightleftharpoons NO(g)+\frac{1}{2}O_2(g) \quad K_{c_2}=\frac{[NO][O_2]^{\frac{1}{2}}}{[NO_2]}$$

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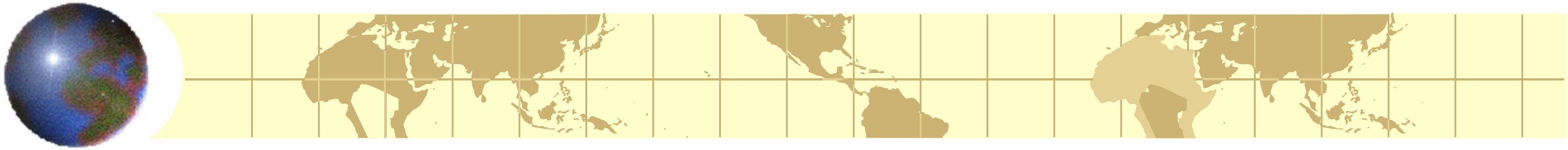
$$SO_2(g)+NO_2(g) \rightleftharpoons SO_3(g)+NO(g)$$

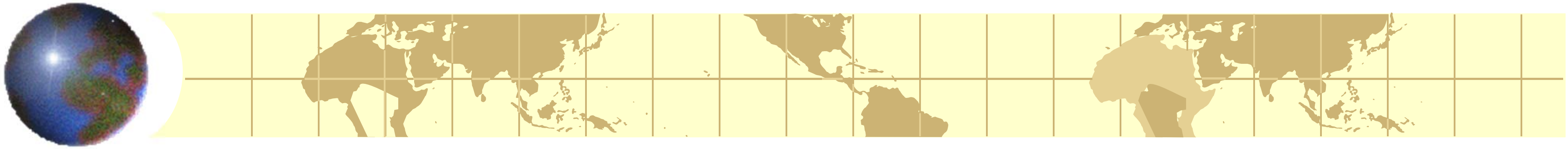
$$K_c=\frac{[NO][SO_3]}{[NO_2][SO_2]}$$



$$K_{c_1} = \frac{[SO_3]}{[SO_2][O_2]^{\frac{1}{2}}} \qquad K_{c_2} = \frac{[NO][O_2]^{\frac{1}{2}}}{[NO_2]}$$

$$K_{c_1} \times K_{c_2} = \frac{[SO_3]}{[SO_2][O_2]^{\frac{1}{2}}} \times \frac{[NO][O_2]^{\frac{1}{2}}}{[NO_2]}$$

$$= \frac{[NO][SO_3]}{[NO_2][SO_2]} = K_c$$



**Example**

$$S(s) + O_2(g) \rightleftharpoons SO_2(g)$$

$K_1 = 5.0\times10^6$

$$K_1 = \frac{[SO_2]}{[O_2]}$$

$$SO_2(g) \rightleftharpoons S(s) + O_2(g)$$

$K_2 = ?$

$$K_2 = \frac{[O_2]}{[SO_2]} \qquad K_2 = \frac{1}{K_1} = \frac{1}{5.0\times10^6}$$

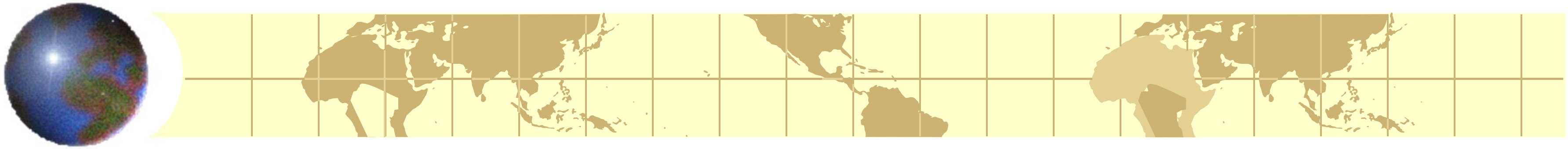
# Example

$$H_2(g) + S(s) \rightleftharpoons H_2S(g)$$ $K_1=1.0\times10^{-3}$

$$S(s) + O_2(g) \rightleftharpoons SO_2(g)$$ $K_2=5.0\times10^{6}$

**Determine $K_c$ for the following reaction**

$$H_2(g) + SO_2(g) \rightleftharpoons H_2S(g) + O_2(g)$$



$$H_2(g) + S(s) \rightleftharpoons H_2S(g)$$

$$SO_2(g) \rightleftharpoons S(s) + O_2(g)$$

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$$H_2(g) + SO_2(g) \rightleftharpoons H_2S(g) + O_2(g)$$

$$K_c = K_1 \times \frac{1}{K_2} = 1.0 \times 10^{-3} \times \frac{1}{5.0 \times 10^{6}} = 2.0 \times 10^{-10}$$

# Example

$$Cl_2(g) + PCl_3(g) \rightleftharpoons PCl_5(g) \qquad K_1 = 8.0 \times 10^{16}$$

$$K_1 = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

$$PCl_5(g) \rightleftharpoons Cl_2(g) + PCl_3(g) \qquad K_2 = ?$$

$$K_2 = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{1}{K_1} = \frac{1}{8.0 \times 10^{16}}$$

$$\frac{1}{2}PCl_5(g) \rightleftharpoons \frac{1}{2}Cl_2(g)+\frac{1}{2}PCl_3(g) \qquad K_3 = ?$$

$$K_3 = \frac{\left[PCl_5\right]^{\frac{1}{2}}}{\left[PCl_3\right]^{\frac{1}{2}}\left[Cl_2\right]^{\frac{1}{2}}} \quad = \left(\frac{1}{K_1}\right)^{\frac{1}{2}} = \left(\frac{1}{8.0\times 10^{16}}\right)^{\frac{1}{2}}$$

$$K_1 = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

$$2PCl_3(g) + 2Cl_2(g) \rightleftharpoons 2PCl_5(g) \qquad K_4 = ?$$

$$K_4 = \frac{[PCl_5]^2}{[PCl_3]^2[Cl_2]^2} = K_1^2 = (8.0 \times 10^{16})^2$$

# Example

**0.100mol of CO was mixed with 0.100mol of $H_2O(g)$ in a 1L vessel and allowed to reach equilibrium at 500ºC.**

**if $K_c$ = 4.06, determine the equilibrium concentrations.**

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

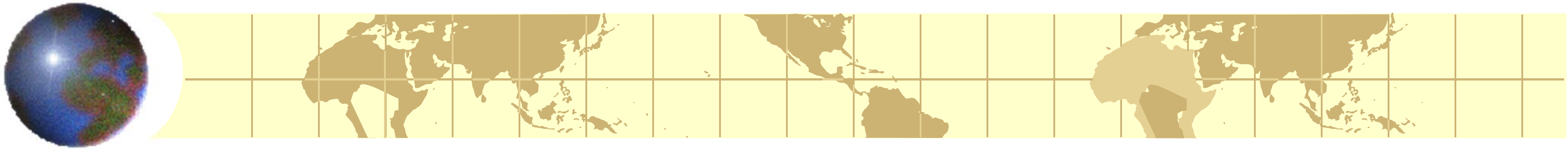
| **Concentrations** ↓ | $CO(g)$ | $H_2O(g)$ | $CO_2(g)$ | $H_2(g)$ |
|---|---|---|---|---|
| **Initial** | **0.100M** | **0.100M** | **0** | **0** |
| **Change** | **- X** | **- X** | **+ X** | **+ X** |
| **Equilibrium** | **0.100M-X** | **0.100M-X** | **X** | **X** |

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(X)(X)}{(0.100 - X)(0.100 - X)} = 4.06$$

$$\frac{(X)(X)}{(0.100 - X)(0.100 - X)} = 4.06$$

$$\frac{(X)^2}{(0.100 - X)^2} = 4.06$$

$$\left(\frac{(X)}{(0.100 - X)}\right)^2 = 4.06$$



$$\frac{(X)}{(0.100 - X)} = \sqrt{4.06} \longrightarrow X = 0.0668$$

$$[CO] = [H_2O] = 0.100 - 0.0668 = 0.033\,M$$

$$[CO_2] = [H_2] = X = 0.0668\,M$$

# Example

**0.20mol of $H_2$ was mixed with 0.20mol of $I_2(g)$ in a 2.0L vessel and allowed to reach equilibrium. At equilibrium $[I_2]$ = 0.020M. What is the value of $K_c$?**

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

| Concentrations ↓ | $H_2(g)$ | $I_2(g)$ | $2HI(g)$ |
|---|---|---|---|
| **Initial** | $\frac{0.20}{2.0}M$ | $\frac{0.20}{2.0}M$ | **0** |
| **Change** | **- X** | **- X** | **+ 2X** |
| **Equilibrium** | $\frac{0.20}{2.0} - X = 0.020$ | $\frac{0.20}{2.0} - X = 0.020$ | **2X** |

$$\frac{0.20}{2.0} - X = 0.020 \longrightarrow X = 0.080$$

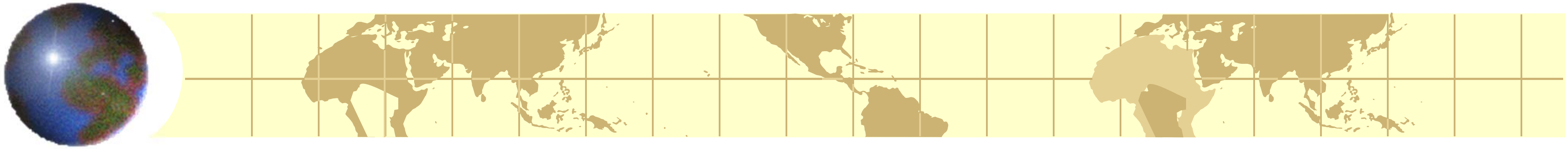
$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_c = \frac{[2 \times 0.080]^2}{[0.020][0.020]} = 64$$

# Example

**0.300mol of $N_2O_4$ is placed in a 2.00L. if $K_c$ =4.50, what are the equilibrium concentrations?**

| **Concentrations** ↓ | $N_2O_4(g)$ | $\rightleftharpoons$ | $2NO_2(g)$ |
|---|---|---|---|
| **Initial** | $\frac{0.300}{2.00}M$ | | **0** |
| **Change** | **- X** | | **+ 2X** |
| **Equilibrium** | $\frac{0.300}{2.00}-X$ | | **2X** |



$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2X)^2}{(0.150 - X)} = 4.50$$

$$4X^2 + 4.50X - 0.675 = 0$$

**Second order equation** $aX^2 + bX + c = 0$

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$X = \frac{-4.5 \pm \sqrt{(4.5)^2 - 4(4)(-0.675)}}{2(4)}$$

**X = 0.134** **or X = -1.26**

**Choose the positive value of X**

$$[NO_2] = 2(0.134) = 0.268\,M$$

$$[N_2O_4] = 0.150 - 0.134 = 0.016\,M$$