Equilibrium Expressions & Equilibrium Constant

- when a system is at equilibrium, the [reactants] and [products] remains constant
- it is found that the **ratio of [products] to [reactants] is constant at a particular temperature**
- even though the **[reactants] and [products] may change** as a result of a shift in equilibrium, the **ratio remains constant**

For an equilibrium equation with the general form:

$$aA + bB \rightleftarrows eE + fF$$

experimentally, it is found that:

$$K_{eq} = \frac{[E]^e[F]^f}{[A]^a[B]^b} = \text{a constant}$$

- this expression of concentrations is called the EQUILIBRIUM EXPRESSION and its numerical value K_{eq} is called the EQUILIBRIUM CONSTANT

- the equilibrium constant is the ratio of product concentration terms to reactant concentration terms

$$K_{eq} = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$$

- in the K_{eq} expression, the **exponent** to which each of the concentrations is raised is equal to its **coefficient** in the balanced reaction
- the units for K_{eq} vary depending on the number of concentration terms in the numerator as compared to the denominator
- these units do not have any particular importance so **units** for K_{eq} are generally **not shown**

Write the K_{eq} expression for the following equilibrium:

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

$$K_{eq} = \frac{[H_2][I_2]}{[HI]^2} = \frac{(.120)(.120)}{(.250)^2}$$

$$K_{eq} = 0.230$$

Given the above equilibrium, what is the value of K_{eq} if the equilibrium concentrations of HI, H_2 and I_2 are 0.250 M, 0.120 M and 0.120 M respectively?

Consider the following equilibrium:

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

If the value of $K_{eq} = 0.230$ at a particular temperature, what is the equilibrium [HI] if the $[H_2]$ = 0.075 M and $[I_2]$ = 0.320 M?

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

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

$$= \sqrt{\frac{(.075)(.320)}{.230}}$$

[HI] = 0.32M

The following substances are not included in the equilibrium expression because their concentrations are essentially constant:

1. **solids** - cannot be compressed and hence their concentrations cannot be changed; concentration determined by **density** of the solid
2. **pure liquids** - cannot be compressed and hence their concentrations cannot be changed; however . . . if there are 2 or more liquids, they may mix and are no longer pure and the concentrations may change due to dilution; **liquids are only pure if there is only one liquid present** in the equilibrium expression

Write the K_{eq} expression for the following equilibrium:

a) $N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$ $K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$

b) $NH_3(g) + 5O_2(g) \rightleftarrows 4NO(g) + 6H_2O(g)$

c) $Si(s) + O_2(g) \rightleftarrows SiO_2(s)$

d) $CH_3COCH_3(l) + Cl_2(g) \rightleftarrows CH_3COCH_2Cl(l) + HCl(g)$

$K_{eq} = \frac{[NO]^4[H_2O]^6}{[NH_3][O_2]^5}$

$K_{eq} = \frac{1}{[O_2]}$

The equilibrium constant, K_{eq}, is a ratio of $\frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$, so numerically, if K_{eq} is large the products are favoured and if K_{eq} is small the reactants are favoured.

$$\text{Large } K_{eq} = \frac{\large[\text{PRODUCTS}]}{\small[\text{REACTANTS}]}$$

$$\text{Small } K_{eq} = \frac{\small[\text{PRODUCTS}]}{\large[\text{REACTANTS}]}$$

$K_{eq} > 1$ then products GREATER THAN reactants
$K_{eq} < 1$ then products LESS THAN reactants
$K_{eq} = 1$ products EQUAL reactants

Predict the relative amount of reactants & products at equilibrium:

a) $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$ R favoured $K_{eq} = 6.3 \times 10^{-11}$

b) $4NH_3(g) + 5O_2(g) \rightleftarrows 4NO(g) + 6H_2O(g)$ $K_{eq} = 5 \times 10^{3}$

P favoured

c) $Si(s) + O_2(g) \rightleftarrows SiO_2(s)$ $K_{eq} = 2 \times 10^{-9}$

R. favoured

Dependence of K_{eq} on Temperature

- K_{eq} remains constant when concentration, pressure or surface area change
- however . . . changing the temperature affects the value of K_{eq}

Why???

- changing **concentration, pressure or surface area** **changes the number of reacting molecules per litre**
  > the equilibrium counteracts these stresses and **shifts to re-establish a new equilibrium**
  > the ratio of [PRODUCT]/[REACTANT] and the **value of K_{eq} remains the same**
- changing **temperature** causes a shift in the equilibrium, but the **number of reacting molecules does not change**
  > therefore the ratio of [PRODUCT]/[REACTANT] changes and the **value of K_{eq} changes**

Varying temperature is the only factor that changes the value of K_{eq}.

Consider the reaction:

$$\text{REACTANTS} \rightleftarrows \text{PRODUCTS} + \uparrow 76\ \text{kJ}$$

- for an **exothermic** reaction, an **increase in temperature** will cause a **shift to the <u>left</u>**
- the [PRODUCTS] decrease while the [REACTANTS] increase . . . and since

$$K_{eq} = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]}$$ **the value of K_{eq} decreases**

- for an **endothermic** reaction, an **increase in temperature** will cause a **shift to the <u>right</u>**
- the [PRODUCTS] increase while the [REACTANTS] decrease and **the value of K_{eq} would increase**

$$\uparrow 76\ \text{kJ} + \text{REACTANTS} \rightleftarrows \text{PRODUCTS}$$

K_{eq} **increases** when the temperature of an **endothermic** reaction is increased
K_{eq} **decreases** when the temperature of an **exothermic** reaction is increased

Consider the following reaction:

energy + $PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$

Is the above reaction endothermic or exothermic if K_{eq} is 2.24 at 227°C and 33.3 at 487°C ?

K_{eq}: 2.24 @ 227°C

↑ 33.3 @ 487°C