Lesson 2 Working with equilibrium expressions and constants of homogeneous systems.

Significance of high equilibrium constant – high equilibrium constants indicate that the reaction will use up a high percentage of the reactants to produce a high amount of product. However it does not indicate the rate at which the reaction takes place..

Units of the equilibrium constant-the units of the equilibrium constant depends on the chemical equation and hence the equilibrium expression.

When the total number of moles of products, in a balanced chemical equation, is equal to the total number of moles of reactants, then K has no units.

For example:

N_2 (g) + O_2 (g) ⇌ 2NO (g)

Units of concentration will cancel out in the expression shown.

$$K = \frac{[NO]^2}{[N_2]\,[O_2]}$$

Expression dependent on equation- before an equilibrium expression can be written the balanced chemical equation has to be known. Reactants appear in the denominator and products in the numerator. Below are a few examples.

aA(g) + bB(g) ⇆ cC(g) + dD(g)

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

cC(g) + dD(g) ⇆ aA(g) + bB(g)

$$\frac{[A]^a\,[B]^b}{[C]^c\,[D]^d} = \frac{1}{K_c}$$

2aA(g) + 2bB(g) ⇆ 2cC(g) + 2dD(g)

$$\frac{[C]^{2c}[D]^{2d}}{[A]^{2a}[B]^{2b}} = K_c^2$$

½aA(g) + ½bB(g) ⇆ ½cC(g) + ½dD(g)

$$\frac{[C]^{\frac{1}{2}c}[D]^{\frac{1}{2}d}}{[A]^{\frac{1}{2}a}[B]^{\frac{1}{2}b}} = K_c^{1/2} = \sqrt{K_c}$$

eg1 Consider the following reaction at equilibrium.

$2SO_2(g) + O_2(g) \leftrightarrows 2SO_3(g)$

The equilibrium constant at 1000 °K is $2.71 \times 10^2\ M^{-1}$.

a) Write the equilibrium expression for the reaction $2SO_2(g) + O_2(g) \leftrightarrows 2SO_3(g)$

$$\frac{[SO_3]^2}{[SO_2]^2\ [O_2]} = K$$

b) Write the equilibrium expression for the reaction $SO_2(g) + \frac{1}{2} O_2(g) \leftrightarrows SO_3(g)$

$$\frac{[SO_3]}{[SO_2]\ [O_2]^{1/2}} = K^{1/2}$$

c) Calculate the equilibrium constant for the reaction below at 1000°K

$2SO_3(g) \leftrightarrows 2SO_2(g) + O_2(g)$

$$\frac{[SO_2]^2\ [O_2]}{[SO_3]^2} = \frac{1}{K} = \frac{1}{271} = 3.69 \times 10^{-3}\ M$$

1) A mixture of nitrogen and hydrogen gases was placed in a sealed vessel and allowed to reach equilibrium according to the equation below at a constant temperature.

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

   When no further change to the mixture was observed the concentration of each gas present was analysed and recorded. The results are given below.

   $[NH_3] = 0.142\ M$

   $[H_2] = 0.121\ M$

   $[N_2] = 0.101\ M$

   a) Write the equilibrium expression for the above reaction.

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

   b) Calculate the value of the equilibrium expression

   $$\frac{[0.142\ M]^2}{[0.121\ M]^3[0.101\ M]} = K_c = 1.13 \times 10^2\ M^{-2}$$

c) The temperature in the reaction vessel above was altered and the mixture was again lowed to reach equilibrium. The equilibrium constant at this new temperature is $1.27 \times 10^4\ M^{-2}$.

i. Write the equilibrium expression for the equation below.

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

$$\frac{[H_2]^3[N_2]}{[NH_3]^2} = \frac{1}{K_c}$$

ii. Calculate the equilibrium constant at this temperature for the reaction in i. above.

$$\frac{[H_2]^3[N_2]}{[NH_3]^2} = \frac{1}{K_c} = \frac{1}{1.27 \times 10^4}\ M^2$$

$7.87 \times 10^{-5}\ M^2$

iii. What can you say about the yield of nitrogen and hydrogen gases at this temperature?

K_c is very low and hence low yields will be achieved at this temperature.

2) A mixture containing 2.00 mol of SO_2 gas and 2.00 mol of O_2 gas was placed in a 2.00 litre, sealed, vessel and allowed to react according to the equation below.

$SO_2(g) + \frac{1}{2} O_2(g) \leftrightarrows SO_3(g)$

The mixture was allowed to reach equilibrium at constant temperature. At equilibrium 0.500 mol of SO_3 gas was present.

a) Write the equilibrium expression for the reaction.

$$\frac{[SO_3]}{[SO_2]\,[O_2]^{1/2}} = K_c$$

b) Calculate the equilibrium constant for the system at the given temperature.

At equilibrium mol of SO_2 present = 1.50, mol of O_2 present = 1.75

$[SO_2] = 1.50/2.00 = 0.750\ M$
$[O_2] = 1.75 / 2.00 = 0.875\ M$
$[SO_3] = 0.500 / 2.00 = 0.250\ M$

$$\frac{[0.250\ M]}{[0.750\ M]\,[0.875\ M]^{1/2}} = K_c$$

$K_c = 0.356\ M^{-1/2}$

3) Consider the production of hydrogen gas according to the equation below.

$$CO(g) + H_2O(g) \leftrightarrows CO_2(g) + H_2(g) \qquad \Delta H = +41 \text{ kJ/mol}$$

A mixture of CO and H_2O gases was placed in a 2.00 litre vessel at 225°C, a few minutes later the mixture was analysed and found to contain 2.00 mol of CO, 1.00 mol of H_2O and 2.00 mol of H_2 gas. At 225°C the equilibrium constant for this reaction is 23.6

a) How many mol of CO_2 was present in the mixture at equilibrium?

The stoichiometry tells us that for every mol of CO_2 formed one mol of H_2 is also formed. The stoichiometric ratio for CO_2 formed to H_2 formed is 1:1. Hence 2.00 mol of CO_2 gas is formed.

b) Write the equilibrium expression for this reaction.

$$\frac{[H_2]\,[CO_2]}{[CO]\,[H_2O]} = K_c$$

c) Calculate the value of the equilibrium expression.

$[H_2]$ = 2.00 / 2.00 = 1.00M

$[CO_2]$ = 2.00 / 2.00 = 1.00M

[CO] = 2.00 / 2.00 =1.00M

$[H_2O]$ = 1.00 / 2.00 = 0.500M

K_c =2.00

d) Had the reaction reached equilibrium? Explain.

No. The equilibrium constant for this reaction at 225°C is 23.6. Since there is no temperature change the equilibrium constant is not change, hence, the reaction is still moving in the forward direction when the sampling was done.

e) What can you say about the forward rate of reaction when compared to the backward rate of reaction? Explain

The forward rate is greater than the backward rate since the reaction is still moving forward to achieve equilibrium once more.

f) In another vessel, of unknown volume, a mixture of CO and H_2O gases was allowed to react and reach equilibrium at 225°C. After reaching equilibrium the mixture was sampled and revealed the following concentrations, [CO] =3.00M and $[H_2O]$ = 2.24 M. Calculate the concentration of H_2 gas.

Since the number of mol of H_2 and CO_2 formed are the same so will their concentrations also be the same.
So we can write the following expression.

$$\frac{[H_2]^2}{[CO]\,[H_2O]} = K_c$$

Now we solve for $[H_2]$

$[H_2]$ =12.6 M

$$\frac{[H_2]^2}{[3.00]\,[2.24]} = 23.6$$