Unit 4, Lesson #3: The Equilibrium Constant

When a reversible reaction occurs in a closed container, the reaction eventually reaches a "balance point" when the rate of the forward reaction is equal to the rate of the reverse reaction. At this point, the system is said to be in dynamic equilibrium. At equilibrium, the tendency toward maximum randomness (entropy) is balanced against and the tendency to minimum enthalpy. At equilibrium, the free energy change (ΔG) is zero.

Consider the reaction: $PCl_3 \text{ (g)} + Cl_2 \text{ (g)} \leftrightarrow PCl_5 \text{ (g)}$

The forward reaction is first order with regard to PCl_3 (g) and Cl_2 (g). The reaction rate for the forward reaction is:

$$rate_{forward} = k_{forward}[PCl_3][Cl_2]$$

The reverse reaction is first order with regard to PCl_5 (g). The rate of the reverse reaction is:

$$rate_{reverse} = k_{reverse}[PCl_5]$$

By definition, equilibrium is reached when the rate of the forward reaction is equal to the rate of the reverse reaction:

$$rate_{forward} = rate_{reverse}$$

If the rates of the forward and reverse reactions are equal, then:

$$k_{forward}[PCl_3][Cl_2] = k_{reverse}[PCl_5]$$

Rearranging gives us: $\dfrac{k_{forward}}{k_{reverse}} = \dfrac{[PCl_5]}{[PCl_3][Cl_2]}$

Because $k_{forward}$ and $k_{reverse}$ are both constants, then $\dfrac{k_{forward}}{k_{reverse}}$ will also be a constant value, called K_{eq}

Therefore, $\boxed{K_{eq} = \dfrac{[PCl_5]}{[PCl_3][Cl_2]}}$

K_{eq}, is called the **equilibrium constant** for this reaction at a specified temperature. Because K_{eq} depends on reaction rates, and reaction rates depend on temperature, the value for K_{eq} is different at different temperatures. The temperature must be reported along with the value of K_{eq}.

The K_{eq} relationship in the example above is for a first order reaction, but scientists have measured the K_{eq} values for many, many reactions with many different reaction orders. Because the K_{eq} is calculated using the rates of both the forward and the reverse reactions, they have found the following relationship:

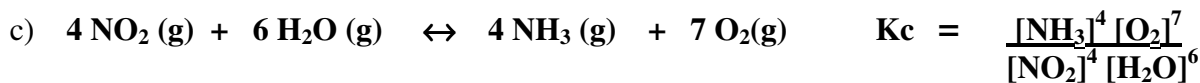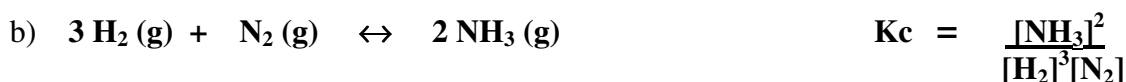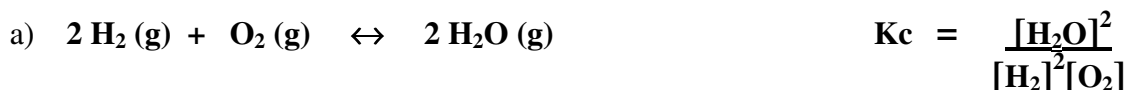For the general **homogeneous**, reversible chemical reaction:

$$aA \ + \ bB \ \leftrightarrow \ cC \ + \ dD$$

At equilibrium, when the rate of the forward and reverse reactions are equal, we can write general equilibrium expression:

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

- When the amounts of the reactants and products are expressed as concentrations, then K_{eq} can also be called the K_c value, where the "c" tells us that K_{eq} was measured using concentrations.
- K_{eq} can also be expressed using the partial pressures of gases
- the only factor that affects the value of K_{eq} (or K_c) for a certain reaction is temperature
- K_{eq} has no units

You may recall that during the unit on rates of reaction, we said over and over again that the molar coefficients in the chemical equation (a,b,c, and d) had no place in the rate equation, because the rate of the overall reaction depends only on the rate of the rate limiting step. Because the K_{eq} equation is calculated using the rates of both the forward and reverse reactions, we do include the molar coefficients in the K_{eq} equation.

eg. For the following **homogeneous** reactions, write the K_c expression:

a) $2 H_2 (g) + O_2 (g) \leftrightarrow 2 H_2O (g)$ $Kc \ = \ \dfrac{[H_2O]^2}{[H_2]^2 [O_2]}$

b) $3 H_2 (g) + N_2 (g) \leftrightarrow 2 NH_3 (g)$ $Kc \ = \ \dfrac{[NH_3]^2}{[H_2]^3 [N_2]}$

c) $4 NO_2 (g) + 6 H_2O (g) \leftrightarrow 4 NH_3 (g) + 7 O_2(g)$ $Kc \ = \ \dfrac{[NH_3]^4 [O_2]^7}{[NO_2]^4 [H_2O]^6}$

The value of K_{eq} is determined experimentally. Chemists allow reactions to occur at stated temperatures, until the system no longer changes. At this point, they measure the amounts of both the reactants and products. Just as chemists monitor changes in pH, colour, gas pressure or conductivity of solutions to calculate the rate of a reaction, measuring these values can also be used to calculate the concentrations of the different species. Once the concentrations have been determined, these values are "plugged into" the expression and K_{eq} is calculated.

The wonderful thing about K_{eq} is that it doesn't matter how much reactant and product you put in the reaction container at the beginning of the reaction, at equilibrium, the ratios of the amounts will always give the same number, the equilibrium constant, K_{eq}. This is because the K_{eq} represents the highest entropy and lowest enthalpy for that system at that temperature.

Heterogeneous systems (chemical reactions in which the species are not all in the same phase) can also reach equilibrium. How do we write the K_{eq} expression for a heterogeneous system?

Recall that gases have the highest entropy, followed by aqueous, liquid and then solid reactants. As the entropy of a reactant increases, the reactant has higher freedom of motion, which means that it will be capable of more collisions and more reactions. For this reason, in a heterogeneous system, only the reactants in the phase with the highest entropy are included in the K_{eq} expression. It is these reactants which will determine the rate of the reaction, so it is these species that are included in the K_{eq}.

eg. For the reaction: **$CaCO_3$ (s) $\leftrightarrow$ CaO (s) + CO_2 (g)**

This is a heterogeneous system, with species in both the solid and gas phases. Because only CO_2 is in the highest entropy phase, only CO_2 is included in the K_{eq} equation. Therefore, the K_{eq} equation for this reaction is $K_{eq} = [CO_2]$

eg. For the reaction: **NH_3 (g)   +   HCl (g) $\leftrightarrow$ NH_4Cl (s)**

We only include the concentrations of the species that are in the highest entropy phase, NH_3 and HCl, in the K_{eq} expression. Therefore, the K_{eq} equation for this reaction is:

$$Keq \; = \; \frac{1}{[NH_3]\,[HCl]}.$$

eg. For the reaction: **$CaCl_2$(s) $\overset{H_2O}{\leftrightarrow}$ Ca^{2+} (aq)   +   2 Cl^{1-} (aq)**

The species in the highest entropy phase are the aqueous calcium and chloride ions, so these are the only species that are included in the K_{eq} expression. The water is not included. This is for two reasons- first of all, liquid water is in a lower entropy phase than the ions (which are spread out through the water), and secondly, the concentration of pure water is a constant 55.5 mol/L. Because the concentration of pure water is constant, it is factored into the K_{eq} already, without having to include it specifically.

The K_{eq} expression for the above reaction is $K_{eq} = [Ca^{2+}]\,[Cl^{1-}]^2$

eg. Calculate the value for K_c at 448 °C for the reaction of hydrogen gas with iodine vapour to produce
     hydrogen iodide, given that the equilibrium concentrations of each species are:
     [HI] = 1.00 mol/L, $[I_2]$ = 0.820 mol/L and $[H_2]$ = 0.0242 mol/L.

The balanced chemical equation for the reaction is: $H_2(g) + I_2(g) \leftrightarrow 2 HI (g)$

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

$K_c = \dfrac{[1.00]^2}{[0.0242][0.820]}$

$\quad = 50.4$

What does this value for K_c for the reaction actually mean?
K_c is the ratio of the concentration (amount) of the products divided by the concentration (amount) of the reactants.
The larger the value of K, the larger the relative amount of product, which means that the reaction proceeded further to the right.
In this example, the ratio of product to reactants is over 50, so the reaction strongly favours the product, HI.

eg. Calculate the value for K_c at certain temperature for the reaction of hydrogen gas and nitrogen gas
     to produce ammonia (NH_3), given that the equilibrium concentrations of each species are:
     $[H_2]$ = 0.746 mol/L, $[N_2]$ = 0.521 mol/L and $[NH_3]$ = 0.0042 mol/L.

The balanced chemical equation for the reaction is: $3 H_2(g) + N_2(g) \leftrightarrow 2 NH_3 (g)$

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

$K_c = \dfrac{[0.0042]^2}{[0.746][0.521]}$

$\quad = 4.54 \times 10^{-5}$

What does this value for K_c for the reaction actually mean?
K_c is the ratio of the concentration (amount) of the products divided by the concentration (amount) of the reactants.
The smaller the value of K, the smaller the relative amount of product, which means that the reaction did not proceed very far to the right.
In this example, the ratio of product to reactants is 0.0000454, so hardly any product formed. The reaction strongly favours the reactants.

Interpreting values of K:
- If K is greater than 1 then the reaction favours the products (the rate of the forward reaction is
  greater than the rate of the reverse reaction)
- If K is less than 1 then the reaction favours the reactants (the rate of the forward reaction is less than
  the rate of the reverse reaction)
- If K equals one, the rates of the forward and reverse reactions are equal. The relative amounts of
 products and reactants is equal.

eg. For the following reactions at the stated temperatures, what does the value of K indicate about the amount of product that will form?

a) **2 H$_2$(g) + O$_2$(g) ↔ 2 H$_2$O (g)**   K$_c$ = 1.4 x 10^{83} at 298 K
K$_c$ >>> 1, so the reaction goes essentially to completion. The amount of product is much much greater than the amount of reactant.

b) **CaCO$_3$ (s) ↔ CaO (s)   +   CO$_2$ (g)**   K$_c$ = 1.9 x 10^{-23} at 298 K
K$_c$ <<< 1, so the reaction does not go anywhere near completion. The amount of reactant is much much greater than the amount of product.
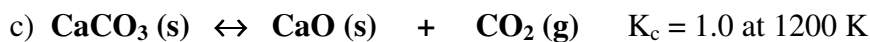
c) **CaCO$_3$ (s) ↔ CaO (s)   +   CO$_2$ (g)**   K$_c$ = 1.0 at 1200 K
K$_c$ = 1.0, so the reaction goes about half-way to completion. The amount of reactant is equal to the amount of product.

d) **2 SO$_2$ (g)   + O$_2$ (g) ↔ 2 SO$_3$ (g)**   Kc = 3.4 at 298 K
K$_c$ > 1.0, so the reaction favours the product. There is about 3 x more product than reactant at equilibrium.

Homework:
1. Read pages 334 to 338 in McGraw-Hill
2. Do problems 1-5 on page 336
3. Do problems 6-10 on page 338.
4. Do problems 16 – 20 on page 349.

answers on page 375 are correct