

Revised August 2011

HONORS TOPIC 11: Chemical Equilibrium

- **Dynamic equilibrium**

A dynamic equilibrium exists in a reversible reaction when the rate of the forward reaction is equal to the rate of the backward reaction. For a reaction to reach equilibrium a finite amount of time must elapse, i.e., the reactants must be allowed to come together and both the forward and backward reactions must be established before the equilibrium position is reached. On a macroscopic scale it appears that the reaction has stopped. Closer inspection on the microscopic scale confirms, it is in fact, still occurring. Consider the equilibrium below where a, b, c and d are the stoichiometric coefficients of substances A, B, C and D respectively.



The equilibrium constant (K_c) is constant at a given temperature. For the reaction above, at equilibrium, at a given temperature

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

Where [] represents concentration. i.e. the product of the concentrations of products raised to their appropriate powers, divided by the product of the concentrations of reactants raised to their appropriate powers.

N.B. K_c expressions do not include values for pure solids or pure liquids since their concentrations are constant and as such are incorporated into the equilibrium constant.



- The use of K_c in calculations

Task 11a

Calculations where Equilibrium has already been established

1. Consider the following gaseous phase esterification reaction, where butanoic acid ($C_3H_7CO_2H_{(g)}$) reacts with ethanol ($C_2H_5OH_{(g)}$) to produce the ester, ethyl butanoate ($C_3H_7CO_2C_2H_5_{(g)}$) and $H_2O_{(g)}$.



In three separate experiments, all at the same temperature, equilibrium was achieved and then the following data were collected.

| Experiment | Moles of butanoic acid | Moles of ethanol | Moles of ethyl butanoate | Moles of water |
|-------------------|-------------------------------|-------------------------|---------------------------------|-----------------------|
| 1 | 10.0 | 10.0 | 20.0 | 20.0 |
| 2 | 5.0 | 20.0 | 10.0 | 40.0 |
| 3 | 30.0 | 1.0 | 12.0 | 10.0 |

Calculate the equilibrium constant K_c , at this temperature in each of the experiments and comment on the values.

Calculations where initial amounts are known, and THEN Equilibrium is established – The use of ICE tables

2. Using the reaction and the K_c calculated in question #1, calculate the number of moles of each substance present at equilibrium when 1.00 moles of butanoic acid and 2.00 moles of ethanol are mixed at the SAME temperature.
3. Another ester, Ethyl ethanoate ($CH_3CO_2C_2H_5$) can be formed by the reaction of ethene (C_2H_4) with ethanoic acid (CH_3COOH) in an inert solvent according to the equation

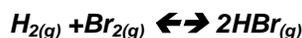




In an experiment 0.50 moles of ethene was allowed to react with 0.25 moles of ethanoic acid and the total volume of the mixture is made up to 500 mL with an inert solvent. When equilibrium had been established, the mixture was found to contain 0.22 moles of the ester. Calculate the molar concentration of all three substances present at equilibrium and hence the value of K_c .

Calculations where K is already known – working backwards

4. *The equilibrium constant for the reaction below has a value of 55 at a certain, given temperature.*



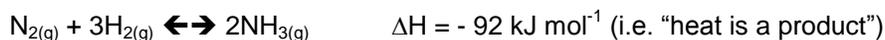
Calculate the number of moles of HBr present in an equilibrium mixture that contains 3.0 moles of hydrogen and 0.45 moles of bromine at this temperature.



- **Le Chatelier's principle and optimum conditions**

Le Chatelier's principle states that in any equilibrium when a change is made to some external factor such as temperature, pressure or concentration then there is a change in the position of the equilibrium so as to oppose that change. Consider two examples;

1. Manufacture of Ammonia (The Haber Process)



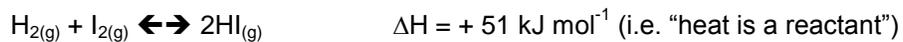
| Change in external factor | Shift in position of equilibrium | Reason |
|--|----------------------------------|--|
| Increase in pressure | Shifts to RHS | Less moles of gas on RHS so pressure is reduced |
| Increase in temperature | Shifts to LHS | Backward reaction is endothermic so removes heat by shifting to the LHS |
| Increase in concentration of nitrogen and hydrogen | Shifts to RHS | Less nitrogen and hydrogen on RHS |
| Increase in concentration of ammonia | Shifts to LHS | Less ammonia on LHS |
| Adding a catalyst | None | Catalyst only increases the speed that equilibrium is established not its position |

According to Le Chatelier's principle the preferred conditions to give a high yield of ammonia (shift to RHS – the product side) are high pressures and low temperatures. However, in practice high pressures are expensive to achieve (requiring stronger plant and thicker pipes that are able to withstand higher pressures), and low temperatures lead to slow rates of reaction which are uneconomic. It is therefore necessary to compromise to achieve an economic process with a reasonable yield at a good rate. Typical conditions 1000 atm and 450°C giving a yield of approximately 15% ammonia (the ammonia in the equilibrium mixture is cooled to liquefy it so it can be removed, and any unreacted gases can be recycled). This appears to be a low percentage of ammonia, but economically it works.

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2. Synthesis of Hydrogen Iodide

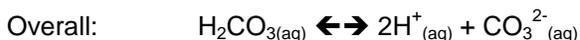
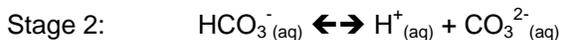
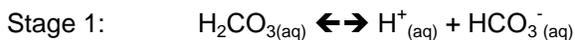


| Change in external factor | Shift in position of equilibrium | Reason |
|--|----------------------------------|--|
| Increase in pressure | No effect | Same moles of gas on LHS and RHS |
| Increase in temperature | Shifts to RHS | Forward reaction is endothermic so removes heat by shifting to the RHS |
| Increase in concentration of hydrogen and iodine | Shifts to RHS | Less hydrogen and iodine on RHS |
| Increase in concentration of hydrogen iodide | Shifts to LHS | Less Hydrogen Iodide on LHS |
| Adding a catalyst | None | Catalyst only increases the speed that equilibrium is established not its position |



- **Simultaneous equilibria**

Consider a situation where two equilibrium reactions occur together. For example, the ionization of a diprotic acid such as carbonic acid occurs in two stages that add up to one overall reaction.



It is possible to write a series of Kc expressions for these equilibria.

Stage 1:
$$\text{Kc stage 1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

Stage 2:
$$\text{Kc stage 2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

Overall:
$$\text{Kc overall} = \frac{[\text{H}^+]^2[\text{CO}_3^{2-}]}{[\text{H}_2\text{CO}_3]}$$

Inspection shows that Kc overall = (Kc stage1)(Kc stage2), and this is true of all multiple, simultaneous equilibria.



- **Format of Kc**

It is helpful to be aware of the possible different formats Kc could take under circumstances that appear very similar. When a reversible reaction is written in the opposite direction the new equilibrium constant is equal to the reciprocal of the original, if a reaction is "halved" or "doubled", then the original Kc will need to be square rooted or squared respectively in order to find the new Kc value. For example for the reaction below



The Kc expression is

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

(i) If the equation is instead written reversed as



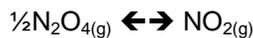
Then the new Kc expression is

$$\text{New Kc} = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

Inspection tells us that

$$\text{New Kc} = \frac{1}{K_c}$$

(ii) If the equation is instead written halved as



Then the New Kc expression is

$$\text{New Kc} = \frac{[\text{NO}_2]}{[\text{N}_2\text{O}_4]^{\frac{1}{2}}}$$

Inspection tells us that

$$\text{New Kc} = \sqrt{K_c}$$

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(iii) If the equation is instead written doubled as



Then the New K_c expression is

$$\text{New K}_c = \frac{[\text{NO}_2]^4}{[\text{N}_2\text{O}_4]^2}$$

Careful inspection tells us that

$$\text{New K}_c = \text{K}_c^2$$