Chemical Equilibrium

Dynamic Equilibrium

A dynamic equilibrium exists in a closed system when the rate of the forward reaction is equal to the rate of the reverse reaction.

When a dynamic equilibrium is set up, the concentrations of reactions and products do not change even though the reactions are proceeding at a finite rate in both directions.

A dynamic equilibrium can be approached from either direction. For example the same equilibrium mixture will be produced regardless of whether you start with just the reactants, just the products, or a mixture of both, given the same temperature and pressure.

Position of Equilibrium

The amounts of reactants and products present in the equilibrium mixture varies depending on the conditions. If there are more products than reactants, we say that the position of equilibrium lies to the right, or favours the forward reaction, and vice versa.

Changes in conditions can change the position of equilibrium, and hence the amounts of reactants and products present in the equilibrium mixture.

> If the position of equilibrium moves to the right or in the forward direction, then the rate of the forward reaction increases. This causes more products to be made, so the equilibrium mixture contains more products and less reactants. The rate of the reverse reaction increases until the two rates are again equal, setting up a new dynamic equilibrium.
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> If the position of equilibrium moves to the left, or in the backward direction, then the rate of the reverse reaction increases. This causes products to be turned into reactants faster than reactants are being turned into products, so the amount of reactants increase and products decrease in the equilibrium mixture

Equilibrium Constant

The **equilibrium constant**, $\mathbf{K_c}$, gives an indication of how far to the left, or right, the equilibrium position lies. If the value of $K_c > 1$, there are more products than reactants and the larger the value of K_c, the more products are present. The lower the value of K_c, the more reactants are present in the equilibrium mixture.

Kc is calculated for homogeneous reactions using the concentrations of the reactants and products at equilibrium:

For the general reaction $aA + bB \rightleftharpoons dD + eE$

$$K_c = \frac{[D]^d \times [E]^e}{[A]^a \times [B]^b}$$

where [D] = concentration of D in mol dm^{-3} etc.

Units of K_c

The units of K_c are found by substituting each concentration for the units of concentration: mol dm^{-3}, then cancelling top and bottom as far as possible. If they all cancel, then K_c has no units. Note that if all the mol dm^{-3} on the top line cancel but some remain on the bottom line:

$1/mol\ dm^{-3} = mol^{-1}dm^{3}$ and $1/(mol\ dm^{-3})^2 = mol^{-2}dm^{6}$ etc. *Check: the power for dm should always be 3x the power for mol, and they should always have opposite signs.*

Application

A sample of HI is placed in a sealed container and left to react equilibrium according to the equation $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$. At equilibrium the concentration of HI is 0.80 mol dm^{-3} and the concentration of I_2 is 0.10 mol dm^{-3}.

i) Write the expression for K_c.

ii) Determine the concentration of H_2 at equilibrium.

iii) Calculate the value of K_c under these conditions.

iv) Calculate the units of K_c, if any.

i) $K_c = [H_2] \times [I_2] / [HI]^2$

ii) H_2 and I_2 are made in equal amounts by the decomposition of HI, so $[H_2] = [I_2] =$ 0.10 mol dm^{-3}.

iii) $K_c = (0.10 \times 0.10) / (0.80)^2 = 0.015625$

iv) No units $Kc = \cancel{mol\ dm^{-3}} \times \cancel{mol\ dm^{-3}} / (\cancel{mol\ dm^{-3}})^2$

Check your understanding

i) The Haber process has equation $N_2 + 3H_2 \rightleftharpoons 2NH_3$. Write the K_c expression, and determine the units of K_c.

ii) At 400°C the concentrations at equilibrium were found to be NH_3: 0.04mol dm^{-3}, H_2: 0.30 mol dm^{-3}, N_2: 0.16mol dm^{-3}. Determine the value of K_c at this temperature. What does this tell you about the position of equilibrium?

Le Chatelier's Principle states that:

When a system in dynamic equilibrium is subjected to a change in the conditions (temperature, pressure or concentration), the position of the equilibrium will shift in the direction that will minimise the effect of the change. ** The shift in position of equilibrium does not "cancel out" the change!*

Effect of Temperature Changes on Position of Equilibrium

An increase in temperature causes the position of equilibrium to shift in the direction for which the reaction is endothermic, i.e. where ΔH is +ve. (it minimises the effect by "taking in" the heat).

Lowering the temperature shifts the position of equilibrium in the exothermic direction, where ΔH is –ve. The reaction generates more heat to minimise the effect of the lower temperature.

Effect of Pressure Changes on Position of Equilibrium

An increase in pressure causes the position of equilibrium to shift in the direction in which the equation has fewer gaseous moles. As a result there are fewer molecules present and the effect of the increased pressure is minimised.

A decrease in pressure causes the position of equilibrium to shift in the direction in which the equation has more gaseous moles.

Note that if there are equal numbers of moles on both sides of the equation, changing the pressure will not affect the position of equilibrium.

Application:
The following two equilibrium reactions are used in the manufacture of methanol. What will be the effect of (i) an increase in pressure and (ii) a decrease in temperature in each case? (iii) How do your answers to (i) and (ii) explain the choice of conditions for each reaction?

$$CH_{4(g)} + H_2O_{(g)} \xrightleftharpoons{\text{Ni at 700°C and 100kPa}} CO_{(g)} + 3H_{2(g)} \qquad \Delta H = +207 \text{ kJ mol}^{-1}$$

$$CO_{(g)} + 2H_{2(g)} \xrightleftharpoons{\text{Cr at 300°C and 30,000kPa}} CH_3OH_{(g)} \qquad \Delta H = -129 \text{ kJ mol}^{-1}$$

(i) An increase in pressure will shift the position of equilibrium in Reaction 1 to left (backward), towards the reactants. Less carbon monoxide will be made. This is because there are two moles of gases on the left side of the equation, and four moles of gases on the right side. An increase in pressure will shift the position of equilibrium in Reaction 2 to right (forward), towards the products. More methanol will be made. This is because there are three moles of gases on the left side of the equation, and one mole of gases on the right side.

(ii) A decrease in temperature will shift any equilibrium reaction in the direction which is exothermic (i.e. the direction in which ΔH is negative). This means that the position of equilibrium in Reaction 1 will shift towards the reactants (backwards direction) and less CO will be made. The position of equilibrium in Reaction 2 will shift in the forward direction (towards the products) producing more methanol.

(iii) In Reaction 1, we move the position of equilibrium to the right to optimise the production of CO by using low pressure (100kPa = atmospheric pressure) and a high temperature of 700°C. In Reaction 2 we move the position of equilibrium to the right to optimise the production of methanol by using a high pressure (300 atmospheres) and a much lower temperature of 300°C.

Effect of Concentration changes on Position of Equilibrium
Changing the concentration of a reactant or product (by adding or removing a substance) causes the position of the equilibrium to shift in the direction where the change is opposed. If a substance is removed, the position of equilibrium is shifted so that more of that substance is made. If a substance is added, the position of equilibrium shifts in the direction that uses up that substance.

This is easily understood in terms of collision theory. Adding a reactant increases the amount of that reactant per unit volume and hence increases the frequency of collisions involving that reactant which increases the rate of the forward reaction. More product is made, so the rate of the reverse reaction then speeds up too, and a new equilibrium is established.

Application
e.g. $$\mathbf{Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons 2\,CrO_4^{2-}{}_{(aq)} + 2H^+_{(aq)}}$$
(orange) (yellow)

A solution made up from acidified K_2CrO_4 will contain an equilibrium mixture of the yellow and orange ions (because it doesn't matter which side the equilibrium is approached from).

(i) Suggest how the equilibrium mixture can be made to contain more of the orange ions.
(ii) Suggest how the equilibrium mixture can be made to contain more of the yellow ions.

(i) If HCl(aq) is added, the concentration of H^+(aq) is increased and the position of equilibrium moves to reduce the concentration of H^+ i.e. it moves to the left, using up H^+ ions. The solution therefore becomes more orange in colour.

(ii) If H_2O is added the position of equilibrium moves in the direction in which H_2O is consumed, i.e. moves in the forward direction so there are more of the yellow ions and less of the orange ones. Alternatively, $OH^-_{(aq)}$ ions can be added to remove $H^+_{(aq)}$ from the solution, which will have exactly the same effect.

<u>The effect of a catalyst on Position of Equilibrium</u>
The effect of a catalyst on a reversible reaction is to lower the activation energy for the forward <u>and</u> backward reaction. This has the effect of speeding up both the forward and reverse reaction **equally**. So there is no change in the position of equilibrium, however equilibrium is reached more rapidly.

Selecting industrial process conditions
When we optimise the conditions for an industrial process that involves a chemical equilibrium we must consider the effect of temperature, pressure, concentration and catalysts on BOTH the position of equilibrium AND the rate of the reaction.

Sometimes the optimum is a compromise because e.g. the position of equilibrium is best when the temperature is low, but the rate of reaction is too slow for economic production. In these circumstances a catalyst might increase the rate sufficiently to allow the lower temperature to be used.

Even when the optimum conditions have been selected, the actual %conversion may be less than the theoretical. Reasons include other products than the required ones being formed, not enough time to allow the equilibrium to be established, and poisoning of the catalyst over time – catalysts do need to be replaced or cleaned and reused periodically

Application
In one of the steps in the manufacture of nitric acid from ammonia, a moderate temperature of 800ºC is used along with a platinum and rhodium catalyst. Suggest why this temperature is chosen.

$$4NH_{3(g)} + 5O_{2(g)} \xrightleftharpoons{Pt/Rh} 4NO_{(g)} + 6H_2O_{(g)} \qquad \Delta H = -950 \text{ kJ mol}^{-1}$$

The chosen temperature is a compromise. The equilibrium is exothermic in the forward direction, so the production of NO is favoured by a low temperature. At low temperatures the rate of reaction is too slow for economic production of NO, so a moderate temperature of 800ºC is used in combination with a catalyst raise the rate of reaction sufficiently without pushing the position of equilibrium back too far to the left.

Check your understanding:

For the two equilibrium reactions below, explain fully the effect of (iii) increasing the pressure or (iv) decreasing the temperature on the production of carbon monoxide and methanol. Make reference to both rate of reaction and position of equilibrium.

$$CH_{4(g)} + H_2O_{(g)} \overset{Ni}{\rightleftharpoons} CO_{(g)} + 3H_{2(g)} \qquad \Delta H = +207\ kJ\ mol^{-1}$$

$$CO_{(g)} + 2H_{2(g)} \overset{Cr}{\rightleftharpoons} CH_3OH_{(g)} \qquad \Delta H = -129\ kJ\ mol^{-1}$$

For the two equilibrium reactions above (manufacture of methanol), explain fully why the following reaction conditions have been selected, and where compromises have been made:

(v) Reaction 1: Ni catalyst at 700ºC and 100kPa
(vi) Reaction 2: Cr at 300ºC and 30,000kPa

Answers to Check your Understanding questions:

i) The Haber process has equation $N_2 + 3H_2 \rightleftharpoons 2NH_3$. Write the K_c expression, and determine the units of K_c.

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad \text{Units: } mol^{-2}dm^{6}$$

ii) At 400°C the concentrations at equilibrium were found to be NH_3: 0.040 mol dm^{-3}, H_2: 0.40 mol dm^{-3}, N_2: 0.16mol dm^{-3}. Determine the value of K_c at this temperature. What does this tell you about the position of equilibrium?

$$K_c = (0.04)^2 / 0.16 \times 0.40^3 \qquad = 0.0016 / 0.01024 = 0.15625$$

This tells us that the position of equilibrium lies to the left: there is more N_2 and H_2 present than there is ammonia.

iii)

REACTION 1 $\quad CH_{4(g)} + H_2O_{(g)} \xrightarrow{\text{Ni at 700ºC and 100kPa}} \!\!\!\!\rightleftharpoons CO_{(g)} + 3H_{2(g)} \quad \Delta H = +207\ kJ\ mol^{-1}$

REACTION 2 $\quad CO_{(g)} + 2H_{2(g)} \xrightarrow{\text{Cr at 300ºC and 30,000kPa}} \!\!\!\!\rightleftharpoons CH_3OH_{(g)} \quad \Delta H = -129\ kJ\ mol^{-1}$

Increase in Pressure
An increase in pressure will shift the position of equilibrium in Reaction 1 to left (backward), towards the reactants because there are two moles of gases on the left side of the equation, and four moles of gases on the right side, and will speed up the forward and reverse reactions. Less carbon monoxide will be made, but it will be made more rapidly.

An increase in pressure will shift the position of equilibrium in Reaction 2 to right (forward), towards the products because there are three moles of gases on the left side of the equation, and one mole of gases on the right side, and will speed up the forward and reverse reactions. More methanol will be made, and it will be made more rapidly.

Decrease in temperature
A decrease in temperature will shift an equilibrium reaction in the direction that is exothermic (i.e. the direction in which ΔH is negative). This means that the position of equilibrium in Reaction 1 will shift in the backward direction. In addition, the rates of the forward and reverse reactions will decrease so less CO will be made and it will be made more slowly.

The position of equilibrium in Reaction 2 will shift in the forward direction (towards the products) producing more methanol, but the rate of the forward and reverse reactions will decrease, so the methanol will be made more slowly.

Choice of conditions

(v) Reaction 1: A moderately high temperature is chosen since at high temperatures the reaction is fast, and the position of equilibrium shifts towards the products. Too high a temperature would be expensive in terms of energy costs, and fuel use, so a catalyst is used to speed up the reaction as well, rather than using an even higher temperature. Atmospheric pressure (100kPa = atmospheric pressure) is used because at high pressures the position of equilibrium shifts towards the reactants, and the cost of reducing the pressure below atmospheric pressure would not be justified (as well as having the effect of reducing the rate of reaction)

(vi) Reaction 2: A moderately low temperature is chosen as a compromise between getting a fast enough rate of reaction and getting a reasonable yield of product, since at high temperatures the position of equilibrium shifts in the backward direction. A lower temperature can be used and still get a reasonable rate of reaction because a catalyst is being used to increase the rate. A high pressure is used which helps increase the rate of reaction as well as shifting the position of equilibrium towards the products, increasing the yield of methanol. An excessively high pressure would result in safety and cost issues, however, so the pressure chosen (300 atmospheres) is also a compromise.