91166 Demonstrate understanding of chemical reactivity
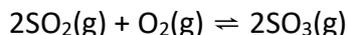## Collated questions on equilibria

(2018:2)

The Contact Process is used industrially in the manufacture of sulfuric acid. One step in this process is the oxidation of sulfur dioxide, $SO_2(g)$, to sulfur trioxide, $SO_3(g)$.
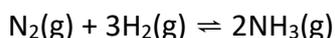
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(a) Write the equilibrium constant expression for this reaction. Kc =

(b) (i) Calculate the equilibrium constant (Kc) for this reaction at 600ºC using the following concentrations: $[SO_2]$ = 0.100 mol L^{-1} $[O_2]$ = 0.200 mol L^{-1} $[SO_3]$ = 0.0930 mol L^{-1}

(ii) Explain what the size of the Kc value indicates about the extent of the reaction at equilibrium.

(c) Explain, using equilibrium principles, why it is important for an industrial plant to continue to remove the sulfur trioxide gas, $SO_3(g)$, as it is produced.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
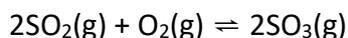
(d) Predict, using equilibrium principles, the effect on the concentration of sulfur trioxide gas, $SO_3(g)$, of carrying out the reaction in a larger reaction vessel.

(e) When the reaction is carried out at 450ºC, the Kc value is higher than the value at 600°C. Justify whether the oxidation of sulfur dioxide gas, $SO_2(g)$, to sulfur trioxide gas, $SO_3(g)$, is exothermic or endothermic.

(2017:2)

The addition of a small amount of iron to a mixture of nitrogen and hydrogen gases helps to speed up the production of ammonia gas. The reaction described above is an equilibrium reaction, as represented by the following equation:

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

(b) (i) Write the equilibrium constant expression for this reaction.

(ii) The value of the equilibrium constant, K_c, is 640 at 25°C. Show, by calculation, using the concentrations of the gases given in the table below, whether or not the reaction is at equilibrium. Explain your answer.

| Gas	N_2	H_2	NH_3
Concentration (mol L^{-1})	0.0821	0.0583	0.105

Is the mixture at equilibrium? (Circle) Yes No

Calculation and explanation:

(c)   As the temperature increases, the value of the equilibrium constant, K_c, decreases from 640 at 25°C to 0.440 at 200°C.

Justify whether the formation of ammonia, $NH_3(g)$, is an endothermic or exothermic reaction.

(2017:3)

(b)   Two different cobalt(II) complex ions, $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-,}$ exist together in a solution in equilibrium with chloride ions, $Cl^-(aq)$. The forward reaction is endothermic; ΔH is positive. The equation for this equilibrium is shown below.

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$
$$\text{pink} \qquad\qquad\qquad \text{blue}$$
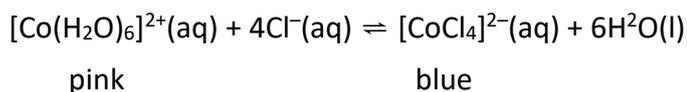
Explain using equilibrium principles, the effect on the colour of the solution if:

(i)   more water is added to the reaction mixture

(ii)   a test tube containing the reaction mixture is placed in a beaker of ice-cold water.

(c)   Brown nitrogen dioxide gas, $NO_2(g)$, exists in equilibrium with the colourless gas, dinitrogen tetroxide, $N_2O_4(g)$.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$
$$\text{brown} \qquad \text{colourless}$$
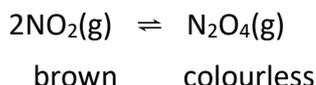
Explain using equilibrium principles, the effect of decreasing the volume of the container (therefore increasing the pressure) on the observations of this equilibrium mixture.
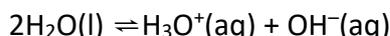
(2016:3)

(a)   The equilibrium constant expression for a reaction is:

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2}$$

Write the equation for this reaction.
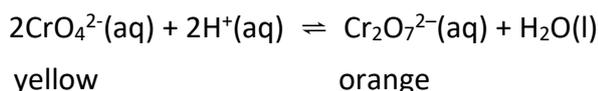
(b)   The ionisation of water is represented by the equation:
$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
Give an account of the extent of ionisation of water, given $K_w = 1 \times 10^{-14}$.

(c)   When acid is added to a yellow solution of chromate ions, $CrO_4^{2-}(aq)$, the following equilibrium is established.

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$
$$\text{yellow} \qquad\qquad \text{orange}$$

Analyse this equilibrium using equilibrium principles to explain the effect on the colour of the solution when:

(i)   more dilute acid is added: (ii)   dilute base is added:

(d)   When hydrogen gas, $H_2(g)$, and iodine gas, $I_2(g)$ are mixed, they react to form $HI(g)$, and an equilibrium is established.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad K_c = 64 \text{ at } 445°C.$$
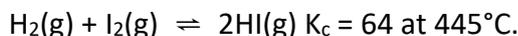
(i)   Calculate the concentration of HI in an equilibrium mixture at 445°C when the concentrations of $H_2(g)$ and $I_2(g)$ are both 0.312 mol L^{-1}.

(ii)   Explain the effect on the position of equilibrium if the overall pressure of the equilibrium system is increased.

(iii)   When the temperature of the equilibrium system is increased to 510°C, the K_c value decreases to 46. Justify, using equilibrium principles, whether the forward reaction is exothermic or endothermic.

(2015:3)
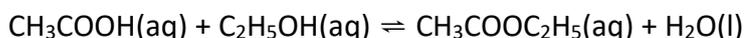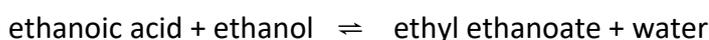
(a)   The equilibrium constant for a reaction involving compounds A, B, C, and D is shown as:

$$K_c = \frac{[C]^3[D]}{[A][B]^2}$$

Write the chemical equation for this reaction.

(b)   The reaction between ethanoic acid and ethanol is reversible. Ethyl ethanoate and water are the products formed. In a closed system, a dynamic equilibrium is set up.

$$\text{ethanoic acid} + \text{ethanol} \rightleftharpoons \text{ethyl ethanoate} + \text{water}$$

$$CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l)$$

(i)   Explain, using equilibrium principles, the effect of adding more ethanol to the reaction mixture.

(ii)   The reaction is quite slow, so a small amount of concentrated sulfuric acid is added as a catalyst.
Explain, using equilibrium principles, the effect of adding this catalyst to the equilibrium mixture.

(c)   The following chemical equation represents a reaction that is part of the Contact Process which produces sulfuric acid.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -200 \text{ kJ mol}^{-1}, \quad K_c = 4.32 \text{ at } 600°C$$
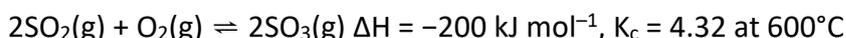
(i)   Write an equilibrium constant expression for this reaction. $K_c =$

(ii)   A reaction mixture has the following concentration of gases at 600°C:

$[SO_2(g)] = 0.300$ mol L^{-1} $[O_2(g)] = 0.100$ mol L^{-1} $[SO_3(g)] = 0.250$ mol L^{-1}

Justify why this reaction mixture is not at equilibrium. In your answer you should use the equilibrium expression from part (c)(i) and the data provided above to show that the reaction mixture is not at equilibrium.
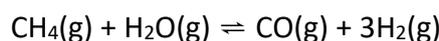
(iii)   The reaction on the previous page was repeated at 450°C.

Explain, using equilibrium principles, how the change in temperature will affect:

- the value of Kc
- the position of equilibrium.

(2014:2)

Hydrogen can be produced industrially by reacting methane with water. An equation for this reaction can be represented by:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

$$K_c = 4.7 \text{ at } 1127°C$$

(a)   (i)   Complete the equilibrium constant expression for this reaction: $K_c =$

(ii)   The concentrations of the four gases in a reaction mixture at 1127°C are found to be:

Gas	CH_4	H_2O	CO	H_2
Concentration / mol L^{-1}	0.0300	0.0500	0.200	0.300

Use these values to carry out a calculation to determine if the reaction is at equilibrium.
Mixture at equilibrium? Yes   No   (circle correct option)

Calculation:

(b)   The reaction shown in the equation below is at equilibrium.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$
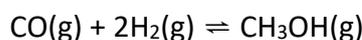
Describe the effect of each of the following changes on the equilibrium concentration of methanol (increase, decrease, stay the same). Justify your answers using equilibrium principles.

A copper oxide, CuO, catalyst is added.

Amount of $CH_3OH(g)$ would: increase OR decrease OR stay the same (circle correct answer)

Reason:

$H_2(g)$ is removed.

Amount of CH3OH(g) would: increase OR decrease OR stay the same (circle correct answer)

Reason:

(d) In a reaction, the brown gas nitrogen dioxide, $NO_2(g)$, exists in equilibrium with the colourless gas dinitrogen tetroxide, $N_2O_4(g)$. The equation for this reaction is represented by:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$
brown gas   colourless gas
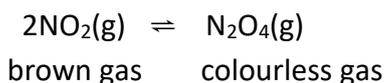
The table below shows the observations when changes were made to the system.

Change		Observations
Pressure	increased (by decreasing the volume of the container)	Colour faded
	decreased (by increasing the volume of the container)	Colour darkened
Temperature	container with reaction mixture put into hot water	Colour darkened
	container with reaction mixture put into ice water	Colour faded

Analyse these experimental observations. In your answer you should:
- link all of the observations to equilibrium principles
- justify whether the formation of dinitrogen tetroxide from nitrogen dioxide is endothermic or exothermic.

(2013:2)

(a) Ammonia gas, $NH_3(g)$, is formed from hydrogen gas and nitrogen gas, as shown in the following equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
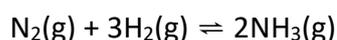
Complete the equilibrium constant expression for this reaction. $K_c =$

(b) The K_c for a different reaction is

$$K_c = \frac{[SO_3(g)]^2}{[SO_2(g)]^2 [O_2(g)]}$$

Write the chemical equation that corresponds to this expression in the box below.

(c) The two reactions shown in the following table are both at equilibrium.

Reaction	Equation	Affected by increased pressure
One	$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	no
Two	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	yes

Compare and contrast the effect of increasing the pressure on both reactions, with reference to the equilibrium positions.

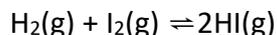(d) For Reaction Two in part (c), the values of K_c at different temperatures are shown below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
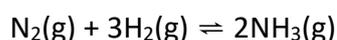
Temperature	227°C	327°C	427°C	527°C
K_c	90	3	0.3	0.04

Use this information to determine whether the formation of $NH_3(g)$ is endothermic or exothermic.
Justify your reasoning using equilibrium principles.

(e)   For Reaction One in part (c), the K_c value is 46.8 at 491°C

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

Calculate the concentration of HI(g), at equilibrium, at 491°C, if the concentration of $H_2(g)$ is 0.0190 mol L^{-1} and the concentration of $I_2(g)$ is 0.210 mol L^{-1}.

(2012:2)

Phosphorus pentachloride gas, $PCl_5(g)$, decomposes to form phosphorus trichloride gas, $PCl_3(g)$, and chlorine gas, $Cl_2(g)$. The equilibrium can be represented as:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(a)   Complete the equilibrium constant expression for this reaction. K_c =

(b)   The table below shows the value of the equilibrium constant, K_c at two different temperatures.

Temperature / °C	Value of K_c
200	8.00×10^{-3}
350	0.612

(i)   Circle the species that will be in the highest concentration at 200°C.

$PCl_5(g)$ $PCl_3(g)$

(ii)   Explain your answer.

(iii)   Calculate the concentration of PCl_5 at equilibrium at 350°C, if the concentrations of PCl_3 and Cl_2 are both 0.352 mol L^{-1}.

(c)   For each of the following changes applied to this system:

(i)   State if the amount of chlorine gas, $Cl_2(g)$, would increase or decrease.

(ii)   Justify your answers using equilibrium principles.

PCl₃(g) is removed.

Amount of $Cl_2(g)$

Reason:

The pressure is decreased.

Amount of $Cl_2(g)$

Reason:

(d)   When the temperature of the equilibrium system is increased from 200°C to 350°C (at constant pressure), the value of K_c increases, as shown in the table above. Use this information to determine whether the decomposition of PCl_5 is endothermic or exothermic.
Justify your reasoning using equilibrium principles.

Answers

(2018:2)

(a) $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$ [A]

(b) (i) $K_c = \dfrac{0.093^2}{0.1^2 \times 0.2} = 4.32$

(ii) The Kc value is larger than 1 so there are more products than reactants at equilibrium.

(c) If the sulfur trioxide is removed as it is produced, [SO₃] will decrease, so the equilibrium will move to minimise the change (stress placed on the system). This means the reaction will move forward to replace the lost sulfur trioxide. This will increase the yield of the desired product.

(d) Increasing the size of the reaction vessel decreases the pressure of the system. In order to minimise this change / stress, the reaction moves to increase the number of gaseous particles. For this reaction, the greatest number of gaseous particles is the reactants side so the reaction will move backwards towards the reactants. This has the effect of decreasing the amount of sulfur trioxide.

(e) When the temperature decreases to 450°C, the reaction moves in the exothermic direction to produce more heat. Since the Kc value increased, more products and less reactants are present. This means the reaction produces more products when the temperature drops. This means the oxidation of sulfur dioxide to sulfur trioxide is an exothermic reaction.

(2017:2)

(b) (i) $K_c = \dfrac{[NH_3(aq)]^2}{[N_2(aq)][H_2(aq)]^3}$

(ii) $K_c = \dfrac{0.105^2}{0.0821 \times 0.0583^3}$

$= 677$

No, the reaction is not at equilibrium because 677 > 640 (values must be equal for a reaction to be at equilibrium). *Accept answers between 676 – 678.*

(c) When temperature increases, the reaction moves in the endothermic direction to absorb the added heat. In this reaction, the value of K decreased, indicating the ratio of products to reactants decreased. Since there will be fewer products and more reactants, the equilibrium is favouring the reactants, so adding heat favours the reverse reaction / the position of equilibrium shifts left. Hence, the formation of ammonia gas / forward reaction, is exothermic.

(Temperature is the only factor that can change the K value in an equilibrium).

(2017:3)

(b) (i) Adding water to this equilibrium means there has been an increase in (concentration of) a product. The system will react to reduce this change, so the backward reaction will be favoured to use up *(idea required for Excellence)* some of the extra product. This results in an increased concentration of the pink $[Co(H_2O)_6]^{2+}$ ion, so the solution will turn pink or the pink colour will intensify.

(ii) The ice-cold water will cause the reaction to move in the exothermic direction to compensate for the loss of heat energy / release heat energy *(for Excellence)* into surroundings. Because this reaction is endothermic (positive ΔH value), the exothermic direction will be backwards, so the colour of the solution will become pink or the pink colour will intensify.

(c) The increase in pressure favours the side with the fewest moles of gas on it, so the reaction will move in the forward direction because there is only one mole of N_2O_4 gas compared to 2 moles of NO_2 gas. This will cause the colour to fade from a darker to a lighter brown. (It won't go colourless because both gases are still present in the mixture.)

(2016:3)

(a) $CO + 2H_2 \rightleftharpoons CH3OH$

(b) The value of K_w at 1×10^{-14} is very small, which means that very little water has ionised / dissociated because there is very little product (i.e. very few ions).

(c) (i) Adding dilute acid increases the concentration of the acid, so the reaction moves in the forward direction / favours the products to use up the added acid, so the colour of the solution will become more orange.

(iii) Adding base means that acid that reacts with the base is removed from the equilibrium / concentration of the acid decreases. This will drive the equilibrium in the backwards direction / favours the reactants to replace the H^+ used up, causing the solution to become more yellow in colour. May include the equation $H^+ + OH^- \rightleftharpoons H_2O$ in their answer.

(d) (i) $$64 = \frac{[HI]^2}{0.312 \times 0.312} \quad [HI] = \sqrt{64 \times 0.312^2} = 2.50 \text{ mol L}^{-1}$$

(ii) There would be no effect on the equilibrium if pressure was increased because there are equal numbers of moles of gas on either side of the equilibrium / in the reactants and products.

(iii) (Temperature is the only factor that can change the K value of an equilibrium). When the temperature increases, the reaction moves in the endothermic direction to absorb the added heat. In this reaction, the value of K decreased, indicating the ratio of products to reactants (numerator to denominator) decreased. Since there will be fewer products and more reactants, adding heat is favouring the backwards reaction. Therefore, the forward reaction is exothermic.

(2015:3)

(a)   A + 2B ⇌ 3C + D

(b)   (i)   Adding more ethanol causes the equilibrium to move in the forward direction in order to use the extra added ethanol. This is because the equilibrium has to re-establish itself with the added reactant in order to maintain K_c.

(ii)   A catalyst speeds up the rate of the reaction so both forward and backward reaction will speed up but no particular reaction is favoured.

(c)   (i)
$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

(ii)
$$Q = \frac{0.250^2}{0.300^2 \times 0.100} = 6.94$$

Since K_c = 4.32, Q ≠ K_c, so this reaction mixture is not at equilibrium. This number is greater than the K_c value, 4.32, which indicates that the reaction lies to the products side as the larger the K_c or Q value, the greater the numerator (products).

(iii)   At 450°C, the temperature has decreased. This reaction is exothermic, as shown by the negative enthalpy. This means that if the temperature is decreased, the reaction will move in the direction that produces more heat. Because this is an exothermic reaction, the exothermic direction is forwards. This will lead to more products and an increase in K_c.

(2014:2)

(a)   (i)
$$K_c = \frac{[H_2]^3[CO]}{[CH_4][H_2O]}$$

(iii)   No K_c = 3.6 which is < 4.7; therefore the reaction is not at equilibrium since if the reaction was at equilibrium, the K_c would be 4.7 at 1127°C.

(b)   CuO catalyst: Amount of methanol stays the same. A catalyst, such as CuO, will speed up the rate of both the forward and the reverse reactions. The proportions of all of the reactants and products remain the same.
H$_2$ removed: Amount of methanol will decrease. As hydrogen gas is removed, the system will oppose the change and the position of the equilibrium will shift in the reverse direction as more hydrogen is formed. This means the amount of methanol will decrease.

(c)   Increasing pressure resulted in the colour fading. This was due to the position of the equilibrium shifting in the forward direction to counteract this change. The system shifts in the direction of the least number of moles of gas since this will decrease the pressure. This forms more N_2O_4 (g), which is colourless, so the colour fades. When the pressure is decreased again the system adjusts to increase the pressure, hence shifts in the direction of a greater number of moles, i.e. in the reverse direction, forming more NO_2, resulting in a darker colour due to the brown colour of this gas. When the reaction container is placed in hot water, the system will adjust so that some of the heat is used up; therefore it will shift in the endothermic direction. In this case, the colour darkened, indicating that this favoured the reverse reaction which must be the endothermic direction. When the container was cooled, the colour faded indicating that the forward reaction, forming colourless N_2O_4, must be exothermic.

(2013:2)

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

(b) $2SO_2 + O_2 \rightleftharpoons 2SO_3$

(c)   When a change is made to a system that is at equilibrium, the system responds to reduce the effect of that change. If there is an increase in pressure, the system responds by decreasing the pressure. This occurs by favouring the reaction that produces fewer gas particles. Because there are now fewer particles hitting the sides of the container, there is less pressure.

In Reaction One there are two moles of gas particles on each side of the equation. Because there are the same numbers of gas particles on both sides of the reaction, then a change in pressure will have no effect as neither reaction will be favoured.

In Reaction Two however, there are four moles of gas particles on the reactant side of the equation and two moles of gas particles on the product side of the equation. Therefore, when there is an increase in pressure, the system would shift and favour the forward reaction meaning there are now fewer gas particles overall and hence fewer gas particles hitting the sides of the container and therefore less pressure overall.

(d)   As the temperature increases, K_c decreases. The decreasing value of K_c indicates that the reaction is reactant-favoured (i.e. more reactants than products). When temperature increases, the system responds and decreases the temperature by shifting in the endothermic direction. Since the increasing temperature favours the reactants, this must mean that the reverse reaction is endothermic and the forward reaction (formation of NH_3) is exothermic.

$$\frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} = 46.8$$

$$\frac{[HI(g)]^2}{[0.0190][0.210]} = 46.8$$

$$\frac{[HI(g)]^2}{3.99 \times 10^{-3}} = 46.8$$

$$[HI(g)]^2 = 0.187$$

$$[HI(g)] = 0.432 \text{ mol L}^{-1}$$

(2012:2)

(a)
$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

(b)   (i) PCl_5

(ii)   The value of Kc is less than 1 /small. This means that the concentration of reactant (PCl_5) is greater than the concentration of products (PCl_3 and Cl_2).

(iii)

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$[PCl_5] = \frac{[PCl_3][Cl_2]}{K_c}$$

$$[PCl_5] = \frac{0.352 \times 0.352}{0.612}$$
$$= 0.202 \text{ mol L}^{-1}$$

(c) When $PCl_3(g)$ is removed: Amount of Cl_2 increases. As $PCl_3(g)$ is removed / concentration decreased, the equilibrium will shift to oppose the change, i.e. increase the concentration of $PCl_3(g)$. This will favour the forward reaction, producing more Cl_2.

When the pressure is decreased: Amount of Cl_2 increases. Decrease in pressure causes the equilibrium to shift to increase the number of gaseous particles, i.e. shifts equilibrium to the side with the greatest number of moles. Since there are two moles of gaseous products and one mole of gaseous reactant, equilibrium will shift to right. This will favour the forward reaction, producing more Cl_2.

(d) At increased temperature the value of Kc increases. This means that equilibrium shifts in favour of products i.e. the forward direction. An increase in temperature causes the equilibrium to shift to favour the reaction that absorbs heat / energy, i.e. the endothermic direction. Hence, the forward reaction is endothermic.