ANSWERS: Equilibria

QUESTION (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. $Kc = \dfrac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$

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

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

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

$PCl_5(g)$ $\qquad$ $PCl_3(g)$

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

(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}.

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} \quad [PCl_5] = \frac{[PCl_3][Cl_2]}{K_c} \quad [PCl_5] = \frac{0.352 \times 0.352}{0.612}$$ = 0.202 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.

$PCl_3(g)$ is removed.

Amount of $Cl_2(g)$ increases

Reason: 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.

The pressure is decreased.

Amount of $Cl_2(g)$ increases

Reason: 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) When the temperature of the equilibrium system is increased from 200°C to 350°C (at constant pressure), the value of *Kc* increases, as shown in the table above (in (b)).

Use this information to determine whether the decomposition of PCl_5 is endothermic or exothermic. Justify your reasoning using equilibrium principles.

At increased temperature the value of K_c increases *(from 8.00×10^{-3} to 0.612)*

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.

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QUESTION (2009:3)

(a) Nitrogen monoxide gas reacts with oxygen gas to form nitrogen dioxide gas. The equilibrium reaction can be represented by:

$$2NO(g) \quad + \quad O_2(g) \quad \rightleftharpoons \quad 2NO_2\,(g)$$

colourless colourless brown

At 230°C the equilibrium constant for this reaction has a value of 6.44×10^5.

(i) Complete the equilibrium constant expression for this reaction. $K_C = \dfrac{[NO_2]^2}{[NO]^2\,[O_2]}$

(ii) State which gas will be in the highest concentration at 230°C. NO_2

Explain your answer in terms of K_C and the colour seen. NO_2 is in the highest concentration. The value of K_c is greater than 1. This means that the amount of the products will be greater than the reactants. Therefore the concentration of $NO_2(g)$ will be greater than $NO(g)$ or $O_2(g)$. This explains the dark brown colour, as there is more $NO_2(g)$, which is a brown colour compared with the other two, which are both colourless.

(b) The following equilibrium system is formed when hydrogen gas is mixed with iodine gas.

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

colourless purple colourless

The reaction has a negative value for Δ_rH.

For each of the following changes applied to this system:

(i) describe the expected observation

(ii) use equilibrium principles to discuss the reason for this observation.

HI(g) is added. Colour will become more purple. As the concentration of HI is increased, the equilibrium will shift to oppose the change, ie decrease the concentration of HI. This will favour the reverse reaction producing more I_2, so more purple

The reaction mixture is cooled. The purple colour fades. Decreased temperature causes the equilibrium to shift to favour the reaction that releases energy/ heat, to replace the heat that has been lost. ie the exothermic direction. This will favour the forward reaction resulting in less I_2 so less purple.

The pressure is increased. No change. Increase in pressure causes the equilibrium to shift to reduce the number of gaseous particles, ie shifts equilibrium to the side with the least number of moles. Since each side of the equilibrium equation has two moles there will be no equilibrium shift. The colour will remain the same.

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QUESTION (2008:2)

Complete the equilibrium constant expressions for the following equations.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

$$2O_3(g) \rightleftharpoons 3O_2(g)$$

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

$$K_c = \frac{[O_2]^3}{[O_3]^2}$$

QUESTION (2008:6)

One step in the production of sulfuric acid involves forming sulfur trioxide from sulfur dioxide.

The equilibrium reaction can be represented by

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta_rH = -196 \text{ kJ mol}^{-1}$$

(a) (i) Explain why a low temperature favours the formation of $SO_3(g)$. The forward reaction is exothermic. A decrease in temperature causes an equilibrium shift to favour reaction that releases energy, i.e. shift in the exothermic direction. So to have a greater amount of $SO_3(g)$ in the equilibrium mixture, the temperature must be low.

(ii) The temperature that is actually used is approximately 450°C. However, this is not considered to be a low temperature. Discuss why this temperature is used. The lower the temperature used, the slower the reaction rate. Although a greater amount of $SO_3(g)$ will be present in the equilibrium mixture, it will be uneconomical if it takes a long time for the reaction to reach that equilibrium. Approximately 450°C is a compromise temperature producing a sufficiently high proportion of sulfur trioxide in the equilibrium mixture, but in a short time.

(b) (i) Describe another way of increasing the amount of $SO_3(g)$ present at equilibrium without adding any more reactants. High pressure / decreasing volume.

(ii) Explain why this will increase the amount of $SO_3(g)$ present at equilibrium. High pressure / decreasing volume. There are 3 gaseous moles / molecules on the left hand side of the equation, but only 2 moles / molecules on the right. If the pressure is increased, the system will move to minimise the effect of this and favour the reaction that produces fewer molecules of gas, since that will cause the pressure to fall again, i.e. will favour formation of $SO_3(g)$.

QUESTION (2008:7)

Carbon dioxide is added to drinks to make them fizzy. The following equilibria are involved:

$CO_2(g) \rightleftharpoons CO_2(aq)$ Equation One

$CO_2(aq) + 2H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$ Equation Two

The drink is fizzy when there is dissolved carbon dioxide, $CO_2(aq)$. The drink stops being fizzy when the carbon dioxide escapes from the drink as a gas.

Using equilibrium principles, discuss the changes that occur as a bottle containing fizzy drink is opened.

Your answer must include reference to:

- equilibrium shift in Equation One and Equation Two

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- changes in the fizziness of the drink
- any change in pH.

Fizziness: As the lid is opened, $CO_2(g)$ escapes from the drink and the pressure is decreased. The equilibrium in Equation One will shift to the left. The position of equilibrium moves to minimise the effect of the change. ie, the decrease in pressure favours formation of more moles / molecules of gas, so the position of equilibrium will move to favour formation of more $CO_2(g)$ in Equation One. This results in a lower concentration of $CO_2(aq)$. As more $CO_2(aq)$ is lost from the drink, there is less fizz in the drink.

pH: As the concentration of $CO_2(aq)$ is decreased, the position of equilibrium in Equation Two will shift to favour formation of reactants, ie form more $CO_2(aq)$. As this occurs, the concentration of H_3O^+ (and HCO_3^-) ions decreases. As the $[H_3O^+]$ decreases, the pH will increase.

QUESTION (2007:5)

The following equilibrium system is formed when potassium thiocyanate solution is added to a solution of iron(III) nitrate.

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

orange colourless dark red

The reaction has a positive value for Δ_rH. For each of the following changes applied to this system:

(i) describe the expected observation

(ii) use equilibrium principles to discuss the reason for this observation.

(a) The reaction mixture is cooled. Colour of solution goes orange / becomes a lighter orange / lighter red / colourless. Decreased temperature causes an equilibrium shift to favour reaction that releases energy / heat, i.e. shift in the exothermic direction. As forward reaction is endothermic having a positive Δ_rH, the reverse reaction is exothermic. Equilibrium shifts in exothermic / reverse direction and the concentration of $FeSCN^{2+}$ will be decreased, so colour of solution is lighter.

(b) Solid sodium fluoride is added to the reaction mixture. The fluoride ions react with Fe^{3+} ions. Colour of solution goes orange / becomes a lighter orange / lighter red / colourless. As the concentration of Fe^{3+} ions is decreased (because of reaction with fluoride ions) equilibrium will move to increase the concentration of Fe^{3+} ions (a reactant). So reverse reaction is favoured, the concentration of $FeSCN^{2+}$ will be decreased so that colour of solution is lighter.

(c) Solid iron(III) chloride is added to the reaction mixture. Colour of solution goes dark red / becomes a darker red. As the concentration of Fe^{3+} ions is increased (due to $FeCl_3$ dissolving), equilibrium will move to decrease the concentration of Fe^{3+} ions (a reactant). So forward reaction is favoured, the concentration of $FeSCN^{2+}$ will be increased so that colour of solution is darker.

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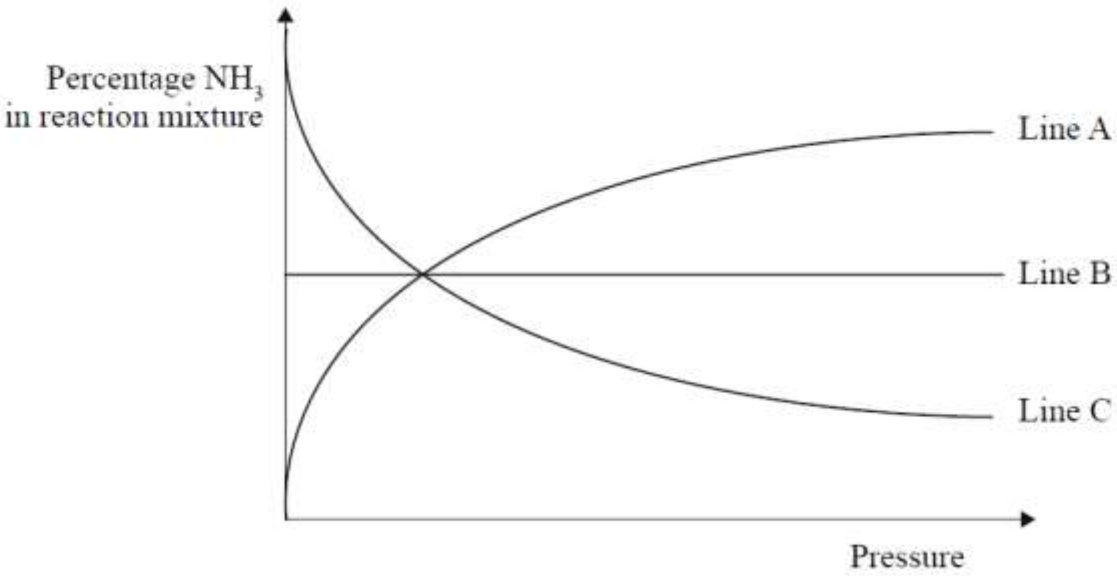
QUESTION (2006:5)

An equilibrium system is shown below.

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

(a) Complete the equilibrium constant expression for this reaction. $\boxed{K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]}}$

The pressure of the system is increased, while maintaining a constant temperature. The percentage of NH_3 in the reaction mixture is recorded and graphed.



(b) On the above graph, identify the line that shows the correct relationship between the percentage of NH_3 in the reaction mixture, and increasing pressure.

Circle the correct answer below.

Line A Line B Line C

Explain your answer by applying knowledge of equilibrium principles.
Line A. Equilibrium shifts to reduce pressure increase. Product side has fewer moles. Equilibrium shifts in forward direction/least amount direction. Therefore increase in % NH_3.

QUESTION (2006:6)

An equilibrium system involving different species of cobalt(II) is shown in the equation below.

$$[CoCl_4]^{2-}(aq) + 6H_2O(l) \rightleftharpoons [Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq)$$

$[CoCl_4]^{2-}$ (aq) is blue and $[Co(H_2O)_6]^{2+}$ (aq) is pink.

At room temperature (25°C) the equilibrium mixture is pink.

(a) Describe the expected observation when solid sodium chloride (NaCl) is added to the equilibrium mixture. Explain your answer. Colour of the solution turns purple or blue. The (concentration) of

Cl^- is increased. Equilibrium shifts to decrease concentration of Cl^-. Equilibrium shifts in favour of reactant. More blue $[CoCl_4]^{2-}$ formed.

(b) The enthalpy change (Δ_rH) for this reaction as written above, has a negative value. Circle the ion that would be present in the higher concentration when the equilibrium mixture is heated.

$[CoCl_4]^{2-}(aq)$ $[Co(H_2O)_6]^{2+}(aq)$

Explain your answer.

$[CoCl_4]^{2-}$. Equilibrium shifts to reduce temperature increase. ΔH is negative/reaction exothermic. Reverse direction endothermic. Equilibrium shifts in endothermic/reverse direction.

QUESTION (2005:2)

(a) Complete the equilibrium constant expression for the following reaction.

(i) $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)^{2+}(aq)$ $\boxed{K_c = \dfrac{[Ag(NH_3)_2^{\ +}]}{[Ag^+][NH_3]^2}}$

(ii) At 25°C the value of *Kc* is 1.70 x 107. Circle the species that would be present in the higher concentration in the equilibrium mixture at this temperature.

$Ag^+(aq)$ or $Ag(NH_3)^{2+}(aq)$

Justify your choice. K_c is very large (10^7), so concentration of product is high compared to that of reactants (as the product concentration is on top of the ratio).

(b) Complete the equilibrium constant expression for the following reaction.

(i) $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ $\boxed{K_c = \dfrac{[NO]^2[O_2]}{[NO_2]^2}}$

(ii) At 200°C the value of *Kc* is 1.10 × 10–5. Circle the species that would be present in the higher concentration in the equilibrium mixture at this temperature.

$NO_2(g)$ or $NO(g)$

Justify your choice. K_c is very small (10^{-5}), so concentration of product is low compared to that of reactants (or concentration of reactant is higher) (as the product concentration is the top of the ratio, or reactant concentration is on the bottom of the ratio.)

QUESTION (2005:4)

The following reaction is exothermic: $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$ Both N_2O_5 and O_2 are colourless gases and NO_2 is a brown gas. A mixture of these gases exists at equilibrium and is observed as a brown colour.

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(a) Complete the equilibrium constant expression for the reaction. $K_c = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$

(b) For each of the following changes applied to the equilibrium system, describe the expected observation and explain why this occurs.

(i) The mixture of gases is heated (at constant pressure).

Expected observation: Lighter brown / brown colour becomes less intense.

Explanation: When the mixture is heated the endothermic reaction / absorption of heat is favoured. This is reverse reaction. So amount of brown NO_2 gas is decreased / N_2O_5 so the observed colour gets lighter.

(ii) The pressure is increased, by decreasing the volume of the container.
Expected observation: Lighter brown / brown colour becomes less intense.

Explanation: As the pressure is increased the formation of fewer moles of gas is favoured. This favours the reverse reaction since there are 5 moles of product gas compared with 2 moles of reactant gas. Thus the amount of brown NO_2 gas is decreased / N_2O_5 increased, so that the observed colour gets lighter.

QUESTION (2004:4)

(a) The following equilibrium system is established when thiocyanate ions (SCN−) are added to iron (III) ions (Fe3+). The resulting aqueous solution is a dark red colour. The equation representing the equilibrium system and the colours of each species involved are given below.

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

pale orange   colourless   dark red

(i) Complete the equilibrium constant expression for the above reaction. $K_C = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$

(ii) When iron (III) ions (Fe^{3+}) are removed from the equilibrium mixture (by adding sodium fluoride), a colour change is observed. Describe the colour change you would expect to see and explain why it occurs. Colour lightens / disappears / goes paler / more orange. Removal of Fe^{3+} causes equilibrium position to shift towards the reactants in order to minimise the change, by replacing some of the Fe^{3+} that has been removed. The new equilibrium mixture will therefore have less $FeSCN^{2+}$ and will be lighter in colour.

(b) Ammonia is produced industrially according to the Haber Process as shown below:

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

(i) Complete the equilibrium constant expression for the above reaction. $Kc = \frac{[NH_3]^2}{[N_2][H_2]^3}$

(ii) The pressure of the system at equilibrium is increased (by decreasing the total volume of the system). Describe the effect of this change on the amount of NH_3 in the system. Explain your answer. Increased pressure of the system causes a shift to the right in order to decrease the pressure by forming fewer moles of gas. Therefore, the amount of NH_3 increases.

(iii) The percentage of NH_3 present in equilibrium mixtures at different temperatures and at constant pressure is shown in the table below.

Temperature (°C)	Percentage NH_3 present in equilibrium mixture
200	63.6
300	27.4
400	8.7
500	2.9

Justify whether the reaction in which NH_3 is formed, is endothermic or exothermic. As the temperature is increased the amount of NH_3 produced decreases, indicating a shift to the reactants. As increasing temperature causes equilibria to shift in the endothermic direction, the forward direction (the reaction producing NH_3) must be exothermic.