CHAPTER 14 - **PROBLEM SHEET**   - CHEMICAL EQUILIBRIUM

1.   Which of the following represent systems at equilibrium?

    a) An open bottle of perfume.

    b) A lump of sugar slowly dissolving in water.

    c) A solution which has been formed from the reaction of copper ions and ammonia
       (Cu^{2+} + $4NH_3 \rightarrow$ $[Cu(NH_3)_4]^{2+}$). The blue colour of the solution remains constant.

    d) A mixture that has been formed by adding silver nitrate solution to sodium chloride solution. The mass of
       precipitate on the bottom of the closed beaker, and the appearance of the solution, remain constant with time.

    e) An open bottle of 'fizzy' drink.

2.   Write the equilibrium law expression for each of the following reactions:

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

    b) $Al^{3+}(aq)$ + $3 OH^-(aq)$ $\rightleftharpoons$ $Al(OH)_3(s)$

    c) $CaCO_3(s)$ $\rightleftharpoons$ $CaO(s)$ + $CO_2(g)$

    d) $2 C_2H_6(g)$ + $7 O_2(g)$ $\rightleftharpoons$ $4 CO_2(g)$ + $6H_2O(l)$

    e) $PbCl_2(s)$ $\rightleftharpoons$ $Pb^{2+}(aq)$ + $2Cl^-(aq)$

    f) $H_2SO_4(aq)$ + $2H_2O(l)$ $\rightleftharpoons$ $2H_3O^+(aq)$ + $SO_4^{2-}(aq)$

3.   i) Comment on the relative concentrations, at the quoted temperatures, of reactants and products in the
      equilibrium mixtures of the following reactions:

    a) $C(s)$ + $O(g)$ $\rightleftharpoons$ $CO(g)$; K = 1×10^{15} at 200^oC.

    b) $AgCl(s)$ $\rightleftharpoons$ $Ag^+(aq)$ + $Cl^-(aq)$; K = 3×10^{-10} at 25^oC.

    c) $H_3PO_4(aq)$ + $H_2O(l)$ $\rightleftharpoons$ $H_2PO_4^-(aq)$ + $H_3O^+(aq)$; K = 2×10^{-3} at 25^oC.

    ii) Comment on the rate of the above reactions in reaching equilibrium, using only the data given.

4.   What will be the effect (increase, decrease, not effect) of the following changes, on the concentrations of all the
    substances in the equilibrium mixture (assuming the temperature and volume remain constant)

$$2SO_2(g) + O_2(g)   \rightleftharpoons   2SO_3(g)?$$

Change made to the equilibrium system	Conc of substances at new equilibrium position		
	$[SO_2]$	$[O_2]$	$[SO_3]$
a) Adding more SO_2 to the reaction vessel.			
b) Increasing the partial pressure of SO_3 in the vessel.			
c) Removing some O_2 from the reaction vessel.			
d) Removing some SO_3 from the reaction vessel.			

5.   What will happen to the number of moles of chlorine, in equilibrium with hydrogen and hydrogen chloride in the reaction $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ when the following changes are made to equilibrium mixtures (assuming the volume and   temperature remain constant)?

a) Hydrogen gas is added

b) A small amount of water is added.

c) Hydrogen gas is removed.

d) Some gaseous ethene is added. Ethene undergoes an addition reaction with chlorine.

e) Argon gas (a noble gas) is added.

6.   Arsenic can be extracted from its ore by first reacting the ore with oxygen (called roasting) to form solid As_4O_6, which is then reduced using carbon:

$$As_4O_6(s) + 6C(s) \rightleftharpoons As_4(g) + 6CO(g)$$
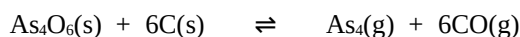
Predict the direction of the shift in the equilibrium position, and whether or not the products are favoured in this shift, in response to each of the following changes in conditions:

Change in conditions	Direction in equilibrium shift	Are the products favoured in this shift?
a) addition of carbon monoxide		
b) addition of carbon or arsenic (III) oxide		
c) removal of gaseous arsenic.		

7.   When a solution containing copper ions is mixed with a solution containing carbonate ions, a precipitate of copper carbonate forms, and the following equilibrium exists:

$$Cu^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CuCO_3(s)$$
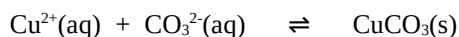
What effect would the following changes have on the amount of precipitate present?

a) A few drops of a concentrated solution of copper sulfate are added.

b) A few drops of concentrated acid are added.

8.   For which of the following equilibrium systems would an <u>increase</u> in volume result in the formation of <u>more</u> product?

a) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

b) $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$

c) $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$

d) $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$

e) $C(s) + O_2(g) \rightleftharpoons CO_2(g)$

f) $2CH_3OH(g) + O_2(g) \rightleftharpoons 2CH_2O(g) + 2H_2O(g)$

g) $CO(g) + NO_2(g) \rightleftharpoons CO_2(g) + NO(g)$

h) $HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$.

9.   Various syringes were fitted with freely moving pistons. Each syringe contained a chemical system which had been
     allowed to come to equilibrium at room temperature. A greater pressure was then exerted on each syringe.
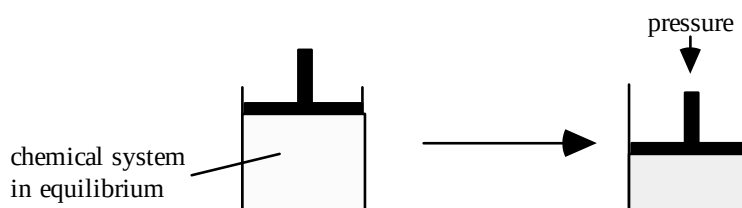
     In which of the following equilibrium systems would this increase in pressure cause <u>less products</u> to be formed?

     a) $CaCO_3(s)$ $\rightleftharpoons$ $CaO(s)$ + $CO_2(g)$

     b) $CO(g)$ + $H_2O(g)$ $\rightleftharpoons$ $CO_2(g)$ + $H_2(g)$

     c) $4NH_3(g)$ + $5 O_2(g)$ $\rightleftharpoons$ $4NO(g)$ + $6H_2O(g)$

     d) $2NO_2(g)$ $\rightleftharpoons$ $N_2O_4(g)$

10.   For each of the following reactions, state the effect on the concentration of the underlined substance if the
      equilibrium system is subjected to an increase in temperature:

      a) $\underline{N_2(g)}$ + $3 H_2(g)$ $\rightleftharpoons$ $2NH_3(g)$ $\Delta H = - 92$ kJ

      b) $2H_2O(g)$ $\rightleftharpoons$ $2H_2(g)$ + $\underline{O_2(g)}$ $\Delta H = + 110$ kJ

      c) $H_2(g)$ + $Cl_2(g)$ $\rightleftharpoons$ $\underline{2HCl(g)}$ $\Delta H = -57$ kJ

11.   For each of the following reactions, state the effect on the concentration of the underlined substance if an
       equilibrium system is subjected to a decrease in temperature:

       a) $N_2(g)$ + $3 H_2(g)$ $\rightleftharpoons$ $2\underline{NH_3}(g)$ $\Delta H = - 92$ kJ

       b) $2H_2O(g)$ $\rightleftharpoons$ $2\underline{H_2(g)}$ + $O_2(g)$ $\Delta H = + 110$ kJ

       c) $H_2(g)$ + $\underline{Cl_2(g)}$ $\rightleftharpoons$ $2HCl(g)$ $\Delta H = -57$ kJ

12.   For each of the following reactions, determine

       a) the direction of the shift in the equilibrium position

       b) whether K will increase or decrease,

         when the temperature of the equilibrium system is <u>increased.</u>

             i) $N_2(g)$ + $O_2(g)$ $\rightleftharpoons$ $2NO(g)$ $\Delta H = + 180.8$ kJ

             ii) $2CO(g)$ + $O_2(g)$ $\rightleftharpoons$ $2CO_2(g)$ $\Delta H = -282$ kJ

13.   1 mole of ammonia was placed in a vessel, and the system was allowed to reach equilibrium according to the reaction

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

Below is a graph showing how the concentrations of the substances varied as the equilibrium position was being reached.
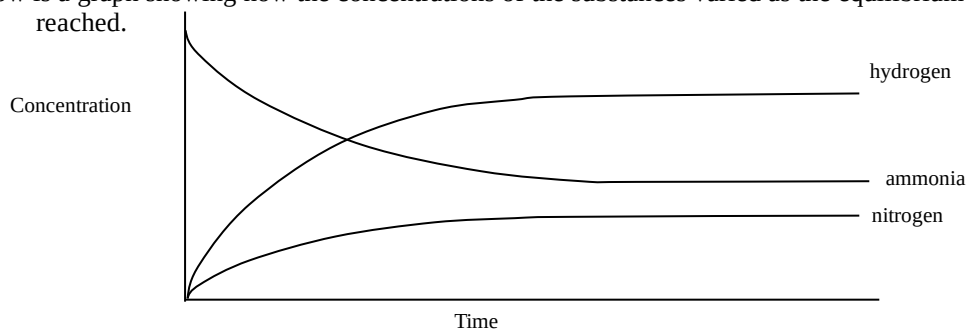
a) Indicate on the graph the time at which equilibrium is reached.

b) The same experiment is repeated, but this time a catalyst is added to the ammonia prior to any reaction. On the same axes , sketch the graphs you would expect for this catalysed reaction.

14.   The dissociation of carbonyl bromide is given by the following equation:

$$COBr_2(g) \quad \rightleftharpoons \quad CO(g) + Br_2(g) \qquad \Delta H = +63 \text{ kJ}$$

Predict in each case whether the number of moles of **carbonyl bromide** is increased, decreased of unaffected in the equilibrium mixture if:

a) carbon monoxide is added to the reaction vessel at constant volume and temperature.

b) the temperature is increased, at constant volume.

c) a catalyst is added.

d) ethene is introduced to the flask at constant volume and temperature. Ethene reacts with bromine.

e) the gas mixture in the reaction flask is allowed to expand by opening a tap leading to an evacuated second vessel of the same volume. The temperature is allowed to return to the original temperature.

15.   Consider the following reaction which is carried out at 800°C:

$$C(s) + O_2(g) \quad \rightleftharpoons \quad CO_2(g) \qquad \Delta H = -830 \text{ kJ}$$
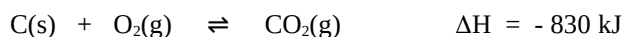
Which of the following conditions will result in a larger yield of CO_2?

        a) decreasing the volume of the reaction vessel

        b) decreasing the reaction temperature

        c) adding a catalyst

        d) increasing the partial pressure of $O_2(g)$ in the reaction mixture

        e) adding more C(s) to the reaction mixture

        f) grinding the carbon before the reaction

16.   Silver ions react with iron (II) ions in the following equilibrium:

$$Ag^+(aq) + Fe^{2+}(aq) \rightleftharpoons Ag(s) + Fe^{3+}(aq)   \Delta H = - 66 \text{ kJ}$$
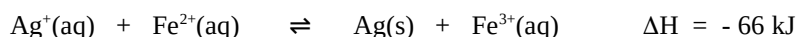
An equilibrium system is created by mixing equal volumes of 0.100 mol L^{-1} silver nitrate solution and 0.100 mol L^{-1} iron (II) sulfate solution at a temperature of 25^0C.

In the table below give the effect of each of the described changes in conditions on the equilibrium amount of iron (III)   ions. Write 'increase', 'decrease' or 'no difference'.

Change in equilibrium system	Effect of this change on amount of iron (III) ions; 'increase', 'decrease' or 'no difference'.
The temperature is decreased to 3ºC.	
An equal volume of water is added whilst the temperature is kept at 25ºC.	
A catalyst is added while the original temperature and volume are maintained.	
A few drops of a concentrated solution of iron (II) nitrate solution is added at 25ºC.	
Some silver foil is added at 25ºC.	
Some sodium chloride is added with stirring at 25ºC.	
Increasing the pressure in the reaction vessel	

17. The concentrations of the three substances in the reaction $POCl_3(g) \rightleftharpoons POCl(g) + Cl_2(g)$ are shown in the graph below
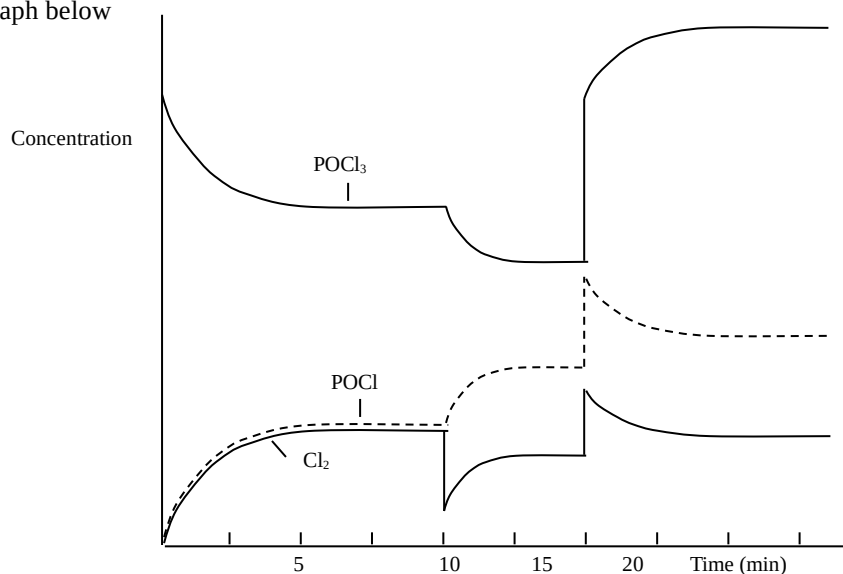
a) What substance, or substances, were initial introduced to the reaction flask at the beginning of the experiment?

b) Account for the horizontal section of the graphs between the 5 and 10 minute marks.

c)   Suggest what might have been done to the system at the 10 minute mark.

d) At approximately what time did the system again reach equilibrium after this first change in conditions?

e) Suggest what might have been done to the system at the 15 minute mark.

f) What was the immediate effect on the concentrations of the substances in the system when the change occurred at   the 15 minutes mark?

g) In which direction did the equilibrium position move to again reach equilibrium after the change at 15 minutes?

18. Identify the following statements as true or false.

    a)   The rates of all chemical reactions increase with temperature.

    b)   Exothermic reactions slow down when the reactants are heated.

    c)   Only endothermic reactions go faster when the reactants are heated.

    d)   Only exothermic reaction proceed spontaneously at room temperature.

ANSWERS - Equilibrium - Problem Sheet

1. c), d)

2. a)   b)   c) $[CO_2]$

    d)   e) $[Pb^{2+}] [Cl^-]^2$ f)

3. i) a) very large amount of products, very small amount of reactants
        b) very small amount of products, very large amount of reactants
        c) small amount of products, large amount of reactants
    ii) equilibrium constants give no indication of the rate of the reaction, so no comment can be made.

4. $[SO_2(g)]$ $[O_2(g)]$ $[SO_3(g)]$
    a)   increase   decrease   increase
    b)   increase   increase   increase
    c)   increase   decrease   decrease
    d)   decrease   decrease   decrease

5. moles of chlorine:
    a) decrease   b) decrease (HCl dissolves in water)   c) increase   d) decrease   e) no effect

6. a) shift towards reactants; products not favoured
    b) no effect
    c) shift towards products; products favoured

7. a) amount of precipitate increases   b) amount of precipitate decreases

8. d), f), h)

9. a) and c)

10. a) $[N_2]$ increases   b) $[O_2]$ increases   c) [HCl] decreases

11. a) $[NH_3]$ increases   b) $[H_2]$ decreases   c) $[Cl_2]$ decreases

12. i) shift towards products, K increases   ii) shift towards reactants, K decreases

13.

14. moles of $COBr_2$:
     a) increased   b) decreased   c) no effect   d) decreased   e) decreased

15. b), d)

16. amount of iron (III) ions: increase
                                     decrease
                                     no effect
                                     increase
                                     no effect
                                     decrease
                                     no effect

17. a) $POCl_3$ b) the system is at equilibrium   c) some Cl_2 is removed   d) at approx 12½ min
     e) volume has been decreased   f) all concentrations immediately increased   g) towards reactants

18. a) true   b) false   c) false   d) false