CHEM 3 EQUILIBRIUM Assignment (Foundations of Chemistry)

1 CO and Cl_2 are mixed in a flask so their concentrations are 0.400 mol L^{-1} and 0.200 mol L^{-1} respectively. The gases react according to the following equation.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

At equilibrium the concentration of CO is 0.304 mol L^{-1}.

a Calculate the equilibrium concentrations of Cl_2 and $COCl_2$.

b Plot qualitative graphs of the concentrations of the three substances from when they are mixed until equilibrium is achieved.

c Plot qualitative graphs of the changes in the rates of the forward and reverse reactions from when the two gases are mixed until equilibrium is established.

2 N_2O_4 is an almost colourless gas whereas NO_2 is dark brown. How would it be possible to determine whether the following system was at equilibrium?

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

3 Chemical equilibrium is described as a dynamic process and yet it is characterised by constant macroscopic properties. How can this be so?

4 a List three factors that can be altered to affect the equilibrium yield of a reaction.

b Which of these factors alters the value of the equilibrium constant?

5 If some ether is poured into a jar and the lid screwed on:

a Describe the molecular processes by which equilibrium becomes established in this system.

b Write an equation to represent the equilibrium.

c Why could equilibrium not be established if the jar was not sealed?

6 A saturated solution of iodine in alcohol at 25 °C is in equilibrium with some undissolved iodine crystals.

a Write an equation for the equilibrium.

b Describe the changes that would occur if the temperature was lowered to 10 °C.

7 Many soft and alcoholic 'fizzy' drinks contain dissolved carbon dioxide in equilibrium with gaseous carbon dioxide.

$$CO_2(g) \rightleftharpoons CO_2(aq) + 19 \text{ kJ}$$

Explain the following.

a Why bubbles of CO_2 come out of solution when a bottle or can is opened.

b Warm 'fizzy' drinks go 'flatter' than cold drinks.

8 For the reaction

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

the equilibrium concentrations at 350 °C are [NO] = 0.30 mol L^{-1}, $[Br_2]$ = 0.11 mol L^{-1} and [NOBr] = 0.046 mol L^{-1}. Calculate the equilibrium constant at 350 °C.

9 For the system

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

the value of K is 0.050 at 250 °C. Two reacting systems were analysed and found to have the following compositions.

System A: $[PCl_3]$ = 0.025 mol L^{-1}, $[Cl_2]$ = 0.040 mol L^{-1} and $[PCl_5]$ = 0.020 mol L^{-1}

System B: $[PCl_3]$ = 0.020 mol L^{-1}, $[Cl_2]$ = 0.025 mol L^{-1} and $[PCl_5]$ = 0.015 mol L^{-1}.

a Calculate the reaction quotient (Q) for both systems and determine if the systems are at equilibrium.

b For any system not at equilibrium, determine the direction in which reaction must occur for equilibrium to be established.

10 Write equilibrium constant expressions for the following reactions:

a $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

b $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$

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

d $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

e $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

f $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$

11 For the decomposition of chlorine molecules into separate atoms,

$$Cl_2(g) \rightleftharpoons 2Cl(g)$$

the equilibrium constant at 25 °C is about 1×10^{-38}. Comment on the relative concentrations of Cl_2 and Cl in an equilibrium system.

Q quotient is while equilibrium is being established.

12 Consider the following reaction at equilibrium.

$$O_3(g) + NO(g) \rightleftharpoons O_2(g) + NO_2(g)$$

How would the concentrations of each of these substances change if:
a The concentration of O_3 was increased.
b The partial pressure of NO_2 was increased.
c The concentration of NO was decreased.
d The partial pressure of O_2 was decreased.

13 For the equilibrium

$$4HBr(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Br_2(g)$$

predict the effect of the following changes on the concentrations of each of the substances.
a Decreasing the volume of the system.
b Decreasing the external pressure on the system.
c Adding some of the noble gas helium to the system but keeping the volume constant.

14 a Predict the effect of increasing the temperature of the following equilibrium systems.
i $3O_2(g) + 286\text{ kJ} \rightleftharpoons 2O_3(g)$
ii $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) + 566\text{ kJ}$
b Predict the effect of decreasing the temperature of the following equilibrium systems
i $N_2(g) + 2O_2(g) + 66\text{ kJ} \rightleftharpoons 2NO_2(g)$
ii $2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g) + 664\text{ kJ}$

15 If the reaction

$$Ca(HCO_3)_2(s) + \text{heat} \rightleftharpoons CaO(s) + 2CO_2(g) + H_2O(g)$$

is at equilibrium, predict the effects of the following changes on the concentration and mass of each substance present.
a Increasing the concentration of CO_2.
b Decreasing the partial pressure of H_2O.
c Decreasing the external pressure.
d Increasing the mass of CaO.
e Decreasing the temperature.

16 Consider the following reaction at equilibrium.

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g) + 42\text{ kJ}$$

If the following changes are made to the system
a The SO_2 concentration is increased.
b The pressure is increased.
c The volume is increased.
d The temperature is increased.
e A catalyst is added.
i Predict the effect on the concentrations of each substance and explain your prediction.
ii Describe what happens to the rates of the forward and reverse reactions.

17 Methanol, a useful fuel and solvent, can be manufactured from hydrogen and carbon monoxide

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -90\text{ kJ}$$

a What conditions would favour a fast reaction rate for this reaction?

b What conditions would favour a high equilibrium yield of methanol?
c Is it likely that compromise conditions would be needed in an industrial process based on this reaction?

18 a Write an equation for the equilibrium between solid NaCl and its saturated aqueous solution.
b If HCl gas is bubbled through saturated NaCl solution the gas dissolves to form H^+ and Cl^- ions but some NaCl crystallises from the solution. Use Le Chatelier's principle to explain the reduced solubility of NaCl in HCl solution.

19 When the equilibrium system

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

is heated, the equilibrium constant increases. Predict whether the forward reaction is exothermic or endothermic and explain your prediction.

20 The following system is at equilibrium.

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$$

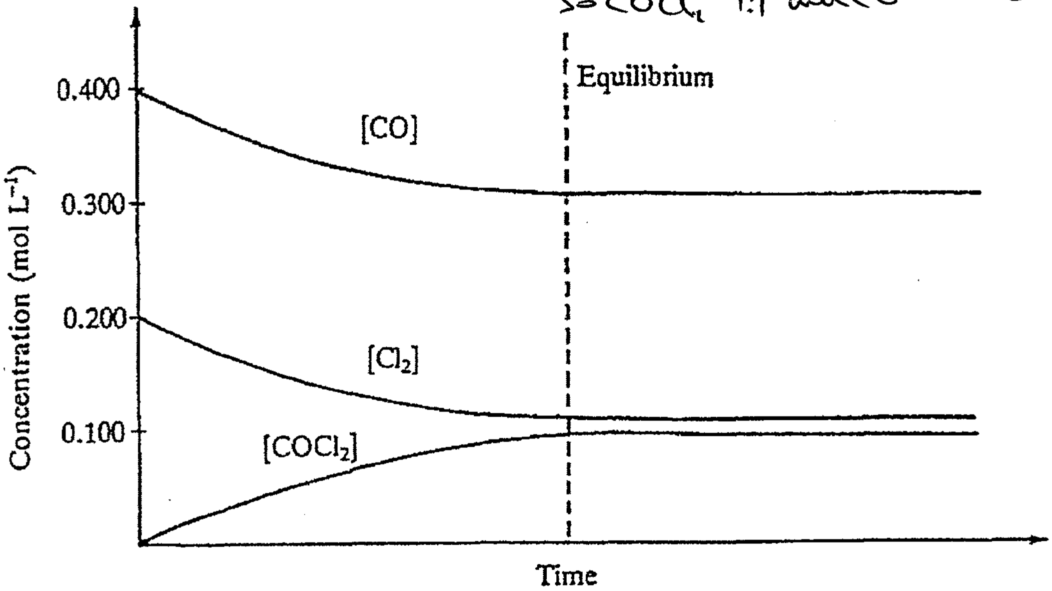
When iodide ions are added silver iodide precipitates. Predict the effect this will have on the ammonia concentration.

CHEM 3. EQUILIBRIUM Assignment (Foundations of Chemistry): SOLUTIONS

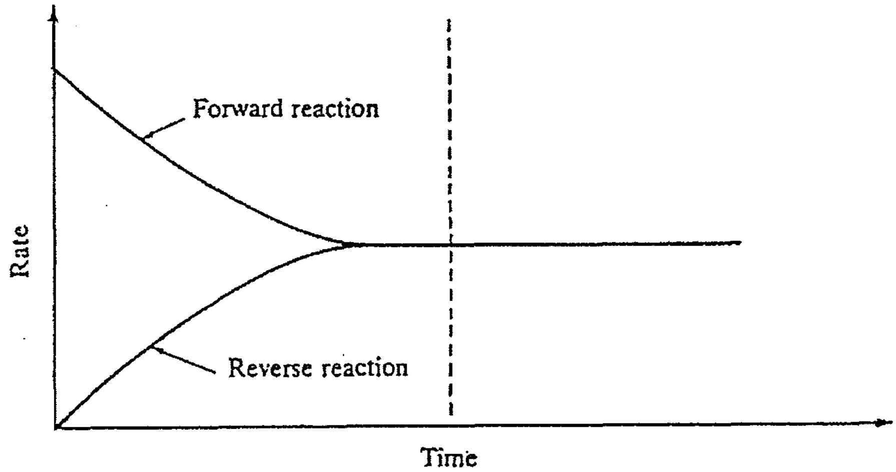
1. a $[Cl_2] = 0.104$ mol L^{-1}
   $[COCl_2] = 0.096$ mol L^{-1}

   So Co used up 0.4 − 0.304 = 0.096 mol L^{-1}
   So Cl_2 is 1:1 0.2 − 0.0906 = 0.104 mol L^{-1}
   So $COCl_2$ 1:1 with CO = 0.096 mol L^{-1}

   b.



   c.



2. Observe the colour of the mixture over a period of time. If the intensity neither increases nor decreases, the system is at equilibrium.

3. The opposing dynamic processes proceed on a molecular scale at equal rates so that no net change occurs.

4. a. Temperature, Pressure and changes in Concentration through injection of reactants or removal of products.

   b. Temperature ONLY!

5. a. High energy ether molecules escape from the liquid into the gaseous state. As the vapour pressure of the ether increases the rate of condensation of gaseous ether back to the liquid state increases until the rates of evaporation and condensation are equal.

b. ether(l) $\rightleftharpoons$ ether(g)

c. Ether would continue to escape from the liquid and leave the jar but the rate of condensation back to the liquid would remain low. Eventually all the ether would evaporate to the surroundings.

6. a. $I_2(s) \rightleftharpoons I_2(alcohol)$

b. The rates of crystallisation and dissolution would both decrease but the rate of crystallisation would be greater than the rate of dissolution. The mass of dissolved iodine would decrease as additional solid iodine crystallised from the solution.

7. a.

When a bottle or can of "fizzy" drink is opened the air space above the drink in the sealed container has a saturation vapour pressure of CO_2 gas. When the container is opened the "closed system" that previously existed is no longer present and carbon dioxide leaves the air space in the bottle or can. There is an immediate shift in equilibrium position to the LEFT in the equilibrium between aqueous and gaseous CO_2. The dissolved carbon dioxide turns rapidly to gas and bubbles or effervescence is formed.

b.

Warm fizzy drinks will go flat as the heat causes the evaporation of CO_2 from the solution which shifts the equilibrium to the left to replace the escaping CO_2. The quantity of dissolved aqueous CO_2 will diminish and so the drink will become increasingly flat. The other factor to consider is that the system as written is EXOTHERMIC and so added heat will shift the equilibrium position towards the LEFT. The system will "***attempt to minimize the effect of the imposed change***" which in this case is added heat energy by shifting in a direction that will use some of it up. For both reasons the concentration of aqueous CO_2 will decrease.

8. $$K = \frac{[NOBr]^2}{[NO]^2[Br_2]} = \frac{(0.046)^2}{(0.30)^2(0.11)} = 0.21$$

9. a. $$Q_A = \frac{(0.025)(0.040)}{(0.020)} = 0.050 \text{ - at equilibrium}$$

$$Q_B = \frac{(0.020)(0.025)}{(0.015)} = 0.033 \text{ - not at equilibrium}$$

b. For system B, the concentration of products must increase.

10. a. $K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$

b. $K = \frac{[CH_3Cl][HCl]}{[CH_4]\,[Cl_2]}$

c. $K = \frac{[CO_2]}{[O_2]}$

d. $K = [Mg^{2+}][OH^-]^2$

e. $K = \frac{[NH_4^+][OH^-]}{[NH_3]}$

f. $K = [CO_2]$

11. The concentration of Cl is extremely low compared with the concentration of Cl_2.

12. a. $[O_2]$, $[NO_2]$ increase, $[NO]$ decreases, $[O_3]$ decreases from adjusted value.

b. $[O_3]$, $[NO]$ increase, $[O_2]$ decreases, $[NO_2]$ decreases from adjusted value.

c. $[O_2]$, $[NO_2]$ decrease, $[O_3]$ increases, $[NO]$ increases from adjusted value.

d. $[O_3]$, $[NO]$ decreases, $[NO_2]$ increases, $[O_2]$ increase from adjusted value.

13. a. All concentrations increase immediately; then $[H_2O]$, $[Br_2]$ increase and $[HBr]$, $[O_2]$ decrease.

b. All concentrations decrease immediately; then $[HBr]$, $[O_2]$ increase and $[H_2O]$, $[Br_2]$ decrease.

c. No effect on concentrations.

14. a. i. $[O_3]$ increases, $[O_2]$ decreases.

ii. $[CO]$, $[O_2]$ increase, $[CO_2]$ decreases.

b. i. $[N_2]$, $[O_2]$ increase, $[NO_2]$ decreases.

ii. $[N_2]$, $[H_2O]$ increase, $[NO]$, $[H_2]$ decrease.

15. a. $[H_2O]$ decreases, $[CO_2]$ decreases from adjusted value, mass (CaO) decreases, mass $(Ca(HCO_3)_2)$ increases.

b. $[CO_2]$ increases, $[H_2O]$ increases from adjusted value, mass (CaO) increases, mass $(Ca(HCO_3)_2)$ decreases.

c. Immediately $[CO_2]$, $[H_2O]$ decrease; then $[CO_2]$, $[H_2O]$ increase above adjusted values; mass (CaO) increases, mass $(Ca(HCO_3)_2)$ decreases.

d. No effect (except to increase mass of CaO).

e. $[CO_2]$, $[H_2O]$ decrease, m(CaO) decreases, $m(Ca(HCO_3)_2)$ increases.

16. a. i. $[SO_3]$, [NO] increase, $[NO_2]$ decreases, $[SO_2]$ decreases from its adjusted value.
ii. Rate of forward reaction increases. Rates of forward and reverse reactions become equal when equilibrium is re-established.
b. i. Concentrations of all species increase immediately but then there is no change i.e. the system remains at equilibrium.
ii. The rates of the forward and reverse reactions increase equally.
c. i. Concentrations of all species decrease immediately but there is no further change.
ii. The rates of the forward and reverse reactions decrease equally.
d. i. $[SO_2]$, $[NO_2]$ increase; $[SO_3]$, [NO] decrease.
ii. Both rates increase but the rate of the reverse reaction is increased more than the rate of the forward reaction. Rates become equal when equilibrium is re-established.
e. i. No effect on concentrations.
ii. The rates of the forward and reverse reactions increase equally.

17. a.

Fast reaction rate will be achieved with **HIGH TEMPERATURE, HIGH PRESSURE** and the **PRESENCE OF A CATALYST**.

b.

High equilibrium YIELD would be obtained with **HIGH PRESSURE** but **LOW TEMPERATURE**.

c.

YES compromise conditions would be required for this reaction. While **HIGH PRESSURE** is of benefit for both rate of attainment of equilibrium and yield Temperature conditions are problematic. A **LOW TEMPERATURE** leads to a **HIGH YIELD** but at a **SLOW RATE OF ATTAINMENT** while **HIGH TEMPERATURE** will attain equilibrium **FASTER** but the **YIELD WILL BE LOWER**. A **COMPROMISE TEMPERATURE** that balances the demands of rate and yield will be required.

18. a. $NaCl \leftrightarrow Na^+ + Cl^-$

b. If HCl is bubbled through a saturated salt (NaCl) solution the concentration of chloride ions in the solution will be raised. As the Cl^- ion is a common ion to the salt saturation equilibrium it will interfere with it. The salt saturation system will respond to the extra chloride ion by SHIFTING to the left it an effort to "***minimise the effect of the imposed change***" and in doing so will use up some of the extra chloride ion but will also produce more undissolved NaCl and hence reduce its solubility.

19. $H_2 + I_2 \leftrightarrow 2HI$

If the equilibrium constant of this reaction is increased by heating then the relative proportion of HI must have increased and so the equilibrium must have shifted to the right. If this is the case then the heat term must have appeared on the left hand side of the equilibrium and hence it must be ENDOTHERMIC.

20. $Ag^+ + 2NH_3 \leftrightarrow [Ag(NH_3)_2]^+$

If iodide ions precipitate out some of the silver ions then this will interfere with the equilibrium above. The system will SHIFT to the left in an effort to "***minimise the effect of the imposed change***" and more of the concentration of the silver complex ion will decrease as more silver ions are produced by the shift. The shift will also cause an increase in the ammonia concentration at the same time.