Chem Factsheet

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How to Answer AS level Questions on Equilibria

This Factsheet gives guidance on how to approach answering questions about equilibria. The answers given are "best answers". However, in some cases, other answers will gain equal or partial credit. Common mistakes are also indicated so they can be avoided. However, this Factsheet is not a substitute for sufficient effort being put in to learn and understand the relevant chemistry, but it should be a big help!

Before starting this Factsheet make sure you know the terms moles, atoms, molecules and ions, endothermic (ΔH + ve) and exothermic (ΔH – ve) and factors that affect reaction rates.

1. Introduction

There are many changes in which all of the starting materials are not converted to products, i.e. the changes do not go to completion. Eventually such systems reach a state of equilibrium (represented using the symbol, $\rightleftharpoons$) where there are no further changes in the concentrations of both the reactants and products.

Examples:
(a) $Br_2(l) \rightleftharpoons Br_2(g)$; (b) $KI(s) \rightleftharpoons KI(aq)$; (c) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; (d) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Characteristics of the Equilibrium State.

1. *The system is closed – materials are neither added nor removed.*
2. *The temperature is constant.*
3. *The concentrations of all substances are constant.*
4. *It is a dynamic as both forward and backward reactions are occurring at equal rates.*
5. *It can be reached by starting from the reactants or starting from the products.*

Note

1. *If the concentrations are constant then if the system is coloured the colour will remain constant. System (a) [see above] will be a shade of orange and system (c) a shade of brown.*
2. *The system can involve physical changes such as (a) and (b) or chemical changes, (c) and (d).*
3. *The system can be homogeneous – one phase – such as (c) or heterogeneous a), b) and d).*

2. Qualitative Effects of Changes of Conditions on a System in Equilibrium

If there are changes such as, temperature, concentration or pressure of gaseous systems, their effect can be predicted by **Le Chatelier's principle**. This states:

*If any change is imposed on a system that is at equilibrium, then the system tends to adjust to a new equilibrium position by **opposing** the change.*

Examples of the application of Le Chatelier's principle

Factor altered is a:	The direction that the system moves to oppose the change is:
(a) concentration increase	that which decreases the increased concentration.
(b) concentration decrease	that which increases the decreased concentration
(c) pressure increase (or volume decrease)	that which decreases the pressure (p). This is the direction in which the number of moles (n) of gas decreases. (since $p \propto n$)
(d) pressure decrease (or volume increase)	that which increases the pressure (p). This is the direction in which the number of moles (n) of gas increases. (since $p \propto n$)
(e) temperature increase	in the endothermic direction as heat energy is absorbed causing the temperature to fall.
(f) temperature decrease	in the exothermic direction as heat energy is evolved causing the temperature to rise.
(g) add a catalyst	**No effect**. (The catalyst will increase the rates of the forward and backward reactions equally.)
(h) adding a solid e.g. Solid $CaCO_3$ in (d)	**No effect**. Adding a solid does not increase the concentration of the solid; it increases its mass.

3. Compromise Conditions and the Chemical Industry.

Le Chatelier's principle can be used to predict the best conditions for the highest equilibrium yield. However, the principle does not predict how quickly equilibrium will be attained or the cost of the process. In some cases compromises have to be made where a lower yield is accepted in order to allow a faster and / or less costly process. These occur when the reaction is exothermic or when there is a decrease in the number of moles of gas during the forward reaction .

Examples	Haber process	Methanol manufacture	Ethanol manufacture
Equation	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$	$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$
Enthalpy change ($\Delta H^{\ominus}_{298K}$)/kJmol^{-1}	- 92	- 91	- 46
Temperature / ^{0}C	450	230	300
Pressure / MPa	20	10	6
Catalyst	Iron	Copper or ZnO/Cr_2O_3	Conc. phosphoric(V) acid

(a) The temperatures used are *compromises* between rate and yield. The higher the temperature the greater the rate of the reaction but the lower the equilibrium yield because the forward reactions are exothermic. At the operating temperature, the rate and yield are both sufficiently high to make the process economically viable.

(b) The pressures used are *compromises* between cost and yield. The higher the pressure, the greater the yield because the forward reaction involves a decrease in the number of gaseous molecules but it also makes it more costly for the chemical plant required to safely contain and control the pressure. Also, the greater the energy cost to generate the pressure. At the operating pressure, the costs are sufficiently low and the yield sufficiently high to make the process economically viable.

Note : A higher pressure also increases the rate of the reaction.

All these processes involve a catalyst to increase the rate of the reaction. The catalyst does not alter the equilibrium yield but, without the catalyst, the process would be uneconomic since even higher temperatures (and pressures) and hence greater costs would be needed to achieve the same rate of reaction.

These processes are not allowed to reach equilibrium since this would take too long and hence be uneconomic. The products are separated from remaining reactants and these are recycled. This increases the atom economy and means expensive reactants are not wasted.

In the manufacture of ethanol, excess steam is used to shift the position of equilibrium to the right increasing the yield of ethanol and reducing the concentration of the more expensive ethene.

Common "Errors" when Answering Questions

(i) In structured questions do not write out the question again before starting the answer.
(ii) confusing terms e.g. atoms and molecules, exothermic and endothermic, actual yield and equilibrium yield, left and right, concentration and amount etc
(iii) not appreciating that pressure changes may only effect reactions involving gases.
(iv) giving an incomplete answer e.g. see answer to Q1 and in Q5 mark 2 depends on mark 1.
(v) not being precise e.g. see answer to 8a) where an answer like "it moves to the right" loses mark 1.;

Practice Questions

1. State and explain the effect of a decrease in
   (i) pressure,
   (ii) temperature, on the yield of nitrogen monoxide in the following equilibrium: $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = + 180$ kJmol^{-1}. (6)

2. (a) Hydrogen can be produced by the dynamic equilibrium reaction: $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
   (i) In terms of rates and of concentrations, what does the term dynamic equilibrium mean?
   (ii) State how an increase in pressure will affect the equilibrium yield of hydrogen. Explain your answer.
   (iii) The equilibrium yield of hydrogen is increased when the reaction is carried out at a higher temperature. What can be deduced about the enthalpy change in this reaction?
   (iv) Explain why the equilibrium yield is unchanged when a catalyst is introduced. (7)

   (b) Ammonia is manufactured by the Haber process:
   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = - 92$ kJmol^{-1}.
   Typical conditions are 450°C and 20 MPa.

   Explain why:
   (i) 450°C is a compromise temperature and
   (ii) 20 MPa is a compromise pressure. (6)

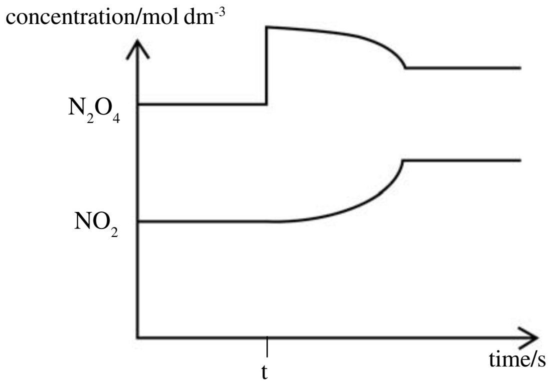
3. An understanding of rates of reaction and of yields at equilibrium is important to find the most economic conditions for an industrial process involving an equilibrium reaction. Consider the production of XY_2 from X_2 and Y_2.
   $X_2(g) + 2Y_2(g) \rightleftharpoons 2XY_2(g)$ $\Delta H = - 20$ kJmol^{-1}

   (a) State Le Chatelier's principle. (2)
   (b) State and explain the effect of a decrease in pressure on:
   (i) the equilibrium position of the reaction (2),
   (ii) the rate of the reaction (2).
   (c) The percentage conversion of X_2 was measured at various temperatures and a graph of percentage conversion (vertically) against temperature was plotted. Draw a sketch showing the shape of this graph. Explain the shape. (3)
   (d) If a catalyst was used in the process to produce XY_2, state the effect of using the catalyst on the equilibrium percentage conversion of X_2 and Y_2 into XY_2. (1).

4. A pale brown mixture of nitrogen dioxide (brown) and dinitrogen tetraoxide (colourless) is in dynamic equilibrium in a closed syringe at constant temperature:

   $2NO_2(g) \rightleftharpoons N_2O_4(g)$ $\Delta H^\ominus = -58\ kJmol^{-1}$.

   (a) Without opening the syringe state two ways of producing a paler colour in the syringe. (2)
   (b) $NO_2(g)$ and $N_2O_4(g)$ were mixed together and allowed to reach equilibrium. At equilibrium, the concentrations of the gases were measured at various times and the results plotted. At time t, a change was made to the composition of the mixture.
   (i) What change of conditions was made to the mixture at time t? (1)
   (ii) Explain the changes that happen to the mixture after time t? (2)



5. Chlorine water, a pale green solution due to the presence of molecular $Cl_2(aq)$, is made by passing chlorine gas into cold water. The following equilibrium exists:
   $Cl_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + Cl^-(aq) + HClO(aq)$

   Use Le Chatelier's principle to explain what will happen to the colour of chlorine water when a concentrated solution of sodium chloride is added. (4)

6. A potentially important future source of natural gas is from solid methane hydrates. They are formed at the bottom of deep seas at places where methane rises.
   $CH_4(g) + 6H_2O(l) \rightleftharpoons [CH_4(H_2O)_6](s)$ ΔH is –ve.
   State and explain two ways of releasing the methane from the methane hydrate. (6)

7. Explain what effect, (if any) the use of a catalyst has on the equilibrium yield of ammonia in the Haber process and also the amount of ammonia produced in a given time. (4)

8. When carbon dioxide from the atmosphere dissolves in the oceans two equilibria that occur are:
   $CO_2(g) \rightleftharpoons CO_2(aq)$ - - - (A)
   and $CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ - - - (B)

   (a) Use Le Chatelier's principle to explain the effect that increased carbon dioxide levels in the atmosphere will have on the HCO_3^- concentration in the oceans. (3)
   (b) Suggest and explain why the balance between gaseous $CO_2(g)$ and $CO_2(aq)$ in the oceans is not a true dynamic equilibrium. (1)

9. Hydrogen is produced from methane as follows: $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$; $\Delta H = +205\ kJmol^{-1}$

   (a) For each of the following changes in conditions, predict what will happen to the equilibrium yield of hydrogen for a given mass of methane and use Le Chatelier's principle to explain your answer.
   (i) the overall pressure is increased, ii) the concentration of steam is increased. (6)

   (b) The temperature used is 750^{0}C. Le Chatelier's principle predicts that the higher the temperature the higher the yield of hydrogen. Suggest two reasons why temperatures higher than 750^{0}C are not used. (2)

10. At 10^{0}C the following dynamic equilibrium exists inside a closed flask.
    $ICl(s) + Cl_2(g) \rightleftharpoons ICl_3(s)$
    (a) State the effect on the amount of iodine(III) chloride of adding more
    (i) solid iodine(I) chloride,
    (ii) chlorine, to the flask. (2)
    (b) Explain what will happen if the stopper is removed from the flask. (4)

Answers

1. (i) No change in yield. (1) Equal numbers of gaseous moles of reactants and products. (1) *(Molecules for moles would be allowed but not atoms.)* So the forward and backward reactions are affected equally. (1)

   (ii) Yield decreases (1). The equilibrium moves to raise the temperature (to oppose the change). (1) so the exothermic backward reaction is favoured. (1)

2. (a) (i) The rates of the forward and backward reactions are equal. (1) The concentrations of the reactants and products are constant. (1) *(Don't say "the same" – they are not!)*

   (ii) Decrease. (1) 2 gas moles produce 4 gas moles. So equilibrium moves to the left to reduce the pressure. (1)

   (iii) Enthalpy change is endothermic (1) – no explanation needed here!

   (iv) The catalyst increases the rate of the forward and backward reactions equally (1) resulting in the same overall equilibrium position being achieved (1).

   (b) (i) The temperature used is a compromise between rate and yield. (1) A higher temperature would increase the rate of reaction but lower the equilibrium yield since the forward reaction is exothermic. (1) A lower temperature would increase the equilibrium yield but lower the rate of reaction. (1) At the given operating temperature, the rate and yield are both sufficiently high to make the process economically viable.

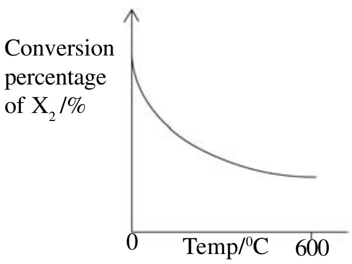
   (ii) The pressure used is a compromise between cost and yield. (1) A higher pressure would increase the cost of the chemical plant required to safely contain and control the pressure and increase the energy costs to generate the pressure even though the equilibrium yield (and rate) would be increased. (1) A lower pressure would lower plant and energy costs but decrease the equilibrium yield (and rate). (1) At the given operating pressure, the costs are sufficiently low and the yield sufficiently high to make the process economically viable.

3. (a) If any change is imposed on a system that is at equilibrium, then the system tends to adjust to a new equilibrium (1) position by opposing the change (1).

   (b) (i) The equilibrium moves to the left since there are more moles of gas on the left. (1) This increases the pressure so opposing the change. (1)

   (ii) Rate decreases. (1) There is a lower concentrations of molecules (don't say "atoms") $\therefore$ less frequent collisions. (1)

   (c) As the temperature increases the % conversion decreases. (1) Equilibrium moves to the left since the forward reaction exothermic.(1)



   (d) Unchanged. (1) (Don't *explain* since this is not asked for in this question.)

4. (a) Decrease the temperature. (1) Increase the pressure. (1)

   (b) (i) N_2O_4 was added (1) .(Not "concentration N_2O_4 increased".)

   (ii) Amount of N_2O_4 goes down / NO_2 goes up (1) as equilibrium moves to the left to remove (some of) the added N_2O_4 (1) until a new equilibrium position is reached. (Not the origional equilibrium.)

5. The concentration of Cl^- is increased [from Na^+Cl^-] (1). The equilibrium moves to the left. (1). This increases the concentration of Cl_2. (1) The green colour is less pale / more green. (1)

6. Reduce the pressure. (1) The equilibrium moves to the left (releasing methane) to increase the pressure (1) (and oppose the change). Since there only moles of gas on the left (1).

   Increase the temperature. (1) The equilibrium shifts to the left releasing methane (1) which is the endothermic direction (1) (to oppose the change).

7. The equilibrium yield is unchanged. (1) The catalyst increases the rates (1) of the forward and backward reactions equally. (1) More ammonia is produced (1) (per second.)

8. (a) To reduce the atmospheric CO_2(g) the equilibrium position of (A) moves to the right. (1) CO_2(aq) concentration increases so the equilibrium position of (B) moves to the right. (1) This increases HCO_3^- conc. (1)

   (b) e.g. the system is not closed ; the temperature is not constant.(1)

9. (a) (i) Decreased. (1) The backward reaction is favoured as this reduces the pressures (1) as there are fewer gaseous moles of reactants than gaseous products. (1).

   (ii) Increased (1). The equilibrium position will move towards the reactants (1) to remove some of the added steam (1)

   (b) Higher temperatures need more (expensive) energy (1) and a more expensive chemical plant (1).

10. (a) (i) No effect, (1) (ii) Increase (1)

    (b) Cl_2 gas escapes. (1) This reduces the concentration of Cl_2 (1) in the flask so the backward reaction is favoured (1) (in attempting to restore equilibrium.) Eventually (only) ICl(s) remains in the flask (1).

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