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# CHEMISTRY

## PHYSICAL CHEMISTRY

Level & Board	CIE (A-LEVEL)
TOPIC:	EQUILIBRIA
PAPER TYPE:	QUESTION PAPER - 2
TOTAL QUESTIONS	10
TOTAL MARKS	112

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## Equilibria - 2

1)

Concern over the ever – increasing use of fossil fuels has led to many suggestions for alternative sources of energy. One of these, suggested by Professor George Olah, winner of a Nobel Prize in chemistry, is to use methanol  $\text{CH}_3\text{OH}$ , which can be obtained in a number of different ways.

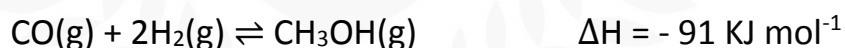
Methanol could be used instead of petrol in a conventional internal combustion engine or used to produce electricity in a fuel cell.

- (a) Construct a balanced equation for the **complete** combustion of methanol. [1]

When hydrocarbon fuels are completely burned in an internal combustion engine, several toxic pollutants may be formed.

- (b) State two toxic pollutants that can be produced after complete combustion of a hydrocarbon fuel in an internal combustion engine. [2]

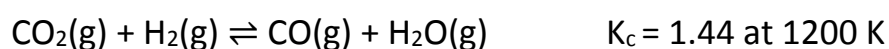
Methanol may be manufactured catalytically from synthesis gas, a mixture of  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2$ . The  $\text{CO}$  is reacted with  $\text{H}_2$  to form methanol,  $\text{CH}_3\text{OH}$ .



- (c) From your understanding of Le Chatelier's principle, state two conditions that could be used in order to produce a high yield of methanol.

In each case, explain why the yield would increase. [4]

Carbon monoxide, which can be used to make methanol, may be formed by reacting carbon dioxide with hydrogen.



- (d) (i) It has been suggested that, on a large scale, this reaction could be helpful to the environment.

Explain, with reasons, why this would be the case.

(ii) A mixture containing 0.50 mol of  $\text{CO}_2$ , 0.50 mol of  $\text{H}_2$ , 0.20 mol  $\text{CO}$  and 0.20 mol of  $\text{H}_2\text{O}$  was placed in a  $1.0 \text{ dm}^3$  flask and allowed to come to equilibrium at 1200 K.

Calculate the amount, in moles, of each substance present in the equilibrium mixture at 1200 K

	$\text{CO}_2$	+	$\text{H}_2$	$\rightleftharpoons$	$\text{CO}$	+	$\text{H}_2\text{O}$	
Initial moles	0.50		0.50		0.20		0.20	[6]

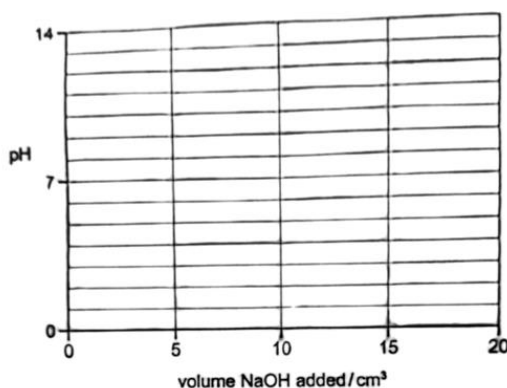
2)

(a) Explain what is meant by the *Bronsted – Lowry* theory of acids and bases. [2]

(b) The  $K_a$  values for some organic acids are listed below.

acid	K <sub>a</sub> /mol dm <sup>-3</sup>
$\text{CH}_3\text{CO}_2\text{H}$	$1.7 \times 10^{-5}$
$\text{ClCH}_2\text{CO}_2\text{H}$	$1.3 \times 10^{-3}$
$\text{Cl}_2\text{CHCO}_2\text{H}$	$5.0 \times 10^{-2}$

- (i) Explain the trend in  $K_a$  values in terms of the structures of these acids.
- (ii) Calculate the pH of a  $0.10 \text{ mol dm}^{-3}$  solution of  $\text{C}/\text{CH}_2\text{CO}_2\text{H}$
- (iii) Use the following axes to sketch the titration curve you would obtain when  $20 \text{ cm}^3$  of  $0.10 \text{ mol dm}^{-3}$  NaOH is added gradually to  $10 \text{ cm}^3$  of  $0.10 \text{ mol dm}^{-3}$   $\text{C}/\text{CH}_2\text{CO}_2\text{H}$ .



- (C) (I) Write suitable equations to show how a mixture of ethanoic acid,  $\text{CH}_3\text{CO}_2\text{H}$ , and sodium ethanoate acts as a buffer solution to control the pH when either an acid or an alkali is added.
- (ii) Calculate the pH of a buffer solution containing  $0.10 \text{ mol dm}^{-3}$  ethanoic acid and  $0.20 \text{ mol dm}^{-3}$  sodium ethanoate. [4]

3)

- (c) Calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , is slightly soluble in water.

(i) Write an expression for  $K_{\text{sp}}$  for calcium hydroxide, and state its units.

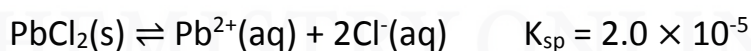
(ii)  $25.0 \text{ cm}^3$  of a saturated solution of  $\text{Ca}(\text{OH})_2$  required  $2.0 \text{ cm}^3$  of  $0.0500 \text{ mol dm}^{-3}$  HCl for complete neutralization.

Calculate the  $[\text{OH}^- (\text{aq})]$  and the  $[\text{Ca}^{2+}(\text{aq})]$  in the saturated solution, and hence calculate a value for  $K_{\text{sp}}$ .

(iii) How would the solubility of  $\text{Ca}(\text{OH})_2$  in  $0.1 \text{ mol dm}^{-3}$  NaOH compare with that in water? Explain your answer. [6]

4)

- (c) Lead (II) chloride is slightly soluble in water.



(i) Write an expression for the solubility product,  $K_{\text{sp}}$  for lead (II) chloride and state its units.

(ii) Calculate  $[\text{Pb}^{2+}(\text{aq})]$  in a saturated solution of  $\text{PbCl}_2$ .

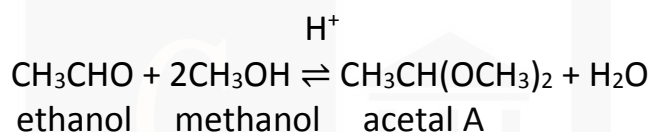
An excess of  $\text{PbCl}_2(\text{s})$  is stirred with  $0.50 \text{ mol dm}^{-3}$  NaCl until equilibrium has been established. The excess  $\text{PbCl}_2(\text{s})$  is then filtered off.

(iii) Assuming  $[\text{Cl}^-]$  remains at  $0.50 \text{ mol dm}^{-3}$  throughout, calculate the  $[\text{Pb}^{2+}(\text{aq})]$  in the remaining solution.

(iv) Suggest an explanation for the difference between this value and the value that you calculated in (ii). [4]

5)

Acetals are compounds formed when aldehydes are reacted with an alcohol and an acid catalyst. The reaction between ethanol and methanol was studied in the inert solvent dioxin.



(a) When the initial rate of this reaction was measured at various starting concentrations of the three reactants, the following results were obtained.

experiment number	[CH <sub>3</sub> CHO] /mol dm <sup>-3</sup>	[CH <sub>3</sub> OH] /mol dm <sup>-3</sup>	[H <sup>+</sup> ] /mol dm <sup>-3</sup>	relative rate
1	0.20	0.10	0.05	1.00
2	0.25	0.10	0.05	1.25
3	0.25	0.16	0.05	2.00
4	0.20	0.16	0.10	3.20

(i) Use the data in the table to determine the order with respect to each reactant.

Order with respect to [CH<sub>3</sub>CHO] .....

Order with respect to [CH<sub>3</sub>OH] .....

Order with respect to [H<sup>+</sup>] .....

(ii) Use your results from part (i) to write the rate equation for the reaction.

(iii) State the units of the rate constant in the rate equation.

(iv) Calculate the relative rate of reaction for a mixture in which the starting

concentrations of all three reactants are 0.20 mol dm<sup>-3</sup>

[5]

	[CH <sub>3</sub> CHO] /mol dm <sup>-3</sup>	[CH <sub>3</sub> OH] /mol dm <sup>-3</sup>	[H <sup>+</sup> ] /mol dm <sup>-3</sup>	[acetal A] /mol dm <sup>-3</sup>	[H <sub>2</sub> O] /mol dm <sup>-3</sup>
at start	0.20	0.10	0.05	0.00	0.00
at equilibrium	(0.20 - x)			x	
at equilibrium				0.025	

(i) Complete the second row of the table in terms of x, the concentration of acetal A at equilibrium. You may wish to consult the chemical equation opposite.

(ii) Using the [acetal A] as given, 0.025 mol dm<sup>-3</sup>, calculate the equilibrium concentrations of the other reactants and products and write them in the third row of the table.

(iii) Write the expression for the equilibrium constant for this reaction, K<sub>c</sub>, starting its units.

(iv) Use your values in the third row of the table to calculate the value of K<sub>c</sub>. [9]

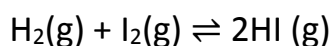
6)

Each of the Group VII elements chlorine, bromine and iodine forms a hydride.

(a) (i) Outline how the relative thermal stabilities of these hydrides change from HCl to HI.

(ii) Explain the variation you have outlined in (i) [3]

Hydrogen iodide can be made by heating together hydrogen gas and iodine vapour. The reaction is incomplete.



(b) Write an expression for K<sub>c</sub> and state the units. [2]

- (c) For this equilibrium, the numerical value of the equilibrium constant  $K_c$  is 140 at 500 K and 59 at 560 K.

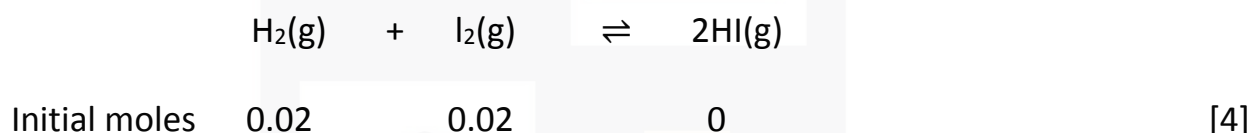
Use this information to state and explain the effect of the following changes on the equilibrium position.

(i) Increasing the pressure applied to the equilibrium

(ii) Decreasing the temperature of the equilibrium [4]

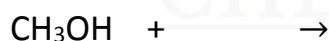
- (d) A mixture of 0.02 mol of hydrogen and 0.02 mol of iodine was placed in a 1 dm<sup>3</sup> flask and allowed to come to equilibrium at 650 K.

Calculate the amount, in moles, of each substance present in the equilibrium mixture at 650 K.



7)

(a) (i) Using the symbol HZ to represent a Bronsted – Lowry acid, write equations which show the following substances acting as Bronsted – Lowry bases.



(ii) Using the symbol B<sup>-</sup> to represent a Bronsted – Lowry base, write equations which show the following substances acting as Bronsted – Lowry acids.



- (a) State briefly what is meant by the following terms.

(i) reversible reaction

(ii) dynamic equilibrium

[2]

(b) (i) Explain what is meant by a buffer solution.

Explain how the working of a buffer solution relies on a reversible reaction involving a Bronsted – Lowry acid such as HZ and a Bronsted – Lowry base such as Z<sup>-</sup>. [4]

(c) Propanoic acid, CH<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>H, is a weak acid with K<sub>a</sub> = 1.34 × 10<sup>-5</sup> mol dm<sup>-3</sup>.(i) Calculate the pH of a 0.500 mol dm<sup>-3</sup> solution of propanoic acid.

Buffer solution **F** was prepared by adding 0.0300 mol of sodium hydroxide to 100 cm<sup>3</sup> of a 0.500 mol dm<sup>-3</sup> solution of propanoic acid.

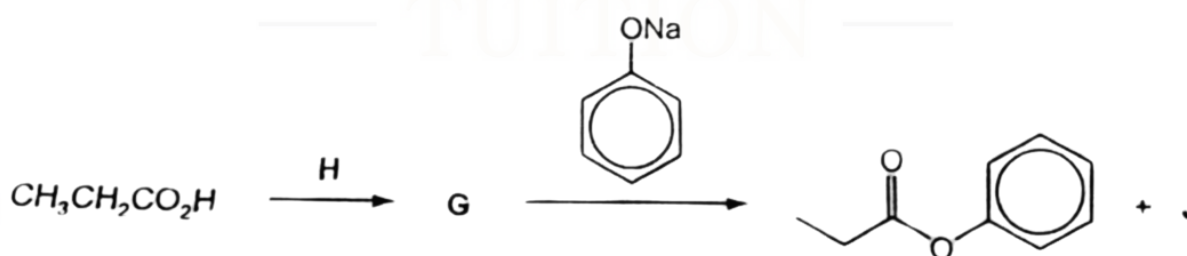
(ii) Write an equation for the reaction between sodium hydroxide and propanoic acid.

(iii) Calculate the concentrations of propanoic acid and sodium propanoate in buffer solution **F**.(i) Calculate the pH of buffer solution **F**.

[6]

(a) Phenyl propanoate cannot be made directly from propanoic acid and phenol.

Suggest the identities of the intermediate **G**, the reagent **H** and the by – product **J** in the following reaction scheme.



[2]



- 8)
- (c) The acid dissociation constant,  $K_a$ , of ethanoic acid is  $1.75 \times 10^{-5} \text{ mol dm}^{-3}$ .

(i) Explain why this value of  $K_a$  is

- Much larger than that of ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ ,
- Smaller than that of chloroethanoic acid,  $\text{ClCH}_2\text{CO}_2\text{H}$ .

(ii) Calculate the pH of a  $0.100 \text{ mol dm}^{-3}$  solution of ethanoic acid. [4]

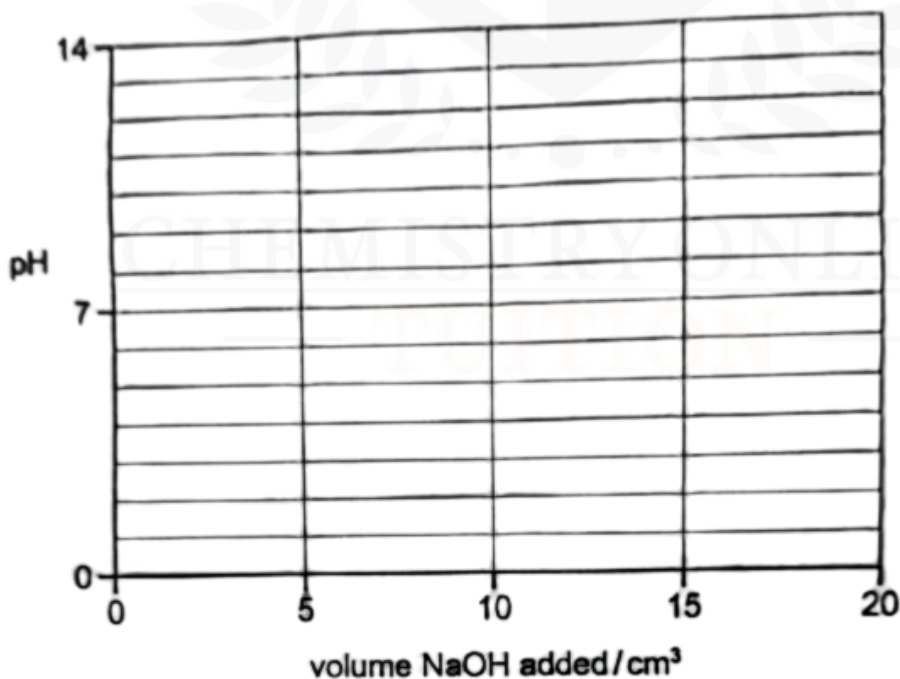
(d)  $20.0 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3}$  NaOH were slowly added to a  $10.0 \text{ cm}^3$  sample of  $0.100 \text{ mol dm}^{-3}$  ethanoic acid, and the pH was measured throughout the addition.

(i) Calculate the number of moles of NaOH remaining at the end of the addition.

(ii) Calculate the  $[\text{OH}^-]$  at the end of the addition.

(iii) Using the expression  $K_w = [\text{H}^+][\text{OH}^-]$  and your value in (ii), calculate  $[\text{H}^+]$  and the pH of the solution at the end of the addition.

(iv) On the following axes, sketch how the pH will change during the addition of a total of  $20.0 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3}$  NaOH. Mark clearly where the end point occurs.



(v) From the following list of indicators, put a tick in the box by the side of the indicator you consider most suitable for this titration.

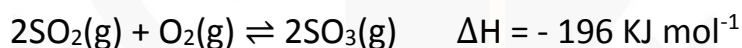
indicator	pH at which color changes	place <b>one</b> tick only in this column
malachite green	0 - 1	
thymol blue	1 - 2	
bromophenol blue	3 - 4	
thymolphthalein	9- 10	

[7]

9)

The Contact process for the manufacture of sulfuric acid was originally patented in the 19<sup>th</sup> century and is still in use today.

The key step in the overall process is the reversible conversion of sulfur dioxide to sulfur trioxide in the presence of a vanadium (V) oxide catalyst.



- (a) One way in which the sulfur dioxide for this reaction is produced is by heating sulfide ore iron pyrites, FeS<sub>2</sub>, in air, iron (III) oxide is also produced. Write an equation for this reaction. [2]
- (b) The sulfur trioxide produced in the Contact process is reacted with 98% sulfuric acid. The resulting compound is then reacted with water to produce sulfuric acid.
- (i) Explain why the sulfur trioxide is not first mixed directly with water. [1]
- (ii) Write equations for the two steps involved in the conversion of sulfur trioxide into sulfuric acid. [2]
- (c) (i) Sulfur dioxide and sulfur trioxide both contain only S = O double bonds. Draw labelled diagrams to show the shapes of these two molecules. [ 2]
- (i) For your diagrams in (i), name the shapes and suggest the bond angles.

SO<sub>2</sub> shape: ..... SO<sub>3</sub> shapes: .....

SO<sub>2</sub> bond angle: ..... SO<sub>3</sub> bond angle: ..... [2]

- (d) The conversion of sulfur dioxide into sulfur trioxide is carried out at a temperature of 400 °C.
- (i) With reference to Le Chateller's Principle and reaction kinetics, state and explain one advantage and one disadvantage of using a higher temperature. [4]
- (ii) State the expression for the equilibrium constant,  $K_p$ , for the formation of sulfur trioxide from sulfur dioxide [1]
- (iii) 2.00 moles of sulfur dioxide and 2.00 moles of oxygen were put in a flask and left to reach equilibrium.
- At equilibrium, the pressure in the flask was  $2.00 \times 10^5$  Pa and the mixture contained 1.80 moles of sulfur trioxide.
- Calculate  $K_p$ . Include the units. [5]

10)

Phosphate ions in water can be removed by adding a solution containing  $\text{Ca}^{2+}(\text{aq})$  ions, which form a precipitate of calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ ,

- (i) Write an expression for the  $K_{sp}$  of  $\text{Ca}_3(\text{PO}_4)_2$ .
- (ii) The solubility of  $\text{Ca}_3(\text{PO}_4)_2$  is  $2.50 \times 10^{-6}$  mol dm<sup>-3</sup> at 298 K.

Calculate the solubility product,  $K_{sp}$ , of  $\text{Ca}_3(\text{PO}_4)_2$  at this temperature. Include the units. [4]

- (a) (i) what is meant by the term lattice energy?
- (ii) Explain why the lattice energy of calcium phosphate is less exothermic than that of magnesium phosphate. [3]



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