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PHYSICAL CHEMISTRY

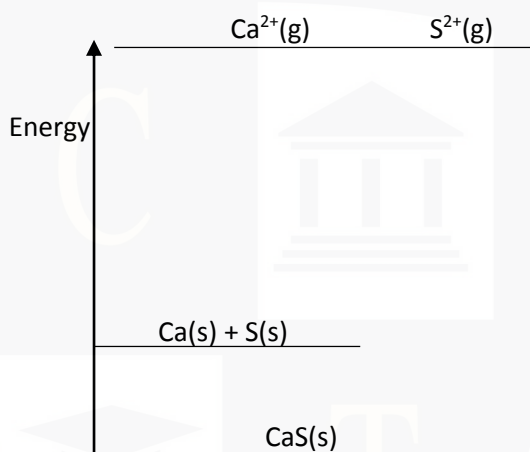
Level & Board	CIE (A-LEVEL)
TOPIC:	CHEMICAL ENERGETICS
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TOTAL QUESTIONS	15
TOTAL MARKS	148

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Chemical Energetics

1)

- (a) On the incomplete outline below sketch the Both – Haber cycle which includes the Standard enthalpy change of formation, ΔH_f^\ominus , and the lattice energy of calcium Sulphide. Label all the enthalpy changes involved and the chemical species at each Stage. [Abbreviations can be used, as in part (b).]



- (b) The standard enthalpy changes of atomization, [5]

$$\Delta H_a^\ominus \text{ of calcium} = 178 \text{ KJ mol}^{-1}$$

$$\Delta H_a^\ominus \text{ of sulphur} = 279 \text{ KJ mol}^{-1}$$

The sum of the first two electron affinities of sulphur = 337 kJ mol^{-1} .

The standard enthalpy change of formation,

$$\Delta H_a^\ominus \text{ of calcium sulphide} = -487 \text{ KJ mol}^{-1}$$

The other enthalpy change values are to be obtained from the Data Booklet.

Use these values to calculate the lattice energy of calcium sulphide. [2]

- (c) (i) The first electron affinity of sulphur is -200 KJ mol^{-1} . Calculate the value of the second Electron affinity of sulphur.

- (ii) Comment on or explain the difference between these two values. [2]

- (d) Suggest and explain how you would expect the value of the lattice energy of calcium oxides to compare with the value you obtained in (b). [2]

2)

- (a) What do you understand by the term lattice energy? [1]

- (b) Write equations to represent

(i) the lattice energy,

The enthalpy changes of formation, of magnesium oxides, MgO. [2]

- (c) Use the following data, together with appropriate data from the Data Booklet, to Calculate the lattice energy of magnesium oxide.

first electron affinity of oxygen ($O(g) + e^- \rightarrow (g)$) -140 mol^{-1}

second electron affinity of oxygen ($O^-(g) + e^- \rightarrow O^{2-}(g)$) $+798 \text{ KJ mol}^{-1}$

enthalpy change of atomization of Mg $+ 148 \text{ KJ mol}^{-1}$

enthalpy change of formation of MgO(s) $- 602 \text{ KJ mol}^{-1}$ [3]

- (d) How would you expect the lattice energy of CaO to differ from that of MgO?

Explain your answer. [2]

- (e) What effect do the relatively high lattice energies of the Group II oxides have on their physical properties? Give one example of a use of these oxides that relies on its high lattice energy. [2]

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3)

One of the most important uses of alkanes is for fuels. In some countries, where crude oil is either scarce or expensive, bio fuels such as ethanol are increasingly being used for fuels instead of hydrocarbons. [1]

(a) What do you understand by the term bond energy?

(b) (i) Write an equation for the complete combustion of octane, C_8H_{18} .

(ii) Use the bond energies given in the Data Booklet to calculate a value for the enthalpy change of combustion of octane. [4]

(c) The accurate experimental enthalpy changes of combustion of three hydrocarbons are

Given are in the table below.

alkane	Formula	$\Delta H_c / \text{KJmol}^{-1}$
heptane	C_7H_{16}	-4817
octane	C_8H_{18}	-5470
nonane	C_9H_{20}	-6125

(i) Suggest a reason for the discrepancy between the ΔH_c for octane you calculated in (b)(i) and that given in the table.

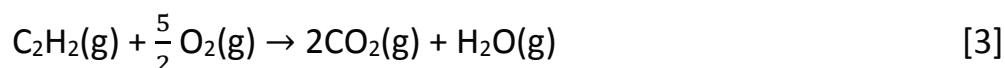
(ii) Suggest what the regular increase in the values of ΔH_c given in the table represents. [2]

(d) The enthalpy change of combustion of ethanol is -1367 KJmol^{-1} , and the densities of Ethanol and octane are 0.79 g cm^{-3} and 0.70 g cm^{-3} respectively. Calculate the heat Produced by the complete combustion of 1.0 dm^3 of each fuel. [3]

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4)

(d) The equation for the complete combustion of ethyne is given below. Use appropriate Bond energy data from the *Data booklet* to calculate a value for the enthalpy change of Combustion of ethyne.



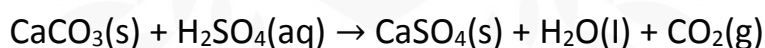
(e) The value for the standard enthalpy change of combustion of ethyne is $-1300 \text{ kJ mol}^{-1}$

(i) Define the term *standard enthalpy change of combustion*.

(ii) Explain why your answer to (d) does not have the same value as the standard enthalpy change of combustion. [3]

5)

Monuments made of marble or limestone, such as the Taj Mahal in India and the Mayan temples in Mexico, in Mexico, are suffering erosion by acid rain. The carbonate stone is converted by the acid rain into the relatively more soluble sulphate.



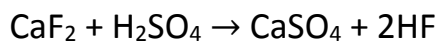
(c) (i) Explain what is meant by the term lattice energy.

(ii) Predict, with a reason, how the lattice energy of BaSO_4 might compare with that of MgSO_4 . [3]

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6)

Fluorspar reacts with concentrated sulphuric acid to form hydrogen fluoride gas.



Data about HF, HCl, HBr, and HI are given below.

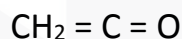
	HF	HCl	HBr	HI
Boiling point / °C	+20	-85	-67	-35
Bond energy / KJmol ⁻¹	562	431	366	299
ΔH_f^\ominus / KJ mol ⁻¹	-269	-92	-36	+26

(c) (i) Explain why the boiling points of HCl, HBr, and HI increase down the Group.

(ii) Suggest why the boiling point of HF is much higher than those of the others. [3]

7)

Ketene, C₂H₂O, is a member of a class unsaturated organic compounds that is widely used in pharmaceutical research for the synthesis of organic compounds.



Ketene

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(c) (i) Define the term standard enthalpy change of formation.

(ii) Use the data below to calculate the standard enthalpy change of formation. Of ketene.

	$\Delta H^\ominus / \text{KJ mol}^{-1}$
Standard enthalpy change of formation of CO_2	-395
Standard enthalpy change of combustion of H_2	-286
Standard enthalpy change of combustion of $\text{CH}_2 = \text{C} = \text{O}$	-1028

[6]

(d) Ketene can be converted directly into ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$, by reaction with a compound **A**. Suggest the identity of **A**.

[1]

8)

(a) What is meant by the term bond energy?

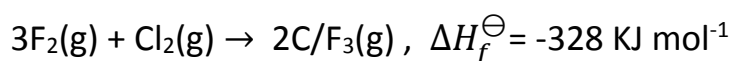
[2]

(b) Describe and explain what is observed when a red – hot wire is plunged into separate samples of the gaseous hydrogen halides HCl and HI .

How are bond energy values useful in interpreting these observations?

[3]

(c) The following reaction occurs in the gas phase.



Use these and other data from the Data Booklet to calculate the average bond energy of the $\text{Cl} - \text{F}$ bond in CF_3

[2]

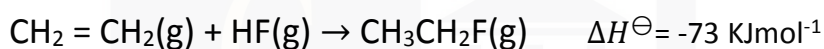
9)

Halogenalkanes have been widely used as aerosol propellants, refrigerants and solvents for many years.

Fluoroethane, $\text{CH}_3\text{CH}_2\text{F}$, has been used as a refrigerant. It may be made by reacting ethene with hydrogen fluoride.

You are to calculate a value for the C – F bond energy in fluoroethane.

(a) Use relevant bond energies from the Data booklet, and the equation below to calculate a value for the bond energy of the C – F bond.



[4]

(b) Another halogenalkane which was used as a refrigerant, and also as an aerosol propellant, is dichlorodifluoromethane, CCl_2F_2 .

State two reasons why compounds such as $\text{CH}_3\text{CH}_2\text{F}$ and CCl_2F_2 have been used as aerosol propellants and refrigerants.

[2]

CCl_2F_2 is one of many chlorofluorocarbon compounds responsible for damage to the ozone layer in the stratosphere.

(c) By using relevant data from the Data booklet, and your answer to (a) suggest why CCl_2F_2 is responsible for damage to the ozone layer in the stratosphere whereas $\text{CH}_3\text{CH}_2\text{F}$ is not.

[2]

Both $\text{CH}_3\text{CH}_2\text{F}$ and CCl_2F_2 are greenhouse gases.

The 'enhanced greenhouse effect' is of great concern to the international community.

(d) (i) What is meant by the term enhanced greenhouse effect?

(ii) Water vapour is the most abundant greenhouse gas.

What is the second most abundant greenhouse gas?

[3]

A greenhouse gas which is present in very small amounts in the atmosphere is sulfur hexafluoride, SF₆, which is used in high voltage electrical switchgear.

(e) What shape is the SF₆ molecule?

[1]

10)

For some chemical reactions, such as the thermal decomposition of potassium hydrogencarbonate, KHCO₃ the enthalpy change of reaction cannot be measured directly.

In such cases, the use of Hess' Law enables the enthalpy change of reaction to be calculated from the enthalpy changes of other reactions.

(a) State Hess' Law.

[2]

in order to determine the enthalpy change for the thermal decomposition of potassium hydrogencarbonate, two separate experiments were carried out.

experiment 1

30.0 cm³ of 2.00 mol dm⁻³ hydrochloric acid (an excess) was placed in a conical flask and the temperature recorded as 21.0 °C .

When 0.0200 mol of potassium carbonate, K₂CO₃, was added to the acid and the mixture stirred with a thermometer, the maximum temperature recorded was 26.2 °C.

(b) (i) Construct a balanced equation for this reaction.

(ii) Calculate the quantity of heat produced in **experiment 1**, stating your units.

Use relevant data from the Data Booklet and assume that all solutions have the same specific heat capacity as water.

(iii) Use your answer to (ii) to calculate the enthalpy change per mole of K₂CO₃.

Give your answer in KJ mol⁻¹ and include a sign in your answer.

(iv) Explain why the hydrochloric acid must be in an excess.

[4]

experiment 2

The experiment was repeated with 0.0200 mol of potassium hydrogencarbonate, KHCO_3 .

All other conditions were the same.

In the second experiment, the temperature fell from 21.0°C to 17.3°C .

(c) (i) Construct a balanced equation for this reaction.

(ii) Calculate the quantity of heat absorbed in **experiment 2**

(iii) Use your answer to (ii) to calculate the enthalpy change per mole of KHCO_3 .

Give your answer in KJ mol^{-1} and include a sign in your answer.

[3]

(d) When KHCO_3 is heated, it decomposes into K_2CO_3 , CO_2 and H_2O .



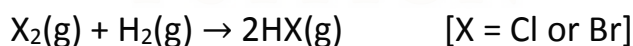
Use Hess' Law and your answers to (b)(iii) and (c)(iii) to calculate the enthalpy change for this reaction.

Give your answer in KJ mol^{-1} and include a sign in your answer.

[2]

11)

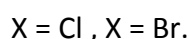
(a) The halogens chlorine and bromine react readily with hydrogen.



(i) Describe how you could carry out this reaction using chlorine.

(ii) Describe two observations you would make if this reaction was carried out with bromine.

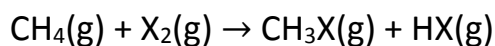
(iii) Use bond energy data from the *Data Booklet* to calculate the ΔH^\ominus for this reaction when



(iv) When is the major reason for the difference in these two ΔH^\ominus values?

[8]

(b) Some halogens also react readily with methane.



- (i) What conditions are needed to carry out this reaction when X is bromine, Br?
- (ii) Use bond energy data from the *Data Booklet* to calculate the ΔH^\ominus of this reaction for the situation where X is iodine, I.
- (iii) Hence suggest why it is not possible to make iodomethane, CH_3I , by this reaction.

[4]

(c) halogen alkanes can undergo homolytic fission in the upper atmosphere.

- (i) Explain the term homolytic fission.
- (ii) Suggest the most likely organic radical that would be formed by the homolytic fission of bromochloromethane, CH_2BrCl . Explain your answer.

[3]

(d) The reaction between propane and chlorine produces a mixture of many compounds

Four of which are structural isomers with the molecular formula $\text{C}_3\text{H}_6\text{Cl}_2$.

Draw the structural or skeletal formulae of these isomers, and indicate any chiral atoms with an asterisk (*).

[3]

12)

Alcohols such as methanol, CH_3OH , are considered to be possible replacements for fossil fuels because they can be used in car engines.

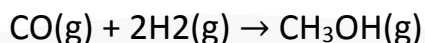
(a) Define, with the aid of an equation which includes state symbols, the standard enthalpy change of combustion, ΔH_c^\ominus for methanol at 298 K.

[3]

Methanol may be synthesized from carbon monoxide and hydrogen. Relevant ΔH_c^\ominus values for this reaction are given in the table below.

Compound	ΔH_c^\ominus
CO(g)	-283
H ₂ (g)	-286
CH ₃ OH(g)	-726

(b) Use these values to calculate $\Delta H_{reaction}^\ominus$ for the synthesis of methanol, using the following equation. Include a sign in your answer.



[3]

(c) The operating conditions for this reaction are as follows.

Pressure	200 atmospheres (2×10^7 Pa)
temperature	600 K
catalyst	oxides of Cr, Cu and Zn

Explain how each of these conditions affects the rate of formation of methanol. [6]

13)

(a) (i) What is meant by the term enthalpy change of hydration, ΔH_{hyd}^\ominus ?

(ii) Write an equation that represents the ΔH_{hyd}^\ominus of the Mg²⁺ ion.

(iii) Suggest a reason why ΔH_{hyd}^\ominus of the Mg²⁺ ion is greater than ΔH_{hyd}^\ominus of the Ca²⁺ ion.

(iv) Suggest why it is impossible to determine the enthalpy change of hydration of the oxide ion, O²⁻ [5]

(b) The enthalpy change of solution for MgCl₂, ΔH_{sol}^\ominus (MgCl₂(s)), is represented by the following equation.



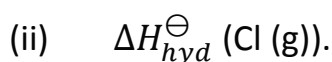
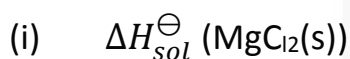
Describe the simple apparatus you could use, and the measurements you would

Make, in order to determine a value for $\Delta H_{sol}^{\ominus}(\text{MgCl}_2(\text{s}))$ in the laboratory. [4]

(c) The table below lists data relevant to the formation of $\text{MgCl}_2(\text{aq})$.

enthalpy change	Value/KJ mol ⁻¹
$\Delta H_f^{\ominus}(\text{MgCl}_2(\text{s}))$	-641
$\Delta H_f^{\ominus}(\text{MgCl}_2(\text{aq}))$	-801
Lattice energy of $(\text{MgCl}_2(\text{s}))$	-2526
$\Delta H_{hyd}^{\ominus}(\text{Mg}^{2+}(\text{g}))$	-1890

By constructing relevant thermochemical cycles, use the above data to calculate a value for



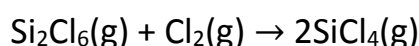
(d) Describe and explain how the solubility of magnesium sulfate compares to that of barium sulfate. [4]

14)

(a) Write down what you would see, and write equations for the reactions that occur, when Silicon (IV) chloride and phosphorus (V) chloride are separately mixed with water. [4]

(c) When SiCl_4 vapour is passed over Si red heat, Si_2Cl_6 is formed Si_2Cl_6 contains a Si – Si bond.

The reaction of Si_2Cl_6 and Cl_2 re – forms SiCl_4 .



Use bond energy data from the *Data Booklet* to calculate ΔH^{\ominus} for this reaction. [2]

(d) Calcium forms three calcium silicides, Ca_2Si , CaSi and CaSi_2 . The first of these reacts

Water as follows.



- (i) Balance this equation. You may find the use of oxidation numbers helpful.
- (ii) During this reaction, state
Which element (s) have been oxidized,
Which element(s) have been reduced. [2]

15)

Propane, C₃H₈, and butane, C₄H₁₀ are components of Liquefied Petroleum Gas (LPG) which is widely used as a fuel for domestic cooking and heating.

- (a) (i) To which class of compounds do these two hydrocarbons belong?
(ii) Write a balanced equation for the complete combustion of butane. [2]
- (b) When propane or butane is used in cooking, the saucepan may become covered by a solid black deposit.
(i) What is the chemical name for this black solid?
(ii) Write a balanced equation for its formation from butane. [2]
- (c) Propane and butane have different values of standard enthalpy change of combustion.
Define the term standard enthalpy change of combustion. [2]
- (d) A 125 cm³ sample of propane gas, measured at 20°C and 101 kPa, was completely burnt in air.
The heat produced raised the temperature of 200 g of water by 13.8 °C. Assume no heat losses occurred during this experiment.
(i) Use the equation $pV = nRT$ to calculate the mass of propane used.
(ii) Use relevant data from the Data Booklet to calculate the amount of heat released in

In this experiment.

(iii) Use the data above and your answers to (i) and (ii) to calculate the energy

Produced by the burning of 1 mol of propane.

[5]

(e) The boiling points of methane, ethane, propane, and butane are given below.

compound	CH ₄	CH ₃ CH ₃	CH ₃ CH ₂ CH ₃	CH ₃ (CH ₂) ₂ CH ₃
boiling point/K	112	185	231	273

(i) Suggest an explanation for the increase in boiling points from methane to butane.

(ii) The isomer of butane, 2 – methylpropane, (CH₂)₃CH, has a boiling point of 261 K.

Suggest an explanation for the difference between this value and that for butane in table above.

[4]

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