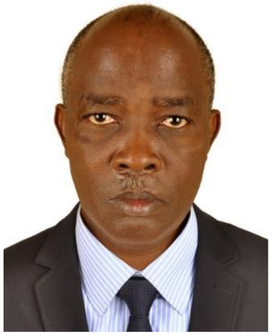

Dr. Bbosa Science

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Thermodynamics (A-level)

In most chemical reactions there is an associated energy change, shown by the evolution of heat in an exothermic reaction /process or by absorption of heat in an endothermic reaction. It is generally possible to measure what the change is, even though it is may not be possible to determine the absolute energy levels before and after the change.

Heat changes at constant volume are known as internal energy change (ΔU) while those at constant pressure are known as enthalpy changes (ΔH). If no volume changes is involved ΔH = ΔU, but with a volume change, the difference between ΔH and ΔU arises because work is involved in expansion or contraction. For practical purposes, these heat changes are used interchangeably.

Heat absorbed or liberated in a reaction varies with the quantities of the reactants, the temperature and pressure at which a reaction is carried out.

Standard enthalpy changes

These are enthalpy changes when molar quantities are considered at 298K and 1 atmospheres.

Standard molar enthalpy changes are then symbolized by $\Delta H_m^{\Theta}(298K)$ but the simpler symbol, ΔH, may be used. ΔH has negative value (heat evolved) for exothermic reaction and positive value for endothermic reaction.

The terms used for the different energy changes are as follows:

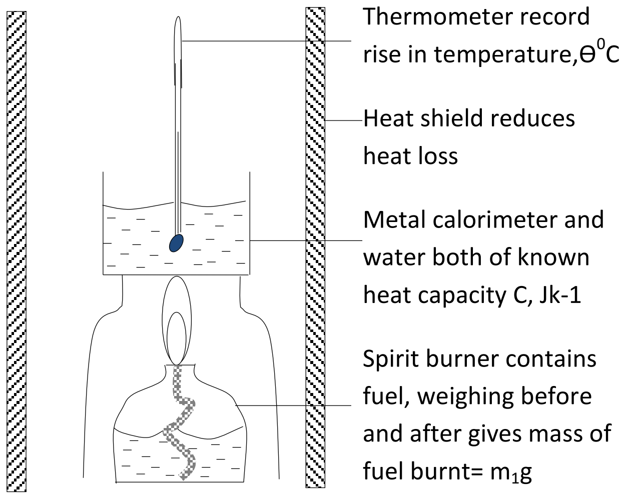
a) Enthalpy of combustions: The standard molar enthalpy of combustion of a substance is the enthalpy changes when 1 mole of it is completely burn in oxygen under standard conditions.

E.g.

	$\Delta H_{c,m}^{\Theta}(298K)$
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$	$-890.5kJmol^{-1}$
$C(s) + O_2(g) \rightarrow CO_2(g)$	$-393.5kJmol^{-1}$

(i) Experimental method for finding enthalpy of combustion a liquid fuel

The figure below shows a simple method for obtaining approximate value for the enthalpy of combustion of a fuel



Calculations

Assumption

Heat produced by combusting fuel = heat gained by water

Heat gained by calorimeter and water = Cϴ joules

It implies that

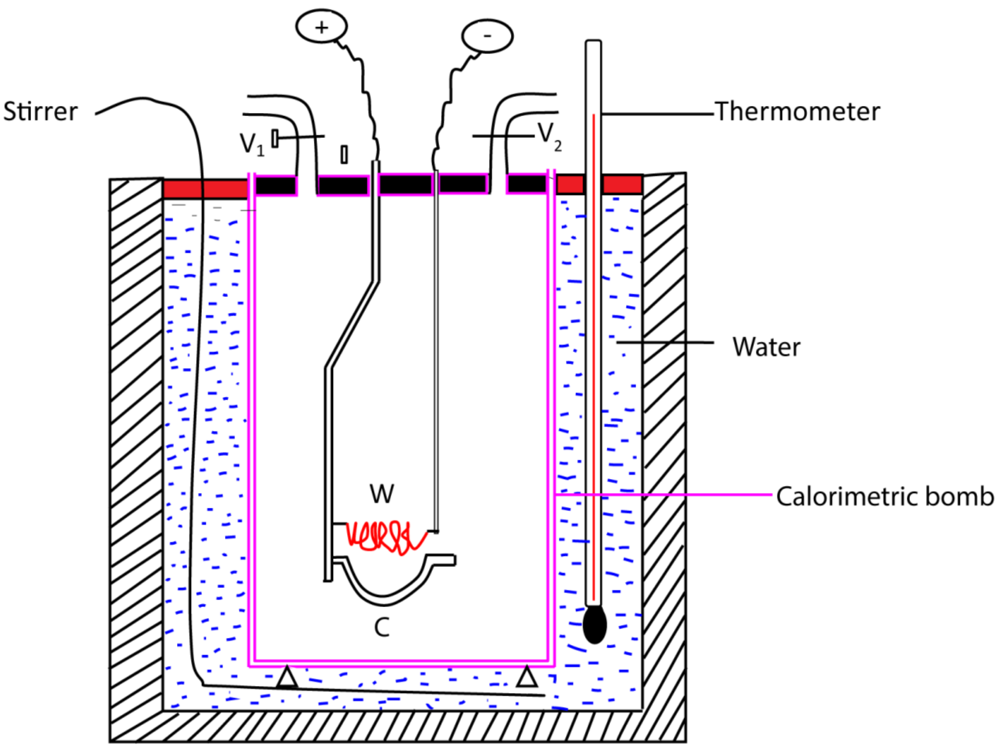
m_1g of fuel produce = Cϴ joules

Mr g (molecular mass of substance) produce = $\frac{MrC\theta}{m_1}$ joulesmol^{-1}

(ii) **Experimental method for finding enthalpy of combustion using a calorimetric bomb.**

This method is suitable for determination of enthalpy of combustion of carbon, Sulphur or sugar but can be used on a liquid fuel

Apparatus



Procedure

1. A known mass, m_1 g, of a substance is placed in a platinum crucible, C.
2. The bomb is filled with oxygen at a pressure of about 20atmospheres and immersed in a known mass (m_w g) of water which is kept stirred.
3. The substance is ignited by passing an electric current through a small coil of iron wire, W.
4. The rise in temperature (θ) of water is read to 0.01^0C with an accurate thermometer.

Calculation

Heat produced by burning m_1 g of substance = heat gained by m_w g of water

= $m_w \times 4.2 \times \theta$ (where 4.2 is specific heat capacity of water)

Therefore, enthalpy of combustion of a substance $= \frac{4.2 m_w \theta M_r}{m_1}$

Where, M_r is the relative molecular mass of the substance.

b) Enthalpy of formation of compounds:

The standard molar enthalpy of formation of a compound is the enthalpy change when 1 mole of the compound is formed from its elements under the standard conditions. e.g.

$H_2(g) + \frac{1}{2} O_2 \rightarrow H_2O(l)$ $\Delta H_{f,m}^{\Theta}(298K) = -285.9 kJmol^{-1}$

As there is no energy change in formation of an element under standard conditions; the standard enthalpies of all pure elements in their standard states is zero

c) Enthalpy of formation of hydrated ions;

This refers to enhtalpy change of the formations of 1mole of hydrated ions from an element in its standard state. e.g.

$Na(s) + aq \rightarrow Na^{+}(aq) + e \quad \Delta H_{f,m}^{\ominus}(298K) = -240kJmol^{-1}$

The figures are usually quoted on arbitrary scale on which the enthalpy of formation of $H^{+}(aq)$ is taken to be zero. i.e.

$\frac{1}{2} H_2(g) \rightarrow H^{+}(aq) + e \quad \Delta H_{f,m}^{\ominus}(298K) = 0kJmol^{-1}$

d) Enthalpy of reaction; is enthalpy change when 1mole of a substance is formed from its reactants at standard conditions. Tabulated values of the standard enthalpies of formation of compounds and or hydrated ions can be used to calculate the standard enthalpy change for any reaction

$$\left\{\text{Standard enthalpy change of a reaction}\right\} = \left\{\text{Sum of standard enthalpy of formation of product}\right\} - \left\{\text{Sum of standard enthalpy of formation of reactants}\right\}$$

Typical examples

$$\underset{(-46)}{NH_3(g)} + \underset{(-92.3)}{HCl(g)} \rightarrow \underset{(-315)}{NH_4Cl(s)}$$

$\Delta H_{r,m}^{\ominus}(298K) = -315 - (-46 + -92.3) = -177kJmol^{-1}$

The negative sign means that reaction is exothermic.

The standard enthalpy depends only on the difference between the standard enthalpy of the reactants and the product and not on the route by which the reaction occurs.

The ideal is embodied in Hess's law, which state that, "*if a reaction take place by more than one route, the overall change in enthalpy is the same whichever route is followed*" or "*enthalpy change of a reaction is independent of the route followed to the product*".

e) Enthalpy of atomization: refers to the enthalpy change for the formation of 1mole of gaseous atoms from an element in its standard state

C(s)(graphite) ⟶ C(g) $\Delta H_{a,m}^{\ominus}(298K) = +715kJmol^{-1}$

½ H_2(g) ⟶ H(g) $\Delta H_{a,m}^{\ominus}(298K) = +218kJmol^{-1}$

f) Enthalpy of ionization: refers to enthalpy change for conversion of gaseous atoms into free gaseous ions, e.g.

Na(g) ⟶ Na+(g)+ e $\Delta H_m^{\ominus}(298K) = +502kJmol^{-1}$

Factors affecting magnitude of ionization energy

(i) **Size of an atom**: Small atoms have strong attraction to outer electrons leading to high ionization energy.

(ii) **Electronegativity**: highly electronegative atoms have high attraction to valence electron causing high ionization energy.

(iii) **Electropositivity:** highly electropositive atoms have low attraction to valence electrons leading low ionization energy.

g) Enthalpy of electron affinity: refers to the enthalpy change for formation of free gaseous anions from1mole of free gaseous atoms.

Cl(g) + e ⟶ Cl^- (g) $\Delta H_m^{\ominus}(298K) = -354kJmol^{-1}$

Factors affecting magnitude of electron affinity

(i) **Size of an atom:** Small atoms have strong attraction to outer electrons leading to high negative electron affinity.

(ii) **Electronegativity:** highly electronegative atoms have high attraction to valence electron causing high negative electron affinity

(iii) **Electropositivity:** highly electropositive atoms have low attraction to valence electrons leading high positive electron affinity.

h) Lattice enthalpy

This is the name given to the enthalpy change for the reaction in which 1mole of crystalline solid is formed from its component ions in the gaseous phase.

Na+(g) + Cl-(g) ⟶ NaCl(s) $\Delta H_m^{\ominus}(298K) = -788\ kJmol^{-1}$

Factors affecting the magnitude of lattice energy

(i) **Size of the ion;** small ions have strong interionic attraction causing high lattice energy

(ii) **Charge on the ions:** ions with big charge have strong interionic attraction leading to high lattice energy.

i) Enthalpy of solution

This refers to the enthalpy change for the formation of an infinitely dilute solution of 1 mole of salt.

NaCl(s) +aq⟶ Na^+(aq) + Cl^- (aq) $\Delta H_m^{\ominus}(298K) = +4\ kJmol^{-1}$

Factors affecting the magnitude of enthalpy of solution

Enthalpy of solution = lattice energy (+ve) + sum of hydration energy of ions (-ve)

When the lattice energy exceeds the sum of hydration energies of the ions, the enthalpy of solution is positive (endothermic) and the salt is insoluble.

When the lattice energy is less than the sum of hydration energies of the ions, the enthalpy of solution is negative (exothermic) and the salt is soluble.

j) Enthalpy of hydration

This refers to the enthalpy change when 1mole of gaseous ions is hydrated. e.g.

$Na^+(g) + aq \rightarrow Na^+(aq)$ $\Delta H_m^\Theta(298K) = -406\ kJmol^{-1}$

Factors affecting the magnitude of lattice energy

(i) **Size of the ion:** small ions have strong attraction to water molecules leading to high hydration energy.

(ii) **Charge on the ions**: ions with high big charge have a strong attraction to water molecules leading to high enthalpy of hydration.

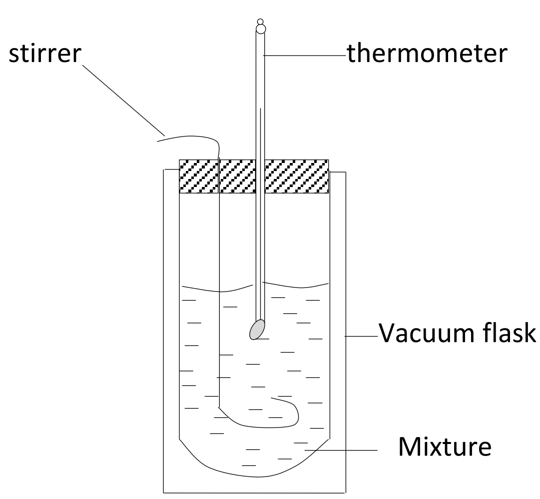
k) Enthalpy of neutralization

This refers to enthalpy change for the formation 1 mole of water is formed from hydrogen and hydroxide ions

$H^+(g) + {}^-OH(aq) \rightarrow H_2O(l)$

Measurement of standard enthalpy of neutralization

The heat released when a known amount of water is formed is found by measuring the temperature produced in a calorimeter and its contents.



A neutralization reaction is carried out in the calorimeter of known heat capacity, C .

Know volume of standard acid (v cm^3) and alkali (v cm^3) are added to calorimeter, and temperature change θ^0C is noted.

The number of moles of water formed, X moles, is calculated

Calculations

Assumptions:

(i) The density of water = density of solution = $1gcm^{-3}$.

(ii) Specific heat of solution = specific heat capacity of water = c $Jg^{-1}K^{-1}$

(iii) Heat given out on neutralization = Heat received by water + calorimeter of capacity, C.

Thus, heat given out = Cθ + (v+v)cθ

Thus X mole of water formed produce = (Cθ + 2vcθ)J

1mole of water will produce $= \frac{(C\theta+2vc\theta)}{X}$ $Jmol^{-1}$

Example

250 cm^3 of 0.40M were added to 250cm^3 of 0.40M HCl in the calorimeter heat capacity of 90 J K^{-1}. The temperature of the two solutions was 17.5^0C and rose to 20.1^0C

Calculate the enthalpy of neutralization assuming that the specific heat capacities of solution are the same as that of water = 4.180J g^{-1} K^{-1}.

Calculation

Temperature change θ = 20.1 – 17.5 = 2.6^0C

Heat liberated = (Cθ + 2vcθ)J

= 90 x 2.6 + (250 + 250) x 4.180 x 2.6)

= 5668J

Moles of water formed = moles of NaOH

$= \frac{250 \; x \; 0.40}{1000}$

= 0.1mole

Molar hat of formation of water $= \frac{5668}{0.1}$ = - 56680$Jmol^{-1}$.

The negative sign signify that heat is liberated.

Enthalpy diagrams

These are constructed by application of Hess's law: that states "enthalpy change of a reaction is independent of the route followed to the product." For instance, the enthalpy change for conversion of carbon into carbon dioxide is the same whether it is carried out in one step;

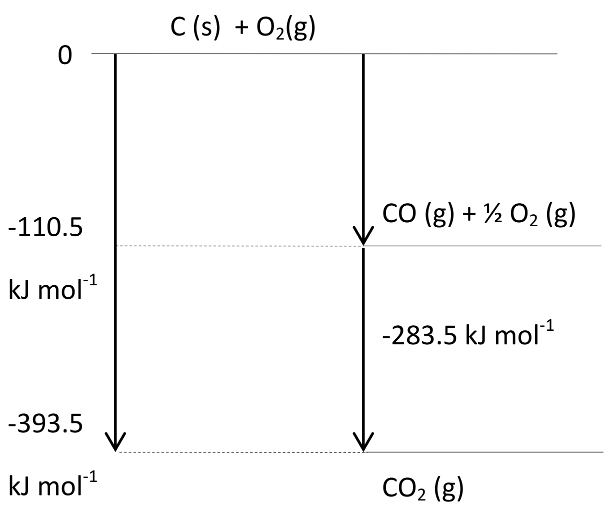
$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_m^{\Theta}(298K)$ $= -393.5$ kJ mol^{-1}

Or two steps

$C(s) + ½ O_2(g) \rightarrow CO(g)$ $\Delta H_m^{\Theta}(298K)$ $= -110.5$ kJ mol^{-1}

$CO(s) + ½ O_2(g) \rightarrow CO_2(g)$ $\Delta H_m^{\Theta}(298K)$ $= -283.0$ kJ mol^{-1}

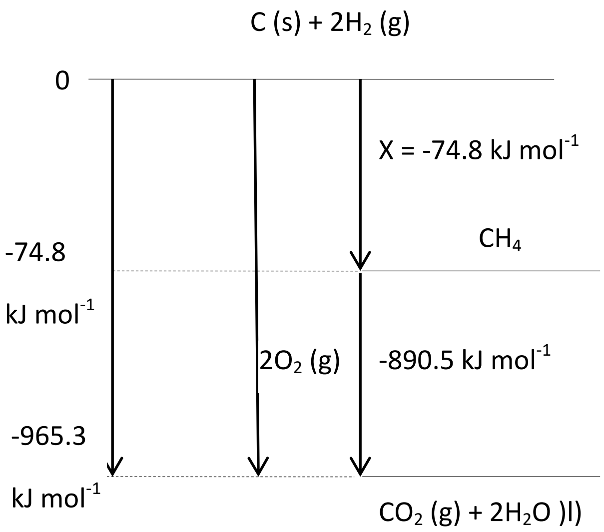
The relationship between various enthalpy changes is conveniently summarized in an enthalpy diagram below.



Such diagrams are used to obtain values for enthalpy changes that cannot be measured directly. The enthalpy of formation of methane cannot be measured directly since carbon and hydrogen do not react for example;

$C(s) + 4H_2(g) \rightarrow CH_4(g)$ $\Delta H_m^{\Theta}(298K) = x$ kJ mol^{-1}

. The enthalpies of combustion of carbon (-393.5 kJ mol^{-1}), hydrogen (-289.9 kJ mol^{-1}) and methane (-890.5 kJ mol^{-1}) can however be measured and the required enthalpy of formation is obtained from them (x = 74.8kJmol^{-1}) as summarized in figure below:



Standard enthalpy for a reaction from average standard bond enthalpies

When the standard enthalpy for a reaction cannot be measured, approximate value can be obtained by using average standard bond enthalpies. During reaction energy must be supplied to break bonds in the reactants and energy is given out when the bonds in the product form.

The Standard enthalpy of reaction	=	**sum of the average bond of reactants**	-	**sum of the average bond of products**

Example

Calculate the standard enthalpy change the reaction

$(CH_3)_2C{=}O\ (g) + HCN \rightarrow (CH_3)_2C(OH)(CN)$

Mean standard enthalpies are C=O = 743, C-H = 412; C-O = 360, C-C = 348, H-O = 463.

Method

Bond broken	One one	C=O C-H	ΔH^{θ} ΔH^{θ}	743 kJ mol^{-1} 412 kJ mol^{-1}
Total energy absorbed				1155 kJ mol^{-1}

Bond formed	One One one	C-O O-H C-C	ΔH^θ ΔH^θ ΔH^θ	360 kJ mol^{-1} 463 kJ mol^{-1} 4348 kJ mol^{-1}
Total energy produced				1171 kJ mol^{-1}

Standard enthalpy of reaction = 1155 -1171

= -16 kJ mol^{-1}.

Exercise

1. (a) The thermo energy changes for some process are shown in the table below

Process	Energy (kjmol^{-1})
Atomization of calcium	+178
First ionization energy of calcium	+590
Second ionization energy of calcium	+1146
Formation of calcium fluoride	-1220
Electron affinity of fluorine	-328
Bond dissociation energy of fluorine	+242.7

(i) Calculate the lattice energy of calcium fluoride crystal. (02marks)

(ii) Determine the enthalpy of solution of calcium fluoride
[enthalpy of hydration of Ca^{2+} and F^- ion are -1587 and – 515 kJmol^{-1} respectively]

(b) (i) state the effect of temperature on solubility of calcium fluoride (01mark)

(ii) give a reason for your answer

2. (a) Define standard enthalpy of formation (01mark)

(b) some thermochemical data for calcium, calcium chloride and chlorine are given below.

	Energy (kjmol^{-1})
Formation of calcium chloride	-763
Atomization of chlorine	+121
Atomization of calcium	+193
First ionization energy of calcium	+590
Second ionization energy of calcium	+1145
Electron affinity of chlorine	-348

(i) Draw an energy diagram for formation of solid calcium chloride (04marks)

(ii) Calculate the lattice energy of calcium chloride. (2 ½ marks)

(c) If calcium formed a chloride in which calcium was in oxidation state of +1, would it be more or less stable than calcium chloride? Explain your answer. (03marks)

(d) (i) Calculate the enthalpy of solution of calcium chloride [enthalpies of hydration of Ca^{2+} and Cl^- are -1689.6 and – 383.7kJmol^{-1} respectively] (2 ½ marks]

(ii) comment on the solubility of calcium chloride. (01mark)

(e) (i) State two factors that can affect the magnitude of hydration energy. (02marks)

(ii) Explain how the factors you have stated in (e)(i) affect hydration energy. (04marks)

3. (a) State

(i) What is meant by the term **first ionization energy**. (01marks)

(ii) Two factors that determine the value of the first ionization energy and explain how the factors affect the value of the first ionization energy

(b) (i) Define the term **first electron affinity**. (01mark)

(ii) Explain why the first electron affinity of oxygen is exothermic process while the second electron affinity is endothermic process

(c) Aluminium reacts with oxygen to form aluminium oxide according to the following equation

$2Al(s) + 3/2\ O_2(g) \longrightarrow Al_2O_3(s) \Delta H0 = -1675.7 kJmole^{-1}$

Some thermodynamic data of aluminium and oxygen are given below

(c)	Enthalpy of atomization of oxygen	=	+249kmol^{-1}
	Enthalpy of atomization of aluminium	=	+324 kmol^{-1}
	First ionization of aluminium	=	+578.0kmol^{-1}
	Second ionization of aluminium	=	+1817.0 kmol^{-1}
	Third ionization of aluminium	=	+2745.0 kmol^{-1}
	First electron affinity for oxygen	=	-141.4 kmol^{-1}
	second electron affinity for oxygen	=	+844.0 kmol^{-1}

(i) Draw an energy level diagram for the formation of aluminium oxide — 5makrs

(ii) Calculate the lattice energy of aluminium III oxide — 2 ½ marks

(iii) Comment on the value of the lattice energy in (c)(ii) — 1 ½ marks

4. The energy changes that take place during the formation barium chloride are shown below

Process	ΔH^{θ} /kJmol^{-1}
Ba (s) $\xrightarrow{A}$ Ba(g)	+176
Ba(g) $\xrightarrow{B}$ Ba_2+(g) + 2e	+1480
Cl2(g) $\xrightarrow{C}$ 2Cl(g)	+224
Cl (g) + e- $\xrightarrow{D}$ Cl^-(g)	-364
Ba^{2+}(g) + 2Cl^-(g) $\xrightarrow{E}$ $BaCl^2$(s)	-2018

(a) Name energy changes for the processes: A, B, C, D, and E.

(b) Calculate the standard enthalpy of formation of barium chloride (03marks)

5. (a) Describe an experiment that can be carried out to determine the enthalpy of solution of sodium chloride (09marks)

(b) In an experiment to determine the enthalpy of anhydrous copper (II) sulphate by indirect method.4.0g of anhydrous salt was added to 50.0g of water and the temperature of water rose 8.0^{0}C. When 4.0g of the hydrated salts was added to 50.0g of water, the temperature of water dropped by 0.90C.

[Specific heat capacity of solution = 4.2Jg^{-1}K^{-1}; Cu = 64, S = 32, O = 16, H = 1)

Calculate the enthalpy of solution of

(i) Anhydrous copper (II) sulphate (3marks)

(ii) Hydrate copper (II) sulphate- 5-water

(c) (i) State which one of two copper salt in (a) is more soluble in water and explain your answer.

(ii) determine the enthalpy of hydration copper (II) sulphate (02marks)

6. Enthalpy of formation of phosphorus trichloride is $-306kJmol^{-1}$ and enthalpy of atomization of phosphorus and chlorine are +314 and $242Kjmol^{-1}$ respectively. Calculate the average bond energy of the P-Cl bond.

7. The enthalpies of some reactions are given below

				$\Delta H\theta f/kJ\ mol^{-1}$
(i)	$Na_2O(s) + H_2O(l)$	$\longrightarrow$	$2NaOH(s)$	ΔH_1^{θ} -205
(ii)	$NaOH(s) + (aq)$	$\longrightarrow$	$NaOH(aq)$	ΔH_2^{θ} -56.5
(iii)	$Na(s) + H_2O(l) + (aq)$	$\longrightarrow$	$NaOH (aq) + ½ H_2(g)$	ΔH_3^{θ} -410
(iv)	$H_2(g) + ½ O_2(g)$	$\longrightarrow$	$H_2O(l)$	ΔH_4^{θ} -285.8

Calculate enthalpy of formation of sodium oxide from its elements (4marks)

8 (a) (i) Define the **enthalpy of solution** (1mark)
  (ii) State the energy terms that determine the magnitude and the sign of the enthalpy of solution of ionic salt.
  (iii) Describe an experiment that can be of used to determine the enthalpy of solution
(b) Some thermochemical data of copper, cupper (II) chloride and chlorine are given below:

Enthalpy of formation of copper chloride	$-220\ kJmol^{-1}$
Enthalpy of sublimation of Cu	$+338.3\ kJmol^{-1}$
First ionization of copper	$+745\ kJmol^{-1}$
Second ionization of copper	$+1954\ kJmol^{-1}$
Electron affinity for chlorine	$-364\ kJmol^{-1}$
Bond dissociation energy of chlorine	$+121\ kJmol^{-1}$

(i) Draw an energy level diagram which can be used to determine the lattice energy of copper (II) chloride. (4marks)
(ii) The hydration energy of copper (II) chloride is -2883.9 kJmol-1. Determine the enthalpy of solution of copper (II) chloride. (3marks)
(iii) Comment on the solubility of copper (II) chloride. (1mark)

9. (a) Define the following terms:
  (i) Hydration energy
  (ii) Lattice energy
  (iii) Enthalpy of solution
(b) State two factors which can affect the magnitude of lattice energy and explain how they affect the lattice energy.
(c) Some thermochemical data are give below

The standard enthalpy of formation of $CaCl_2$ (s)	=	$-795\ kJmol^{-1}$
The standard enthalpy of atomization of calcium		$+177kJmol^{-1}$
The first ionization of calcium	=	$+590kJmol^{-1}$
The second ionization of calcium	=	$+1100kJmol^{-1}$

The standard enthalpy of atomization of chlorine = $+121kJmol^{-1}$

The first electron affinity of chlorine = $-364kJmol^{-1}$

Calculate the lattice energy of calcium chloride

(2marks)

(d) The lattice and hydration energies of salts AX and BX are given in the table below

	Lattice energy/$kJmol^{-1}$	Hydration energy/$kJmol^{-1}$
AX	+880	-860
BX	+790	-800

(i) Calculate the enthalpy of solution of each salt (3marks)

(ii) Which of the two salts is more soluble in water at a gives temperature? Give a reason.

(e) Explain why hydrated copper sulphate crystals dissolve endothermically whereas anhydrous copper sulphate dissolve exothermically

10.(a) (i) Explain what is meant by the term *lattice energy.* (2marks)

(ii) State two factors that affect the magnitude of lattice energy. (2marks)

(iii) Describe how the factors you have stated in (ii) affect lattice energy. (6marks)

(b) (i) Draw a Born-Haber cycle for the formation of solid rubidium chloride from its elements (6marks)

(ii) Calculate the electron affinity of chlorine atom. Use the following data (3marks)

Lattice energy of rubidium chloride = $665kJmol^{-1}$

Dissociation energy of chlorine gas molecule = $226kJmol^{-1}$

Heat of atomization of rubidium meal = $84kJmol^{-1}$

Ionization energy of rubidium atom = $397kJmol^{-1}$

Standard heat of formation of solid rubidium chloride = $-439kJmol^{-1}$

(c) Calculate the heat of hydrogenation of ethane from the following thermodynamic data.

$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$ $\Delta H = -1393kJmol^{-1}$

$C_2H_2(g) + 2\frac{1}{2} O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$ $\Delta H = -1310kJmol^{-1}$

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$ $\Delta H = -285kJmol^{-1}$

(3marks)

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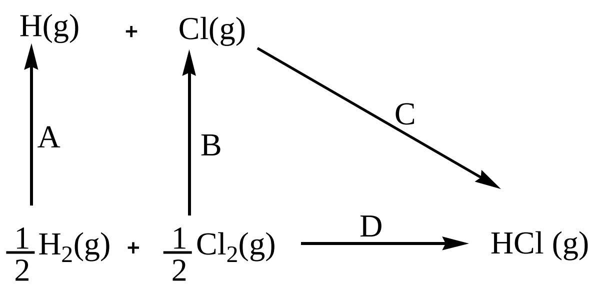
11. The energy diagram for the reaction between hydrogen and chlorine is given below



(a)Identify the energy changes

A………………………………………………………………….

B ………………………………………………………………….

C ………………………………………………………………….

D ………………………………………………………………….

(b) Calculate the enthalpy change for the reaction.

(The H-H, Cl-Cl and H-Cl bond energies are 435.9, 241.8 and 431.0 $kJmol^{-1}$ respectively) (1½ marks).

12. (a) Some bond energies are given in the table below

Bond	Energy ($kJmol^{-1}$)
C-C	-337
C-H	-414
C-O	-360
O-H	-123

Calculate the heat of formation of gaseous ethanol (3marks)

(b) Carbon monoxide burns in oxygen according to the following equation.

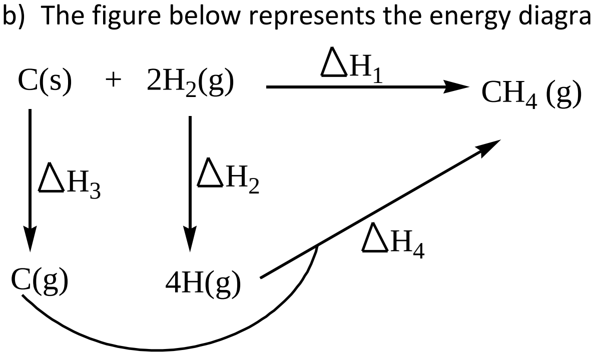
$2CO (g) + O_2(g) \longrightarrow 2CO_2(g)$

Calculate the enthalpy of combustion of carbon monoxide.

(Heats of formation of carbon monoxide and carbon dioxide are -108 and -393$kJmol^{-1}$ respectively.)

13(a) What is bond energy? (2marls)

(b) The figure below represents the energy diagram for formation of methane



Identify the following energy changes: 3marks

ΔH_1 ………………………………………………………………

ΔH_2 ………………………………………………………………

ΔH_3 ………………………………………………………………

Given that ΔH_1 = -75 $kJmol^{-1}$

ΔH_2 = +218 $kJmol^{-1}$ of hydrogen atom

ΔH_3 = +715 $kJmol^{-1}$

Calculate the value of:

(i) ΔH_4 (2marks)

(ii) The bond energy for C-H bond (2marks)

14 (a) Methane reacts with chlorine in the presence of sun light to form chloromethane. write equation for the reaction and outline mechanism for the reaction.

(b) Some bond energies are given below

Bond	Energy/$kJmol^{-1}$
Cl-Cl	242
C-H	435
Cl-H	431
C-Cl	339

Determine the enthalpy change for the reaction.

(3marks)

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Suggested answers

1(a) (i) -1220 = 178 + 590 + 1146- 328 x 2 +242.7 + ΔH Lattice

- ⇨ ΔH Lattice = -2720kJmol^{-1}

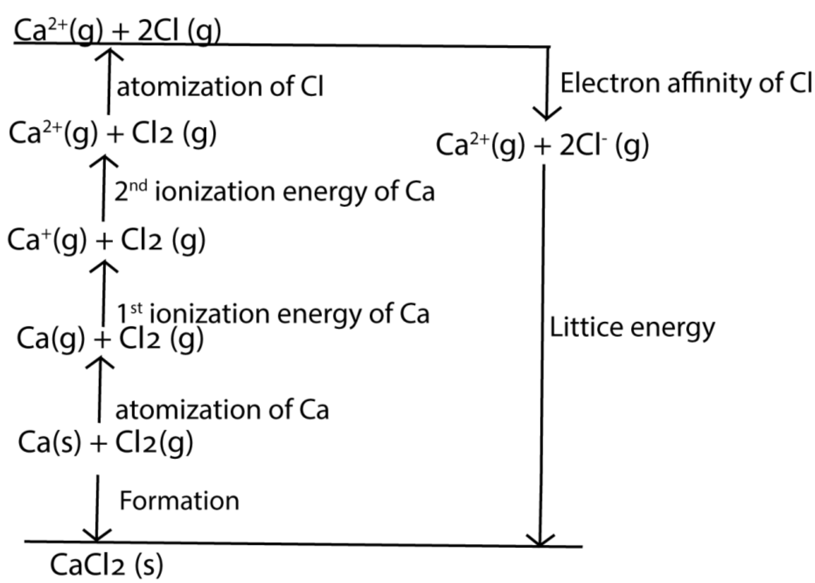
(ii) Δsolution = lattice + hydration energies
=2720.7 –(1587 + 515 x2)
= 103.7 kJmol^{-1}

(b) (i) Increasing temperature increases solubility of calcium fluoride.

(ii) enthalpy of solution for CaF_2 is endothermic

2. (a) Standard enthalpy of formation is enthalpy change when 1 mole of a substance is formed from it elements at 298K and 1 atmosphere.

(b)(i)



(ii) -763 = 193 + 590 + 1145 + 121 x 2 – 348 x 2 + lattice energy
Lattice energy = -2237 kJmol^{-1}

(a) It would be less stable because Ca+ has unstable electron configuration.

(b) (i) enthalpy of solution = lattice energy + hydration energy
= 2237 –(1689.6 + 383.7 x 2)
= -220kJmol-1

(ii) Calcium chloride is soluble because its enthapy of solution is negative

(e)(i) Charge on the ions

Size of the ions

(ii) – The bigger the charge on the ions, the higher the hydration energy because of strong forces between the ion ans water molecules

- The smoller the ions the stronger the force of attration between the ion and water molecules and the higher the hydration enrgy.

3.(a)(i) First inosation energy is the enthalpy change when 1 mole of gaseous atoms are converted into 1 mole of gaseous ions with a single postive charge

(ii) Factor affecting first ionization energy

- Nuclear charge on valence electrons:the higher the nuclear charge on the valence electron the higher the first ionization energy due to strong attaction of the nucleus to valence elelctrons.
- Electronegativity: the higher the electronegativity, the higher the first ionization energy due to strong nuclear attraction on the valence electrons.
- Atomic radius: increase in atomic radius reduce attraction of the nucleus on the valence electrons and reduces first ionization energy.
- Electropositivity: the higher the electronegativity, the lower the first ionization energy due to low nuclear attraction on the valence electrons

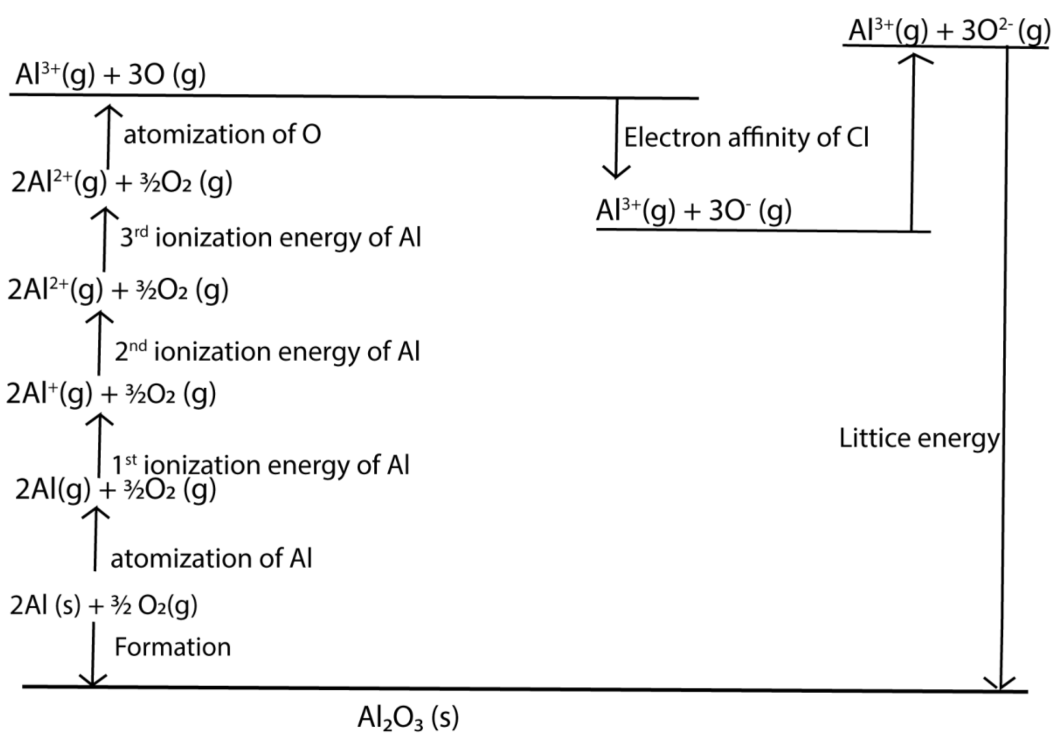
(b) (i) First electron affinity is the enthalpy change when 1mole of gaseous atoms is converted into 1 mole of gaseous anions with single negative charge

(ii) $O(g) \rightarrow O^-(g)$

(iii) - first electron affinity of oxygen is exothermic bcause oxygen atoms are highly electronegative with strong attraction to valency electrons.

- The second electron affinity is positive because the added electron added repels the second electrons.

(c)



(ii) -1675.7 = 324.5 x 2 +578 x 2 + 1817 x 2 + 2745 x 2 +249.2 x 3- 141.4 x 3 + 844 x 3 +ΔH lattice

ΔH lattice = -15460.1kJmol-1

(iii) Lattice energy is very high showing that aluminium oxide is very stable.

4. (a) A – atomization energy of barium

B – ionization energy of of barium

C – bond energy of chlorine

D – electron affinity of chlorine

E – lattice energy

(b) ΔHf = +176+ 1480 + 242 +-364 x 2 – 2018 = -848kJmol^{-1}.

5. (a) A given mass m g of sodium chloride is dissolved in x g of excess water and the temperature change θ^{0}C is measured.

Assumptions

Heat liberated = heat absorbed by water

= xcθ (where c is specific heat capacity of water)

Formula mass of NaCl = 23 + 35.5 = 58.5g

- ⇨ m g of NaCl liberate xcθ J
- ⇨ 58.5g of NaCl will liberate $\left(\frac{58.5\ x\ xc\theta}{m}\right)$Jmol^{-1}

(b) (i) Heat liberated = mcθ

= 50 x 4.2 x 8

= 1689 joules

Formula mass of $CuSO_4$ = 64 + 32 + 16 x 4

= 160g

4.0g of CuSO4 liberate 1680J

∴ 160g of $CuSO_4$ liberate 67.2kJmol^{-1}

ii) Heat absorbed = mcθ

= 50 x 4.2 x 0.9

= 189 joules

Formula mass of $CuSO_4.5H_2O$ = 64 + 32 + 16 x 4 + 5(2 + 16)

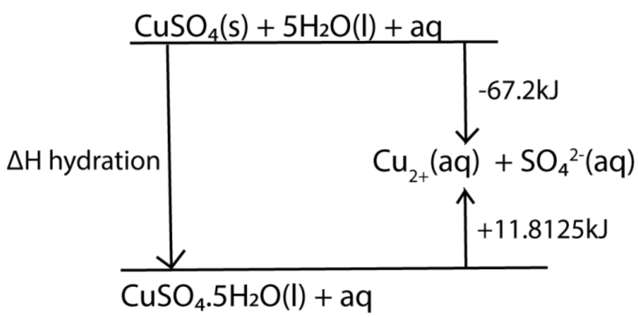
= 250g

4.0g of CuSO4 absord 189J

∴ 250g of $CuSO_4$ liberate 11.812kJmol^{-1}

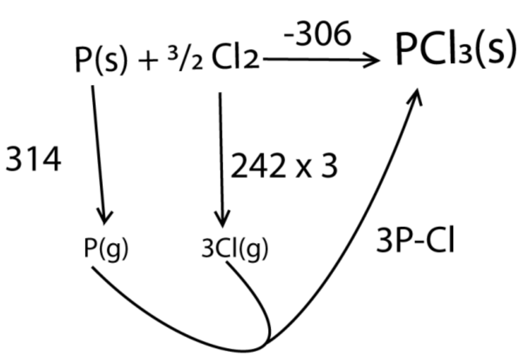
(c) (i) anhydrous copper (II) sulphate is more soluble because it liberates heat on dissolving.

(ii)



Enthalpy of hydration = -67.2 – 11.8125 = 79.125kJ

6.



-306 = 314 + 242 x 3 + 3P-Cl

P-Cl = 448.7kJmol^{-1}

7.

					ΔHθf/kJ mol^{-1}
reverse equation (i)	$2NaOH(s)$	→	$Na_2O(s) + H_2O(l)$		205
reverse (ii) x 2	$2NaOH(aq)$	→	$2NaOH(s) + 2(aq)$	2 x 56.5	113
equation (iii) x2	$2Na(s) + 2H_2O(l) + (aq)$	→	$2NaOH(aq) + H_2(g)$	2 x-410 =	-820
equation (iv)	$H_2(g) + ½ O_2(g)$	→	$H_2O(l)$		-285.8
	2Na(s) + ½ O2	→	$N_2O(s)$		**-787.8**

8 (a)(i) Enthalpy of solution is enthalpy change when 1 mole of ionic salt is dissolved in excess water.

(ii) Lattice energy and hydration energy

(iii) Experiment to determine enthalpy of solution

A given mass m g of ionic salt of molecular mass (Mr) is dissolved in x g of excess water and the temperature change θ^0C is measured.

Assumptions

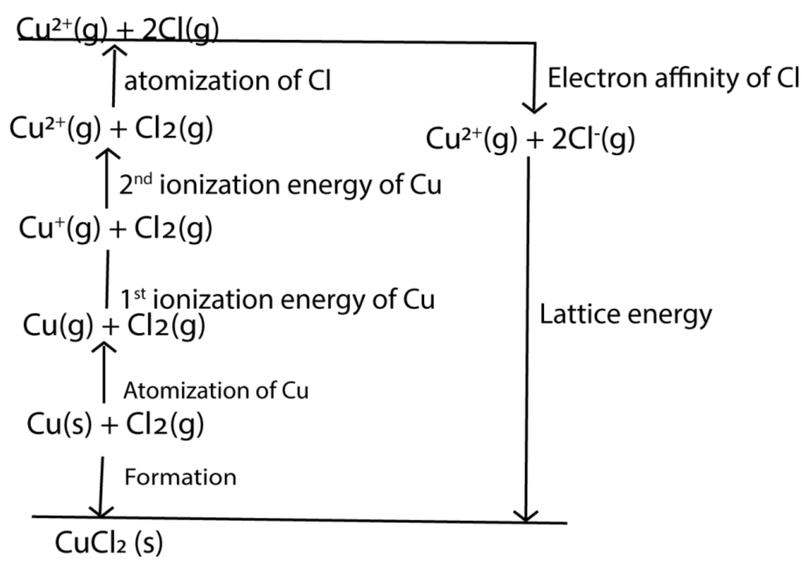
Heat liberated = heat absorbed by water

= xcθ (where c is specific heat capacity of water)

m g of NaCl liberate xcθ J

⇨ Mr g of NaCl will liberate $\left(\frac{Mr\ x\ xc\theta}{m}\right)$Jmol^{-1}

(b)



Lattice energy = -220-338.3-745-1958-121.1+364 x 2 = 2654.4kJmol-1

(ii) Enthalpy of solution = lattice energy + hydration energy

= 2654.4 -2883.9

= 229.5kJmol-1

(iii) Cupper II chloride is soluble because enthalpy of solution is negative

9. (a) (i) Hydration energy is enthalpy change that occur when 1mole of gaseous ions is hydrated at 298K and 1 atmosphere.

(ii) Lattice energy is enthalpy change when 1 mole of crystalline ionic compound is dissolved in excess water.

(iii) Enthalpy of solution is enthalpy change when 1 mole of ionic salt is dissolved in excess water

(b) (i) charge on the ions: the bigger the charge on ions the bigger the lattice energy due to strong attraction

(ii) size of the ion: small ions give high lattice energy due to strong attraction.

(c) -795 = 177 + 590+ 1100+121 x2 – 364 x 2 + ΔHL

ΔHL = -2176kJmol^{-1}

(d)(i) enthalpy of solution of AX = 880-860 = 20kJmol-1

(ii) enthalpy of solution of BX = 790-800 = -10kJmol^{-1}

(iii) Bx is more soluble because enthalpy of solution is negative

(e) Enthalpy of solution of hydrated copper (II) sulphate is positive because it involves breakage of bonds of hydration in the crystal lattice during dissolving

Enthalpy of solution of anhydrous copper (II) sulphate is exothermic due to formation of coordinate bonds between the copper ions or sulphate ions with water molecules to form complex ions

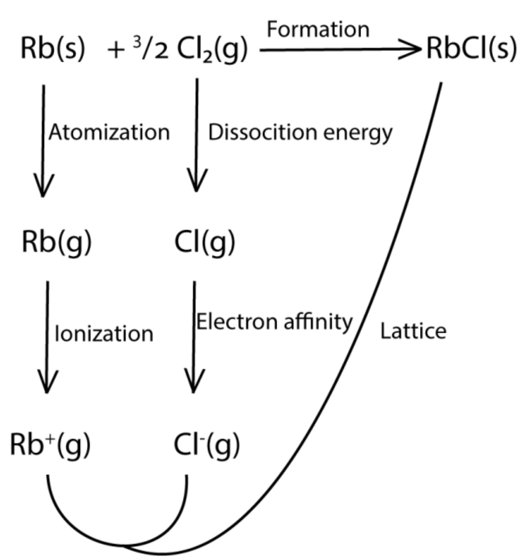
10. (a) (i) Lattice energy is enthalpy change when 1 mole of crystalline ionic compound is dissolved in excess water.

(ii) charge on the ion and size of the ion

(iii) - charge on the ions: the bigger the charge on ions the bigger the lattice energy due to strong attraction

- size of the ion: small ions give high lattice energy due to strong attraction.

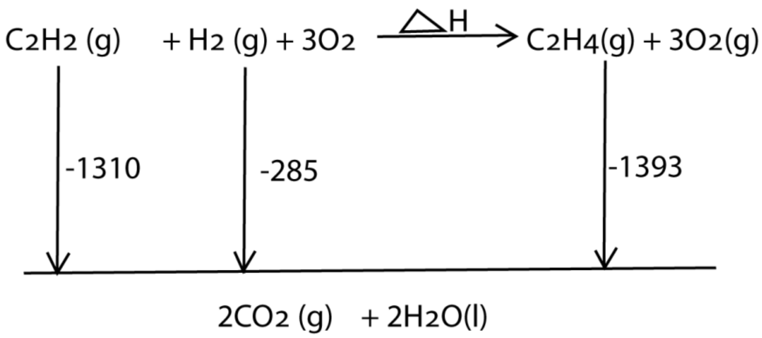
(b)



-439 = 84 + 397 + ½ x 226 + electron affinity – 665

Electron affinity = -368kJmol^{-1}

(c)



-1310 – 285 = ΔH – 1393

ΔH = -202kJmol^{-1}

11. (a) A – atomization of hydrogen gas

B – atomization of chlorine gas

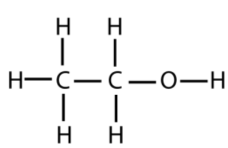
C – bond energy

D – formation

(b) D = $\frac{435.9}{2} + \frac{241.8}{2} - 431$ = -92.15kJmol^{-1}

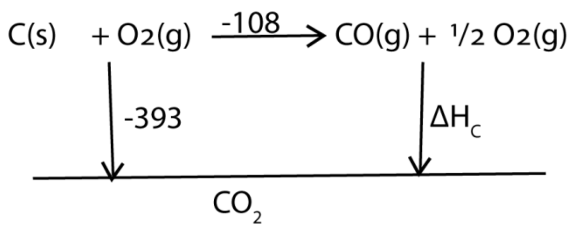
12.

Ethanol



Ethanol has	5C-H bonds	= -414 x 5
	1C-C bond	= -337 x 1
	1C-O bond	= -360 x 1
	1O-H bond	= -123 x 1
Heat of formation = (sum)		= -2890kJmol^{-1}

(b)



$-393 = -108 + \Delta Hc$

$\Delta Hc = -385 kJmol^{-1}$

13. (a) Bond energy is energy change required to form 1 mole of a gaseous covalent bond.
    (b) ΔH1 = enthalpy of formation
    ΔH2 = atomization energy of hydrogen
    ΔH3 = atomization of energy carbon

    $\Delta H1 = \Delta H3 + \Delta H2 + \Delta H4$
    $-75 = 715 + 218 \times 4 + \Delta H4$
    $\Delta H4 = -1662$

    C-H bond = $\frac{-1662}{4} = 415.5$ kJmol-1

14. CH_4 (g) + Cl_2(g) CH_3Cl (g) + HCl(g)
    Enthalpy change = sum of enthalpies of bonds broken – sum of enthalpies of bonds formed
    = [4C-H +1Cl-Cl] –[3C-H + 1C-Cl + 1 H-Cl]
    = [4 x 435 + 242] – [3 x435 + 339 + 431]
    = $93 kJmol^{-1}$