**UPGRADING**

**CHEMISTRY**

 **FORM 4**

 **AA Thermochemistry**

 **Comprehensive tutorial notes**

 **1.Introduction to Energy changes**

Energy is the capacity to do **work**. There are many/various **forms** of energy like heat, electric, mechanical, and/ or chemical energy.There are two types of energy:

 (i)Kinetic Energy(KE) ;the energy in motion.

 (ii)Potential Energy(PE); the stored/internal energy.

Energy like matter , is **neither created nor destroyed** but can be transformed /changed from one form to the other/ is interconvertible. This is the **principle of conservation** of energy. e.g. Electrical energy into heat through a filament in bulb.

Chemical and physical processes take place with **absorption** or **evolution**/production of energy mainly in form of **heat**

The study of energy changes that accompany physical/chemical reaction/changes is called **Thermochemistry.** Physical/chemical reaction/changes that involve energy changes are called **thermochemical reactions.** The SI unit of energy is the **Joule**(**J**).Kilo Joules(**kJ**)and megaJoules(**MJ**) are also used. The Joule(J) is defined as the:

(i) quantity of energy transferred when a force of one **newton** acts through a distance of one **metre**.

(ii) quantity of energy transferred when one **coulomb** of electric charge is passed through a potential difference of one **volt**.

All thermochemical reactions should be carried out at standard conditions of:

 (i) **298K /25oC** temperature

 (ii)**101300Pa/101300N/m2 /760mmHg/1** atmosphere pressure.

**2.Exothermic and endothermic processes/reactions**

Some reactions **/** processes take place with evolution/production of energy. They are said to be **exothermic** while others take place with **absorption** of energy. They are said to be **endothermic.**

Practically exothermic reactions **/** processes cause a rise in temperature (by a rise in thermometer reading/mercury or alcohol level rise)

 Practically endothermic reactions **/** processes cause a fall in temperature (by a fall in thermometer reading/mercury or alcohol level decrease)

**To demonstrate/illustrate exothermic and endothermic processes/reactions**

1. Dissolving Potassium nitrate(V)/ammonium chloride crystals

**Procedure:**

 Measure 20cm3 of water in a beaker. Determine and record its temperature T1.Put about 1.0g of Potassium nitrate(V) crystals into the beaker. Stir the mixture carefully and note the highest temperature rise /fall T2.Repeat the whole procedure by using ammonium chloride in place of Potassium nitrate (V) crystals.

Sample results

|  |  |  |
| --- | --- | --- |
| **Temperture (oC)** | **Using Potassium nitrate(V) crystals**  | **Using Ammonium chloride crystals**  |
| T2(Final temperature) |  21.0 |  23.0 |
| T1 (Initial temperature) |  25.0 |  26.0 |
| Change in temperature(T2 –T1) |  **4.0** |  **3.0** |

Note:

(i)Initial(**T1**) temperature of dissolution of both potassium nitrate(V) crystals and ammonium chloride crystals is **higher** than the final temperature(**T2**)

(ii) Change in temperature(T2 –T1) is **not** a mathematical “-**4.0”** or“-**3.0”**.

(iii)Dissolution of both potassium nitrate(V) and ammonium chloride crystals isan **endothermic** process becauseinitial(**T1**) temperatureis **higher** than the final temperature(**T2**) thus causes a **fall/drop** in temperature.

1. Dissolving concentrated sulphuric(VI) acid/sodium hydroxide crystals

**Procedure:**

 Measure 20cm3 of water in a beaker. Determine and record its temperature T1.**Carefully** put about 1.0g/four pellets of sodium hydroxide crystals into the beaker. Stir the mixture carefully and note the highest temperature rise /fall T2.Repeat the whole procedure by using 2cm3 of concentrated sulphuric(VI) acid in place of sodium hydroxide crystals.

**CAUTION:**

(i)Sodium hydroxide crystals are **caustic** and cause painful blisters on contact with skin.

(ii) Concentrated sulphuric (VI) acid is **corrosive** and cause painful wounds on contact with skin.

Sample results

|  |  |  |
| --- | --- | --- |
| **Temperture (oC)** | **Using Sodium hydroxide pellets**  | **Using Concentrated sulphuric(VI) acid**  |
| T2(Final temperature) |  30.0 |  32.0 |
| T1 (Initial temperature) |  24.0 |  25.0 |
| Change in temperature(T2 –T1) |  **6.0** |  **7.0** |

Note:

(i)Initial (**T1**) temperature of dissolution of both concentrated sulphuric (VI) acid and sodium hydroxide pellets is **lower** than the final temperature (**T2**).

(ii)Dissolution of both Sodium hydroxide pellets and concentrated sulphuric (VI) acid isan **exothermic** process becausefinal (**T2**) temperatureis **higher** than the initial temperature (**T1**) thus causes a **rise** in temperature.

The above reactions show heat loss **to** and heat gain **from** the surrounding as illustrated by a **rise** and **fall** in temperature/thermometer readings.

Dissolving both potassium nitrate(V) and ammonium chloride crystals causes heat **gain** **from** the **surrounding** that causes **fall** in thermometer reading.

 Dissolving both Sodium hydroxide pellets and concentrated sulphuric (VI) acid causes heat **loss to** the **surrounding** that causes **rise** in thermometer reading.

At the same temperature and pressure ,heat absorbed and released is called enthalpy/ heat content denoted **H.**

Energy change is measured from the heat content/enthalpy of the **final** and **initial** products. It is denoted **∆H(**delta H**)**.i.e.

 Enthalpy/energy/ change in heat content ∆H = H**final** – H**initial**

For chemical reactions:

 ∆H = H**products** – H**reactants**

For exothermic reactions, the heat contents of the **reactants** is **more** than/**higher** than the heat contents of **products**, therefore the ∆H is negative (**-∆H**)

For endothermic reactions, the heat contents of the **reactants** is **less** than/**lower** than the heat contents of **products**, therefore the ∆H is negative (**+∆H**)

Graphically, in a **sketch** energy level diagram:

(i)For endothermic reactions the heat content of the reactants should be relatively/slightly **lower** than the heat content of the products

(ii)For exothermic reactions the heat content of the reactants should be relatively/slightly **higher** than the heat content of the products

Sketch energy level diagrams for endothermic dissolution

 Energy

 (kJ) H2 KNO3(aq)

 **+**∆H = H**2** – H**1**

 H1 KNO3(s)

 Reaction path/coordinate/progress

 Energy

 (kJ) H2 NH4Cl (aq)

 **+**∆H = H**2** – H**1**

 H1 NH4Cl (s)

 Reaction path/coordinate/progress

Sketch energy level diagrams for exothermic dissolution

 H2 NaOH(s)

 Energy(kJ)

 -∆H = H**2** – H**1**

 H1 NaOH (aq)

Reaction path/coordinate/progress

 H2 H2SO4 (l)

Energy

 (kJ)

 -∆H = H**2** – H**1**

 H1 H2SO4 (aq)

Reaction path/coordinate/progress

**3.Energy changes in physical processes**

**Melting/freezing/fusion/solidification** and **boiling/vaporization/evaporation** are the two physical processes. Melting /freezing point of pure substances is fixed /constant. The boiling point of pure substance depend on **external** atmospheric **pressure**.

Melting/fusion is the physical change of a **solid** to **liquid**. Freezing is the physical change of a **liquid** to **solid**.

Melting/freezing/fusion/solidification are therefore two **opposite** but **same** reversible physical processes. i.e

 A (**s**) ========A(**l**)

Boiling/vaporization/evaporation is the physical change of a **liquid** to **gas/vapour**. Condensation/liquidification is the physical change of **gas/vapour** to **liquid**. Boiling/vaporization/evaporation and condensation/liquidification are therefore two **opposite** but **same** reversible physical processes. i.e

 B (**l**) ========B(**g**)

Practically

(i) Melting/liquidification/fusion involves **heating** a solid to **weaken** the strong bonds holding the solid particles together. Solids are made up of very strong bonds holding the particles **very close** to each other (**Kinetic Theory of matter**).On heating these particles gain energy/heat from the surrounding heat source to form a liquid with **weaker** bonds holding the particles close together but with some degree of **freedom**. Melting/freezing/fusion is an **endothermic** (**+**∆H)process that require/absorb energy from the surrounding.

(ii)Freezing/fusion/solidification involves cooling a a liquid to reform /rejoin the very strong bonds to hold the particles **very close** to each other as solid and thus lose their degree of **freedom** (**Kinetic Theory of matter**). Freezing /fusion / solidification is an **exothermic** (**-**∆H)process that require particles holding the liquid together to lose energy to the surrounding.

(iii)Boiling/vaporization/evaporation involves **heating** a liquid to completely **break/free** the bonds holding the liquid particles together. Gaseous particles have high degree of **freedom** (**Kinetic Theory of matter**). Boiling /vaporization / evaporation is an **endothermic** (**+**∆H) process that require/absorb energy from the surrounding.

(iv)Condensation/liquidification is **reverse** process of boiling /vaporization / evaporation.It involves gaseous particles losing energy to the surrounding to form a liquid.It is an **exothermic**(**+**∆H) process.

The quantity of energy required to **change** one mole of a solid **to** liquid or to **form** one mole of a solid **from** liquid at constant temperature is called **molar enthalpy/latent heat of fusion**. e.g.

 H2O(**s**) -> H2O(**l**) ∆H = **+6.0kJ mole-1** (endothermic process)

 H2O(**l**) -> H2O(**s**) ∆H = **-6.0kJ mole-1** (exothermic process)

The quantity of energy required to **change** one mole of a liquid **to** gas/vapour or to **form** one mole of a liquid **from** gas/vapour at constant temperature is called **molar enthalpy/latent heat of vapourization**. e.g.

 H2O(**l**) -> H2O(**g**) ∆H = **+44.0kJ mole-1** (endothermic process)

 H2O(**g**) -> H2O(**l**) ∆H = **-44.0kJ mole-1** (exothermic process)

The following experiments illustrate/demonstrate practical determination of melting and boiling

1. **To determine the boiling point of water**

**Procedure:**

Measure 20cm3 of tap water into a 50cm3 glass beaker. Determine and record its temperature.Heat the water on a strong Bunsen burner flame and record its temperature after every thirty seconds for four minutes.

 Sample results

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Time(seconds) | 0 | 30 | 60 | 90 | 120 | 150 | 180 | 210 | 240 |
| Temperature(oC) | 25.0 | 45.0 | 85.0 | 95.0 | 96.0 | 96.0 | 96.0 | 97.0 | 98.0 |

Questions

**1.Plot a graph of temperature against time(y-axis)**

 Sketch graph of temperature against time

 boiling point

 96 oC

 Temperature(0C)

 25oC

 time(seconds)

**2.From the graph show and determine the boiling point of water**

Note:

 Water boils at 100oC at sea level/one atmosphere pressure/101300Pa **but** boils at **below** 100oC at **higher** altitudes. The sample results above are from Kiriari Girls High School-Embu County on the slopes of Mt Kenya in Kenya. Water here boils at 96oC.

**3.Calculate the molar heat of vaporization of water.(H= 1.0,O= 16.O)**

Working:

Mass of water = density x volume => (20 x 1) /1000 = **0.02kg**

Quantity of heat produced

= mass of water x specific heat capacity of water x temperature change

 =>0.02kg x 4.2 x ( 96 – 25 ) = **5.964kJ**

Heat of vaporization of one mole H2O = Quantity of heat

 Molar mass of H2O

=>5.964kJ = **0.3313 kJ mole -1**

 18

 **To determine the melting point of candle wax**

**Procedure**

Weigh exactly 5.0 g of candle wax into a boiling tube. Heat it on a strongly Bunsen burner flame until it completely melts. Insert a thermometer and remove the boiling tube from the flame. Stir continuously. Determine and record the temperature after every 30seconds for four minutes.

**Sample results**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Time(seconds) | 0 | 30 | 60 | 90 | 120 | 150 | 180 | 210 | 240 |
| Temperature(oC) | 93.0 | 85.0 | 78.0 | 70.0 | 69.0 | 69.0 | 69.0 | 67.0 | 65.0 |

Questions

**1.Plot a graph of temperature against time(y-axis)**

 Sketch graph of temperature against time

 93 oC

 Temperature(0C) melting point

 69oC

 time(seconds)

2.From the graph show and determine the melting point of the candle wax

**4.Energy changes in chemical processes**

Thermochemical reactions measured at **standard** conditions of 298K(25oC) and 101300Pa/101300Nm2/ 1 atmospheres/760mmHg/76cmHg produce standard **enthalpies** denoted **∆Hᶿ.**

Thermochemical reactions are named from the type of reaction producing the energy change. Below are some thermochemical reactions:

1. Standard enthalpy/heat of reaction **∆Hᶿr**
2. Standard enthalpy/heat of combustion **∆Hᶿc**
3. Standard enthalpy/heat of displacement **∆Hᶿd**
4. Standard enthalpy/heat of neutralization **∆Hᶿn**
5. Standard enthalpy/heat of solution/dissolution **∆Hᶿs**
6. Standard enthalpy/heat of formation **∆Hᶿf**

**(a)Standard enthalpy/heat of reaction ∆Hᶿr**

The molar standard enthalpy/heat of reaction may be defined as the energy/heat change when one mole of products is formed at standard conditions

A chemical reaction involves the reactants forming products. For the reaction to take place the bonds holding the reactants must be broken so that new bonds of the products are formed. i.e.

 **A**-**B** + C-D -> **A**-C + **B**-D

 Old Bonds **broken** A-B and C-D on reactants

 New Bonds **formed** A-C and B-D on products

The energy required to break one mole of a (covalent) bond is called **bond dissociation energy**. The SI unit of bond dissociation energy is **kJmole-1**

The higher the bond dissociation energy the stronger the (covalent)bond

**Bond dissociation energies of some (covalent)bonds**

|  |  |  |  |
| --- | --- | --- | --- |
| Bond | Bond dissociation energy (kJmole-1) |  | Bond dissociation energy (kJmole-1) |
| H-H | 431 | I-I | 151 |
| C-C | 436 | C-H | 413 |
| C=C | 612 | O-H | 463 |
| C = C | 836 | C-O | 358 |
| N = N | 945 | H-Cl | 428 |
| N-H | 391 | H-Br | 366 |
| F-F | 158 | C-Cl | 346 |
| Cl-Cl | 239 | C-Br | 276 |
| Br-Br | 193 | C-I | 338 |
| H-I | 299 | O=O | 497 |
| Si-Si | 226 | C-F | 494 |

The molar enthalpy of reaction can be calculated from the bond dissociation energy by:

 (i)**adding** the total bond dissociation energy of the **reactants**(endothermic process/**+∆H**) and total bond dissociation energy of the **products**(exothermic process/**-∆H**).

 (ii)**subtracting** total bond dissociation energy of the **reactants** **from** the total bond dissociation energy of the **products**(exothermic process/**-∆H less/minus** endothermic process/**+∆H**).

 **Practice examples/Calculating ∆Hr**

**1.Calculate ∆Hr from the following reaction:**

1. **H2(g)+ Cl2(g)-> 2HCl(g)**

Working

Old bonds broken (endothermic process/**+∆H** )

= (H-H + Cl-Cl) => (+431 + (+ 239)) = **+ 670kJ**

New bonds broken (exothermic process/**-∆H** )

= (2(H-Cl ) => (- 428 x 2)) = **-856kJ**

 ∆Hr =(+ 670kJ + -856kJ) = 186 kJ = **-93kJ mole-1**

 2

The above reaction has negative **-∆H** enthalpy change and is therefore practically exothermic.

The thermochemical reaction is thus:

½ H2(g)+ ½ Cl2(g)-> HCl(g) ∆Hr = -93kJ

1. **CH4(g)+ Cl2(g)-> CH3Cl + HCl(g)**

Working

Old bonds broken (endothermic process/**+∆H** )

= (4(C-H) + Cl-Cl)

 => ((4 x +413) + (+ 239)) = **+ 1891kJ**

New bonds broken (exothermic process/**-∆H** )

= (3(C-H + H-Cl + C-Cl)

=> (( 3 x - 413) + 428 + 346) = -**2013 kJ**

 ∆Hr =( + 1891kJ + -2013 kJ) = **-122 kJ mole-1**

The above reaction has negative **-∆H** enthalpy change and is therefore practically exothermic.

The thermochemical reaction is thus:

CH4(g)+ Cl2(g)-> CH3Cl(g) + HCl(g) ∆H = -122 kJ

1. **CH2CH2(g)+ Cl2(g)-> CH3Cl CH3Cl (g)**

Working

Old bonds broken (endothermic process/**+∆H** )

= (4(C-H) + Cl-Cl + C=C)

 => ((4 x +413) + (+ 239) +(612)) = **+ 2503kJ**

New bonds broken (exothermic process/**-∆H** )

= (4(C-H + C-C + 2(C-Cl) )

=> (( 3 x - 413) + -436 +2 x 346 = -**2367 kJ**

 ∆Hr =( + 2503kJ + -2367 kJ) = **+136 kJ mole-1**

The above reaction has negative **+∆H** enthalpy change and is therefore practically endothermic.

The thermochemical reaction is thus:

CH2CH2(g)+ Cl2(g)-> CH3Cl CH3Cl (g) ∆H = +136 kJ

Note that:

 (i)a reaction is **exothermic** if the bond dissociation energy of **reactants** is **more** than bond dissociation energy of products.

 (ii)a reaction is **endothermic** if the bond dissociation energy of **reactants** is **less** than bond dissociation energy of products.





**(b)Standard enthalpy/heat of combustion ∆Hᶿc**

The molar standard enthalpy/heat of **combustion(∆Hᶿc**) is defined as the energy/heat change when one mole of a substance is burnt in oxygen/excess air at standard conditions.

Burning is the reaction of a substance with oxygen/air. It is an exothermic process producing a lot of energy in form of heat.

A substance that undergoes burning is called a **fuel.** A fuel is defined as the combustible substance which burns in air to give heat energy for domestic or industrial use. A fuel may be **solid** (e.g coal, wood, charcoal) **liquid** (e.g petrol, paraffin, ethanol, kerosene) or **gas** (e.g liquefied petroleum gas/LPG, Water gas-CO2/H2, biogas-methane, Natural gas-mixture of hydrocarbons)

To determine the molar standard enthalpy/heat of **combustion(∆Hᶿc**) of ethanol

**Procedure**

Put 20cm3 of distilled water into a 50cm3 beaker. Clamp the beaker. Determine the temperature of the water T1.Weigh an empty burner(empty tin with wick).

Record its mass M1.Put some ethanol into the burner. Weigh again the burner with the ethanol and record its mass M2. Ignite the burner and place it below the clamped 50cm3 beaker. Heat the water in the beaker for about one minute. Put off the burner. Record the highest temperature rise of the water, T2. Weigh the burner again and record its mass M3

**Sample results:**

|  |  |
| --- | --- |
| Volume of water used |  20cm3 |
| Temperature of the water before heating T1 |  25.0oC |
| Temperature of the water after heating T2 |  35.0oC |
| Mass of empty burner M1 |  28.3g |
| Mass of empty burner + ethanol before igniting M2 |  29.1g |
| Mass of empty burner + ethanol after igniting M3 |  28.7g |

**Sample calculations:**

**1.Calculate:**

**(a) ∆T the change in temperature**

 **∆T =** T2 – T1  => (35.0oC – 25.0oC) = **10.0oC**

**(b) the mass of ethanol used in burning**

mass of ethanol used = M2 – M1 => 29.1g – 28.7g = **0.4g**

**(c) the number of moles of ethanol used in burning**

 moles of ethanol = mass used => 0.4 = **0.0087 /8.7 x 10-3**moles

 molar mass of ethanol 46

**2. Given that the specific heat capacity of water is 4.2 kJ-1kg-1K-1,determine the heat produced during the burning.**

Heat produced **∆H** = mass of water(**m)** x specific heat capacity (**c**)x **∆T**

 => 20 x 4.2 x 10 = **840 J**oules = **0.84 kJ**

1000

**3.Calculate the molar heat of combustion of ethanol**

Molar heat of combustion ∆Hc = Heat produced ∆H

 Number of moles of fuel

=> 0.84 kJ = **96.5517 kJmole-1**

 0.0087 /8.7 x 10-3 moles

**4.List two sources of error in the above experiment.**

(i)Heat loss to the surrounding **lowers** the practical value of the molar heat of combustion of ethanol.

 A draught shield tries to minimize the loss by protecting wind from wobbling the flame.

 (ii) Heat gain by reaction vessels/beaker **lowers** ∆T and hence ∆Hc

**5.Calculate the heating value of the fuel.**

Heating value = molar heat of combustion => 96.5517 kJmole-1 = **2.0989 kJg-1**

 Molar mass of fuel 46 g

**Heating value is the enrgy produced when a unit mass/gram of a fuel is completely burnt**

**6.Explain other factors used to determine the choice of fuel for domestic and industrial use.**

(i) **availability and affordability**-some fuels are more available cheaply in rural than in urban areas at a lower cost.

 (ii)**cost of storage and transmission**-a fuel should be easy to transport and store safely. e.g LPG is very convenient to store and use. Charcoal and wood are bulky.

 (iii)**environmental effects –**Most fuels after burning produce carbon(IV) oxide gas as a byproduct. Carbon(IV) oxide gas is green house gas that causes global warming. Some other fuel produce acidic gases like sulphur(IV) oxide ,and nitrogen(IV) oxide. These gases cause acid rain. Internal combustion engines exhaust produce lead vapour from leaded petrol and diesel. Lead is carcinogenic.

(iv)**ignition point-**The temperature at which a fuel must be heated before it burns in air is the ignition point. Fuels like petrol have very low ignition point, making it highly flammable. Charcoal and wood have very high ignition point.

**7.Explain the methods used to reduce pollution from common fuels.**

**(i)Planting trees-**Plants absorb excess carbon(IV)oxide for photosynthesis and release oxygen gas to the atmosphere.

**(ii)using catalytic converters** in internal combustion engines that convert harmful/toxic/poisonous gases like carbon(II)oxide and nitrogen(IV)oxide to harmless non-poisonous carbon(IV)oxide, water and nitrogen gas by using platinum-rhodium catalyst along the engine exhaust pipes.

Further practice calculations

**1.Calculate the heating value of methanol CH3OH given that 0.87g of the fuel burn in air to raise the temperature of 500g of water from 20oC to 27oC.(C-12.0,H=1.0 O=16.0).**

Moles of methanol used = Mass of methanol used => 0.87 g = **0.02718 moles**

 Molar mass of methanol 32

Heat produced **∆H** = mass of water(**m)** x specific heat capacity (**c**)x **∆T**

 => 500 x 4.2 x 7 = 14700 **J**oules = **14.7 kJ**

1000

Molar heat of combustion ∆Hc = Heat produced ∆H

 Number of moles of fuel

=> 14.7 kJ = **540.8389 kJmole-1**

 0.02718 moles

Heating value = molar heat of combustion => 540.8389 kJmole-1 = **16.9012 kJg-1**

 Molar mass of fuel 32 g

**2. 1.0 g of carbon burn in excess air to raise the temperature of 400g of water by 18oC.Determine the molar heat of combustion and hence the heating value of carbon(C-12.0,).**

Moles of carbon used = Mass of carbon used => 1.0 g = **0.0833 moles**

 Molar mass of carbon 12

Heat produced **∆H** = mass of water(**m)** x specific heat capacity (**c**)x **∆T**

 => 400 x 4.2 x 18 = 30240 **J**oules = **30.24 kJ**

1000

Molar heat of combustion ∆Hc = Heat produced ∆H

 Number of moles of fuel

=> 30.24 kJ = **363.0252 kJmole-1**

 0.0833 moles

Heating value = molar heat of combustion => 363.0252 kJmole-1= **30.2521 kJg-1**

 Molar mass of fuel 12 g

**(c)Standard enthalpy/heat of displacement ∆Hᶿd**

The molar standard enthalpy/heat of **displacement ∆Hᶿd** is defined as the energy/heat change when one mole of a substance is displaced from its solution.

A displacement reaction takes place when a more reactive element/with less electrode potential **Eᶿ** /negative Eᶿ /higher in the reactivity/electrochemical series remove/displace another with less reactive element/with higher electrode potential **Eᶿ** /positive Eᶿ /lower in the reactivity/electrochemical series **from** its solution.e.g.

(i)Zn(s) + CuSO4(aq) -> Cu(s) + ZnSO4(aq)

Ionically: Zn(s) + Cu2+(aq) -> Cu(s) + Zn2+ (aq)

(ii)Fe(s) + CuSO4(aq) -> Cu(s) + FeSO4(aq)

Ionically: Fe(s) + Cu2+(aq) -> Cu(s) + Fe2+ (aq)

(iii)Pb(s) + CuSO4(aq) -> Cu(s) + PbSO4(**s**)

This reaction stops after some time as insoluble PbSO4(**s**) coat/cover unreacted lead.

 (iv)Cl2(g) + 2NaBr(aq) -> Br2(aq) + 2NaCl(aq)

Ionically: Cl2(g)+ 2Br- (aq) -> Br2(aq) + 2Cl- (aq)

Practically, a displacement reaction takes place when a known amount /volume of a solution is added excess of a more reactive metal.

To determine the molar standard enthalpy/heat of **displacement(∆Hᶿd**) of copper

**Procedure**

Place 20cm3 of 0.2M copper(II)sulphate(VI)solution into a 50cm3 plastic beaker/calorimeter. Determine and record the temperature of the solution T1.Put all the Zinc powder provided into the plastic beaker. Stir the mixture using the thermometer. Determine and record the highest temperature change to the nearest 0.5oC- T2 . Repeat the experiment to complete table 1 below

Table 1

|  |  |  |
| --- | --- | --- |
| Experiment | I | II |
| Final temperature of solution(T2) | 30.0oC | 31.0oC |
| Final temperature of solution(T1) | 25.0oC | 24.0oC |
| Change in temperature(∆T) | 5.0 | 6.0 |

**Questions**

 **1.(a) Calculate:**

 **(i)average ∆T**

Average∆T = change in temperature in experiment I and II

=>5.0 + 6.0 = **5.5oC**

 2

 **(ii)the number of moles of solution used**

Moles used = molarity x volume of solution = 0.2 x 20 = **0.004 moles**

1000 1000

 **(iii)the enthalpy change ∆H for the reaction**

Heat produced **∆H** = mass of solution(**m)** x specific heat capacity (**c**)x **∆T**

 => 20 x 4.2 x 5.5 = 462 **J**oules = **0.462 kJ**

1000

 **(iv)State two assumptions made in the above calculations.**

Density of solution = density of water = 1gcm-3

Specific heat capacity of solution=Specific heat capacity of solution=4.2 kJ-1kg-1K

This is because the solution is assumed to be **infinite dilute.**

**2. Calculate the enthalpy change for one mole of displacement of Cu2+ (aq) ions.**

Molar heat of displacement ∆Hd = Heat produced ∆H

 Number of moles of fuel

=> 0.462 kJ = **115.5 kJmole-1**

 0.004

**3.Write an ionic equation for the reaction taking place.**

 Zn(s) + Cu2+(aq) -> Cu(s) + Zn2+(aq)

**4.State the observation made during the reaction.**

 Blue colour of copper(II)sulphate(VI) fades/becomes less blue/colourless.

Brown solid deposits are formed at the bottom of reaction vessel/ beaker.

**5.Illustrate the above reaction using an energy level diagram.**

Zn(s) + Cu2+(aq)

 Energy ∆H = -115.5 kJmole-1

(kJ)

Cu(s) + Zn2+(aq)

 Reaction progress/path/coordinates

**6. Iron is less reactive than Zinc. Explain the effect of using iron instead of Zinc on the standard molar heat of displacement ∆Hd of copper(II)sulphate (VI) solution.**

No effect.Cu2+ (aq) are displaced from their solution.The element used to displace it does not matter.The reaction however faster if a more reactive metal is used.

**7.(a)If the standard molar heat of displacement ∆Hd of copper(II)sulphate (VI) solution is 209kJmole-1 calculate the temperature change if 50cm3 of 0.2M solution was displaced by excess magnesium.**

Moles used = molarity x volume of solution = 0.2 x 50 = **0.01 moles**

1000 1000

Heat produced ∆H = Molar heat of displacement ∆Hd x Number of moles

 =>209kJmole-1x 0.01 moles = **2.09 kJ**

**∆**T (change in temperature) **=**  Heat produced ∆H Molar heat of displacement ∆Hd x Number of moles

=>2.09 kJ = **9.9524K**elvin

 0.01 moles

**(b)Draw an energy level diagram to show the above energy changes**

Mg(s) + Cu2+(aq)

 Energy ∆H = -209 kJmole-1

(kJ)

Cu(s) + Mg2+(aq)

 Reaction progress/path/coordinates

**8. The enthalpy of displacement ∆Hd of copper(II)sulphate (VI) solution is 12k6kJmole-1.Calculate the molarity of the solution given that 40cm3 of this solution produces 2.204kJ of energy during a displacement reaction with excess iron filings.**

 Number of moles **=**  Heat produced ∆H Molar heat of displacement ∆Hd

=>2.204 kJ = **0.0206moles**

 126 moles

Molarity of the solution = moles x 1000 Volume of solution used

 = 0.0206moles x 1000 = **0.5167 M**

 40

**9. If the molar heat of displacement of Zinc(II)nitrate(V)by magnesium powder is 25.05kJmole-1 ,calculate the volume of solution which must be added 0.5 moles solution if there was a 3.0K rise in temperature.**

Heat produced ∆H = Molar heat of displacement ∆Hd x Number of moles

 =>25.08kJmole-1x 0.5 moles = **1.254 kJ** x 1000 **=1254J**

Mass of solution (**m) =** Heat produced **∆H**

 specific heat capacity (**c**)x **∆T**

=> 1254J = **99.5238 g**

 4.2 x 3

Volume = mass x density = 99.5238 g x 1 = **99.5238cm3**

Note: The solution assumes to be too dilute /infinite dilute such that the density and specific heat capacity is assumed to be that of water.

**Graphical determination of the molar enthalpy of displacement of copper**

**Procedure:**

Place 20cm3 of 0.2M copper(II)sulphate (VI) solution into a calorimeter/50cm3 of plastic beaker wrapped in cotton wool/tissue paper.

Record its temperature at time T= 0.

Stir the solution with the thermometer carefully and continue recording the temperature after every 30 seconds .

Place all the (1.5g) Zinc powder provided.

Stir the solution with the thermometer carefully and continue recording the temperature after every 30 seconds for five minutes.

Determine the highest temperature change to the nearest 0.5oC.

**Sample results**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Time oC | 0.0 | 30.0 | 60.0 | 90.0 | 120.0 | 150.0 | 180.0 | 210.0 | 240.0 | 270.0 |
| Temperature | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 | xxx | 36.0 | 35.5 | 35.0 | 34.5 |

**Sketch graph of temperature against time**

36.5

 Extrapolation

 Temperature point ∆T

oC

130Time(seconds)

**Questions**

1. **Show and determine the change in temperature ∆T**

From a well constructed graph ∆T= T2 –T1 at **150** second by **extrapolation**

 ∆T = 36.5 – 25.0 = 11.5oC

**2.Calculate the number of moles of copper(II) sulphate(VI)used given the molar heat of displacement of Cu2+ (aq)ions is 125kJmole-1**

Heat produced **∆H** = mass of solution(**m)** x specific heat capacity (**c**)x **∆T**

 => 20 x 4.2 x 11.5 = 966 **J**oules = **0.966 kJ**

1000

Number of moles **=**  Heat produced ∆H Molar heat of displacement ∆Hd

=>.966 kJ = **0.007728moles**

 125 moles **7.728 x 10-3moles**

1. **What was the concentration of copper(II)sulphate(VI) in moles per litre.**

 Molarity = moles x 1000 => 7.728 x 10-3moles x 1000 = **0.3864M**

 Volume used 20

 **4.The actual concentration of copper(II)sulphate(VI) solution was 0.4M.Explain the differences between the two.**

Practical value is **lower** than theoretical. Heat/energy **loss** to the surrounding and that absorbed by the reaction vessel **decreases** ∆T hence **lowering** the practical number of moles and molarity against the theoretical value

5.a) In an experiment to determine the molar heat of reaction when magnesium displaces copper ,0.15g of magnesium powder were added to 25.0cm3 of 2.0M copper (II) chloride solution. The temperature of copper (II) chloride solution was 25oC.While that of the mixture was 43oC.

i)Other than increase in temperature, state and explain the observations which were made during the reaction.(3mks)

ii)Calculate the heat change during the reaction (specific heat capacity of the solution = 4.2jg-1k-1and the density of the solution = 1g/cm3(2mks)

iii)Determine the molar heat of displacement of copper by magnesium.(Mg=24.0).

iv)Write the ionic equation for the reaction.(1mk)

v)Sketch an energy level diagram for the reaction.(2mks)

**(c)Standard enthalpy/heat of neutralization ∆Hᶿn**

The molar standard enthalpy/heat of **neutralization ∆Hᶿn** is defined as the energy/heat change when one mole of a H+ (H3O+)ions react completely with one mole of OH- ions to form one mole of H2O/water.

Neutralization is thus a reaction of an acid /H+ (H3O+)ions with a base/alkali/ OH- ions to form salt and water only.

Strong acids/bases/alkalis are completely dissociated to **many** free ions(H+ /H3O+ and OH- ions).

Weak acids/bases/alkalis are partially dissociated to **few** free ions(H+ (H3O+ and OH- ions) and exist **more** as molecules.

Neutralization is an exothermic(-∆H) process.The enrgy produced during neutralization depend on the amount of free ions (H+ H3O+ and OH-)ions existing in the acid/base/alkali reactant:

(i)for weak acid-base/alkali neutralization,some of the **energy** is used to dissociate /ionize the **molecule** into free H+ H3O+ and OH- ions therefore the overall energy evolved is comparatively **lower/lesser/smaller** than strong acid / base/ alkali neutralizations.

 (ii) (i)for strong acid/base/alkali neutralization, no **energy** is used to dissociate /ionize since **molecule** is wholly/fully dissociated/ionized into free H+ H3O+ and OH- ions.The overall energy evolved is comparatively **higher/more** than weak acid-base/ alkali neutralizations. For strong acid-base/alkali neutralization, the enthalpy of neutralization is **constant** at about **57.3**kJmole-1 irrespective of the acid-base used. This is because ionically:

 **OH-(aq)+ H+(aq) -> H2O(l)** for any wholly dissociated acid/base/alkali

Practically ∆Hᶿn can be determined as in the examples below:

To determine the molar enthalpy of neutralization ∆Hn of Hydrochloric acid

**Procedure**

Place 50cm3 of 2M hydrochloric acid into a calorimeter/200cm3 plastic beaker wrapped in cotton wool/tissue paper. Record its temperature T1.Using a clean measuring cylinder, measure another 50cm3 of 2M sodium hydroxide. Rinse the bulb of the thermometer in distilled water. Determine the temperature of the sodium hydroxide T2.Average T2 andT1 to get the initial temperature of the mixture T3.

Carefully add all the alkali into the calorimeter/200cm3 plastic beaker wrapped in cotton wool/tissue paper containing the acid. Stir vigorously the mixture with the thermometer.

Determine the highest temperature change to the nearest 0.5oC T4 as the final temperature of the mixture. Repeat the experiment to complete table 1.

 Table I . **Sample results**

|  |  |  |
| --- | --- | --- |
| Experiment |  I |  II |
| Temperature of acid T1 (oC) | 22.5 | 22.5 |
| Temperature of base T2 (oC) | 22.0 | 23.0 |
| Final temperature of solution T4(oC) | 35.5 | 36.0 |
| Initial temperature of solution T3(oC) | 22.25 | 22.75 |
| Temperature change( T5) | 13.25 | 13.75 |

 **(a)Calculate T6 the average temperature change**  T6 = 13.25 +13.75 = 13.5 oC 2

 **(b)Why should the apparatus be very clean?**

 Impurities present in the apparatus reacts with acid /base lowering the overall temperature change and hence ∆Hᶿn.

**(c)Calculate the:**

**(i)number of moles of the acid used**

 number of moles = molarity x volume => 2 x 50 = **0.1moles** 1000 1000

**(ii)enthalpy change** ∆H **of neutralization.**

∆H = (**m**)mass of solution(acid+base) x (**c**)specific heat capacity of solution x **∆T**(T6) => (50 +50) x 4.2 x 13.5 = **5670J**oules = **5.67kJ**

 **(iii) the molar heat of neutralization the acid.**

 ∆Hn = Enthalpy change ∆H => 5.67kJ = **56.7kJ mole-1**

 Number of moles 0.1moles

**(c)Write the ionic equation for the reaction that takes place**

OH-(aq)+ H+(aq) -> H2O(l)

**(d)The theoretical enthalpy change is 57.4kJ. Explain the difference with the results above.**

The theoretical value is higher

 Heat/energy loss to the surrounding/environment lowers **∆T**/T6 and thus ∆Hn

 Heat/energy is absorbed by the reaction vessel/calorimeter/plastic cup lowers ∆T and hence ∆Hn

**(e)Compare the ∆Hn of the experiment above with similar experiment repeated with neutralization of a solution of:**

 **(i) potassium hydroxide with nitric(V) acid**

The results would be the same/similar.

Both are neutralization reactions of strong acids and bases/alkalis that are fully /wholly dissociated into many free H+ / H3O+ and OH- ions.

 **(ii) ammonia with ethanoic acid**

The results would be lower/∆Hn would be less.

Both are neutralization reactions of weak acids and bases/alkalis that are partially /partly dissociated into few free H+ / H3O+ and OH- ions. Some energy is used to ionize the molecule.

**(f)Draw an energy level diagram to illustrate the energy changes**

 H**2** H+(aq)+OH-(aq)

 Energy

 (kJ)

 ∆H = **-56.7kJ**

 H1 H2O (l)

 Reaction path/coordinate/progress

**Theoretical examples**

**1.The molar enthalpy of neutralization was experimentary shown to be 51.5kJ per mole of 0.5M hydrochloric acid and 0.5M sodium hydroxide. If the volume of sodium hydroxide was 20cm3, what was the volume of hydrochloric acid used if the reaction produced a 5.0oC rise in temperature?**

Working:

Moles ofsodium hydroxide = molarity x volume => 0.5 M x 20cm3 = **0.01 moles**

 1000 1000

Enthalpy change∆H **=**  ∆Hn =>51.5 = **0.515kJ**

 Molessodium hydroxide 0.01 moles

Mass of base + acid = Enthalpy change∆H in Joules

 Specific heat capacity x ∆T

 => 0.515kJ x 1000 = **24.5238**g

 4.2 x 5

Mass/volume of HCl = Total volume – volume of NaOH

=>24.5238 - 20.0 = **4.5238 cm3**

1. **∆Hn of potassium hydroxide was practically determined to be 56.7kJmole-1.Calculate the molarity of 50.0 cm3 potassium hydroxide used to neutralize 25.0cm3 of dilute sulphuric(VI) acid raising the temperature of the solution from 10.0oC to 16.5oC.**

∆H = (**m**)mass of solution(acid+base) x (**c**)specific heat capacity of solution x **∆T**

=> (50 +25) x 4.2 x 6.5 = **2047.5J**oules

Molespotassium hydroxide =Enthalpy change∆H

∆Hn

 2047.5Joules = **0.0361 moles**

 56700Joules

Molarity of KOH = moles x 1000 => 0.0361 moles x 1000 = **0.722M**

Volume used 50cm3

**3.Determine the specific heat capacity of a solution of a solution mixture of 50.0cm3 of 2M potassium hydroxide neutralizing 50.0cm3 of 2M nitric(V) acid if a 13.25oC rise in temperature is recorded.(1mole of potassium hydroxide produce 55.4kJ of energy)**

Moles ofpotassium hydroxide = molarity KOH x volume

 1000

 => 2 M x 50cm3 = **0.1 moles**

 1000

Enthalpy change∆H  **=** ∆Hn x Molespotassium hydroxide => 55.4kJ x 0.1 moles = 5.54kJ x 1000=**5540J**oules

Specific heat capacity = Enthalpy change∆H in Joules

 Mass of base + acid x ∆T

 => 5540 =  **4.1811J-1g-1K-1**

 (50+50) x 13.25

Graphically ∆Hn can be determined as in the example below:

**Procedure**

Place 8 test tubes in a test tube rack .Put 5cm3 of 2M sodium hydroxide solution into each test tube.

 Measure 25cm3 of 1M hydrochloric acid into 100cm3 plastic beaker.

 Record its initial temperature at volume of base =0. Put one portion of the base into the beaker containing the acid.

Stir carefully with the thermometer and record the highest temperature change to the nearest 0.5oC.

Repeat the procedure above with other portions of the base to complete table 1 below

**Table 1:Sample results.**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| olume of acid(cm3) | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 |
| Volume of alkali(cm3) | 0 | 5.0 | 10.0 | 15.0 | 20.0 | 25.0 | 30.0 | 35.0 | 40.0 |
| Final temperature(oC) | **22.0** | **24.0** | **26.0** | **28.0** | **28.0** | **27.0** | **26.0** | **25.0** | **24.0** |
| Initial temperature(oC) | **22.0** | **22.0** | **22.0** | **22.0** | **22.0** | **22.0** | **22.0** | **22.0** | **22.0** |
| Change in temperature | **0.0** | **2.0** | **4.0** | **6.0** | **6.0** | **5.0** | **4.0** | **3.0** | **2.0** |

 (a)Complete the table to determine the change in temperature.

(b)Plot a graph of volume of sodium hydroxide against temperature change.

 **6.7=**T2

Volume of sodium hydroxide(cm3)

 ∆T (oC)

 **0 =T1**

**From the graph show and determine :**

 **(i)the highest temperature change ∆T**

 ∆T =T2-T1 => highest temperature-T2 (from extrapolating a correctly plotted graph) less lowest temperature at volume of base=0 :T1

=>∆T = 6.7 – 0.0 = **6.70C**

  **(ii)the volume of sodium hydroxide used for complete neutralization**

From a correctly plotted graph – **16.75cm3**

**(c)Calculate the number of moles of the alkali used**

 Moles NaOH = molarity x volume =>2M x 16.75cm3 = **0.0335 moles**

 1000 1000

**(d)Calculate ∆H for the reaction**

∆H = mass of solution(acid+base) x c x ∆T

 =>(25.0 + 16.75) x 4.2 x 6.7 = 1174.845 J = **1.174845kJ**

1000

**(e)Calculate the molar enthalpy of neutralization of the alkali.**

 ∆Hn  = ∆Hn  = 1.174845kJ =  **35.0701kJ**

Number of moles 0.0335

**(d)Standard enthalpy/heat of solution ∆Hᶿs**

The standard enthalpy of solution ∆Hᶿsis defined as the energy change when one mole of a substance is dissolve in excess distilled water to form an infinite dilute solution. An infinite dilute solution is one which is **too** dilute to be diluted further.

Dissolving a solid involves two processes:

 (i) **breaking** the **crystal** of the solid into **free ions**(cations and anion).This process is the **opposite** of the **formation** of the crystal itself. The energy required to form one mole of a crystal structure from its **gaseous ions** is called **Lattice energy**/heat/enthalpy of lattice (**∆Hl**).Lattice energy /heat/enthalpy of lattice (**∆**Hl) is an endothermic process (**+∆Hl**).

The table below shows some **∆Hl** in kJ for the process MX(s) -> M+ (g) + X- (g)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Li | Na | K | Ca | Mg |
| F | +1022 | +900 | +800 | +760 | +631 |
| Cl | +846 | +771 | +690 | +2237 | +2493 |
| Br | +800 | +733 | +670 | +2173 | +2226 |

 (ii)**surrounding** the free ions by polar **water** molecules. This process is called **hydration.** The energy produced when one mole of ions are completely hydrated is called **hydration energy**/ heat/enthalpy of hydration(**∆Hh**).Hydration energy /enthalpy of hydration(∆Hh) is an **exothermic** process(∆Hh).

The table below shows some ∆Hhin kJ for some ions;

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| ion | Li+ | Na+ | K+ | Mg2+ | Ca2+ | F- | Cl- | Br- |
| ∆Hh | -1091 | -406 | -322 | -1920 | -1650 | -506 | -364 | -335 |

The **sum** of the **lattice** energy **+∆Hl**(endothermic) and **hydration** energy **-∆Hh** (exothermic) gives the heat of solution**-∆Hs**

**∆Hs = ∆Hl +∆Hh**

**Note**

Since ∆Hl is an endothermic process and ∆Hh is an exothermic process then ∆Hs is**:**

(i)**exothermic** if **∆Hl** is **less** than **∆Hh** and hence a solid **dissolve** easily in water.

 (ii)**endothermic** if **∆Hl** is **more** than **∆Hh** and hence a solid does not **dissolve** easily in water.

(a)Dissolving sodium chloride crystal/s:

(i) **NaCl -**---breaking the crystal into free ions--**-> Na +(g)+ Cl-(g) ∆**Hl **=+771 kJ**

(ii) Hydrating the ions;

Na +(g) + **aq** -> Na(aq) **∆Hh = - 406 kJ**

Cl-(g) + aq -> Cl-(aq) **∆Hh = - 364 kJ**

 **∆Hs =∆Hh** +**∆Hs** ->(- 406 kJ + - 364 kJ) + +771 kJ = **+ 1.0 kJmole-1**

NaCl does not **dissolve** easily in water because overall **∆Hs** is **endothermic**

Solubility of NaCl therefore increases with increase in temperature.

 Increase in temperature increases the energy to break the crystal lattice of NaCl to freeNa +(g)+ Cl-(g)

**(b)Dissolving magnesium chloride crystal/s//**  **MgCl2 (s) ->MgCl2 (aq)**

(i) MgCl2 **-**-breaking the crystal into free ions-**->**Mg 2+(g)+ 2Cl-(g) ∆Hl =+2493 kJ

(ii) Hydrating the ions;

 Mg 2+(g) + aq -> Mg 2+(g) (aq) ∆Hh = - 1920 kJ

 2Cl-(g) + aq -> 2Cl-(aq) ∆Hh = (- 364 x 2) kJ

 ∆Hs =∆Hh +∆Hs -> (- 1920 kJ + (- 364 x 2 kJ)) + +2493 kJ = -**155.0 kJmole-1**

MgCl2 (s) **dissolve** easily in water because overall **∆Hs** is **exothermic** .

Solubility of MgCl2 (s) therefore decreases with increase in temperature.

**(c)Dissolving Calcium floride crystal/s//**  **CaF2 (s) -> CaF2 (aq)**

(i) **CaF2 -->**Ca 2+(g)+ 2F-(g) ∆Hl =+760 kJ

(ii) Hydrating the ions;

 Ca 2+(g) + aq -> Ca 2+(g) (aq) ∆Hh = - 1650 kJ

 2F-(g) + aq -> 2F-(aq) ∆Hh = (- 506 x 2) kJ

 ∆Hs =∆Hh +∆Hs -> (- 1650 kJ + (- 506 x 2 kJ)) + +760 kJ = -**1902.0 kJmole-1**

CaF2 (s) **dissolve** easily in water because overall **∆Hs** is **exothermic** .

Solubility of CaF2 (s) therefore decreases with increase in temperature.

**(d)Dissolving magnesium bromide crystal/s//**  **MgBr2 (s) ->MgBr2 (aq)**

(i) MgCl2 **-**-breaking the crystal into free ions-**->**Mg 2+(g)+ 2Br-(g) ∆Hl =+2226 kJ

(ii) Hydrating the ions;

 Mg 2+(g) + aq -> Mg 2+(g) (aq) ∆Hh = - 1920 kJ

 2Br-(g) + aq -> 2Br-(aq) ∆Hh = (- 335x 2) kJ

 ∆Hs =∆Hh +∆Hs -> (- 1920 kJ + (- 335 x 2 kJ)) + +2226 kJ = -**364.0 kJmole-1**

MgBr2 (s) **dissolve** easily in water because overall **∆Hs** is **exothermic** .

Solubility of MgBr2(s) therefore decreases with increase in temperature.

Practically the heat of solution can be determined from dissolving known amount /mass/volume of solute in known mass /volume of water/solvent.

 From the temperature of solvent **before** and **after** dissolving the change in temperature(∆T) during dissolution is determined.

To determine the ∆Hs ammonium nitrate

Place 100cm3 of distilled water into a plastic beaker/calorimeter. Determine its temperature and record it at time =0 in table I below.

Put all the 5.0g of ammonium nitrate (potassium nitrate/ammonium chloride can also be used)provided into the plastic beaker/calorimeter, stir using a thermometer and record the highest temperature change to the nearest 0.5oCafter every ½ minute to complete table I.

Continue stirring the mixture throughout the experiment.

**Sample results: Table I**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Time (minutes) | 0.0 | ½  | 1 | 1 ½  | 2 | 2 ½  | 3 | 3 ½  |
| Temperature()oC | **22.0** | **21.0** | **20.0** | **19.0** | **19.0** | **19.5** | **20.0** | **20.5** |

(a)Plot a graph of temperature against time(x-axis)

22.0**=**T1

 temperature(oC) ∆T

 18.7. oC T1

Time (minutes)

**(b)From the graph show and determine the highest temperature change ∆T**

 ∆T =T2-T1 => lowest temperature-T2 (from extrapolating a correctly plotted graph) less highest temperature at volume of base=0 :T1

=>∆T =18.7 – 22.0 = **3.30C**

**(c)Calculate the number of moles of ammonium nitrate(V) used**

 Moles NH4NO3 = mass used => 5.0 = **0.0625 moles**

 Molar mass 80

**(d)Calculate ∆H for the reaction**

∆H = mass of water x c x ∆T

->100 x 4.2 x 3.3 = **+**1386 J = **+1.386kJ**

1000

**(e)Calculate the molar enthalpy of dissolution of ammonium nitrate(V).**

 ∆Hs  = ∆H = +1.386kJ = + 22.176kJ mole-1

 Number of moles 0.0625 moles

**(f)What would happen if the distilled water was heated before the experiment was performed.**

The ammonium nitrate(V)would take less time to dissolves. Increase in temperature reduces lattice energy causing endothermic dissolution to be faster

**(g)Illustrate the process above in an energy level diagram**

 NH4+ (g) + NO3-(g)

 +∆H NH4+ (aq)+NO3-(aq) Energy(kJ) +∆H ∆H = **-22.176kJ** NH4NO3-(s) Reaction path /progress/coordinate

**(h) 100cm3 of distilled water at 25oC was added carefully 3cm3 concentrated sulphuric(VI)acid of density 1.84gcm-3.The temperature of the mixture rose from 250C to 38oC.Calculate the molar heat of solution of sulphuric(VI)acid (S=32.0,H=1.0,0=16.0)**

 Working

 Molar mass of H2SO4 = 98g

 Mass of H2SO4= Density x volume => 1.84gcm-3  x 3cm3 = **5.52 g**

 Mass of H2O = Density x volume => 1.00gcm-3  x 100cm3 = **100 g**

 Moles of H2SO4= mass => 5.52 g = **0.0563 moles**

 Molar mass of H2SO4  98g

Enthalpy change ∆H= (mass of acid + water) x specific heat capacity of water x ∆T => (100 +5.52 g) x 4.2 x 13oC = 5761.392 J = **5.761392 kJ**

 1000

∆Hs of H2SO4= ∆H => 5.761392 kJ = **-102.33378kJmoles-1**

 Moles of H2SO4  0.0563 moles

**(e)Standard enthalpy/heat of formation ∆Hᶿf**

The molar enthalpy of formation ∆Hᶿf is defined as the energy change when one mole of a compound is formed from its elements at 298K(25oC) and 101325Pa(one atmosphere)pressure. ∆Hᶿf is practically difficult to determine in a school laboratory.

It is determined normally determined by applying Hess’ law of constant heat summation.

Hess’ law of constant heat summation states that **“the total enthalpy/heat/energy change of a reaction is the same regardless of the route taken from reactants to products at the same temperature and pressure”.**

Hess’ law of constant heat summation is as a result of a series of experiments done by the German Scientist Henri Hess(1802-1850).

He found that the total energy change from the reactants to products was the same irrespective of the intermediate products between. i.e.

 A(s) --**∆H1**-->C(s) = A(s) --**∆H2**-->B(s)--**∆H3**-->C(s)

Applying Hess’ law of constant heat summation then:

 A(s) **∆H2** B(s)

 **∆H1** **∆H3**

 C(s)

The above is called an **energy cycle diagram**. It can be used to calculate any of the missing energy changes since:

 (i) ∆H1 =∆H2 + ∆H3

 (ii) ∆H2 =∆H1 + -∆H3

 (iii) ∆H3 = - ∆H1 + ∆H2

 Examples of applying Hess’ law of constant heat summation

**1.Calculate the molar enthalpy of formation of methane (CH4) given that ∆Hᶿc of carbon-graphite is -393.5kJmole-1,Hydrogen is -285.7 kJmole-1 and that of methane is 890 kJmole-1**

Working

Carbon-graphite ,hydrogen and oxygen can react to first form methane.

Methane will then burn in the oxygen present to form carbon(IV)oxide and water. Carbon-graphite can burn in the oxygen to form carbon(IV)oxide.

Hydrogen can burn in the oxygen to form water.

C(s)+ 2H2 (g)+2O2 (g) --**∆H1**--> CH4(g) +2O2(g) --**∆H2**--> **CO2(g)+2H2O(l)**

C(s)+ 2H2 (g)+2O2 (g) --**∆H3**--> **CO2(g)+2H2O(l)**

Energy cycle diagram

 C(s) + 2H2 (g) + 2O2(g) ∆H1=∆Hᶿc =-890.4kJ CH4(g)+2O2(g)

 ∆H3=∆Hᶿc =-393.5kJ ∆H3=∆Hᶿc =-285.7kJ x 2 ∆H2= ∆Hᶿf= x

 CO2(g) + 2H2O(l)

Substituting:

 ∆H3 = ∆H1 + ∆H2

 -393.5 + (-285.7 x 2) = -890.4kJ + x

 x = -74.5 kJ

 Heat of formation ∆Hᶿf CH4 = -74.5 kJmole-1

**2. Calculate the molar enthalpy of formation of ethyne (C2H2) given : ∆Hᶿc of carbon-graphite = -394kJmole-1,Hydrogen = -286 kJmole-1 , (C2H2) = -1300 kJmole-1**

Working

Carbon-graphite ,hydrogen and oxygen can react to first form ethyne.

Ethyne will then burn in the oxygen present to form carbon(IV)oxide and water. Carbon-graphite can burn in the oxygen to form carbon(IV)oxide.

Hydrogen can burn in the oxygen to form water.

2C(s)+ H2 (g)+2 ½ O2 (g) --**∆H1**--> C2H2 (g) +2 ½ O2(g) --**∆H2**--> **CO2(g)+H2O(l)**

2C(s)+ H2 (g)+ 2 ½ O2 (g) --**∆H3**--> 2**CO2(g)+H2O(l)**

Energy cycle diagram

 2C(s) + H2 (g) +2½O2(g) **∆H1**=∆Hᶿf =x C2H2+2½O2(g)

 ∆H3=∆Hᶿc =-394kJx 2 ∆H3=∆Hᶿc =-286kJ ∆H2= ∆Hᶿc= -1300kJ

 2CO2(g) + H2O(l)

Substituting:

 ∆H3 = ∆H1 + ∆H2

 ( -394 x 2) + -286 = -1300kJ + x

 x = +244 kJ

 Heat of formation ∆Hᶿf CH4 = **+244 kJmole-1**

**3. Calculate the molar enthalpy of formation of carbon(II)oxide (CO) given : ∆Hᶿc of carbon-graphite = -393.5kJmole-1, ∆Hᶿc of carbon(II)oxide (CO)= -283 kJmole-1**

Working

Carbon-graphite reacts with oxygen first to formcarbon (II)oxide (CO).

Carbon(II)oxide (CO) then burn in the excess oxygen to form carbon(IV)oxide. Carbon-graphite can burn in excess oxygen to form carbon (IV) oxide.

C(s)+ ½O2 (g) --**∆H1**--> CO (g) + ½ O2(g) --**∆H2**--> **CO2(g)**

 C(s)+ O2 (g) --**∆H3**--> **CO2(g)**

Energy cycle diagram

 C(s) + ½O2(g) ∆H1=∆Hᶿf =x CO+½O2(g)

 ∆H3=∆Hᶿc =-393.5kJ ∆H2= ∆Hᶿc= -283kJ

 CO2(g)

Substituting:

 ∆H3 = ∆H1 + ∆H2

 -393.5kJ = -283kJ + x

 x = -110 kJ

 Heat of formation ∆Hᶿf CO = -110 kJmole-1

**4.Study the information below:**

 **H2(g) + ½ O2(g)-> H2O(l) ∆H1=-286 kJmole-1**

**C(s) + O2(g)-> CO2(g) ∆H2=-393 kJmole-1**

**2C(s) + H2(g) + ½ O2(g)->C2H5OH(l) ∆H3=-277 kJmole-1**

**Use the information to calculate the molar enthalpy of combustion ∆H4 of ethanol**

Energy cycle diagram

 2C(s) + 3H2 (g) +3½O2(g) **∆H3**=∆Hᶿf =-227kJ C2H5OH +3O2(g)

 ∆H2=∆Hᶿc =-394kJx 2 ∆H1=∆Hᶿc =-286kJx 3 ∆H4= ∆Hᶿc= x

 **2CO2(g) + 3H2O(l)**

Substituting:

 ∆H1 + ∆H2 = ∆H3 + ∆H4

 ( -394 x 2) + -286 x 3 = -277 + x

 ∆H4 = -1369 kJ

 Heat of combustion ∆Hᶿc C2H5OH = **-1369 kJmole-1**

**5.Given the following information below:**

 **CuSO4(s) + (aq)-> CuSO4(aq) ∆H=-66.1 kJmole-1**

**CuSO4(s) + (aq)+5H2O(l)-> CuSO4 .5H2O (aq) ∆H=-77.4 kJmole-1**

 **Calculate ∆Hfor the reaction;**

**CuSO4(aq) + 5H2O-> CuSO4 .5H2O (aq) ∆H=-77.4 kJmole-1**

Working

**CuSO4(s) + (aq)+5H2O(l)-> CuSO4(aq)+ 5H2O(l)-> CuSO4 .5H2O (aq)**

**CuSO4(s) + (aq)+5H2O(l)-> CuSO4 .5H2O (aq)**

Energy cycle diagram

 CuSO4(s) + (aq)+5H2O(l) ∆H1=+66.1kJ CuSO4(aq)+ 5H2O(l)

 ∆H3= =-77.4kJ ∆H2= x

 CuSO4 .5H2O (aq)

Substituting:

∆H3 = ∆H2 + ∆H1

 ( -77.4kJ = x + +66.1kJ

 ∆H4 = **-10.9 kJ**

 Heat of dissolution of CuSO4 = **-10.9kJmole-1**

Practically, Hess’ law can be applied practically as in the following examples

**a)Practical example 1**

Determination of the enthalpy of formation of CuSO4.5H2O

**Experiment I**

Weigh accurately 12.5 g of copper(II)sulphate(VI)pentahydrate. Measure 100cm3 of distilled water into a beaker. Determine its temperature T1 .Put all the crystals of the copper(II)sulphate(VI)pentahydrate carefully into the beaker. Stir using a thermometer and determine the highest temperature change T2 Repeat the procedure again to complete table 1.

Table 1:Sample results

|  |  |  |
| --- | --- | --- |
| Experiment | I | II |
| Highest /lowest temperature T2 | 27.0 | 29.0 |
| Initial temperature T1 | 24.0 | 25.0 |
| Change in temperature ∆T | 3.0 | 4.0 |

**Experiment II**

Weigh accurately 8.0g of anhydrous copper(II)sulphate(VI). Measure 100cm3 of distilled water into a beaker. Determine its temperature T1 .Put all the crystals of the copper(II)sulphate(VI)pentahydrate carefully into the beaker. Stir using a thermometer and determine the highest temperature change T2 Repeat the procedure again to complete table II.

Table II :Sample results

|  |  |  |
| --- | --- | --- |
| Experiment | I | II |
| Highest /lowest temperature T2 | 26.0 | 27.0 |
| Initial temperature T1 | 25.0 | 25.0 |
| Change in temperature ∆T | 1.0 | 2.0 |

**Questions**

**(a)Calculate the average ∆T in**

 **(i)Table I**

 ∆T= T2 -T1 => 3.0 +4.0 = **3.5 oC**

2

 **(ii)Table II**

 ∆T= T2 -T1 => 1.0 +2.0 = **1.5 oC**

2

**(b)Calculate the number of moles of solid used in:**

 **(i)Experiment I**

 Moles of CuSO4.5H2O = Mass => 12.5 = **0.05 moles**

 Molar mass 250

 **(ii)Experiment II**

 Moles of CuSO4 = Mass => 8.0 = **0.05 moles**

 Molar mass 160

**(c)Calculate the enthalpy change for the reaction in:**

 **(i)Experiment I**

Enthalpy change of CuSO4.5H2O= mass of Water(**m**) x **c** x **∆T**

=>100cm3 x 4.2 x 3.5 oC = **-1.47kJ**

 1000

 **(ii)Experiment II**

Enthalpy change of CuSO4 = mass of water(**m**) x **c** x **∆T**

=>100cm3 x 4.2 x 1.5 oC = **-0.63kJ**

 1000

**(c)Calculate the molar enthalpy of solution CuSO4 .5H2O (s) form the results in (i)experiment I.**

∆Hs = CuSO4.5H2O= ∆H => -1.47kJ = **29.4kJ**

 Number of Moles 0.05 moles

**(ii)experiment II.**

∆Hs = CuSO4= ∆H => -0.63kJ = **12.6kJ**

 Number of Moles 0.05 moles

**(d) Using an energy level diagram, calculate the molar enthalpy change for the reaction:**

**CuSO4 .5H2O (s) -> CuSO4(s)+5H2O(l)**

Energy cycle diagram

 CuSO4(s) + (aq)+5H2O(l) ∆H1=x CuSO4. 5H2O (s)+ (aq)

 ∆H3= =-29.4kJ ∆H2= -12.6kJ

 CuSO4 .5H2O (aq)

∆H3 = ∆H1 +∆H2

=>-29.4kJ = -12.6kJ + x

=>-29.4kJ - (+12.6kJ) = x

**x = 16.8kJ**

**b)Practical example II**

Determination of enthalpy of solution of ammonium chloride

Theoretical information.

Ammonium chloride dissolves in water to form ammonium chloride solution. Aqueous ammonia can react with excess dilute hydrochloric acid to form ammonium chloride solution. The heat change taking place can be calculated from the heat of reactions:

(i) NH3(aq) + HCl(aq) -> NH4Cl(s)

(ii) NH4Cl(s) + (aq) -> NH4Cl(aq)

(iii) NH3(aq) + HCl(aq) -> NH4Cl(aq)

Experiment procedure I

Measure 50cm3 of water into a 100cm3 beaker. Record its temperature T1 as initial temperature to the nearest 0.5oC in table I. Add exactly 5.0g of ammonium chloride crystals weighed carefully into the water. Stir and record the highest temperature change T2 as the final temperature change. Repeat the above procedure to complete table I.

Sample results TableI

|  |  |  |
| --- | --- | --- |
| Experiment | I | II |
| final temperature(oC) | 19.0 | 20.0 |
| initial temperature(oC) | 22.0 | 22.0 |
|  temperature change ∆T(oC) | 3.0 | 2.0 |

Experiment procedure II

Measure 25cm3 of 2M aqueous ammonia into a 100cm3 beaker. Record its temperature T1 as initial temperature to the nearest 0.5oC in table II. Measure 25cm3 of 2M hydrochloric acid solution. Add the acid into the beaker containing aqueous ammonia. Stir and record the highest temperature change T2 as the final temperature change. Repeat the above procedure to complete table II.

Sample results:Table II

|  |  |  |
| --- | --- | --- |
| Experiment | I | II |
| final temperature(oC) | 29.0 | 29.0 |
| initial temperature(oC) | 22.0 | 22.0 |
|  temperature change ∆T(oC) | 7.0 | 7.0 |

**Sample Calculations:**

**(a)Calculate the average ∆T in**

 **(i)Table I**

 ∆T= T2 -T1 => -3.0 +-2.0 = **2.5 oC**

2

 **(ii)Table II**

 ∆T= T2 -T1 => 7.0 +7.0 = **7.0 oC**

2

**(b)Calculate the enthalpy change for the reaction in:**

 **(i)Experiment I**

 Enthalpy change ∆H = mass of Water(**m**) x **c** x **∆T**

 =>50cm3 x 4.2 x 2.5 oC = **+0.525kJ**

 1000

 **(ii)Experiment II**

 Enthalpy change of CuSO4 = mass of water(**m**) x **c** x **∆T**

 =>25+25cm3 x 4.2 x 7 oC = **+1.47kJ**

 1000

**(c)Write the equation for the reaction taking place in:**

 **(i)Experiment I**

 NH4Cl(**s**) + (aq) -> NH4Cl(**aq**)

**(ii)Experiment I**

 NH3(aq) + HCl(aq) -> NH4Cl(aq)

**(d)Calculate the enthalpy change ∆H for the reaction:**

 NH3(g) + HCl(g) -> NH4Cl(s) given that:

(i) NH3(g) + (aq) -> NH3(aq) ∆H= -40.3kJ

(ii) (aq) + HCl(g) -> HCl(aq) ∆H= -16.45kJ

**(e)Applying Hess’ Law of constant heat summation:**

 Energy level diagram

 N2(g) + 1½ H2(g) + ½ Cl2 **∆Hf** NH4Cl(s) + aq

 **+0.525kJ**=∆H4

 (aq) (aq)

 **- 40.3kJ**=∆H1  **-16.43kJ**=∆H2

 NH3 (aq) + HCl(aq) **-1.47kJ**=∆H3 NH4Cl(s)

∆H1 + ∆H2 + ∆H3  = ∆H4  + ∆Hf

 **- 40.3kJ + -16.43kJ + -1.47kJ = +0.525kJ + ∆Hf**

 =>**∆Hf = -58.865kJ.**

Practice theoretical examples:

**1. Using an energy level diagram calculate the ∆Hs  of ammonium chloride crystals given that.**

 **∆Hf  of NH3 (aq) = -80.54kJ mole-1**

**∆Hf  of HCl (aq) = -164.46kJ mole-1**

**∆Hf  of NH4Cl (aq) = -261.7483kJ mole-1**

**∆Hs  of NH4Cl (aq) = -16.8517kJ mole-1**

 N2(g) + 1½ H2(g) + ½ Cl2  **∆Hf**=-261.7483kJ NH4Cl(s) + aq

 **x**=∆Hs

 (aq) (aq)

**- 80.54kJ**=∆H1  **-164.46kJ**=∆H2

 NH3 (aq) + HCl(aq) **16.8517kJ**=∆H3 NH4Cl(s)

∆H1 + ∆H2 + ∆H3  = ∆H4  + ∆Hf

 - 80.54kJ + -164.46kJ + -16.8517kJ = -261.7483kJ + ∆Hf

 =>∆Hf = **-33.6kJmole-1**.

Study the energy cycle diagram below and use it to:

(a)Identify the energy changes ∆H1 ∆H2 ∆H3 ∆H4 ∆H5 ∆H6



∆H1  - enthalpy/heat of formation of sodium chloride (∆Hf)

∆H2 -enthalpy/heat of atomization of sodium (∆Hat)

∆H3  -enthalpy/heat of ionization/ionization energy of sodium (∆H i)

 ∆H4 -enthalpy/heat of atomization of chlorine (∆Hat)

∆H5 -enthalpy/heat of electron affinity of chlorine (∆He)

∆H6 enthalpy/heat of lattice/Lattice energy of sodium chloride(∆H l)

**(b) Calculate ∆H1  given that ∆H2 =+108kJ , ∆H3=+500kJ, ∆H4 =+121kJ ,∆H5 =-364kJ and ∆H6 =-766kJ**

Working:

∆H1 =∆H2 +∆H3 +∆H4 +∆H5 +∆H6

Substituting:

∆H1= +108kJ + +500kJ + +121kJ +-364kJ + -766kJ

∆H1= **-401kJmole-1**

**(c) Given the that:**

 **(i) Ionization energy of sodium = + 500kJmole-1**

**(ii)∆Hat of sodium = + 110kJmole-1**

**(iii) Electron affinity of chlorine = - 363kJmole-1**

 **(iv)∆Hat of chlorine = + 120kJmole-1**

 **(v) ∆Hf  of sodium chloride = -411kJ , calculate the lattice energy of sodium chloride using an energy cycle diagram.**

****

Working:

Applying Hess law then:

∆Hf =∆Ha  +∆Hi +∆Ha +∆He +∆Hl

Substituting:

-411= +108kJ + +500kJ + +121kJ +-364kJ + x

-411 + -108kJ + -500kJ + -121kJ + +364kJ = x

 x= **-776kJmole-1**

****