Department of Chemostry

College of Science

Al-Mustansiriyah University

The Scintific Course
1st Semister
2nd Stage
Physical Chemistry Lab.

By

Lecturer Athraa Salman Ahmed

Supervised by:

Dr. Hussain Ismaiel

1st Semester Experiments

1. Finding the molecular weight for a volatile liquid (Dumas Method).
2. The relation between gas volume and temperature, and finding the absolute Zero.
3. Finding liquid viscosity.
4. Finding constant calorimeter.
5. Finding a strong acid and strong base reaction temperature.
6. Finding reaction temperature of weak acid and weak base.
7. Finding magnesium electrode voltage using a thermodynamic method.

Introduction

Chemistry deals with materials formula and structure besides the changes that happen to the structure of materials.

However, physical chemistry deals with the material physical characteristics and structure besides the rules that control the chemical reaction.

The main objective of the physical chemistry is to accumulate experimental information that is needed to decide gases, liquids, solids, solutions and colloid solutions desperation characteristics, besides providing the theoretical principles as rules.

FIRST EXPERIMENT

The Theoretical Part:

The importance of this method is to find the molecular weight of volatile liquid, when the molecular formula of the compound is not available. In the normal conditions (the pressure and temperature), the general equation of gases can be applied considering that the gas of volatile liquid is a typical gas.

$$PV = nRT$$
$$PV = \frac{wt}{M.wt} RT$$

Where:

P= pressure

V= steam volume = flask volume

n= number of moles = $\frac{weight}{molecular\ weightt}$
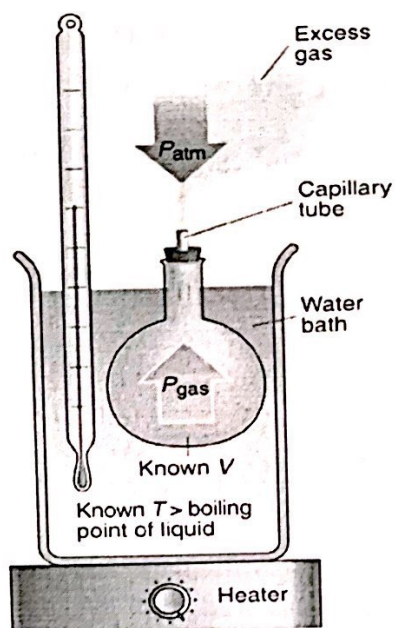
R= gases general constant

T= absolute temperature

Dumas method is considered convenient to get correct results. It depends on finding volatile liquid steam weight that fills certain volume in standard conditions.

Procedure:

1) Take a rounded flask, close it with aluminum foil, and punch it with a pin to get rid of the air and to get equal internal and external pressure, and then record the weight of the empty flask.

2) Put (3ml) of an anonymous volatile liquid in the flask, put aluminum foil, put the flask in water bath at 100°C, and wait till liquid boiling and last drop vapors.

3) Close the hole with your hand, weight the flask, and record the weight, which represents flask weight + liquid vapor weight.

Excess gas

P_{atm}

Capillary tube

Water bath

P_{gas}

Known V

Known T > boiling point of liquid

Heater

4) Take to the rounded flask, fill it with water then pour the water into a graduated cylinder whose volume similar to water volume=flask volume.

Calculations:

Apply the general law for gases.

$$PV = nRT$$

$$PV = \frac{wt}{M.wt} RT$$

Where:

P= pressure (1 atm)

V= flask volume = steam volume (ml) convey to (ltr)

n= number of moles $= \dfrac{wt}{m.\,wt}$ where

wt= liquid vapor weight = weight of the flask with vapor − empty flask weight in gr.

m. wt = molecular weight in gr/mol

R= gases general constant $= 0.082 \dfrac{ltr.atm}{mol.Kelvin}$

T= temperature of water bath = (100+273)K

$$1atm \times ltr = \frac{gm}{?} \times \frac{ltr.atm}{mol.\,K} * K$$

$$M.wt = gm/mol$$

SECOND EXPIREMENT

The relation between gas volume and temperature, and finding the absolute Zero

3

THIRD EXPIREMENT
Finding viscosity, absolute density and ratio of volatile liquid

The Theoretical Part:

Viscosity can be defined as liquid reluctance during its flow; it can be measured using Viscometer. To understand viscosity concept river strips flow is taken as an example; it is noticed that the water strips that are close to the coast are mostly static, while distance increases water flow becomes faster, which is the most at the center of the river. The dynamic strip tries to slow dawn the neighboring strips, however there is a friction between strips.

Accordingly, the dynamic liquid in a tube can be regarded as strips moving in different speeds, and the strips that are close to the tube static and the speed increases as we become close to the center; so there will be a decline in speed between strips due to the affective friction force between the different strips, and this power is responsible for liquid viscosity. Experiment shows that the force needed to get constant difference between balanced strips for a liquid moving in same direction is directly proportional with speed difference (u) and area (A) for two strips surface tangency, and is inversely proportional with distance (d) between the two strips, as:

$$F \propto \frac{Au}{d} \dots\dots\dots\dots\dots\dots\dots (1)$$

$$F = \mu \frac{Au}{d} \dots\dots\dots\dots\dots\dots (2)$$

Where μ is proportional constant that is pronounced ('eta) and is called viscosity coefficient.

Viscosity measuring unit is (poise) which equals (dyn.cm^{-2}.sec), which the force needed to move liquid strip area (cm^2) with (1cm/sec) speed and 1 cm far from another neighboring strip. The name (Poise) taken from the scientist (Poiseuille) who identified viscosity concept.

Viscosity can be defined using two general methods, both depend on Stokes and Poiseuille equations, here we will practically measure viscosity depending on Poiseuille equation by which he show the relation between viscosity and liquid flow speed in a thin long tube its radius (r) in time (t) under constant pressure (p) and its length (l) 1 cm.

$$\mu = \frac{\pi p r^4 t}{8LV} \dots\dots\dots\dots\dots\dots (3)$$

Where, V represents liquid volume that flows in the capillary, so if times of flowing of equal volumes of two liquids in the same capillaries and under same conditions, equation will be:

$$\frac{\mu_1}{\mu_2} = \frac{p_1 . t_1}{p_2 . t_2} = \frac{d_1 . t_1}{d_2 . t_2} \dots\dots\dots\dots\dots (4)$$
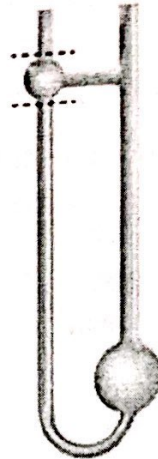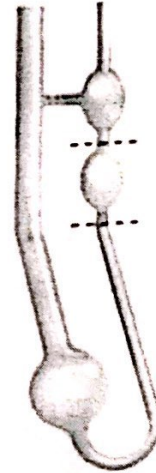
4

Where $p \propto d$

Viscosity can be measured using viscometer, which is used to measure polymeric solutions viscosity and their molecular weights, so there are three types of viscometer, as follows:


Ubbelhode   Ostwald   Cannon-Fenske

Procedure:

1. Take a dry and clean viscometer, and put a volatile liquid from (f) till the distention (e) get fill.
2. Pull the liquid using rubber tube from (a) side till it reached remark (c), then calculate the time that liquid needs to descent from (a) to (d), this step should be repeated until make sure of descent time (t_1) in sec.
3. Repeat step 2 after viscometer get dry and calculate water descent time (t_2) in sec, using same method.
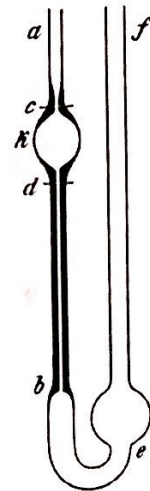
Calculations:

The proportion of the liquid to the distilled water is to be calculated:

$$\frac{\mu_1}{\mu_2} = \frac{t_1.d_1 \, Liquid}{t_2.d_2 \, H2O}$$

Where, μ_1 = volatile liquid viscosity

    μ_2 = distilled water viscosity = 909×10^{-4} n/m^2.sec

    t_1 = time of liquid descent in sec.

    t_2 = time of distilled water descent in sec

    d_1 = liquid density kg/m^3

    d_2 = distilled water density kg/m^3

5

# Finding the Absolute Density and Relative Density of a Volatile Liquid:

The **absolute density** can be defined as "substance volumetric mass density, i.e. substance mass per unit volume at a specified temperature". It is measured in gm/vm^3 or kg/m^3.

$$Absolute\ density(\rho) = \frac{mass\ (m)}{volume\ (V)}$$
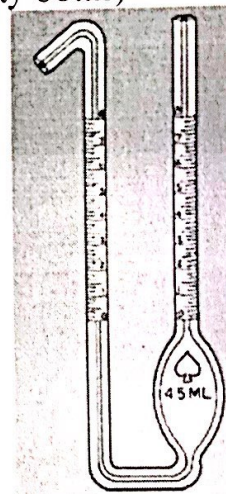
Relative density: is the ratio of the density of a substance (volatile liquid) to the density of a given reference material (distilled water). It has no units.

$$Relative\ density\ (RD) = \frac{density\ of\ volatile\ liquid}{density\ of\ distilled\ water}$$

Density is measured using pycnometere (density bottle)
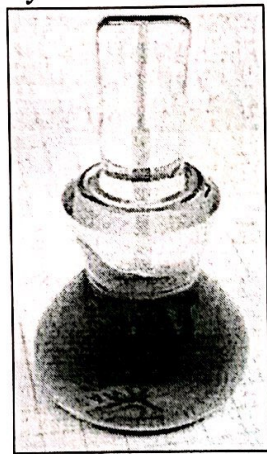
Density Bottle

Pycnometere

Procedure:
1. Take a clean and dry density bottle, weight it empty with the stopper, and then record the weight.
2. Fill the bottle with the volatile liquid up to the nozzle and close it with the stopper and dry its external side, and weight it (bottle + volatile liquid).
3. Spill the liquid and wait until the bottle get dry, repeat step 2 using distilled water, and record the weight.

Calculations:
a. Absolute density:
$w_1 = volatile\ liquid\ weight = bottle\ with\ luiquid - empty\ bottle\ weight$
$w_2 = distilled\ water\ weight = bottle\ with\ water - empty\ bottle\ weight$
$$V = volatile\ liquid\ volume$$
$$d_1 = volatile\ liquid\ absolute\ density = \frac{w_1}{V}\ (gm/cm^3)$$
$$d_2 = distilled\ water\ absolute\ density = \frac{w_2}{V}\ (gm/cm^3)$$

6

Density should be transferred from (gm/cm^3) into (kg/m^3) after multiply by 10^3.

b. Relative density for the volatile liquid:

$$Relative \ density \ of \ volatile \ liquid = \frac{d_1}{d_2} \quad OR \quad \frac{w_1}{w_2}$$

To verify results:

$$Absolute \ density \cong Relative \ dnsity$$

FOURTH EXPIREMENT

Finding Constant of Calorimeter

The Theoretical Part:

Most reactions are accompanied with temperature emission or absorption proportional to:

1. Substance quantity.
2. Substance physical state.
3. It does not depend on reaction path.

This temperature is called Enthalpy or heat content which is state function, i. e., it depends on substances state (reacted and products), and does not depend on reaction path. To measure such temperature, the calorimeter is used, which is a hollow metal container has two layers of glass vacuumed from air, coated with silver and put in an iron container has a wooden isolator.

Measuring temperature is carried out by reaction of known quantities of the reacted substances in the calorimeter where the emission or absorbed reaction temperature equals the emission or absorbed calorimeter temperature.

Each calorimeter has a constant called calorimeter constant (**thermal capacity** is a measurable physical quantity equals the ratio of the heat that is added to or removed from an object leads to temperature change for $1^{\circ}C$). This constant is used in all experiments but the same calorimeter has to be used.

The specific heat is defined as "the amount of heat per unit mass (1gr) that is required to raise the temperature one degree Celsius.

7
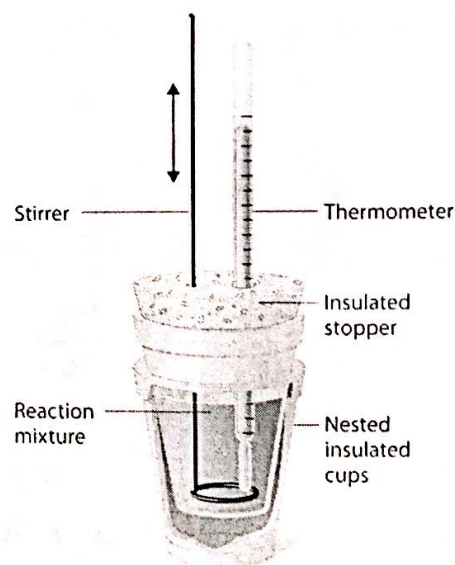
$$spcific\ heat = \frac{thermal\ capacity}{mass}$$

$$heat\ quantity = (mass \times spesific\ heat) \times temperature\ difference$$

$$heat\ quantity = thermal\ capacity \times temperature\ difference$$

$$q = C.\Delta t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where $q = heat\ quantity$

$C = thermal\ capacity$

$\Delta t = temperature\ difference$

Due to the fact that enthalpy or heat content ΔH:

Then

$$\Delta H = q_p \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Then compensate (2) in (1):

$$\Delta H = C.\Delta t$$

$$\therefore C = \frac{\Delta H}{\Delta t}$$

N.B.:

$$Thermal\ capacity = \frac{\Delta H}{\Delta t}$$

$$Spcific\ heat = \frac{thermal\ capacity}{mass}$$

Calorimeter constant units are $cal/\,^{\circ}C\ or\ K$ OR $Kcal/\,^{\circ}C\ or\ K$

Procedure:

1. Clean the calorimeter, put (100 ml) of distilled water, stir with a stir rod, and then record temperature each 30 sec. till its constancy.
2. Add (3 ml) of concentrate H_2SO_4 to the distilled water, so temperature will rise when acid is added and then it reduces. Record temperature each 30 sec. till its constancy.

8

3. Using a pipette, suck (10 ml) of solution, put in a conical flask, add 2 drops of phenolphthalein, then titrate solution by adding (NaOH 1N) until pick color appears, and record the volume.

Calculations:

1) Draw the chart between temperature and time firstly for the distilled water only, and then after adding H_2SO_4.
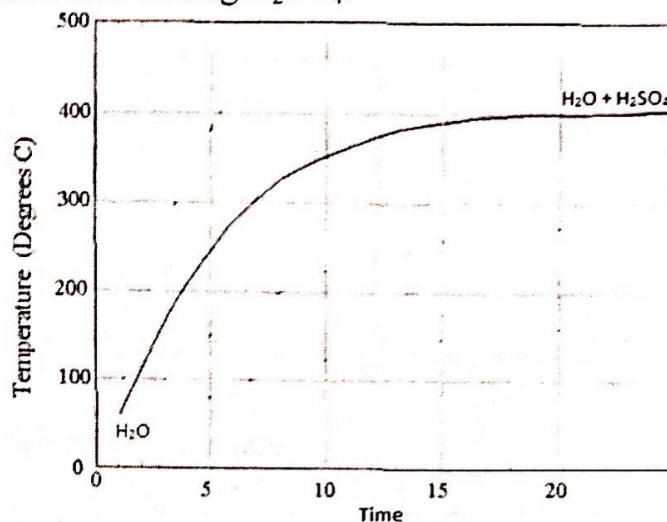
2) Measure H_2SO_4 normality resulted from its titration with NaOH using drying law.

$$N_1 V_1 = N_2 V_2$$
$$\text{NaOH} \qquad H_2SO_4$$
$$N_1 \times V_1 \,(from\ burette) = N_2 \times 10ml$$

3) Calculate (ΔH) from the following table depending on the calculated normality value; if it was equal to one of the available values then the equivalent value of (ΔH) should be taken and be compensated in calorimeter constant law.

(ΔH) Emission Temperature Quantity in $((Kcal)$	Final Normality of Solution $((Eq.\,L^{-1})$	Volume of added Acid
0.945	1.100	3.00
0.784	0.918	2.50
0.718	0.842	2.30
0.473	0.552	1.50
0.242	0.227	0.75
0.191	0.217	0.60

9

While, when the value was not available in the above table; the correlation between (ΔH) and normality (N) found in the table is draw, and then the calculated normality is to be drawing on the chart and draw a vertical line on (ΔH), the equivalent value is compensated in the calorimeter constant law:
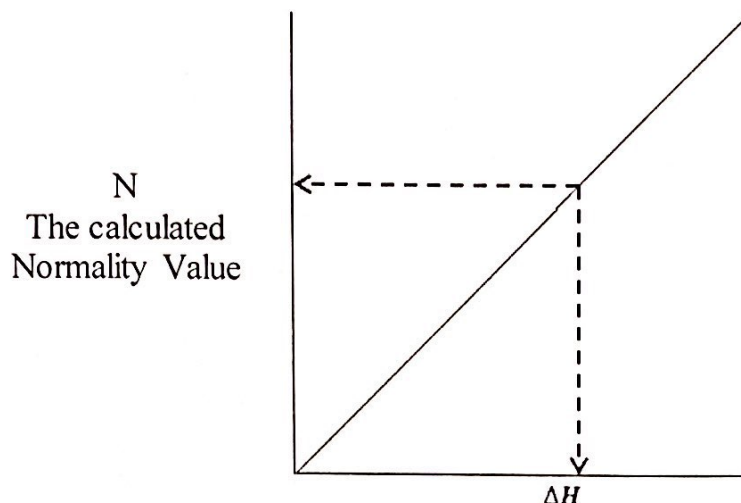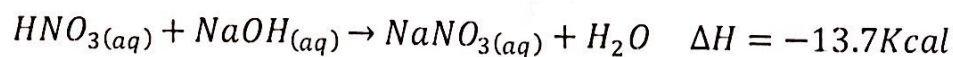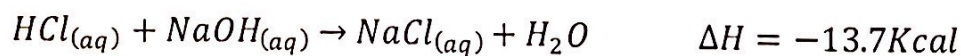

4) Calculate calorimeter constant.

$$C = \frac{\Delta H \ (from \ the \ table)}{\Delta t (from \ the \ chart \ for \ H_2O \ and \ H_2O + H_2SO_4)} = \frac{Kcal}{^\circ C \ OR \ K}$$

FIFTH EXPERIMENT

Finding a strong acid and strong base reaction temperature

The Theoretical Part:

The enthalpy of neutralization (ΔHn) is the change in enthalpy that occurs when one equivalent of an acid and one equivalent of a base undergo a neutralization reaction to form water and a salt. It has been shown that enthalpy neutralization for any strong acid and strong base is as follows:

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O \qquad \Delta H = -13.7 Kcal$$

$$HNO_{3(aq)} + NaOH_{(aq)} \rightarrow NaNO_{3(aq)} + H_2O \quad \Delta H = -13.7 Kcal$$

The value ($-13.7 Kcal$) represents enthalpy of neutralization for a strong acid and strong base, and it is a constant value because it represents the neutralization for all acids.

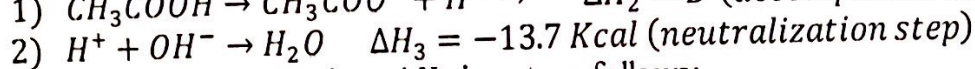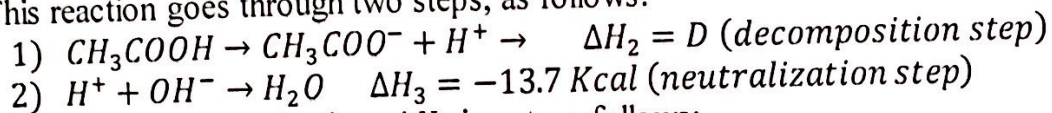$$H^+ + OH^- \rightarrow H_2O \qquad \Delta H = -13.7 Kcal$$

For this reason, each neutralization reaction consists of H^+ and OH^- ions union that produce unionized water, this for the strong acid. Whereas, the weak acid with base the enthalpy of neutralization value differs from that of the

10

strong acid, because of the fact that the weak acid firstly suffers decomposition and then union of H^+ and OH^- ion, as shown below:

$$CH_3COO^-H^+ + Na^+OH^- \rightarrow CH_3COONa + H_2O$$
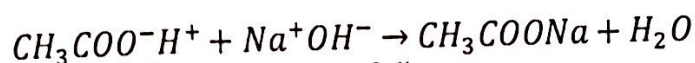
This reaction goes through two steps, as follows:

1) $CH_3COOH \rightarrow CH_3COO^- + H^+ \rightarrow \quad \Delta H_2 = D \ (decomposition \ step)$
2) $H^+ + OH^- \rightarrow H_2O \quad \Delta H_3 = -13.7 \ Kcal \ (neutralization \ step)$

By combining both equations ΔH_1 is got, as follows:

$$\Delta H_{1(nut)} = \Delta H_{2(ion)} + \Delta H_3$$

$$\Delta H_{nut} = D + (-13.7)$$

∴ The decomposition temperature (D) of the weak acid can be calculated by using enthalpy neutralization.

So,

$$heat \ of \ neutralization = heat \ of \ ionization \mp 13.7$$

Procedure:

1. Mix (3.5 ml) of distilled water with (6.5 ml) of the concentrated nitric acid (HNO_3) to prepare (10 ml) of nitric acid solution.
   This step is the most important step in which a graduated cylinder because the acid is very strong (the prepared acid consists of 50% water).
2. Clean the calorimeter well, put (33 ml) of NaOH (1N) solution and (66 ml) of distilled water (H_2O), mix substances well using stirring rod, and then record reaction temperature each (30 sec.) until consistency.
3. Add (3.3 ml) of diluted nitric acid that prepared in step (1) to the calorimeter contains.
4. Add two drops of orange methyl to calorimeter contains, the following are to be noticed:
   a) If the contains of the calorimeter were yellow, it means that a portion of the base is not neutralized with nitric acid, in this case (10 ml) of contains are taken and titrate with HCl 0.1N until the neutral point is reached.
   b) If the contains of the calorimeter were red, it means that all the base is neutralized with the acid, in this case no need for titration with HCl.

N.B.: the above mentioned reaction is considered two reactions, in the first one the reaction is between acid and water so dilution heat is got, while in the second the reaction is between acid and base so neutralization heat is got. However, dilution heat (solution heat) should be found and subtracted from the total value (dilution heat + neutralization heat) to get neutralization heat only.

5. To calculate dilution heat, pour the calorimeter contains, clean it well, put (99 ml) of distilled water, and then record temperature each 30 sec. till its constancy. Afterwards, add (3.3 ml) of nitric acid prepared in step (1), mix substances well using stirring rod, and then record temperature each 30 sec. till its constancy.
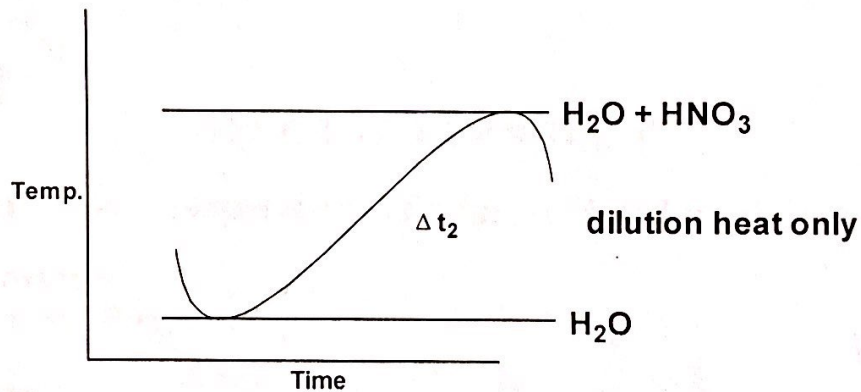
Calculations:

1) In steps (2 and 3) of the procedures, draw the chart for correlation between time and temperature.
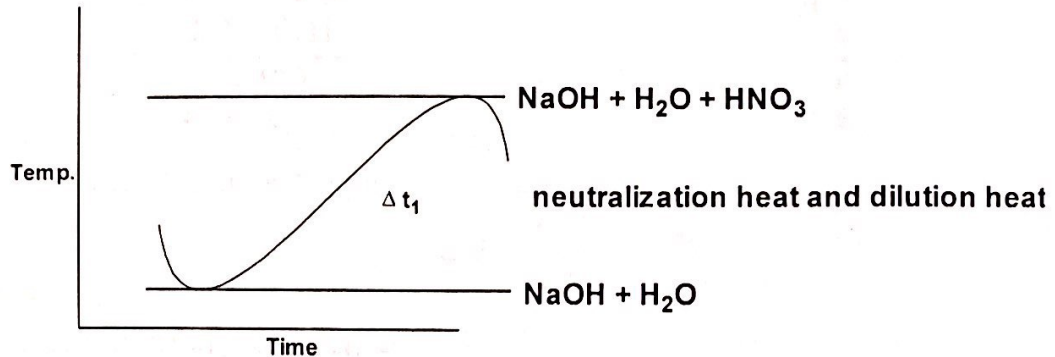
Neutralization and Dilution Process

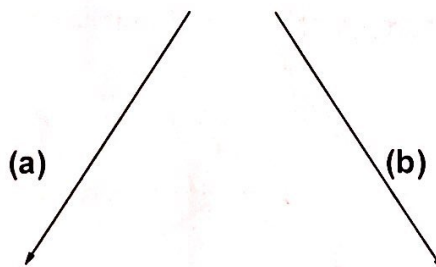2) Draw a chart between temperature and time, in step (5).

Dilution Process

Calculate the temperature raise due to neutralization that equals:

$$\Delta t = \Delta t_1 - \Delta t_2$$

3) Calculate the number of base (Y) equivalents, as follows:

(a)   (b)

If calorimeter contains were **yellow**:
Calculate the volume of nonequivalent base with HNO_3 by titrating it with

If calorimeter contains were **red**:

12

HCl 0.1N

$$N_1V_1 = N_2V_2$$
$$HCl = NaOH$$
$$0.1 \times V_1 = N_2V_2$$
$$Y = \frac{33 - 0.1V}{1000}$$
$$Y = eq$$

$$Y = \frac{33}{1000} \times 1N$$
$$Y = \frac{33}{1000}$$
$$Y = eq$$

4) Calculate reaction temperature as follows:

$$\Delta H = \frac{C.\Delta t}{Y}$$

Where,

ΔH: Neutralization temperature.

C: Calorimeter constant.

Y: The number of base (Y) equivalents.

Δt: Difference in temperature raise due to neutralization.

$$\Delta H = \frac{Kacl/^{\circ}C \cdot ^{\circ}C}{eq} = \frac{Kcal}{eq}$$

SIXTH EXPERIMENT

## Finding reaction temperature of weak acid and weak base

The Theoretical Part:
It is same as in Experiment (5).

Procedure:
1. Take calorimeter with a known constant, put (25 ml) of $NaOH$ (1N), add (75 ml) of distilled water, and then record temperature each 30 sec. till its constancy.
2. Open calorimeter stopper; add to the above base solution (25 ml) of acetic acid (1N), and then record temperature each 30 sec. till its constancy.

Calculations:
1) Draw the chart for correlation between temperature in ºC and time in sec to get Δt.
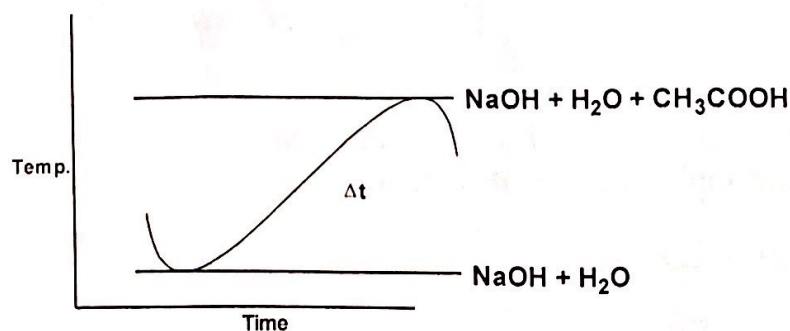
2) Calculate neutralization temperature (ΔH) for the weak acid, as follows:

$$\Delta H = \frac{C.\Delta t}{Y}$$

Where,
C: Calorimeter constant (0.1 Kcal/^{o}C).
ΔH: Neutralization temperature (Kcal/eq).
Δt: Difference in temperatures.
Y: The number of base (Y) equivalents that neutralized the acid (eq).

$$Y = \frac{1N \times 25ml}{1000L} = 0.025eq$$

3) Calculate decomposition temperature (D), as follows:

$\Delta t_{neut} = D + (-13.7)$
$D = (\quad)????$
$\Delta H = -13.7$ that is neutralization or union temperature.

$$H^+ + OH^- \rightarrow H_2O$$

SEVENTH EXPIREMENT

Finding magnesium electrode voltage using a thermodynamic method

The Theoretical Part:
This electrode can be found using the electrical methods, which are easier than the other methods, because they are direct ones.
In this experiment, the voltage will be measured using the thermodynamic method using   and thermodynamic laws as in the following reaction:

$$Mg + 2H^+ \rightarrow Mg^{+2} + H_2 \uparrow$$
$$(s) \quad (eq) \quad (aq) \quad (g)$$
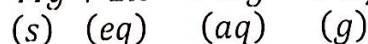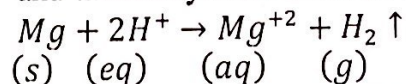
To find electrode voltage (E^o), it is required to find (ΔH^o, ΔS^o and ΔG^o).

Procedure:
1. In a clean calorimeter, put (100 ml) of H_2SO_4 (1N), stir with stirring rod, and then record temperature each 30 sec. until constancy.
2. Weight (0.25 gr) of Magnesium bar, add water; the temperature will rise directly after addition, record this temperature, and then record temperature each 30 sec. until constancy.

Calculations:
1) Calculate the standard reaction temperature (ΔH^o) for each mole of Mg, which represents the emission temperature from magnesium bar to H_2SO_4.

$$\Delta H^o = \frac{C.\Delta t(t_1 - t_2)}{Y}$$

Where,

قيمة DH سالبة

14

ΔH^o: The standard reaction temperature (Kcal/mol).

C: Calorimeter constant (Kcal/°C OR Kcal/K).

Δt: Difference in temperature between before and after adding Mg.

Y: Number of moles

$$Mg = \frac{weight}{atomic\ weight} = \frac{0.25}{24.3} = 0.0103\ mol$$

2) Use entropy molar that is calculate at ($298K^o$) and equals ($20.5 \frac{Jol}{mol.K}$)

$$\Delta S^o = \left(S^o_{Product} - S^o_{Reactant} \right)$$

$$\Delta S^o = \left(S^o_{Hz} - S^o_{Mg^{+2}} \right) - \left(S^o_{Mg} - S^o_{H^+} \right)$$

3) Calculate the change in standard free energy, as follows:

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Where,

T: is the highest temperature that the thermometer records after adding magnesium bar.

$$T = (T^oC + 273)$$

ΔH^o must be transfer from Kcal/mol into J/mol, as follows:

$1 cal = 4.18 J$

So,

$$Kcal \rightarrow cal \rightarrow J \xrightarrow{it\ becomes} J/mol$$

4) Calculate electrode voltage (E^o) whose unit is (V), as follows:

$$E^o = \frac{-\Delta G^o}{nF}$$

Where,

$n = 2$: Oxidation number of Mg^{+2}

F: Faraday constant which equals 96500 C/mol.

E^o: Electrode voltage in (V) (J/C).

ΔG^o: The Standard free energy in J/mol.

5) Draw the chart of the correlation between temperature and time, as follows:

15