## PHYSICAL CHEMISTRY PRACTICALS USING THERMO-CHEMISTRY

## Introductory Remarks

Thermochemistry deals with heat changes taking place during chemical reactions. Reactions accompanying evolution or absorption of heat are known as exothermic or endo thermic reactions, respectively. The heat of reaction for a chemical process depends upon the following factors:

1) Nature of reacting substances
2) Physical state of reacting substances (e.g. solid, liquid and gaseous state are a particular allotropic form)
3) The fraction of reactive species taking part in the reaction

Heat changes are generally expressed in calorie. It is defined as the amount of heat required to raise the temperature of 1 g of water from $15^{\circ} \mathrm{C}-16^{\circ} \mathrm{C}$. It is represented as cal. Another conventional unit is joule (J) (Came by the name of James Prescott Joule). 1 cal=4.184 J.

A thermochemical result is expressed by writing chemical formula of reacting substances separated by coma (,) together with the amount of heat change which has accompanied the reaction. A coma is used to separate the chemical formula of reacting species when they combined directly, while a colon (:) when the reaction take place, but there is no direct combination. Thus, $(\mathrm{N}, 3 \mathrm{H})$ indicates that nitrogen and hydrogen react directly to form $\mathrm{NH}_{3}$, while $\left(\mathrm{NH}_{3}: 3 \mathrm{Cl}_{2}\right)$ indicates that ammonia and chlorine react to form HCl and $\mathrm{NCl}_{3}$.

Thermochemical variables can be classified as follows
i) Heat of formation
ii) Heat of solution
iii) Heat of dilution
iv) Heat of hydration
v) Heat of neutralisation
vi) Heat of reaction
vii) Heat of combustion

Demonstration of measurement of all these are beyond scope in this book. We will demonstrate only Heat of dilution, Heat of neutralisation and Heat of reaction.

## Description of calorimeter

A calorimeter is a device used to measure the heat flow of a chemical reaction or physical change. The process of measuring this heat is called calorimetry. A basic calorimeter consists of a metal container of water above a combustion chamber, in which a thermometer is used to measure the change in water temperature. However, there are many types of more complex calorimeters.

The basic principle is that heat released by the combustion chamber increases the temperature of the water in a measurable way. The temperature change may then be used to calculate the enthalpy change per mole of substance A when substances A and B are reacted.

The equation used is:

$$
\mathrm{q}=\mathrm{C}_{\mathrm{v}}\left(\mathrm{~T}_{\mathrm{f}}-\mathrm{T}_{\mathrm{i}}\right)
$$

where:

- $q$ is the amount of heat in joules
- Cv is the calorimeter's heat capacity in joules per Kelvin ( $\mathrm{J} / \mathrm{K}$ )
- $\mathrm{T}_{\mathrm{f}}$ and $\mathrm{T}_{\mathrm{i}}$ are the final and initial temperatures


## (I) TO FIND WATER EQUIVALENT OF CALORIMETER AND DETERMINATION OF HEAT OF DILUTION OF $\mathrm{H}_{2} \mathrm{SO}_{4}$.

Chemicals and Apparatus: Sulphuric acid, oxalic acid, NaOH , distilled water, calorimeter.

Theory: Heat capacity or water equivalent of a calorimeter is defined as the number of calories required to heat the calorimeter by unit temperature. If $M$ is mass of the calorimeter and S is the specific heat then heat capacity is obtained by multiplying M by S . During the heat changes the calorimeter takes up some of the heat evolved, it should be taken into account by determining the water equivalent (w.e.) or heat capacity of the calorimeter.

In case of glass vessels, the value of w.e. is found for such part of the vessel which is actually in contact with the reacting system. In this case the method of obtaining w.e by multiplying the mass and specific heat of the material of the vessel is not significant. During the experiments equal volumes are used so that the area of the calorimeter in contact with the system remains unaltered as far as possible.

Heat of dilution is a quantity of heat evolved or absorbed when a solution containing 1 g -mol of a substance in unknown quantity of water or other solvent is diluted by known quantity of that solvent.

## Procedure:

1) Calculate density of water at two different temperatures, sulphuric acid using method described in Expt. 2, Chap 4.
2) Prepare 0.1 (M) 100 mL oxalic acid by accurate weighing (Table 1) and then standardize freshly prepared NaOH solution (Table 2). With this standardized NaOH solution calculate the strength of the supplied sulphuric acid exactly (Table $3)$.
3) Take 25 mL of distilled water in the calorimeter and record its temperature. Take some water in a beaker and heat it up to a temperature about $30-35^{\circ} \mathrm{C}$ than the room temperature.
4) Pipette out 24 mL hot water and add it to another beaker and record its temperature after every half minute for five minutes
5) Add this hot water quickly to the water in calorimeter.
6) Mix the content properly and record the temperature after every half minute.
7) Plot a graph of Temperature versus time and from it findout the temperature of hot water and that of mixture at the time of mixing.
8) On the graph draw a vertical line for the moment of mixing (when half volume of water has been transferred) and extrapolate the temperature time curve of hot water and mixture to this vertical line. The point of intersection gives the desire temperature (Figure 2.1).


Figure 2.1: Experimental plot Time Versus. Temperature
9) Now perform another experiment and take 25 mL distilled water in the calorimeter and note its temperature.
10) Pipette out known quantity (say 5 mL ) sulphuric acid of known strength. Transfer this acid into the calorimeter and mix the content of calorimeter with the pipette itself. Record the temperature with time as done in previous part of the experiment and plot temperature-time curve. Note the maximum temperature attained.

## Observations:

Temperature $=$. $\qquad$ ${ }^{\circ} \mathrm{C}$
$\mathrm{W}_{1}=$ weight of density bottle
$\mathrm{W}_{2}=$ weight of pyknometer + water
$\mathrm{W}_{3}=$ weight of pyknometer + liquid
Therefore, $\left(\mathrm{W}_{2}-\mathrm{W}_{1}\right)=\mathrm{W}=$ weight of water at $\mathrm{t}^{\circ} \mathrm{C}$
$\left(W_{3}-W_{1}\right)=W^{\prime}=$ weight of liquid at $t^{\circ} \mathrm{C}$
Thus, Density of liquid/water $\left(\mathrm{d}^{t}\right)=\left(\mathrm{W}^{\prime} / \mathrm{W}\right) * \mathrm{D}$.
Table 1: Preparation of 100 mL 0.1 (M) Oxalic acid
Molecular weight of oxalic acid $\left(\mathrm{C}_{2} \mathrm{O}_{4} \mathrm{H}_{2} .2 \mathrm{H}_{2} \mathrm{O}=126.03\right)$

| Initial <br> mass (g) | Final mass <br> $(\mathrm{g})$ | Mass of oxalic <br> acid transferred <br> $(\mathrm{g})$ | Mass of <br> oxalic acid to <br> be taken <br> $(\mathbf{g})$ | Strength of <br> oxalic acid <br> solution (M) |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | 0.12603 |  |

Table 2: Standardization of NaOH against oxalic acid

| S. No. | Vol. of oxalic <br> acid taken (mL) | Volume of NaOH <br> consumed (mL) | Most precise <br> reading (mL) |
| :---: | :---: | :---: | :---: |
| 1 | 10 |  |  |
| 2 |  |  |  |
|  |  |  |  |
| 3 |  |  |  |

Table 3: Standardization of sulphuric acid against $\mathbf{N a O H}$

| S. No. | Vol. of sulphuric <br> acid taken (mL) | Volume of NaOH <br> consumed (mL) | Most precise <br> reading (mL) |
| :---: | :---: | :---: | :---: |
| 1 | 10 |  |  |
| 2 |  |  |  |
| 3 |  |  |  |

## I) General Observations

Volume of cold water $=\mathrm{V}_{1} \mathrm{~mL}$
Initial temperature of water $=t_{1}{ }^{\circ} \mathrm{C}$.
Volume of hot water mixed $=V_{1} \mathrm{~mL}$
Temperature of hot water $=\mathrm{t}_{2}{ }^{\circ} \mathrm{C}$
Temperature of mixed solution $=t_{3}{ }^{\circ} \mathrm{C}$

## II) Calculation of Density (D) Of Liquid/Water

Volume of cold water taken $=V_{3} \mathrm{~mL}$
Initial temperature of water $=\mathrm{t}_{1}{ }^{\circ} \mathrm{C}$
Volume of sulphuric acid $=\mathrm{V}_{4} \mathrm{~mL}$
Highest temperature after addition $=\mathrm{t}_{4}{ }^{\circ} \mathrm{C}$
Strength of sulphuric acid=x (M)

## Calculations:

I) Heat taken by calorimeter and water $=\left(W+V_{1} \times d_{1}\right) \times\left(\mathrm{t}_{3}-\mathrm{t}_{1}\right) \mathrm{cal}$.

Here $\mathrm{d}_{1}$ is the density
$\mathrm{W}=$ weight of calorimeter .
Heat given out by hot water $=V_{2} \times \mathrm{d}_{2} \times\left(\mathrm{t}_{2}-\mathrm{t}_{3}\right)$
Heat taken up=heat given up
Thus, $\left(\mathrm{W}+\mathrm{V}_{1} \times d_{1}\right) \times\left(\mathrm{t}_{3}-\mathrm{t}_{1}\right)=V_{2} \times \mathrm{d}_{2} \times\left(\mathrm{t}_{2}-\mathrm{t}_{3}\right)$

$$
\mathrm{W}=\frac{V_{2} \times \mathrm{d}_{2} \times\left(\mathrm{t}_{2}-\mathrm{t}_{3}\right)-V_{1} \times \mathrm{d}_{1} \times\left(\mathrm{t}_{3}-\mathrm{t}_{1}\right)}{\left(\mathrm{t}_{3}-\mathrm{t}_{1}\right)}
$$

II Heat of dilution of $x(M)$ sulphuric acid $=\left(W+V_{3} d_{1}+V_{4} d_{4}\right) \times\left(t_{4}-\mathrm{t}_{1}\right) \mathrm{cal}$.
Results: Heat capacity of the calorimeter $=\ldots \ldots . \mathrm{Cal}$.
Heat of dilution of sulphuric acid $=\ldots . \mathrm{Cal}$
Precautions: 1) The temperatures should be recorded accurately up to the least count of the thermometer
2) The calorimeter should be completely insulated.

# (II) TO FIND OUT HEAT OF NEUTRALISATION OF NaOH AND HCl 

Chemicals and Apparatus: Oxalic acid, HCl and NaOH , calorimeter, thermometer, stirrer and burette, pipette, measuring flask

Theory: Heat of neutralisation is the quantity of heat evolved on neutralisation of 1 g -equivalent of an acid by 1 g -equivalent of a base in dilute solution. When dilute solutions of strong acids are neutralised by strong base of about same concentration. The heat evolved is found to be practically constant ( 13.7 kcal ) for all strong acids and bases. Strong acids and bases in their dilute solutions are almost completely ionized and on neutralisation they result in formation of salt formed by their union, so that the only change can be said to be the formation of water by reaction of $\mathrm{H}^{+}$and ${ }^{-} \mathrm{OH}$ ions, as shown below:

$$
\begin{aligned}
& \mathrm{NaOH}+\mathrm{HCl}=\mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}+13.7 \mathrm{kcal} \\
& \text { or, } \mathrm{Na}^{+}+{ }^{-} \mathrm{OH}+\mathrm{H}^{+}+{ }^{-} \mathrm{Cl}=\mathrm{Na}^{+}+\mathrm{Cl}^{-}+\mathrm{H}_{2} \mathrm{O}+13.7 \mathrm{kcal} \\
& \text { or, } \mathrm{H}^{+}+{ }^{-} \mathrm{OH}=\mathrm{H}_{2} \mathrm{O}+13.7 \mathrm{kcal}
\end{aligned}
$$

It is obvious from the above reactions that heat of neutralisation of strong acids by strong bases represents the heat of combination of 1 g -eqv $\mathrm{H}^{+}$ion with same g-eqv of ${ }^{-} \mathrm{OH}$ to form water.

Procedure:1) Determine water equivalent of calorimeter as described in Expt. 1
2) Prepare ( $\mathrm{M} / 2$ ) oxalic acid by dissolving 15.75 g oxalic acid in 250 mL distilled water
3) Prepare $\sim 2$ (M) NaOH by dissolving 85 g NaOH in 1 litre.
4) Standardise the NaOH solution against oxalic acid and prepare exact 1 (M) 250 mL NaOH .
5) Prepare nearly 2 (M) HCl by diluting 50 mL concentrated HCl to 250 mL and standardize it by titrating against standard $1(\mathrm{M}) \mathrm{NaOH}$.
6) Prepare exact 1 (M) 250 mL HCl by proper dilution. Recheck it by titrating against standard NaOH solution.
7) Take 100 mL 1 (M) HCl in calorimeter and record the temperature after every half minute for five minutes. Repeat the procedure for 100 mL 1 (M) NaOH and plot the temperature time curve for both the experiments
8) Pour NaOH quickly into the calorimeter containing HCl , taking care to avoid splashing. Mix it properly and record the temperature readings after every half minute for five minutes. After the completion of experiments add 1 drop of phenolphthalein to ascertain the complete neutralisation.
9) Plot a graph between temperature and time (Figure 2.2).
10) It has been observed that after mixing HCl and NaOH the temperature rises quickly in the beginning and starts to form irregularly in the beginning and later on in a regular manner. Record the temperature of mixture at the time of mixing
11) Draw a vertical line at the time of mixing (when half quantity of NaOH has been added). Extend the curves through the points when temperature begins to fall regularly. The point of intersection will give the final temperature after mixing
12) To obtain the actual temperature at the time of mixing plot the temperature vs. time for each solution. The temperature of solution before mixing can be taken as: $\left(\frac{t_{1}+\mathrm{t}_{2}}{2}\right)$, as they are mixed in equal volumes.


Figure 2.2: Plot of temperature versus Time
Observations: Volume of cold water $=\mathrm{V}_{1} \mathrm{~mL}$
Initial temperature $=\mathrm{t}_{1}{ }^{\circ} \mathrm{C}$
Volume of hot water added $=\mathrm{V}_{1} \mathrm{~mL}$
Temperature of hot water $=\mathrm{t}_{2}{ }^{\circ} \mathrm{C}$
Final temperature after mixing $=\mathrm{t}_{3}{ }^{\circ} \mathrm{C}$
Calculation: (I) If W is water equivalent of calorimeter, then, heat taken by calorimeter and water $=\left(W+V_{1}\right) \times\left(t_{3}-t_{1}\right) c a l$.

Heat released by hot water $=V_{2} \times\left(t_{2}-\mathrm{t}_{3}\right) \mathrm{cal}$
Heat taken up= heat given out

$$
\left(W+V_{1}\right) \times\left(t_{3}-t_{1}\right)=V_{2} \times\left(t_{2}-t_{3}\right)
$$

Or, $W=\frac{V_{2} \times\left(t_{2}-t_{3}\right)-V_{1} \times\left(t_{3}-t_{1}\right)}{\left(t_{3}-t_{1}\right)}$

Rise in temperature $=\left(t_{5}-\mathrm{t}_{4}\right)^{\circ} \mathrm{C}$
Heat given out by the solution $=\left(V_{3}+V_{4}+W\right) \times\left(t_{5}-\mathrm{t}_{4}\right)=\mathrm{Q}$ cal
Therefore, Q cal. of heat is given out by reaction of $0.1(\mathrm{M})$ of HCl and $0.1(\mathrm{M})$ NaOH .

So, molar heat of neutralisation $=\frac{\mathrm{Q} \times 1 \text { mole }}{0.1} \operatorname{cal}=(10 \times \mathrm{Q})$ cal.
Result: Heat of neutralisation of HCl and $\mathrm{NaOH}=\ldots . \mathrm{Cal}$

## (III) TO FIND RELATIVE STRENGTH OF TWO ACIDS BY ESTIMATING HEAT OF NEUTRALISATION

Chemicals and Apparatus: Oxalic acid, $\mathrm{NaOH}, \mathrm{HCl}$ and acetic acid, calorimeter set up

Theory: The strength of an acid or is the measure of its extent of ionization (Degree of dissociation) at a given concentration. If the heats of neutralisation of HCl acid (here onward hydrochloric acid or HCl acid will be denoted as HCl only) and acetic acid against NaOH are x and y calories, respectively. If to a mixture containing 1 g -eqv of each acid, 1 g -eqv of NaOH is added, HCl and acetic acid will consume NaOH in the ratio of their ionization. Assuming n g-eqv out of 1 g -eqv of NaOH are consumed by HCl and remaining (1-n) by acetic acid. nx and (1-n)*y cal will be produced by neutralisation of HCl and acetic acid, respectively. Suppose $z$ is experimental heat evolved by the mixture, then:

$$
\text { or, } n=\left(\frac{z-y}{x-y}\right) \quad n x+(1-n) y=z
$$

The ratio n : (1-n) gives the relative strength of HCl and acetic acid
Procedure:1) Determine water equivalent of calorimeter as described in Expt. I
2) Prepare (M/2) oxalic acid by dissolving 15.75 g oxalic acid in 250 mL distilled water (Table 1).
3) Prepare $\sim 2$ (M) NaOH by dissolving 85 g NaOH in 1 litre
4) Standardise the NaOH solution against oxalic acid (Table 2) and prepare exact 1 (M) 250 mL NaOH .
5) Prepare nearly $2(\mathrm{M}) \mathrm{HCl}$ by diluting 50 mL concentrated HCl to 250 mL and standardize it by titrating against standard $1(\mathrm{M}) \mathrm{NaOH}$ (Table 3).
6) Prepare exact 1 (M) 250 mL HCl by proper dilution.
6) Prepare $\sim 2(\mathrm{M})$ acetic acid by diluting 30 mL glacial acetic acid to 250 mL and standardize it by titrating against standard 1 (M) NaOH (Table 4).
6) Prepare exact 1 (M) 250 mL acetic acid by proper dilution.
7) Take 100 mL of HCl in calorimeter and neutralise it with same quantity of NaOH solution. Record the heat of neutralisation for this process. This gives x.
8) Repeat Step 7) with acetic acid. This gives y.
8) Take 125 mL of each of $1(\mathrm{M})$ acetic acid and HCl in a 250 mL volumetric flask and shake thoroughly to make a uniform mixture. This mixture contains 0.5 g-eqv per litre of each acid.
8) Add 250 mL of 0.5 (M) NaOH to this mixture and determine the heat evolved during the reaction. On multiplying this quantity by 8 (the value of heat evolved for solution containing 1 g -eqv in 1 litre), we can evaluate z .
9) Calculate the ratio $n:(1-n)$ using Eq (1).

## Observations:

Table 1: Preparation of (M/2) $\mathbf{2 5 0} \mathbf{m L}$ oxalic acid solution
Molecular weight of oxalic acid $\left(\mathrm{C}_{2} \mathrm{O}_{4} \mathrm{H}_{2} .2 \mathrm{H}_{2} \mathrm{O}=126.03\right)$

| Initial <br> mass $(\mathbf{g})$ | Final mass <br> $(\mathrm{g})$ | Mass of oxalic <br> acid transferred <br> $(\mathbf{g})$ | Mass of <br> oxalic acid to <br> be taken <br> $(\mathbf{g})$ | Strength of <br> oxalic acid <br> solution (M) |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | 15.75 |  |

Table 2: Standardization of $\mathbf{N a O H}$ against oxalic acid

| Sl. No. | Vol. of oxalic <br> acid taken (mL) | Volume of NaOH <br> consumed (mL) | Most precise <br> reading (mL) |
| :---: | :---: | :---: | :---: |
| 1 | 10 |  |  |
| 2 |  |  |  |
| 3 |  |  |  |
|  |  |  |  |

Table 3: Standardization of $\mathbf{H C l}$ acid against $\mathbf{N a O H}$

| Sl. No. | Vol. of sulphuric <br> acid taken (mL) | Volume of NaOH <br> consumed (mL) | Most precise <br> reading (mL) |
| :---: | :---: | :---: | :---: |
| 1 | 10 |  |  |
| 2 |  |  |  |
| 2 |  |  |  |


| 3 |  |  |  |
| :--- | :--- | :--- | :--- |

Table 4: Standardization of acetic acid against $\mathbf{N a O H}$

| Sl. No. | Vol. of sulphuric <br> acid taken (mL) | Volume of NaOH <br> consumed (mL) | Most precise <br> reading (mL) |
| :---: | :---: | :---: | :---: |
| 1 | 10 |  |  |
| 2 |  |  |  |
| 3 |  |  |  |

RESULT: Thus, heat of neutralisation of mixture of HCl and acetic acid is= $\left(\frac{z-y}{x-y}\right) \mathrm{cal}$

## (IV) TO FIND HEAT OF FORMATION OF MgO CALORIMETRICALLY

Chemicals and Apparatus: Mg powder, $0.5(\mathrm{M}) \mathrm{HCl}$, calorimeter set up
Theory: The thermochemical reactions involved are
(1) $\mathrm{Mg}(\mathrm{s})+2 \mathrm{H}^{+}($aq. $)=\mathrm{Mg}^{2+}($ aq. $)+\mathrm{H}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}_{1}$
(2) $\mathrm{MgO}(\mathrm{s})+2 \mathrm{H}^{+}$(aq.) $=\mathrm{Mg}^{2+}$ (aq.) $+\mathrm{H}_{2} \mathrm{O}$ (1) $\Delta \mathrm{H}_{2}$
(3) $1 / 2 \mathrm{O}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})=\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
$\Delta \mathrm{H}_{3}$
(4) $\mathrm{Mg}(\mathrm{s})+1 / 2 \mathrm{O}_{2}(\mathrm{~g})=\mathrm{MgO}(\mathrm{s})$
$\Delta \mathrm{H}_{4}$
Thus, $\Delta \mathrm{H}_{4}=\Delta \mathrm{H}_{1}-\Delta \mathrm{H}_{2}+\Delta \mathrm{H}_{3}$
The standard value of $\Delta \mathrm{H}_{3}$ at 298 K is $-68.32 \mathrm{kcal} / \mathrm{mole}$. By measuring the values of $\Delta \mathrm{H}_{1}$ and $\Delta \mathrm{H}_{2}$ we can calculate the heat of formation of $\mathrm{MgO}\left(\Delta \mathrm{H}_{4}\right)$.

Procedure:1) Determine the water equivalent of calorimeter as described in Expt. I.
2) Weigh 0.4 g of Mg metal powder.
3) Prepare standard solution of HCl of strength 0.5 (M) as described in Experiment III (Table 1, 2, 3).
4) Take 200 mL of $0.5(\mathrm{M}) \mathrm{HCl}$ in the calorimeter and record the temperature with time.
5) Add Mg metal powder to this acid and stir gently
6) Record variation in temperature with time even after Mg has dissolved. Now calculate heat of reaction $\Delta \mathrm{H}_{1}$ (Table 4).
7) Weigh 0.705 g of MgO powder and dissolve it in 200 mL 0.5 (M) HCl and calculate the heat of reaction $\Delta \mathrm{H}_{2}$ in the similar manner as described in the last step.

## Observation:

Table 1: Preparation of (M/2) $\mathbf{2 5 0} \mathbf{m L}$ oxalic acid solution

Molecular weight of oxalic $\operatorname{acid}\left(\mathrm{C}_{2} \mathrm{O}_{4} \mathrm{H}_{2} .2 \mathrm{H}_{2} \mathrm{O}=126.03\right)$

| Initial <br> mass (g) | Final mass <br> $(\mathrm{g})$ | Mass of oxalic <br> acid transferred <br> $(\mathrm{g})$ | Mass of <br> oxalic acid to <br> be taken <br> $(\mathbf{g})$ | Strength of <br> oxalic acid <br> solution (M) |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | 15.75 |  |

Table 2: Standardization of NaOH against oxalic acid

| S. No. | Vol. of oxalic <br> acid taken (mL) | Volume of NaOH <br> consumed (mL) | Most precise <br> reading (mL) |
| :---: | :---: | :---: | :---: |
| 1 | 10 |  |  |
| 2 |  |  |  |
| 2 |  |  |  |
|  |  |  |  |

Table 3: Standardization of $\mathbf{H C l}$ acid against $\mathbf{N a O H}$

| S. No. | Vol. of sulphuric <br> acid taken $(\mathbf{m L})$ | Volume of NaOH <br> consumed $(\mathbf{m L})$ | Most precise <br> reading (mL) |
| :---: | :---: | :---: | :---: |
| 1 | 10 |  |  |
| 2 |  |  |  |
| 2 |  |  |  |
|  |  |  |  |

Table 4: Calculation of heat of formation:

| Serial No. | $\Delta \mathbf{H}_{1}$ <br> $\left(\mathbf{M g}+\mathbf{2 H} \mathbf{H}^{+}\right)$ <br> cal | $\Delta \mathbf{H}_{\mathbf{2}}$ <br> $\left(\mathbf{M g O}+\mathbf{2 H} \mathbf{H}^{+}\right)$ | $\Delta \mathbf{H}_{3}$ <br> $\left(\mathbf{1} / 2 \mathbf{O}_{\mathbf{2}}+\mathbf{H}_{\mathbf{2}}\right)$ <br> cal | $\Delta \mathbf{H}_{\mathbf{3}}=\Delta \mathbf{H}_{1}-$ <br> $\Delta \mathbf{H}_{\mathbf{2}}+\Delta \mathbf{H}_{\mathbf{3}}$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 |  |  |  |  |
| 2 |  |  |  |  |
| 3 |  |  |  |  |

Result: The heat of formation of MgO is $=\ldots . \mathrm{Cal}$

## CRYOSCOPY AND EBULLIOSCOPY

## V. TO DETERMINE THE MOLECULAR WEIGHT OF THE GIVEN SOLUTE IN WATER BY DEPRESSION IN FREEZING POINT METHOD

Chemicals and Apparatus: NaCl , ice, Beckmann freezing point apparatus,
Theory: The molecular weight of a solute is determined from the formula
$m_{1}=\frac{1000 \mathrm{~K}_{f} w_{1}}{w_{2} \Delta T}$
Where, $\mathrm{K}_{\mathrm{f}}$ is freezing point constant. $\mathrm{w}_{1}$ and $\mathrm{w}_{2}$ are weight of solute and solvent. $\Delta \mathrm{T}$ is depression in freezing point.

Description of Beckmann Apparatus: The Beckmann apparatus consists of an inner tube A possessing a side tube introduces the solute. The inner tube is fitted inside another tube $\mathrm{A}_{1}$ which acts as an air jacket and ensures uniform and slower cooling of the liquid. The whole apparatus is capped in a glass jar B containing freezing mixture. Beckmann thermometer T and a small stirrer S are dipped through two holes in a cork of inner tube. A larger stirrer $S_{1}$ is introduced in the outer vessel as shown in Figure 2.3.

Setting of Beckmann Thermometer: Beckmann thermometer is constructed for measuring out small difference of temperatures at any point of the ordinary thermometer scale, but not the actual freezing points (or boiling point in specific cases). It consists of an open scale of only 5-6degree graduated in 0.01 degree. It possesses a large bulb connected with an undulated glass tubing at the top which is closed at the upper end, with the help of a fine capillary glass tube having uniform bore which runs over the porcelain scale. If we assume the zero of the thermometer is set at $20^{\circ} \mathrm{C}$ and that it is desired to set a new setting in such a way that $0{ }^{\circ} \mathrm{C}$ fall on the upper part of the scale.


Figure 2.3: Beckmann Apparatus and Beckmann thermometer
In the beginning the thermometer does not contain enough mercury and if the bulb were immersed in ice water, the mercury column would disappear into the bulb. Tilt the thermometer to transfer the mercury from the reservoir to the space above the fine capillary inseal. If the thermometer is kept in upright position, the mercury can be frequently caused to run down from the space and join the main column by a quick jerk. If this does not take place readily, the bulb of thermometer should be held in warm water, till mercury in main column rises to join the mercury at the top. On cooling the mercury will go down.

Now the bulb of thermometer is placed in a beaker containing ice. The excess mercury in the top space can return to the reservoir by inverting the thermometer and giving it a sharp tap or jerk. This process should be carried out quickly, before the mercury in the bulb become appreciable warmer. On again keeping the thermometer to ice bath the quantity of mercury increases in the thermometer. The excess amount of mercury should be removed cautiously by heating the bulb with warm water or even with the palm and forcing the excess mercury dropwise out of the capillary inseal.

If we desire to set a thermometer to a temperature above that of initial setting, the procedure will be similar.

For setting the Beckmann thermometer its bulb is placed in a beaker containing ice and then it is observed whether the mercury level is stationary on the thermometer scale or not. Stationarity indicates the proper setting of thermometer. If a stationary condition is not achieved and mercury level is much below then, it is required to add mercury from the upper reservoir. For this purpose, mercury thread is broken near the top by giving a sharp tap when the temperature of bath is slightly higher than the freezing point of pure solvent.

If mercury level is above the scale then it is required to transfer it to the upper reservoir. For this purpose, thermometer is placed in hot water and mercury is expelled until its amount is so adjusted that mercury level stays on the scale.

## Procedure:

1) Beckmann thermometer is set following the procedure described above.
2) The whole apparatus is fitted as shown in Figure 2.3.
3) 20 mL of water is taken in inner tube (A) and Beckamann thermometer is immersed in such a manner that it's bulb dips in the liquid. The liquid is stirred gently with the stirrer $S_{1}$ and allowed to super cool a bit below its freezing point.
4) Stir it vigorously when crystallization of ice starts. As the freezing initiates the thread of mercury begins to rise till it becomes stationary at a particular level.
This reading gives freezing point of pure solvent.
5) The inner tube is removed and warmed to melt the solid solvent
6) A definite weight of solute is added through side tube. It is mixed thoroughly to obtain a homogeneous solution
7) The freezing point of the solution is recorded (Table 1) following step 1-4.

## Observation:

Weight of solvent $\left(W_{2}\right)=\ldots . g$
Freezing point of pure solvent $\left(\mathrm{T}^{\circ} \mathrm{C}\right)=\ldots$.
Table 1: Depression in freezing point of solvent

| SI. | Amount of | Freezing point <br> No | Depression in <br> solute $\left(w_{1}\right) g$ <br> of solution $\left(T_{1}\right)$ | Molecular |
| :---: | :---: | :---: | :---: | :---: |
| Freezing point | weight |  |  |  |


|  |  | ${ }^{\circ} \mathbf{C}$ | $\left(\mathbf{D T}=\mathbf{T}-\mathbf{T}_{\mathbf{1}}\right)^{\circ} \mathbf{C}$ |  |
| :--- | :--- | :--- | :--- | :--- |
|  |  |  |  |  |
|  |  |  |  |  |
|  |  |  |  |  |

Calculations: The molecular weight $\left(\mathrm{m}_{1}\right)$ of the solute $=\frac{1000 \mathrm{~K}_{f} w_{1}}{w_{2} \Delta T}$
Result: Molecular weight of the given solute $=\ldots .$.
Precautions:1) The temperature of freezing mixture should be only 5 degree below the freezing point of the pure solvent.
2) The reading of the freezing point must be noted as soon as crystallization starts, $i . e$, when the level of mercury becomes fixed.

## VI. TO DETERMINE MOLECULAR WEIGHT OF GIVEN SOLUTE IN WATER BY ELEVATION OF BOILING POINT METHOD

Chemicals and Apparatus: Given solute (say sugar), water, Landsberger boiling point apparatus and steam generating flask, Beckmann thermometer or any other accurate thermometer

Theory: The molecular weight of the solute is given by the formula

$$
\begin{equation*}
m_{1}=\frac{1000 K_{b} w_{1}}{w_{2} \Delta T} \tag{2.4}
\end{equation*}
$$

$\mathrm{K}_{\mathrm{b}}$ is molal elevation constant. Other symbols have already mentioned in the earlier experiment.

Procedure:1) Set the Beckmann thermometer as explained in the previous experiment. However, for practical purposes we can use any other accurate thermometer.
2) Landsberger type boiling point apparatus is used to perform the experiment they rose head ensures uniform distribution of steam through the liquid.
3) A known quantity (say 20 mL ) of water is taken in inner graduated tube. The thermometer is adjusted in such a manner that its bulb lies about 1 cm above the level of water.
4) Water is boiled in the vessel and steam is passed through a delivery tube.
5) The temperature (boiling point of pure water) is recorded when it becomes constant.
6) Take out the tube and dissolve a weighed quantity of the given solute in water.
7) Boiling temperature of this solution is recorded as described in step 5.
8) Record another set of reading by dissolving 0.5 g more solute and record the boiling point of resulting solution (Table 1).

Observations: Weight of solvent $\left(w_{2}\right)=\ldots$. g
Boiling point of pure solvent $\left(\mathrm{T}^{\circ} \mathrm{C}\right)=\ldots$.

Table 1: Elevation in boiling point of solvent

| S. <br> No | Amount of <br> solute $\left(\mathbf{w}_{\mathbf{1}}\right) \mathbf{g}$ | Boiling point of <br> solution $\left(\mathrm{T}_{\mathbf{1}}\right){ }^{\circ} \mathrm{C}$ | Elevation in <br> boiling point <br> $\left(\Delta \mathrm{T}=\mathrm{T}_{1}-\mathrm{T}\right){ }^{\circ} \mathrm{C}$ | Molecular <br> weight |
| :--- | :---: | :---: | :---: | :---: |
|  |  |  |  |  |
|  |  |  |  |  |
|  |  |  |  |  |

Calculations: The molecular weight $\left(\mathrm{m}_{1}\right)$ of the solute $=\frac{1000 \mathrm{~K}_{f} w_{1}}{w_{2} \Delta T}$
Result: Molecular weight of the given solute $=\ldots .$.
Precautions:1) The relation holds good for dilute solutions so take a small quantity of solute.
2) The rose head should be used for uniform heating of the liquid.

## Further Reading

1) Schulte M.; Thermochemistry. In: Geochemistry. Encyclopedia of Earth Science. Springer, Dordrecht. 1998. https://doi.org/10.1007/1-4020-4496-8_320
2) West, C. J.; New books: the thermochemistry of the chemical substances. Journal of Physical Chemistry 193741 (2), 333-333. DOI: 10.1021/j150380a014.
