
UNIT 7 DETERMINATION OF ENTHALPY OF NEUTRALISATION AND IONISATION

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7.1 INTRODUCTION

In the last unit, you have studied about the determination of the integral enthalpy of solution. There are other kinds of enthalpies which are named according to the type of transformation or reaction they are associated with. The examples of some such enthalpies include **enthalpy of combustion, enthalpy of fusion, enthalpy of formation, enthalpy of hydration, enthalpy of neutralisation, enthalpy of ionisation**, etc. In this unit, we will be discussing the determination of

- (i) the enthalpy of neutralisation and
- (ii) the enthalpy of ionisation, using the enthalpy of neutralisation.

Objectives

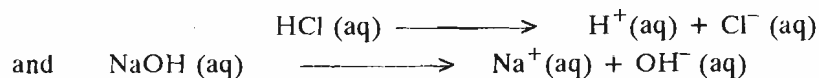
After studying this unit and having the experiments performed, you should be able to:

- define the enthalpy (heat) of neutralisation,
- give reason for the constant value of ΔH_{neut} for the neutralisation of a strong acid with a strong base, and
- explain how to calculate the enthalpy of ionisation of a weak acid or a weak base from the enthalpy of its neutralisation.

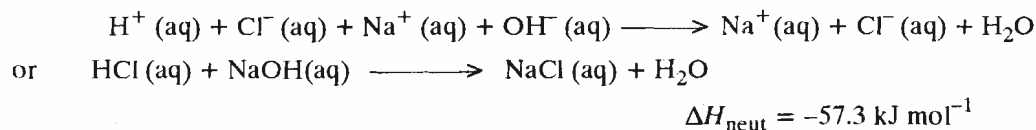
7.2 THE ENTHALPY OF NEUTRALISATION

The **enthalpy of neutralisation** (ΔH_{neut}) of an acid can be defined as the enthalpy change associated with the complete neutralisation of its dilute aqueous solution

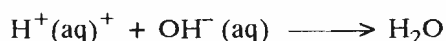
containing one mole of H^+ ions by a dilute aqueous solution of a base containing one mole of OH^- ions. Let us consider the example of neutralisation of hydrochloric acid with sodium hydroxide. You are aware that hydrochloric acid is a **strong acid** and sodium hydroxide is a **strong base**. This means that both hydrochloric acid and sodium hydroxide are completely dissociated in aqueous solution. Therefore, we can write



The neutralisation reaction can be represented as



Thus, the neutralisation of a strong acid with a strong base can be considered as the combination or reaction of $H^+(aq)$ ions with $OH^-(aq)$ ions and can be represented as



because Na^+ and Cl^- remain unchanged in the reaction.

In other words, the enthalpy of neutralisation of strong acids and strong bases is the enthalpy of formation of 1 mole of water from one mole each of H^+ and OH^- ions.

You must then also expect that the enthalpy of neutralisation of the strong acids with strong bases to be of a constant value irrespective of the strong acid or the strong base used.

Let us now focus our attention on the actual determination of the enthalpy of neutralisation.

7.2.1 EXPERIMENT 5 : DETERMINATION OF THE ENTHALPY OF NEUTRALISATION OF HYDROCHLORIC ACID WITH SODIUM HYDROXIDE

Requirements

Apparatus			Chemicals
Thermos Flask	—	1	Sodium hydroxide
Glass Stirrer	—	1	Hydrochloric acid
Thermometer 110° (1/10°C)	—	1	
Stop Watch or Stop Clock	—	1	
Beaker 250/400 cm ³	—	2	
(1 as calorimeter)			
Measuring Cylinder 100 cm ³	—	1	

Solutions Provided

0.50 mol dm⁻³ NaOH
0.50 mol dm⁻³ HCl

Procedure

Measure 100 cm³ of HCl in a beaker for which heat capacity has already been determined in Experiment 3. Place it in a thermos flask. Insert the stirrer and the thermometer through the two holes and cover the thermos flask with the lid. Stir

Calculations

- (1) Plot temperature — time curve for the neutralisation of HCl with NaOH data. You will get a plot as given in Fig. 7.1. From the graph, calculate T_b and T_a (the temperature of the reactants: base and acid, respectively) and T_m , the temperature of the products.
- (2) The heat evolved during neutralisation will raise the temperature of the solution and that of the beaker (calorimeter). In other words, the enthalpy change for the neutralisation of the given amount of the acid with the given amount of the base is equal in magnitude but opposite in sign to the heat gained by the calorimeter and its contents. That is why there is a negative sign in the right hand side of Eq. 7.1 as given below:

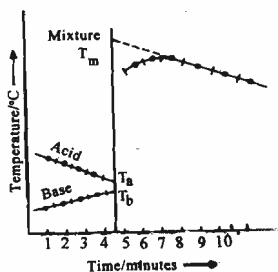


Fig. 7.1 : Temperature-time curve for neutralisation.

For dilute solutions of acids and bases, mass can be assumed to be equal to volume because density could be taken as 1 kg dm^{-3} for them.

The specific heat of water is $4.185 \text{ J K}^{-1} \text{ kg}^{-1}$. For a dilute solution of an acid and a base, the specific heats can be assumed to be equal to the specific heat of water. Let us denote the specific heat of water as s . Hence, specific heat of acid = specific heat of base = specific heat of water = s ... (7.3)

0.5 M HCl means 0.5 mole of HCl present in 1 dm^3 of the solution. Thus, amount (no. of moles) of HCl present in 100 cm^3 of HCl (or 200 cm^3 of the solution)

$$= \frac{0.5}{10} \text{ mole} = 0.05 \text{ mole}$$

Because $1 \text{ dm} = 10 \text{ cm}$

and $(1 \text{ dm})^3 = (10 \text{ cm})^3$

$$1 \text{ dm}^3 = 1000 \text{ cm}^3 \text{ or } 100 \text{ cm}^3 = \frac{1}{10} \text{ dm}^3$$

Thus, to get the amount (number of moles) present in 100 cm^3 of 0.5 M HCl or 200 cm^3 of the solution from the molarity (or amount in no. of moles of substance present in 1 dm^3), we have to divide the molarity by 10 as done above.

$$\Delta H = - [\text{Heat gained by the calorimeter} + \text{Heat gained by the solution}] \quad \dots (7.1)$$

$$= - [(\text{Heat capacity of the calorimeter} \times \text{Rise in temperature of the calorimeter}) + (\text{Mass of base} \times \text{Specific heat of base} \times \text{Rise in temperature of base}) + (\text{Mass of acid} \times \text{Specific heat of acid} \times \text{Rise in temperature of acid})]$$

$$= - \{ [C_p (c) \text{ as obtained in the earlier experiment} \times (T_m - T_a)] + \{V_{\text{base}} \times \text{sp. heat of base} \times (T_m - T_b)\} + \{V_{\text{acid}} \times \text{sp. heat of acid} \times (T_m - T_a)\} \} \quad \dots (7.2)$$

Using Eq. 7.3,

$$\Delta H = - [C_p (c) (T_m - T_a) + V_{\text{base}} s (T_m - T_b) + V_{\text{acid}} s (T_m - T_a)] \quad \dots (7.4)$$

Calculate ΔH from Eq. 7.4 by substituting the values of T_m , T_a and T_b as obtained by the plot of temperature versus time curve and those of heat capacity of calorimeter [$C_p(C)$ from Experiment 3] and specific heat ($s = 4.185 \text{ J K}^{-1} \text{ kg}^{-1}$). ΔH so obtained in the above equation is the enthalpy change for the neutralisation of 100 cm^3 of 0.5 M HCl with 100 cm^3 of 0.5 M NaOH. From this ΔH , you can now calculate the ΔH_{neut} as follows.

You know that the enthalpy of neutralisation is the enthalpy change per mole of the substance neutralised. Thus, we have to first calculate the amount (number of moles) of HCl present in the volume of solution taken for neutralisation in the experiment. As given in the procedure, when 100 cm^3 of 0.5 M HCl is neutralised using 100 cm^3 of 0.5 M NaOH, then, the amount (no. of moles) of HCl present in the 200 cm^3 solution (100 cm^3 acid + 100 cm^3 base) will be equal to 0.05 mole.

To calculate the heat of neutralisation, we have to divide the ΔH obtained by Eq. 7.4 by amount (the number of moles) of hydrochloric acid, i.e.,

$$\begin{aligned} \Delta H_{\text{neut}} &= \frac{\Delta H (\text{obtained from Eq. 7.4})}{\text{amount (No. of moles) of HCl}} \\ &= \frac{\Delta H (\text{obtained from Eq. 7.4})}{0.05} \\ &= \dots \text{ J mol}^{-1} \end{aligned}$$

Now report your result as given below:

Result

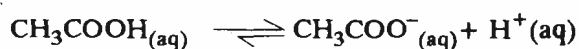
The heat of neutralisation of hydrochloric acid with sodium hydroxide is $\dots \text{ J mol}^{-1}$

Let us now turn to a similar experiment using acetic acid instead of hydrochloric acid.

7.2.2 EXPERIMENT 6: DETERMINATION OF THE ENTHALPIES OF NEUTRALISATION AND IONISATION OF ACETIC ACID

Principle

The enthalpy of neutralisation of acetic acid can be determined by the similar method as done above for the hydrochloric acid. The acetic acid, in contrast to the hydrochloric acid, is a **weak acid** and is **not completely** dissociated in dilute aqueous solutions into H^+ and CH_3COO^- ions.



When acetic acid is neutralised with a base (NaOH), some of the heat evolved during the neutralisation is used in the process of dissociating the acetic acid to allow the completion of neutralisation. Therefore, you can expect that the enthalpy change associated with the neutralisation of acetic acid (a weak acid) with a strong base to be lower than that of the enthalpy of neutralisation of a strong acid with a strong base (i.e., $-57.3 \text{ kJ mol}^{-1}$). Similarly, the value of enthalpy of neutralisation of a weak base with a strong acid will also be lower than that of the enthalpy of neutralisation of a strong base with a strong acid.

The difference in the enthalpy of neutralisation of a strong acid (HCl) with a strong base (NaOH) and enthalpy of neutralisation of weak acid (CH_3COOH) with strong base (NaOH) will give the enthalpy of ionisation of the weak acid (CH_3COOH).

Since the ionisation proceeds simultaneously with neutralisation, the enthalpy change observed is the sum of enthalpy of ionisation and enthalpy of neutralisation, i.e.,

$$\begin{aligned} \Delta H_{\text{ionis}} + \Delta H_{\text{neut}} &= \Delta H_{\text{observed}} \\ \Delta H_{\text{ionis}} &= \Delta H_{\text{obs}} - \Delta H_{\text{neut}} \\ &= \Delta H_{\text{obs}} - (-57.3 \text{ kJ mol}^{-1}) \\ \Delta H_{\text{ionis}} &= \Delta H_{\text{obs}} + 57.3 \text{ kJ mol}^{-1} \end{aligned}$$

Since the ΔH_{obs} has a negative sign and is smaller in value than 57.3, ΔH_{ionis} is positive. Thus, ionisation is endothermic.

Requirements

Apparatus

Thermos flask	—	1
Glass stirrer	—	1
Thermometer — 110°C (1/10th $^\circ\text{C}$)	—	1
Stop Watch or Stop Clock	—	1
Beaker 250/400 cm^3	—	2
Measuring cylinder 100 cm^3	—	1

Chemicals

Acetic acid
Sodium Hydroxide

Solutions Provided

$0.50 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$
 $0.50 \text{ mol dm}^{-3} \text{ NaOH}$

Procedure

Do exactly in a similar way as done in the previous experiment using acetic acid instead of hydrochloric acid.

Calculations

From the observations that you have recorded, plot a graph of temperature versus time for the acid, the base and the mixture. You will get a similar plot as you got in the previous experiment. From this plot, note down the temperature of the acid (T_a), the base (T_b) and the mixture (T_m). Now, substitute the values of T_a , T_b and T_m in Eq. 7.4 and get the value of enthalpy change (ΔH) or heat evolved during the neutralisation of 100 cm^3 of $0.5 \text{ M CH}_3\text{COOH}$ with 100 cm^3 of 0.5 M NaOH . Then divide the above value of enthalpy change with the number of moles of acetic acid present in the amount of solution taken for neutralisation.

Remember ΔH_{neut} has a negative sign.

$$\begin{aligned}\Delta H_{\text{neut}} \text{ of acetic acid} &= \frac{\Delta H \text{ (obtained above)}}{0.05 \text{ mol}} \\ &= \dots\dots \text{ kJ mol}^{-1}\end{aligned}$$

Now calculate the enthalpy of ionisation of acetic acid as given below:

$$\begin{aligned}\Delta H_{\text{ionis}} &= \Delta H_{\text{neut}} \text{ (strong acid with strong base)} - \\ &\quad \Delta H_{\text{neut}} \text{ (acetic acid with NaOH)} \\ &= (57.3 \text{ kJ mol}^{-1}) - (\text{value of } \Delta H_{\text{neut}} \text{ as obtained above)} \\ &= \dots\dots\dots \text{ kJ mol}^{-1}\end{aligned}$$

Result

The enthalpy of neutralisation of acetic acid with sodium hydroxide is kJ mol^{-1} and the enthalpy of ionisation of acetic acid is kJ mol^{-1}

SAQ 1

Calculate the mass of acetic acid present in 75.0 cm^3 of 0.150 molar solution.

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7.3 ANSWERS

Self Assessment Questions

1 1000 cm^3 acetic acid solution contains 0.150 mol acetic acid

$$75.0 \text{ cm}^3 \text{ acetic acid solution will contain } \frac{0.150 \text{ mol} \times 75.0 \text{ cm}^3}{1000 \text{ cm}^3}$$

$$= 0.01125 \text{ mol}$$

$$= 0.01125 \text{ mol} \times 0.0600 \text{ kg mol}^{-1}$$

$$= 6.75 \times 10^{-4} \text{ kg}$$

The molar mass of acetic acid is $0.0600 \text{ kg mol}^{-1}$

Appendix
Density of water at different temperatures

Temperature/°C	Density/ g cm ⁻³
10	0.9997
15	0.9991
20	0.9982
21	0.9980
22	0.9978
23	0.9975
24	0.9973
25	0.9970
26	0.9968
27	0.9965
28	0.9962
29	0.9959
30	0.9956
31	0.9953
32	0.9950
33	0.9947
34	0.9944
35	0.9941
40	0.9922

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