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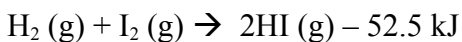
Thermo chemistry

Thermo chemistry is that branch of chemistry which deals with heat changes accompanying chemical reactions or change of phase. It is based on **first law of thermodynamics**.

Chemical reactions are accompanied by energy changes. These changes appear in the form of evolution or absorption of heat. If chemical reaction is accompanied by evolution of heat, it is called exothermic reaction e.g.



On the other hand, if chemical reaction is accompanied by absorption of heat, it is called endothermic reaction e.g.



A balanced chemical equation which indicates the amount of heat absorbed or evolved in the reaction process is called **thermo chemical equation**.

Heat of Reaction or Enthalpy of Reaction

Heat of reaction is defined as the amount of heat absorbed or evolved in a chemical reaction when the number of moles of reactants as represented by balanced chemical equation, are converted into products at constant pressure. Since most of the reactions

occur at constant pressure, it is usual to express heat of reaction as enthalpy change of the reaction.

Factors Affecting Heat of Reaction

- i) Physical State of Reactants and Products: A physical state of Reactants and Products affects the heat of reaction.
- ii) Amounts of Reactants involved: If amount of reactants is doubled, the heat of reaction is also doubled.

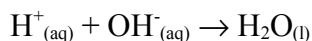
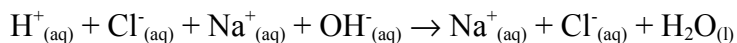
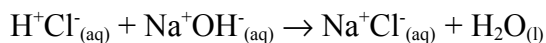
Heat of reactions is generally reported for 1 mole of the reactants.

- iii) Whether the reaction is taking place at constant pressure or volume.
- iv) Temperature: The enthalpy change of chemical reaction varies with temperature. **The values are generally reported at 298 K.**
- v) Concentration of the solution: If the solutions are involved in the reaction, their concentration may affect the heat of reaction.

Aim: Determination of Heat of Neutralization of Strong acid with Strong base e.g. hydrochloric acid with Sodium Hydroxide.

Theory: Heat of neutralization of an acid is defined as the amount of heat evolved when 1 gram equivalent of an acid is neutralized completely by a 1 gram equivalent of strong base in a dilute solution. Similarly, heat of neutralization of a base is the amount of heat evolved when 1 g equivalent of the base is completely neutralized by strong acid in dilute solution.

The neutralization of any strong acid by any alkali always produces the same final equation and the same value for the change in enthalpy. It is found that heat of neutralization for all strong acids and strong bases is practically a constant quantity i.e. -57.2 kJ/mole. This can be explained on the basis of theory of ionization. Strong acids and strong bases are assumed to be completely ionized in dilute solutions; moreover, the salts they form on mixing are also completely ionized in dilute solution. The reaction between strong acid and strong base can be written as:



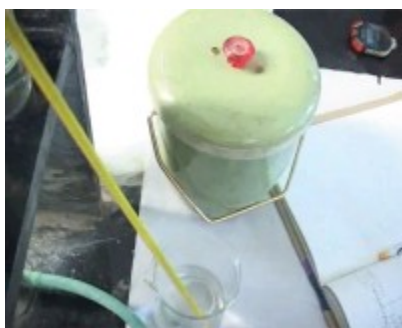
$$\Delta H = -57.2 \text{ kJ mol}^{-1}$$

So, it is heat released when 1 mole of water is formed during the neutralization of strong acid by an alkali as shown above. Thus neutralization is simply a reaction between H^+ ions given by strong acid and OH^- ions given by strong base. In case of all strong acids and strong bases, the number of H^+ and OH^- ions produced by one gram equivalent of any strong acid or strong base is always same. Hence the enthalpy of neutralization of a strong acid with strong base is always same.

Principle: A known volume of strong acid solution of known concentration is allowed to react completely with a strong alkali in a dilute solution. The rise in temperature is noted. Knowing the heat capacity (water equivalent) of calorimeter, masses of acid and base and their specific heat in dilute solutions, heat of neutralization can be calculated.

$$\Delta H = - [\text{Heat gained by calorimeter} + \text{Heat gained by solution}]$$

Apparatus Required: Thermos flask, glass stirrer, stop watch, thermometers, beakers, and burette.



Chemicals Required: Hydrochloric acid (strong acid) (1 N), Sodium Hydroxide (strong base) (1 N) and distilled water.

Procedure:

1. Calibrate two thermometers by putting them in 20.0 cm³ distilled water. Leave them in water for 10 minutes and note down the temperature shown by both thermometers. Note down the difference in reading of two thermometers and do either addition in reading of that thermometer which shows less reading or subtract the difference from the reading of that thermometer which shows high reading.
2. Determine heat capacity of calorimeter by mixing equal amount (50 cm³) of hot water and cold water as explained in earlier experiment.
3. Prepare 1 N HCl solution and 1N NaOH solution.
4. Prepare 250 cm³ of 0.5 N standard solution of oxalic acid in distilled water in a standard flask.
5. Titrate the NaOH solution with standard solution of oxalic acid using phenolphthalein as indicator and find out its normality.
6. Dilute the NaOH solution to prepare 250 cm³ of 1 N solution.
7. Titrate HCl solution with 1 N NaOH using phenolphthalein as indicator and calculate its normality.
8. Dilute HCl solution to prepare 250 cm³ of 1 N solution.
9. Recheck the normalities of HCl and NaOH solutions by titrating them.
10. Rinse a beaker with 1 N HCl solution and then measure 50 cm³ of this solution in it. Fix 0.1°C thermometer in it and keep it in thermos flask.
11. Similarly take 50 cm³ of 1N NaOH solution in beaker outside the thermos flask and fix another thermometer in it. Start the stop watch and record the temperatures of HCl and NaOH solutions alternately after every 30 seconds till the last reading is taken 30 seconds before the time of mixing (5.0 min.)



12. Remove the thermometer from HCl solution, open the lid of thermos flask partly and pour NaOH solution into the beaker containing HCl solution which is already placed in thermos flask such that one half of mixing would occur by the time of mixing.
13. Replace the lid as soon as the pouring is complete and start stirring the mixture solution in the thermos flask gently but continuously.
14. The mixing of reactants is started by pouring about 3-4 seconds before the time of mixing and it continues for an equal interval of time after it. When the pouring/mixing is complete, the reaction mixture is stirred continuously but gently.
15. Note down the temperature of mixture after every half minute for next ten minutes.
16. Record observations as given below:
17. Calculate the temperature of acid, base and mixture at the time of mixing (from graph).
18. Add a drop of phenolphthalein to the solution in calorimeter to check whether the neutralization process is complete or not.
19. Repeat the experiment (steps 10-18) one more time to obtain second value of enthalpy of neutralization using the same solutions

Observations:

I. Preparation of standard solution of oxalic acid

Mass of oxalic acid dissolved = m g

Volume of solution prepared = 250 cm^3

Equivalent mass of oxalic acid = 63 g eqvt⁻¹

$$\text{Normality of oxalic acid solution} = \frac{m \times 1000}{63 \times 250}$$

II. Standardization and preparation of 1 N solution of HCl and NaOH.

Table 1: Titration of oxalic acid against NaOH

S.No.	Initial Reading	Final Reading	Volume of NaOH (cm ³)

Table 2: Titration of HCl against NaOH

S.No.	Initial Reading	Final Reading	Volume of NaOH (cm ³)

Temperature of measurement = ---- °C

Normality of HCl solution = 1 N

Normality of NaOH solution = 1 N

Volume of HCl taken = 50 cm³

Volume of NaOH taken = 50 cm³

Table 3: Variation of Temperature with Time for HCl - NaOH pair.

S. No.	Time (Min.)	Temperature ($^{\circ}\text{C}$)		
		Acid	Base	Mixture
1	0.5			
2	1.0			
3	1.5			

Calculations

Plot a graph between temperature and time (as shown in Figure 1). Calculate temperature of acid (T_a), base (T_b) and mixture (T_m) at the time of mixing.

The points of each solution are joined by the best straight line and these lines are all extended (extrapolated) up to this vertical line. The point of intersections of these lines with the vertical line (T_a , T_b and T_m) gives the temperatures of all the solutions at the *time of mixing*. In case of two reactants with different initial temperatures, their mean gives the initial temperature (T_i). A vertical line is drawn at the time of mixing on the graph.

The heat evolved during the neutralization will raise the temperature of the solution and that of calorimeter i.e.

$$\Delta H = - [\text{Heat gained by calorimeter} + \text{Heat gained by solution}]$$

$$\Delta H = - C_p \Delta T$$

$$\text{Increase in temperature } (\Delta T) = T_m - T_i$$

$$\text{Initial Temperature } (T_i) = T_a + T_b / 2$$

$$C_p = C_p (\text{Calorimeter}) + C_p (\text{Solution})$$

$$C_p (\text{Solution}) = \text{mass of solution} \times \text{specific heat of solution}$$

For a very dilute solution

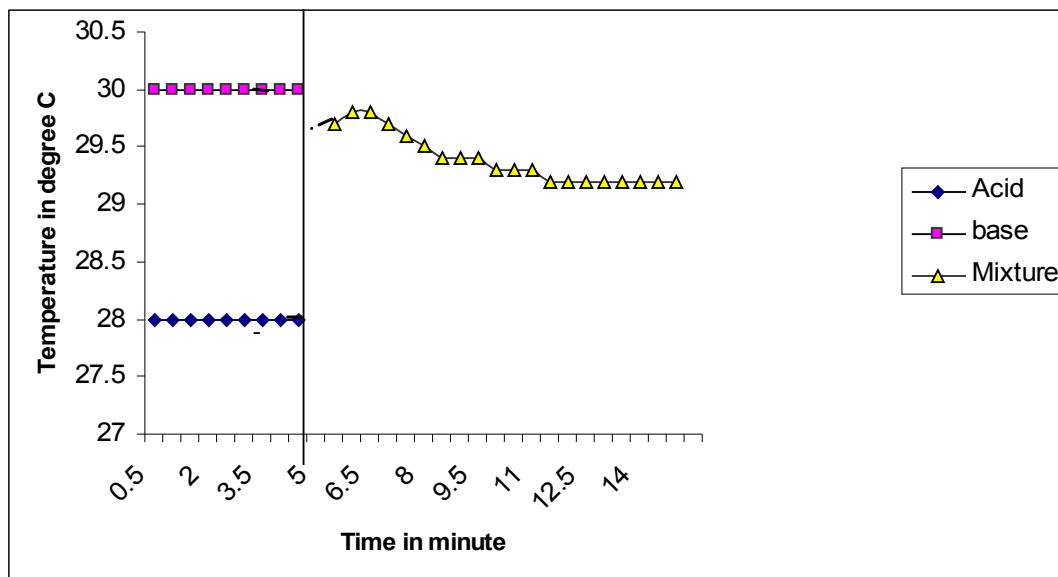


Figure 1: Temperature versus Time graph for determination of enthalpy of neutralization of HCl and NaOH

Specific heat of solution \approx specific heat of solvent (water) = $4.182 \text{ J g}^{-1} \text{ deg}^{-1}$

Density of solution \approx Density of water = 1 g/cm^3

Volume of solution taken = 100 cm^3

So, mass of solution = 100 g

$C_p = (C_p (\text{Cal}) + 100 \times 4.182) \text{ J deg}^{-1}$

So, $\Delta H = - (C_p (\text{Cal}) + 100 \times 4.182) \Delta T \text{ J}$

$\Delta H = \text{----- kJ}$

$\Delta_n H = - \Delta H / \text{Amount of acid in moles}$

Nos of moles of acid present in 50 cm^3 of 1M acid = $1 \times 50/1000 = 1 / 20$ moles

So, $\Delta_n H = - \Delta H / 1/20 \text{ kJ mol}^{-1}$

Precautions:

- i. Both the thermometers should be kept in cold water to know their temperature difference.

- ii. The thermometers should be marked properly to avoid any confusion.
- iii. Stop watch should not be stopped during the experiment.
- iv. Thermos flask should be properly closed from the top and it should have the opening only for stirrer and thermometer.
- v. Volume of HCl and NaOH taken should be same.
- vi. Volume of cold and hot water taken for water equivalent calculation should be same as that of acid and base.
- vii. The mixing of reactants should be carried out quickly to avoid heat loss.
- viii. Standardization of NaOH and HCl solution should be done carefully.
- ix. The normalities of HCl and NaOH solutions prepared by dilution must be checked finally by titrating these solutions.

Result: Heat of neutralization for HCl and NaOH is - ----- kJ/mole.

Learning Objectives

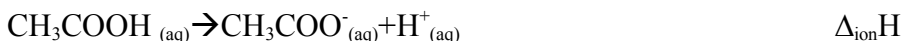
After performing this experiment student will be able to:

- correlate the change in thermal energy with heat gained or lost by the system;
- define the terms calorimetric formula, heat capacity of calorimeter, water equivalent of calorimeter, enthalpy of neutralization;
- explain why the enthalpy of neutralization of any strong acid with a strong base is the same;
- set up the apparatus for determination of heat capacity of calorimeter and enthalpy of neutralization;
- record the data and plot the required graph to determine the initial and final temperatures at the ‘time of mixing’;
- identify the common sources of error and suggest their preventive measures.

Aim: Determination of heat of Neutralization of weak acid - strong base e.g. acetic acid – Sodium Hydroxide and heat of Ionization of Acetic Acid.

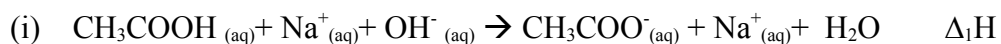
Theory: Heat of neutralization of acetic acid with sodium hydroxide can be determined by the same method as discussed for the neutralization of hydrochloric acid in earlier experiment. Acetic acid is a weak acid and is not completely dissociated in dilute aqueous solutions. Thus heat of neutralization is always less than that of HCl i.e. -57.2 kJ. The reason is that the neutralization process not only involves the combination of hydronium and hydroxide ions, but also the dissociation of weak acid or weak base. During the neutralization of weak acid like acetic acid with strong base like sodium hydroxide, acetic acid dissociates to a small extent whereas NaOH ionizes completely as shown in equation (i).

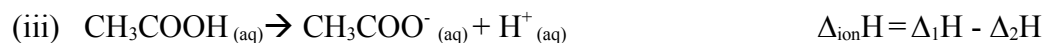
Heat of Ionization: Heat of ionization of weak acid or weak base is defined as the amount of heat required to completely ionize weak acid or base in aqueous solution and it is always positive. In case of acetic acid, heat of ionization is enthalpy change for the following equation:



As H^+ ions given by the acid combine with OH^- ions given by the base, the equilibrium of above equation shifts to the right till acetic acid is completely neutralized, thus a part of heat produced by the combination of H^+ and OH^- ion (net neutralization reaction in case of strong acid and strong base) is used up for complete dissociation of acetic acid. Thus, heat of neutralization in is always less than -57.2 kJ.

Principle: A known volume of CH_3COOH solution of known concentration is allowed to react completely with NaOH in dilute solution. The rise in temperature is noted. Knowing the heat capacity of calorimeter, masses of acid and base and their specific heats in dilute solutions, the heat of neutralization is calculated as shown below:





On subtracting equation (ii) from equation (i), one can obtain equation (iii) i.e. heat of ionization of acetic acid. Since heat of neutralization of acetic acid with sodium hydroxide is negative and less than -57.2 kJ, so $\Delta_{\text{ion}}H$ is positive i.e. ionization is an endothermic process.

Apparatus Required: Thermos flask, glass stirrer, stop watch, thermometers, beakers, and burette.



Chemicals Required: Acetic acid (weak acid) (1 N), Sodium Hydroxide (strong base) (1 N) and oxalic acid.

Procedure: Procedure is exactly same as explained in earlier experiment.

Plot a graph to explain the calculation of T_a , T_b and T_m at the time of mixing.

Precautions: Same as in earlier experiment.

Result: i) Heat of neutralization of acetic acid - sodium hydroxide pair is - ---- kJ/ mole.

ii) Heat of ionization of acetic acid is ----- kJ/mole.

Learning Objectives

After performing this experiment students will be able to

- Define enthalpy of ionization.

- Explain the reason for different values of enthalpy of neutralization for different weak acids.
- Correlate the difference between the observed value of enthalpy of neutralization of a weak acid with a strong base and the standard expected value for a strong acid and a strong base.