



DETERMINATION OF THERMODYNAMIC PARAMETERS FOR THE NEUTRALIZATION REACTION BETWEEN HYDROCHLORIC ACID AND SODIUM HYDROXIDE USING TITRATION METHOD

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Abstract

This research was aimed at determining the thermodynamic parameters for the neutralization reaction between Hydrochloric acid and Sodium hydroxide using titration method. In the process, standard solutions of HCl were prepared and titrated against the unknown concentration of NaOH solutions. After determining the concentrations of NaOH and volumes of HCl required for the neutralization reaction, the heat given out at various temperature rise (ΔT) were equally calculated and values are 2800, 3192, 3864, 4480 and 5152j. These values were used in the determination of the total heat content enthalpy (ΔH) followed by the other thermodynamic parameters ie ΔS and ΔG . In this research work, the values of the thermodynamic parameters (ΔH , ΔS and ΔG) determined are -51.52, 0.17 and -102.69 kJmol⁻¹ respectively.

Key words: Thermodynamic parameters, determination, titration



INTRODUCTION

Thermodynamic is a branch of science that deals with the quantitative relationships between heat and other forms of energy. Its objectives as applied to chemistry include; To predict the feasibility of a process: whether or not a process will occur under a given set of conditions can be predicted by applying the principle of thermodynamic. To estimate the yield of the product i.e. thermodynamic relationship helps to predict the yield of a product obtainable in a process or a reaction. It is possible to know the extent to which the reaction takes place before attaining equilibrium, also to deduce some important relationships in physical chemistry that is, it has been possible to deduce some important and useful results such as Raoult's Law of lowering of vapour pressure and expression for the depression of freezing point, elevation of boiling point, distribution law and phase rule from the study of thermodynamic (Silberberg, 2007).

The limitation of thermodynamic include the following; It deals with the properties like temperature, pressure etc of the matter in bulk ie with macroscopic quantities and not with microscopic quantities. In other words it deals with large groups of atoms, molecules and ions rather than individual atoms, molecules or ions. It helps to predict the feasibility of a process but does not tell anything about the time taken for the process to complete or the rate at which the process would proceed. It concerns itself only with initial and final states of a system and is not concern with path by which the change is brought about, that is, it throws no light on the mechanism of a process (Madan, 1939).

Specifically, in studying and evaluating the flow of energy in to or out of a system it will be useful to consider changes in certain properties like temperature, pressure, volume and concentration of the system. Measuring the changes in these properties from initial state to the final state, can provide information concerning changes in energy and related parameters such as entropy and Gibb's free energy. It is noticed that energy in the form of heat is generally evolved or absorbed as a result of chemical changes (Robert et al ., 2007).

Thermo chemistry is the study of heat change in a chemical reaction. During a chemical reaction, there is an associated energy change which is due to the difference in the energy contents between the reactants and the products. This change is as a result of the transfer of energy between the reacting system and its surroundings. Such energy is in the form of heat (The Chemical age 2007). The measurement of the heat change of a system may be carried out at a constant volume, and is called the change in internal energy of the system, or at constant pressure, which is called the enthalpy change of the system. However, chemical reactions are commonly carried out at atmospheric pressure. The heat change of the system at atmospheric pressure may not be the same as the change in the internal energy of the system. The internal energy of the system is represented by the symbol E . it is neither possible nor necessary to



calculate the absolute value of internal energy of the system. In thermodynamics we are concern only with the energy changes when a system changes from one state to another. If ΔE be the difference of energy of the initial (E_{initial}) and the final states (E_{final}). We can write; $\Delta E = E_f - E_i$ (Gupta, 2011).

Therefore, in order to study the heat changes for a reaction taking place at constant pressure and constant temperature a new term called enthalpy was introduced. This gave rise to the study of thermodynamic parameters i.e. enthalpy, entropy and Gibb's free energy. Enthalpy of a system is defined as the sum of the internal energy and product of its pressure and volume i.e. $H = E + PV$; Where E is the internal energy, P is the pressure and V is the volume of the system. It is also called heat content, just like internal energy the exact value of enthalpy cannot be measured. However a change in it (ΔH) accompanying a process can be measured accurately, given by the expression; $\Delta H = H_{\text{product}} - H_{\text{reactant}}$ (Wang et al., 1998).

In general, the tendency of a process or a reaction to occur naturally, is called spontaneity, therefore, spontaneous process like heat flow from hot object to cold one or gas flow occur with the decrease in internal energy or enthalpy. However, there are spontaneous processes that occur endothermically i.e. without any decrease in internal energy or enthalpy. Some examples are melting of ice and evaporation of water (Arun *et al.* , 1977).

It therefore, means that beside internal energy and enthalpy, there is another parameter that determines the spontaneity of a reaction and is called entropy i.e. S or slight change in it ΔS . Careful explanation shows that in each of the above two mentioned spontaneous processes i.e. melting of ice and evaporation of water, there is an increase in randomness or disorder of a system. The water molecules in ice are arranged in highly organized crystal patterns which permit very little movement. However as the ice melts, the water molecules become disorganized and can move freely. The atmospheric movement of molecules becomes free still when the water evaporates as now they can roam about throughout the entire atmosphere. In view of this therefore, one can say that the entropy of water molecules increases as ice melts into water or water evaporates into space (Arun *et al.* , 1977).

Entropy is a thermodynamic state quantity that is a measure of the randomness or disorder of molecules of the system. The symbol of entropy is S , while the change in disorder accompanying a process from start to completion is represented by ΔS . The entropy of a system is a state function and depends on the initial and the final states of a system. The change in entropy, ΔS , for any process is given by the equation; $\Delta S = S_{\text{final}} - S_{\text{initial}}$ (Osei-Yaw, 1990).

Gibb's Free Energy, the free energy, G , of a chemical system is the energy which is available for doing work. It is the driving force that brings about a chemical change. The Gibbs free energy



ΔG is a state function as it depends on the initial and final states of the system. i.e. $\Delta G = G_2 - G_1$ (Robert et al., 2007).

Volumetric analysis is a method used by chemists to determine the concentration of a substance by measuring volumes of solutions through titration. During titration, a solution is run from a burette into a known volume of another solution measured out from a pipette into a conical flask. In the process, one of the solutions involved should be a standard solution. In order to determine the concentration of the other unknown solution which is usually expressed in moles

per dm^3 , the following equation should be applied;
$$\frac{M_1 V_1}{N_1} = \frac{M_2 V_2}{N_2}$$

Where M_1 = molar concentration of standard solution, V_1 = volume of the standard solution from the burette, N_1 = number of moles of the standard solution, M_2 = molarity of a solution of unknown concentration, V_2 = volume of a solution of unknown concentration pipetted out into the conical flask which will react with the standard solution discharged from the burette, N_2 = number of moles of a solution of unknown concentration. In a typical acid base titration, the point at which neutralization takes place is called the end point which is determined by a suitable indicator (Jumoke, 1999).

BACKGROUND OF THE RESEARCH

First law of thermodynamics states that one form of energy can change in to another form but the total amount of energy remains the same (Atkins P. Julio p, 2010). It means that once a particular process or change is specified, the law will help us to balance the internal energy ΔE , heat released ΔH and work done W in the process. But the law did not say anything about whether the process of change we specify can, in fact, occur and if so in which direction. The knowledge of Gibb's free energy ΔG which determines the feasibility and direction of a reaction as well as the amount of work done either on the system or by the system is very essential

Most of the natural processes that occur are spontaneous and proceed with an increase in entropy ΔS . (Lionel M.R ,2014) . Entropy measures the degree of disorder and randomness of a process or reaction. Some spontaneous reactions are slow e.g rusting of iron while some are very fast and explosive e.g nuclear reactions and hydrolysis of sodium metals .A fair knowledge of thermodynamic will enable one to conduct spontaneous and explosive reactions safely and economically. Suitable catalyst will be applied to reduce the speed of such reactions with a view to avoiding damages to equipment, products, chemicals and even the researcher. In addition to this, the researcher is in a better position to select appropriate personal protective equipment and effectively utilize same for safety .Those reactions that occur at very slow rates, suitable catalysts should be used to increase their speed with a view to minimizing waste of time, energy and materials resources.



Some industrial operations take place in alkaline medium e.g. soap making industry during saponification. Those that favoured acidic medium include glucose making industry where sugarcane is hydrolyzed in the presence of mineral acid. In fertilizer company, urea is hydrolyzed in acidic medium by an enzyme urease present in soya beans. Chemists with good thermodynamic background will ensure safe, efficient and effective operations in these industries.

MATERIALS AND METHOD

The reagents used in this work are BDH grade obtained from chemical vendors here in Azare and Bauchi towns in Bauchi state. They include the following: Sodium hydroxide pellets, Hydrochloric acid (concentrated), phenolphthalein and distilled water.

APPARATUS/MATERIALS: The apparatus used in this work are routine laboratory glass wares in addition to other normal equipment and they include the following; Burette, Pipette, Conical flasks, Weighing balance, Thermometer, Calorimeter, Beakers, Measuring cylinder, Retort stand and White tiles.

METHODOLOGY

Preparation of 1.0 M solution of HCl

21.50cm³ of concentrated HCl was accurately measured using a measuring cylinder. This was transferred into a 1000cm³ volumetric flask. The measuring cylinder was rinsed five (5) times each with 20cm³ of distilled water and washings were transferred into 1000cm³ volumetric flask. Distilled water was continuously added to the content of the flask up to the mark. The flask was shaken vigorously to ensure proper dilution. This solution was allowed to cool to room temperature and kept for further usage. However, the following concentrations of HCl; 1.25M, 1.50M, 1.75M and 2.0M were similarly prepared using the above procedure (Daniel, 2007).

DATA ANALYSIS

The data obtained from titration was used to determine the molar concentrations of NaOH. Also, heat evolved or given out during the reaction was calculated using the following equation; heat evolved or given out = $M_1C_1 + M_2C_2 (\Delta T)$. Where M_1 = mass of water, M_2 = mass of calorimeter, C_1 = Specific heat capacity of water, C_2 = Specific heat capacity of calorimeter and ΔT == temperature rise during the reaction. Furthermore, number of moles of either HCl or NaOH was calculated using the following relation. i.e. number of moles of HCl or NaOH =

$$\text{Molarity} \times \frac{\text{volume}}{1000}$$

From the equation for the reaction, $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$, the number of moles of HCl = number of moles of NaOH = number of moles of water formed. However, the heat given out



per mole of water formed which is equivalent to the enthalpy change of neutralization (ΔH) was calculated using the equation: Heat given out per mole of water formed =

$$\frac{\text{Heat given out}}{\text{Number of moles of water formed}}$$

The entropy change (ΔS) was calculated using the following relationship; $\Delta S = \frac{\Delta H}{T}$

Gibb's free energy (ΔG) was determined using the following formular; $\Delta G = \Delta H - T\Delta S$

RESULTS

TABLE 1: The result of titration between standard solutions of HCl and NaOH

S/N	STANDARD SOLUTION OF HCl (moldm ⁻³)	VOLUME OF HCL CONSUMED (cm ³)	VOLUME OF NaOH PIPETTED	CONCENTRATION OF NaOH (moldm ⁻³) DETERMINED OUT(cm ³)
1	1.00	25.00	25	1.00
2	1.25	24.90	25	1.25
3	1.50	25.00	25	1.50
4	1.75	24.70	25	1.75
5	2.00	24.80	25	2.00

TABLE 2: The temperature differences (ΔT (°C)) and the Heat given out (J) when equal volumes of HCl and NaOH reacted

S/N	CONCENTRATION OF HCl (moldm ⁻³)	ΔT (°C)	HEAT GIVEN OUT (J)
1	1.00	5.00	2800
2	1.25	5.70	3192
3	1.50	6.90	3864
4	1.75	8.00	4480
5	2.00	9.20	5152

TABLE 3: The result of thermodynamic parameters (ΔH , ΔS and ΔG) when HCl reacted with equal volumes and concentrations of NaOH

S/N	CONCENTRATION OF HCl (moldm ⁻³)	ΔH (kJmol ⁻¹)	ΔS (kJmol ⁻¹)	ΔG (kJmol ⁻¹)
1	1.00	-56.00	0.19	-111.99
2	1.25	-51.07	0.17	-102.24
3	1.50	-51.52	0.17	-102.69
4	1.75	-51.20	0.17	-102.87
5	2.00	-52.52	0.17	-102.69



DISCUSSION

In the titrations between standard solutions of Hydrochloric acid (HCl) and Sodium hydroxide (NaOH) of unknown concentrations, nearly equal volume of Hydrochloric acid was required to neutralize 25cm³ of Sodium hydroxide (Table 1). This is due to the fact that HCl is monoacid while NaOH is monobasic in nature. For the same reason, the concentrations of NaOH determined were found to be equal to those of standard solutions of HCl as presented in table 1. Although, phenolphthalein and methyl orange are suitable indicators for the titration between a strong acid and strong base, (Mendham *et al.*, 2000), however, in this research, phenolphthalein was used at the researchers' discretion.

In an effort to determine the heat given out and the temperature rise when equal volumes of HCl and NaOH were allowed to react in a calorimeter, the result shows an increase in temperature difference (ΔT) with increase in concentrations of both NaOH and HCl as indicated in Table 2. With increase in concentrations of the reacting species, their rate of collisions also increased. This accounted for the increase in temperature rise (ΔT) and for the same reason, the amount of heat given out during the reaction also increased. These observations therefore, suggest that the value of heat evolved or given out is a function of temperature difference and the concentrations of the acid and base.

Determination of total heat content enthalpy (ΔH) was done with the help of the heat given out and the number of moles of water formed during the reaction. The number of moles of water formed is equal to the number of moles of either HCl or NaOH. The values of enthalpy change ΔH for the neutralization reaction of the various concentrations of HCl and NaOH were found to be almost constant as shown in Table 3. This is due to the fact that the mole ratio of HCl and NaOH in the reaction is 1:1. This is expected from the reaction between monoacid and monobasic compounds. However, the values determined slightly differed from that of the literature due to the fact that some heat were lost from the system to the surroundings. Also, the experiments were carried out at room temperature. The reason for the negative sign of the enthalpy change was due to the fact that heat was given out from the system to the surrounding (Hilary, 2008).

The entropy values were found to be small and constant at 0.17kJmol⁻¹ as can be seen in table 3. This was partly due to the fact that there was no change in state between the reactants and products i.e. they were all in liquid form. The reaction mixture did not boil let alone to produce gaseous product which would have accounted for high entropy value.

Gibb's free energy, which determines the feasibility, magnitude and direction of a reaction, (Greiner, *et al.*, 1995) in this work, its (ΔG) values were found to be negative, large and almost constant at -102kJmol⁻¹ irrespective of the changes in concentration of Hydrochloric acid



(HCl). This could be due to nature of the reacting species, and constant values of the other thermodynamic parameters like ΔH and ΔS . The negative sign of ΔG is due to the high and negative value of ΔH (Table 3).

CONCLUSION

The enthalpy changes in this work were found to differ (although not very much) from the standard value of -57.00kJmol^{-1} due to the following reasons: firstly, some reasonable amounts of heat were lost to the surroundings. Secondly, the experiments were carried out at room temperature and pressure. The entropy values determined in this research work were found to be constant, simply because there were no changes of state either from solid to liquid or liquid to gas between the reactants and products i.e they were all in liquid state. Gibb's free energy values calculated in this work were almost constant partly due to the nature of the reactant species and partly due to the constant values of ΔH and ΔS .

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