Exercise 2

Determination of the molar enthalpy of neutralization reaction

Topics: Basic thermodynamic concepts: system (isolated, closed, open), surroundings of the system, state variables, intensive and extensive properties, state functions. Internal energy of the system and the first law of thermodynamics. Enthalpy and the first law of thermodynamics expressed in terms of enthalpy. Energetic effects in perfect gas transformations: isobaric, isochoric, and adiabatic processes. Thermochemical equation. Experimental methods for determining heat of reaction - calorimetry. Hess's law (derivation). The dependence of heat of reaction on temperature. Enthalpy of dissolution, hydration, dilution, and neutralization.

Introduction

Thermodynamics, the study of energy transformations and their relationships, plays a fundamental role in understanding the behavior of chemical reactions and physical processes. One of the key principles in thermodynamics is the first law, which states that every chemical reaction is accompanied by the exchange of energy, either in the form of heat or work, with the system.

Thermochemistry, a branch of thermodynamics, specifically focuses on studying the thermal effects that occur during chemical reactions. This field relies on the laws of thermodynamics, particularly the first law, also known as the law of conservation of energy. According to this law, energy cannot be created or destroyed; it can only change its form.

To delve deeper into the thermal effects accompanying chemical reactions, we first need to understand the concept of internal energy (U). The internal energy of a system refers to the sum of its kinetic and potential energies at the molecular level. It is a function of state parameters, such as temperature, pressure, and volume. However, it does not include the kinetic energy of the system as a whole or its potential energy in an external force field.

The first law of thermodynamics can be mathematically expressed as $dU = \text{đ}q + \text{đ}w_{vol} + \text{đ}w_e$, where dU represents the change in internal energy, and $\text{đ}q$, $\text{đ}w_{vol}$, and $\text{đ}w_e$ represent the heat, work done on the system due to volume changes, and work done on the system not associated with volume changes, respectively, during an infinitely small change in the system.

One crucial aspect to note is that work and heat are not state functions. In other words, their values depend on the specific path taken during a process, not just the initial and final states. As a result, their differentials are incomplete (∂). Nonetheless, their sum, ΔU, which is the change in internal energy, is indeed a state function.

At this point, it is essential to differentiate between heat and work. Heat ($\text{đ}q$) is the energy transferred between the system and its surroundings due to temperature differences, while work involves mechanical energy transfer that results in changes in volume or pressure.

In specific cases, where the process occurs at constant volume (V = const) and no non-expansion work is done ($w_e = 0$), the change in internal energy (dU) becomes equal to the heat exchanged with the surroundings (q_V). Similarly, if the process takes place under constant pressure (p = const) and no non-expansion work occurs ($w_e = 0$), the change in enthalpy (dH) is equivalent to the heat exchanged at constant pressure (q_p).

Enthalpy (*H*), another essential thermodynamic function, is particularly useful when dealing with processes at constant pressure (isobaric processes). It is defined as $H = U + pV$, where pV represents the pressure-volume work. Enthalpy, like internal energy, is a function of state parameters and, in a finite change, only depends on the initial and final states of the system.

Hess's Law, a fundamental principle in thermochemistry, is based on the first law of thermodynamics. It was discovered empirically in the mid-19th century before the formalization of the first law. Hess's Law states that in an isochoric or isobaric process where no non-expansion work is done, the heat effect of the process is equal to the change in internal energy or enthalpy. Since internal energy and enthalpy are state functions, the heat effect of such processes does not depend on the process path; rather, it solely depends on the initial and final states of the system.

This law has profound implications for calculating the heat effects of chemical reactions. By using the heat effects of other reactions whose combination leads to the desired chemical process, one can determine the heat effect of the reaction in question. This method is particularly valuable for reactions whose heat effects cannot be directly measured.

In the context of thermochemistry, the term "system" refers to the object under investigation, while "surroundings" encompass the rest of nature that interacts with the system. A closed system is one that does not exchange mass with its surroundings, while an isolated system is one that does not exchange energy either. Understanding these distinctions is crucial for accurate thermodynamic analysis.

To fully describe the state of a closed system, one needs to know its composition (number of moles of each substance) and two other independent parameters, which are typically temperature and pressure or temperature and volume. These independent parameters are known as state parameters or thermodynamic coordinates. All other quantities characterizing the system, which are functions of these independent parameters, are referred to as state functions. Internal energy (*U*) is one such state function that represents the energy stored within the system.

Thermochemistry delves into the heat effects accompanying chemical reactions and various physical processes, including phase transitions, mixing, dissolution, adsorption, and more. The standardization of heat effects is crucial to compare the heat effects of different processes, allowing for a standardized comparison. The concept of standard heat effect, denoted as $\Delta H°$, involves considering the reaction under specific conditions, typically at a temperature of 25°C (298 K) and at a pressure of 1 atm (101.325 kPa). The standard enthalpy of reaction is the change in enthalpy when reactants in their standard states undergo transformation into products that are also in their standard states.

The standard enthalpy of reaction can be represented as:

$\Delta H° = \Sigma n \Delta H°(\text{products}) - \Sigma m \Delta H°(\text{reactants})$

where n and m are the stoichiometric coefficients of the products and reactants, respectively. $\Delta H°$(products) and $\Delta H°$(reactants) are the standard enthalpies of formation of the products and reactants, respectively.

Thermochemical equations are used to represent the heat effects of chemical reactions. The enthalpy change ($\Delta H°$) is often given per mole, specifying whether it refers to 1 mole of the product or substrate, to ensure clarity and precision in its interpretation.

One fascinating application of thermochemistry is the study of the enthalpy of neutralization. This process involves the reaction of hydrogen ions (H^+) with hydroxide ions (OH^-) to form water (H_2O). The heat or enthalpy of neutralization represents the heat effect of this reaction, where 1 mole of H^+ ions reacts with 1 mole of OH^- ions without a change in the concentration of the solution. In practice, a strong monoprotic acid (e.g., HCl) is neutralized with a strong monohydroxy base (e.g., NaOH). During this process, ions are transferred from one solution to another (dilution processes) before the actual neutralization reaction occurs.

It is essential to consider that the heat effect measured in a calorimeter during neutralization includes contributions from these dilution processes and other accompanying reactions, such as the formation of salts. The heat effect of neutralization is usually referred to an infinitely diluted solution for better comparison and standardization.

Furthermore, during the dissolution of solids in liquid solvents, enthalpy changes result from the sum of two partial processes: the disruption of the crystal lattice of the solid substance, associated with heat absorption (positive energy effect), and solvation of the released lattice elements, associated with heat release (negative energy effect). Depending on the predominance of one process over the other, the overall enthalpy change during dissolution can be either positive or negative.

On the other hand, when a liquid substance dissolves in a liquid solvent, there is always heat released, associated with the solvation process (negative energy effect). The heat exchanged during dissolution is typically expressed per 1 mol of dissolved substance and depends on the nature of the substances being mixed.

Enthalpies of dissolution ($\Delta_{\mathrm{dis}}H$) are determined through direct calorimetric measurements.

Exercise Execution

The aim of this exercise is to determine the molar enthalpy of neutralization ($\Delta^{z}_{H_2O}H_m$) in the reaction between sulfuric acid(VI) and potassium hydroxide. This objective can be achieved by:

- Determining the average heat capacity of the calorimeter ($\bar{c}_{cal}$),
- Determining the molar enthalpy of dissolution of sulfuric acid(VI) ($\Delta_{dis}H_{H_2SO_4,m}$),
- Determining the overall heat effect accompanying the addition of sulfuric acid(VI) to the potassium hydroxide solution, per 1 mole of sulfuric acid(VI) ($\Delta_{\Sigma}H_m$).

Measurements are carried out using a Dewar flask (serving as the calorimeter) equipped with a thermometer and a stirrer.

Ad 1) Determining the average heat capacity of the calorimeter ($\bar{c}_{cal}$)

The average heat capacity of the calorimetric system is determined by measuring the change in temperature of the system during the dissolution of a substance if its molar enthalpy of dissolution ($\Delta_{\mathrm{dis}}H_m$) is known:

$$\bar{c}_{cal} = \sum c_J m_J = -\left(\frac{\partial \Delta_{dis}H_m}{\partial T}\right)_p$$

where c_J is the specific heat of materials, individual components of the calorimetric system, with a mass of m_J. In the exercise, substances with known values of molar enthalpy of dissolution are used, for example, NH_4Cl and KCl.

Table 1. NH_4Cl and KCl molar enthalpies of dissolution.

Substance	molar enthalpy of dissolution $\Delta_{dis}H_{J,m}$ [kJ mol^{-1}]	Recommended substance amount m [g]
NH_4Cl	15.99	12
KCl	18.33	10

300 cm^3 of distilled water is poured into the Dewar flask, and its temperature is measured at 10-second intervals. Once the temperature stabilizes, the T_0 value is recorded. Next, a weighed amount of one of the substances given in Table 1 is added to the Dewar flask (the weighed substance should be crushed in a mortar before adding it to the flask). While continuously stirring, the temperature of the system is noted every 10 seconds until it reaches equilibrium (the system attains a constant T_1 temperature). The temperature readings during the dissolution process are recorded in the table.

Ad 2) Determination of the molar enthalpy of dissolution of sulfuric acid(VI)

300 cm^3 of distilled water is poured into the Dewar flask, and its temperature is measured every 10 seconds. Once the temperature stabilizes, the T_0 value is recorded. Then, using a measuring cylinder, 5 cm^3 of concentrated sulfuric acid(VI) (ρ = 1.84 g cm^{-3}) is added to the Dewar flask. The changes in temperature are measured every 10 seconds during the dissolution process and recorded in the table, similar to step 1.

Ad 3) Determination of the molar enthalpy of neutralization in the reaction

$$H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O$$

In a 500 cm^3 beaker, 300 cm^3 of distilled water is poured, and the appropriate amount of KOH is dissolved in it to neutralize the previously used quantity of H_2SO_4. The prepared KOH solution is then transferred to a Dewar flask, and while continuously stirring, the temperature of the system is recorded every 10 seconds until it reaches equilibrium (T_0). Next, 5 cm^3 of H_2SO_4 is added to the Dewar flask, and using the procedure mentioned above, the changes in temperature are noted until the value of T_1 stabilizes.

Remarks:

- The cover of the Dewar flask must be closed during the measurement.
- Sulfuric acid(VI) should be added through the central opening of the cover.
- The amount of water used in successive determinations must be the same.

Calculations

1. Calculation of the average heat capacity of the calorimeter ($\bar{c}_{cal}$).

From the given equations, it follows that the heat effect $\Delta_{dis}H$ associated with the dissolution of the substance is described by the expression:

$$\Delta_{dis}H = -\bar{c}_{cal}\Delta T$$

Taking into account that: $\Delta_{dis}H = n_J\Delta_{dis}H_{J,m}$ and $n_J = m_J/M_J$ and the fact that the molar enthalpy of the substance J used in the dissolution, the expression is described as:

$$\Delta_{dis}H_{J,m} = -\bar{c}_{cal}\frac{M_J\Delta T}{m_J}$$

where n_J, m_J, M_J respectively represent the number of moles, mass [g], and molar mass [g mol^{-1}] of the substance used (NH_4Cl or KCl).

From rearranging this formula, it follows:

$$\bar{c}_{cal} = -\frac{\Delta_{dis}H_{J,m}m_J}{M_J\Delta T}$$

to find the value of $\Delta T = \Delta_1 T$, a graph is prepared showing the relationship between temperature (T) and time (Δt). From the graph, ΔT is obtained as the difference $T_1 - T_0$ in the salt dissolution process, as shown in the manner described in Figure 1 and explained below.

Regardless of the type of calorimeter, a calorimetric measurement consists of three periods: the initial period, the main period, and the final period. The initial period is the time from the start of temperature observation to the beginning of the studied process. From that point until reaching the maximum temperature, the main period occurs. Directly after that, the final period follows, lasting until the temperature readings are completed.

To determine the value of $\Delta T = \Delta_1 T$, a graph is plotted showing the relationship between temperature (T) and time (t) (curve *abcd*). Then, two tangents parallel to this curve are drawn, passing through the points corresponding to the initial period (segment *ab*) and the final period (segment *cd*). These drawn tangents are extended on both sides to obtain auxiliary lines I and II, which are then connected with a line *ef* drawn perpendicular to the *x*-axis. The middle segment *eg* is then drawn in such a way that the lengths of segments *eg* and *gf* are equal. The segment *ef* determined in this way unequivocally defines the value of $\Delta T = \Delta_1 T = T_1 - T_2$. The temperature values at points *e* (T_0) and *f* (T_1) are read from the graph by extrapolation to $t = 0$.

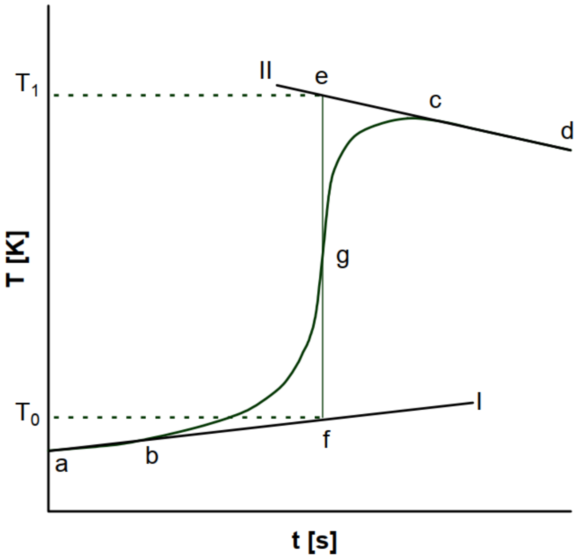

Figure 1. The graphical method of determining $\Delta T = T_1 - T_0$.

2. Calculation of the molar enthalpy of dissolution of sulfuric acid(VI) ($\Delta_{dis}H_{H_2SO_4,m}$).

This value is determined using equation

$$\Delta_{dis}H_{J,m} = -\bar{c}_{cal}\frac{M_J\Delta T}{m_J}$$

by finding the value of $\Delta_2 T$ through the preparation of a graph showing the change in temperature during the dissolution process of sulfuric acid(VI) over time.

3. Calculation of the molar enthalpy of neutralization in the reaction between sulfuric acid(VI) and potassium hydroxide.

The total heat effect accompanying the addition of H_2SO_4 to the KOH solution (per 1 mole of sulfuric acid(VI), denoted by symbol ($\Delta_\Sigma H_m$), consists of the molar enthalpy of dissolution of sulfuric acid(VI) ($\Delta_{\mathrm{dis}} H_{H_2SO_4,m}$) and the enthalpy of forming 2 moles of water. In the following equation, the molar enthalpy of forming 1 mole of H_2O is denoted by $\Delta^z_{\mathrm{H_2O}} H_m$. Therefore:

$$\Delta_\Sigma H_m = \Delta_{\mathrm{dis}} H_{H_2SO_4,m} + 2\Delta^z_{\mathrm{H_2O}} H_m$$

After reading the value of $\Delta_3 T$ from the graph of temperature changes over time (similarly to points 1 and 2), the total heat effect during the addition of sulfuric acid(VI) to the potassium hydroxide solution is calculated:

$$\Delta_\Sigma H_m = -\frac{\bar{c}_{cal} M_{H_2SO_4} \Delta_3 T}{m_{H_2SO_4}}$$

Using experimentally determined values of $\Delta_\Sigma H_m$ and $\Delta_{\mathrm{dis}} H_{H_2SO_4,m}$ and after rearranging equation:

$\Delta_\Sigma H_m = \Delta_{\mathrm{dis}} H_{H_2SO_4,m} + 2\Delta^z_{\mathrm{H_2O}} H_m$

one can calculate $\Delta^z_{\mathrm{H_2O}} H_m$.

The results obtained in points 1, 2, and 3 are compiled in a table. It should be assumed that the main source of errors during the determination of $\bar{c}_{cal}$, $\Delta_{\mathrm{dis}} H_{H_2SO_4,m}$, $\Delta^z_{\mathrm{H_2O}} H_m$ are errors resulting from the measurements of ΔT (in points 1, 2, and 3), while other quantities are determined with negligible errors.