Thermochemical Approaches to Neutralization Reaction between Weak Acid and Strong Base

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Abstract

As an advanced laboratory activity at high school, thermochemical approaches to neutralization reactions between weak acids and strong base are proposed. For the reactions of organic acids and sodium hydroxide in aqueous media, the total enthalpy change ΔH_{total} can be determined by means of calorimetry using a thermometer with a thermistor sensor. For determining the dissociation enthalpy $\Delta_d H$ of the weak acid, a simple procedure of measuring the acid dissociation constant K_a at different temperatures was developed. Using the experimental values of ΔH_{total} and $\Delta_d H$, students can study the thermochemical relation for the neutralization between weak acid and strong base. The practical usefulness of the present laboratory activity as an advanced thermochemical experiment at high school and as an introductory experiment to chemical thermodynamics at college was discussed.

Introduction

In the high school chemistry, the reaction enthalpy $\Delta_r H$ for the formation of water from aqueous hydrogen ion and hydroxide ion is treated as being equal to -56.5 kJ mol^{-1}. This thermochemical relation is demonstrated easily by a simple calorimetric experiment for the neutralization between strong acid and strong base. However, this is not applicable to the neutralization reactions where weak acid and/or weak base is taking part in, due to the participation of the dissociation enthalpy $\Delta_d H$ of the weak acid and/or weak base. The thermochemical understanding of this chemical phenomena is based on the fundamental concepts of neutralization heat and chemical equilibrium of acid and/or base dissociation studied in the chemistry course at high school. For the quantitative understanding, it is required to introduce fundamental thermodynamic relationship in the chemical equilibrium. From this point of view, thermochemical approach to the neutralization reactions, where weak acid and/or weak base is taking part in, is a valuable teaching material for an inquiry-based laboratory work for integrating the learning outcomes at high school and also for introducing chemical thermodynamics in a basic chemistry course at college.

In the present study, appropriate experimental procedures to construct a

guided-inquiry for understanding the thermochemical relation of the neutralization between weak acid and strong base were investigated. The reactions of organic weak acids, i.e., phenol, p-cresol, o-chlorophenol, and p-nitorophenol, with sodium hydroxide in aqueous media were selected as the possible reaction systems. A convenient procedure of calorimetry for determining the total enthalpy change ΔH_{total} of the reaction was developed using a hand-made calorimetry vessel and a thermistor sensor [1]. The equilibrium constant K_a of acid dissociation and its temperature dependence were measured using a pH meter. By introducing the van't Hoff equation, the value of $\Delta_d H^o$ was calculated from the slope of the van't Hoff plot. The value of $\Delta_r H$ for the formation of water from aqueous hydrogen and hydroxide ions was successfully estimated from ΔH_{total} and $\Delta_d H^o$ using the Hess's law. The practical usefulness of the present laboratory activity as an advanced thermochemical experiment at high school and as an introductory experiment to chemical thermodynamics at college is discussed by reviewing typical experimental data.

Experimental

A convenient calorimeter. As is shown in Fig.1, a calorimetry vessel was constructed by inserting a polystyrene cup (200 cm^3) into a stainless-steel vacuum-insulation vessel (250 cm^3), where the space between the cup and vessel was filled with polystyrene foam. The opening of the calorimetry vessel was closed doubly with two polystyrene lids. A Teflon-coated themistor sensor (Techno seven; R_0=2.207 kΩ(T_0=273.15 K), 15.00 kΩ(327.15 K), B=3383 K) guided by a thin glass tube was inserted into the calorimetry vessel. The resistance of the thermistor sensor R was measured using a digital multi-meter (Advantest TR6851) connected to a PC via GPIB. Temperature T was estimated using the following relationship between R and T [1].

$$R = R_0 \cdot \exp\left[B(T^{-1} - T_0^{-1})\right] \qquad (1)$$

For calibrating the calorimeter, temperature change during dissolution of sodium hydroxide into 100 cm^3 of water was measured using different amounts of the solute (0.5~1.5 g). As the reference data, temperature change during the neutralization between hydrochloric acid and sodium hydroxide solution was measured by adding 0.10 mol dm^{-3} of HCl$_{aq}$ (50 cm^3) to 0.10 mol dm^{-3} of NaOH$_{aq}$ (50 cm^3) in the calorimeter.

Four aqueous solutions of organic acids were prepared, i.e., phenol (0.10 mol dm^{-3}), p-cresol (0.10 mol dm^{-3}), o-chlorophenol (0.10 mol dm^{-3}), and p-nitrophenol (0.05 mol dm^{-3}). Temperature changes during the reactions between the respective organic acid solutions and sodium hydroxide solution were measured by mixing every 50 cm^3 of acid and base solutions of the same concentration in the calorimetry vessel.

Measurements of acid dissociation constant at different temperatures. The respective solutions of organic acids prepared above were titrated with $NaOH_{aq}$ (the same concentration with the counter organic acid) up to the point of half-neutralization. Using a pH meter (Horiba F-22), pH values of the resultant solutions were measured at different temperatures by switching off the temperature compensation function.
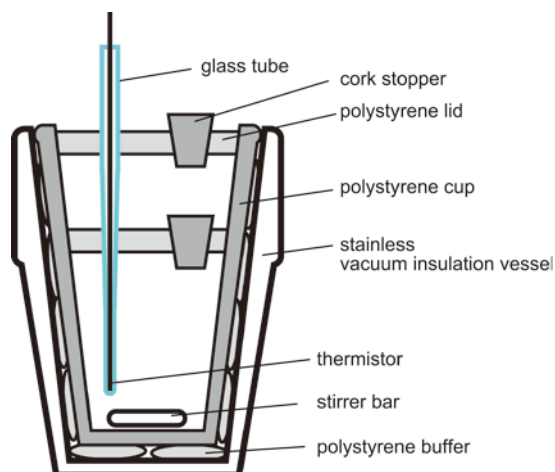

Figure 1   A schematic view of the simple calorimetry vessel used in the present study.
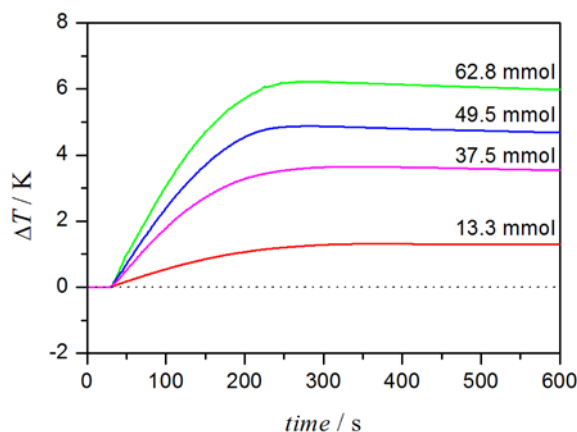

Figure 2   Temperature changes ΔT measured for the dissolution of different molar amounts of $NaOH_{(s)}$ into 100 cm^3 water.

Results and discussion

Calibration for the calorimetry system. Figure 2 shows typical experimental data of temperature change during dissolving different molar amounts of $NaOH_{(s)}$ into 100 cm^3 of water. It is noted that after completing the dissolution the temperature of the resultant solution was kept constant for a certain time, especially when the observed temperature change is less than 4 K. This indicates the good heat-retaining property of the present calorimetry vessel. In this case, the temperature change ΔT during the reaction can be determined by the difference

between two plateau temperatures of the sample solution before and after reaction, without any corrections due to thermal leak. By assuming the heat capacity of the resultant solution is comparable with that of water, $C_p = 4.184$ J g^{-1}, the experimental value of the enthalpy change of solution for NaOH$_{(s)}$, $\Delta_s H_{exp}$, is calculated by the following equation.

$$\Delta_s H_{exp} = -\frac{m \Delta T C_p}{n} \qquad (2)$$

where m and n are the mass of the resultant solution and molar amount of the solute, respectively. The value of $\Delta_s H_{exp}$ determined in the present study was -41.4 ± 0.4 kJ mol^{-1}, which is slightly smaller than that of literature value $\Delta_s H_{ref} = -44.5$ kJ mol^{-1} [2]. The ratio $C = \Delta_s H_{ref} / \Delta_s H_{exp}$ was 1.06, which can be treated as the correction constant for the heat calibration of the entire calorimetric system by considering the temperature changes of the parts of the calorimetry vessel other than the sample solution, i.e., cup, stirrer bar, thermometer, and so on [3].

Total enthalpy change for the reaction. Figure 3 compares the temperature changes due to the reactions of 0.10 mol dm^{-3} NaOH$_{aq}$ with the same concentration of HCl$_{aq}$ and phenol$_{aq}$. Because the low concentrations of the acid and base should be selected due to the limited solubility of phenolic compounds, the temperature changes for the reactions are small. Utilization of the thermometer with a thermistor sensor was thus required to detect such small temperature change with reading digits as many as possible. It is apparent from Fig. 3 that the smaller temperature change is observed for the reaction of phenol$_{aq}$. The values of ΔT observed for the respective reactions are listed in Table 1. In comparison with the value for the reaction of HCl$_{aq}$ and NaOH$_{aq}$, the smaller values of ΔT for the reactions of the aqueous solutions of phenolic compounds with NaOH$_{aq}$ are observed as the general trend.
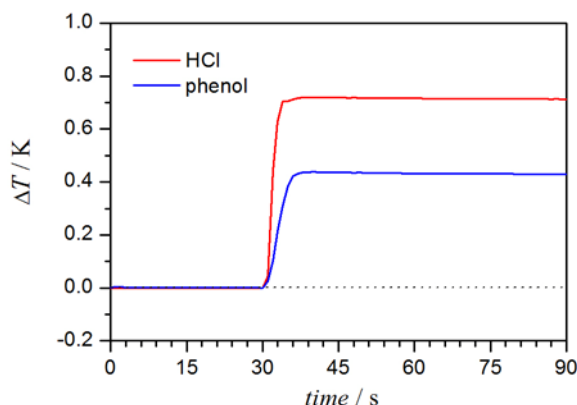

Figure 3   Comparison of temperature changes for the reactions of NaOH$_{aq}$ with HCl$_{aq}$ and phenol$_{aq}$: 50 cm^3 of 0.10 mol dm^{-3} acid and base were mixed at 30 sec.

Table 1   The temperature change ΔT and the total enthalpy change ΔH_{total} for the neutralization reactions determined experimentally

Acid	Concentration[*1]	ΔT	ΔH_{total}	ΔH_{ref}[*2]
	mol dm^{-3}	K	kJ mol^{-1}	kJ mol^{-1}
HCl	0.10	0.704 ± 0.012	−62.4 ± 1.0	−56.5
Phenol	0.10	0.443 ± 0.017	−39.3 ± 1.5	−33.1
p-cresol	0.10	0.519 ± 0.042	−46.0 ± 3.7	−38.8
o-chlorophenol	0.10	0.509 ± 0.046	−45.1 ± 4.0	−32.2
p-nitrophenol	0.05	0.278 ± 0.029	−49.3 ± 5.1	−36.8

[*1] Concentrations for the acid and sodium hydroxide solutions.

[*2] Literature values for the infinite dilution at 298 K [2].

The total enthalpy change ΔH_{total} of the reaction can be estimated from the value of ΔT according to the equation.

$$\Delta H_{total} = -\frac{m\Delta T C_p}{n} C \qquad (3)$$

where n and C are the molar amount of the product water and the correction constant 1.06 determined above, respectively. The values of ΔH_{total} determined experimentally were listed in Table 1, together with the literature values [2]. The larger values of ΔH_{total} were obtained in comparison with the respective literature values for the infinite dilution at 298 K. At the same time, it is clear that the values of ΔH_{total} for the weak acid-strong base reactions are smaller than that for strong acid-strong base reaction.

Dissociation enthalpy of the weak acid. The acid dissociation constants K_a of the aqueous solutions of phenolic compounds at different temperatures were determined by measuring pH values of the mixed solutions of the weak acids and $NaOH_{aq}$ in the fixed molar ratio of 2:1, because pK_a of the weak acid is approximately equivalent to pH value of the reacting solution at the point of half-neutralization [4]. Figure 4(a) shows the temperature dependence of pK_a thus obtained for the aqueous solutions of phenolic compounds. Irrespective of the phenolic compounds, the values of pK_a decrease systematically with increasing temperature.

The variation of K_a with temperature is given by the van't Hoff equation [5]:

$$\ln K_a = -\frac{\Delta_d H^\circ}{RT} + \frac{\Delta_d S^\circ}{R} \qquad (4)$$

where R, $\Delta_d H^\circ$, and $\Delta_d S^\circ$ are the gas constant (8.314 J K^{-1} mol^{-1}), standard enthalpy of the dissociation, standard entropy of the dissociation, respectively. The van't Hoff plots, $\ln K_a$ vs. T^{-1}, for the acid dissociation equilibria of the aqueous solutions of phenolic compounds are

shown in Fig. 4(b). These linear plots with the negative slopes indicate the endothermic behavior of the acid dissociations, $\Delta_d H^o > 0$. Table 2 lists the values of $\Delta_d H^o$ calculated from the slopes of the respective van't Hoff plots. The values of $\Delta_d H^o$ determined experimentally are close to the literature values $\Delta_d H^o_{ref}$ [2], but the deviation from $\Delta_d H^o_{ref}$ is about 30 % in the largest case.
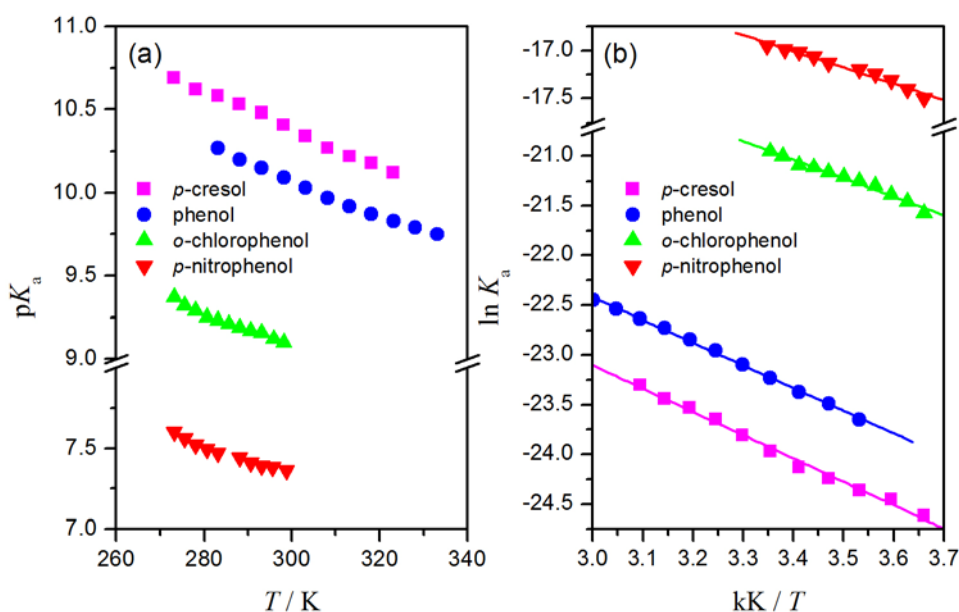

Figure 4   Temperature dependence of pK_a of the phenolic compounds (a) and the van't Hoff plots for the equilibrium of the acid dissociation (b).

Table 2   The enthalpy change of acid dissociation $\Delta_d H^o$ calculated from the slope of van't Hoff plot

Acid	Temp. range	Correl. coeff., γ^2 [*1]	$\Delta_d H^o$	$\Delta_d H^o_{ref}$ [*2]
	K		kJ mol^{-1}	kJ mol^{-1}
phenol	283–333	0.9981	18.9 ± 0.1	23.6
p-cresol	273–323	0.9927	19.5 ± 0.3	17.9
o-chlorophenol	273–298	0.9791	15.5 ± 0.2	19.4
p-nitrophenol	273–299	0.9747	14.1 ± 0.2	19.7

[*1] Square of the correlation coefficient of the linear regression for the van't Hoff plot.

[*2] Literature values [2].

Table 3   The reaction enthalpy $\Delta_r H$ of the formation of water from aqueous hydrogen ion and hydroxide ion

Acid	ΔH_{total}	$\Delta_d H^\circ$	$\Delta_r H = \Delta H_{total} - \Delta_d H^\circ$
	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
phenol	-39.3 ± 1.5	18.9 ± 0.1	-58.2
p-cresol	-46.0 ± 3.7	19.5 ± 0.3	-65.5
o-chlorophenol	-45.1 ± 4.0	15.5 ± 0.2	-60.6
p-nitrophenol	-49.3 ± 5.1	14.1 ± 0.2	-63.4
HCl	-62.4 ± 1.0	—————	-62.4

Reaction enthalpy for the formation of water from aqueous hydrogen ion and hydroxide ion. Assuming simply the reaction is composed of the acid dissociation of penolic compounds in aqueous solutions and the formation of water from aqueous hydrogen ion and hydroxide ion, the value of $\Delta_r H$ is estimated according to the Hess's law. The values of $\Delta_r H$ evaluated from the thermochemical relationship of the neutralization between aqueous solutions of phenolic compounds and NaOH$_{aq}$ are listed in Table 3. The values of $\Delta_r H$ are nearly equivalent to that determined directly by calorimetric method for the neutralization of strong acid and strong base.

For designing an inquiry. At the high school chemistry courses, the dissolution of NaOH$_{(s)}$ and neutralization between HCl$_{aq}$ and NaOH$_{aq}$ have widely been utilized as learning materials of reaction calorimetry. The definite discrepancy between the neutralization enthalpies of weak acid-strong base from that of strong acid-strong base is a key question to be a starting point of inquiry-based learning. Through discussion, the contribution of dissociation of weak acid to the overall reaction between weak acid and strong base can be recalled from the student knowledge of the chemical equilibrium. A hypothesis on the contribution of the enthalpy change of the acid dissociation to the total enthalpy change may be constructed. The hypothesis is verified qualitatively by measuring the temperature-dependent change of the equilibrium constant. It is expected through such an inquiry that students learn more about the thermochemistry and chemical equilibrium on the basis of high school chemistry. The inquiry can be extended further by determining the enthalpy change of the acid dissociation from the temperature dependence of the equilibrium constant using the van't Hoff equation, which is appropriate as an introductory experiment of chemical thermodynamics at colleges and universities.

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