College Students' Misconception about the Volume Change of Solution during Acid/Base Titration: Partial Molar Volume of Salt

Nak Han Jang*
Kongju National University

산 · 염기 적정에서 용액의 부피 변화에 대한 대학생들의 오개념 연구

장 낙 한*
공주대학교

국문 요약

부피 측정법을 이용하여 산 · 염기 적정 실험에서 중화점을 측정할 때, 나는 용액의 부피 변화에 대한 한국 대학생들의 개념을 조사하였다. 이 연구에 의하면, 대부분의 대학생들은 산 · 염기 적정 동안 중화반응에 의해 물이 생성되기 때문에 부피가 증가한다는 오개념을 갖고 있었다. 그러나 이것은 용액에 있는 염에 의한 효과를 무시한 것이기 때문에, 부피 변화를 설명하는데 충분하지 않다. HCl/NaOH 중화반응 동안 용액의 부피 증가를 설명하기 위해, 나는 생성된 NaCl의 부분 몰부피를 계산하였다. 실험 결과와 계산된 부분 몰부피를 비교할 때, 나는 부피 증가의 주요 효과는 HCl/NaOH 중화반응 동안 생성된 NaCl의 부분 몰부피 때문이라는 것을 밝혔다. 여기서 산 · 염기 중화 적정 동안 용액의 부피 변화에 대한 오개념을 줄이기 위해, 나는 부분 몰부피의 개념을 대학생들에게 도입하도록 제안한다.

주요어: 오개념, 중화, 부피 변화, 부분 몰부피

I. Introduction

Titration is an analytical method in which a standard solution is used to determine the concentration of another solution. In aqueous solutions, addition of bases to water leads to an increase in the pH of the solution, while the addition of acids leads to a decrease in the pH. The changes in pH can be followed using either specific dyes, called – indicators, or a pH electrode (Barnum, 1999; Charlesworth *et al.*, 2003). Acids and bases neutralize, or reverse, the action of one another. By adding a known amount of acid to a basic solution, until it completely reacts with it, the amount of the base can be determined. This procedure is called: acid – base titration.

An acid/base titration uses the fact that one can be neutralized with the other. In this neutralization reaction, the acid and base will combine with each other to produce ionic substances, called salts, plus water. When done correctly, the resulting solution will be neutral – neither acid nor base. In a titration, this is known as the end point. The change in pH of the solution can be monitored using an indicator or pH meter (Harris, 2001). In addition, the end point can be determined with temperature or volume measurement (Loucks, 1999; Lunelli & Scagnolari, 2002). It is extremely important that the exact amounts of each solution used be known at the end point.

In this study, the volume change of solution, occurring while an acid (hydrochloric acid) is added to a base (sodium hydroxide) solution, is followed using a volumetric flask with volume graduation during acid/base titration.

$$HCl + NaOH \Rightarrow NaCl + H_2O \quad (1)$$

*교신저자: 장낙한(nhjang@kongju.ac.kr)
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This balanced equation indicates that one mole of sodium hydroxide will combine with one mole of hydrochloric acid to produce one mole of sodium chloride and one mole of water. The only variable is the concentration of the two solutions. I measured volume changes at various concentrations of acid and base and analyzed the reason why the volume of solution increased during HCl/NaOH titration.

Ⅱ. Method

1. Partial M●lar V●lume

The partial molar volume is defined as the change in volume of a mixture when a mole of a substance is added. The formal definition of the partial molar volume of the jth component in a mixture is $\overline{V}_j = \left(\frac{\partial V}{\partial n_j}\right)_{p,T,n_j}$. It is important to note that V is a function of p, T and the composition of the mixture. The result of this is that I can write that for a two component system, $V = V(p, T, n_A, n_B)$. This means that I can write the differential of V at constant T and p as

$$dV_{T,p} = \left(\frac{\partial V}{\partial n_A}\right)_{n_A,T,P} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{n_B,T,P} dn_B = \overline{V}_A dn_A + \overline{V}_B dn_B \quad (2)$$

In other words for small changes in the mole number of the components of a mixture, the change in volume equals the partial molar volume times the change in mole number. I can also write the modification of equation (2).

$$V = \overline{V}_A n_A + \overline{V}_B n_B \quad (3)$$

However, great care must be taken in using both of these equations since the partial molar volume changes as the composition changes. Unlike molar volumes, partial molar volumes can be negative. As an illustration, if I take one mole of $MgSO_4$ and add it to one liter of water I find that the volume decreases by 1.4 mL. Thus the partial molar volume of $MgSO_4$ in pure water is −1.4 cm^3, *i.e.*, $\left(\frac{\partial V}{\partial n}\right) = -1.4$ mL. This leads to an interesting and important distinction − partial molar volumes can be negative   molar volumes cannot be negative (Atkins & de Paula, 2002).

For a two-component solution: NaCl (A) + water (B) ⇒ NaCl solution, dV can be computed from equation (3) as

$$dV = n_A d\overline{V}_A + \overline{V}_A dn_A + n_B d\overline{V}_B + \overline{V}_B dn_B \quad (4)$$

Comparing equations (2) with (4), I can find that

$$n_A d\overline{V}_A + n_B d\overline{V}_B = 0 \quad (5)$$

This is known as the *Gibbs-Duhem equation*. It cabalsobemodifiedas

$$d\overline{V}_A = -\left(\frac{n_B}{n_A}\right) d\overline{V}_B \quad (6)$$

For the total volume V of a solution containing 1kg(55.51 mol) of water (A) and m mol of NaCl (B),

$$d\overline{V}_A = -\left(\frac{n_B}{55.51}\right) d\overline{V}_B \quad (7)$$

Because the partial molar volume of NaCl, $\overline{V}_B$, is best determined from the slope of a plot of V vs n_B, the partial molar volume of water, $\overline{V}_A$, can also be determined using equation(7).

2. Ex●erimental Secti●n

Students must make sure all glassware is clean and dry. Acetone will be helpful to get rid of excess water. Drying ovens are available under the hoods at the laboratory and also on the benchtop.

Both stock solutions of 2M aqueous HCl and 2M aqueous NaOH were prepared using a 200 mL of volumetric flask. The 50 mL of volumetric flask was modified with a 0.1 mL of volume graduation mark after calibrating with the deionized water as shown in Fig. 1.

Students add a known volume of 2 M HCl to a known volume of 2 M NaOH into a 50 mL of graduated volumetric flask one by one as shown in Table 1. After completing a pair of solution, dry the volumetric flask with acetone to get rid of water prior to filling with each new solution. Rinse the volumetric flask three times with each solution prior to filling. Pour each pair of solutions into the volumetric flask one by one with the procedure.

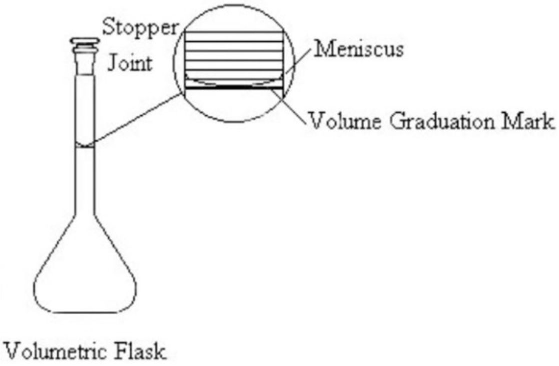

Fig. 1 Diagram of modified volumetric flask with volume graduation

Students must make sure solutions are thoroughly mixed, shaking vigorously. They observe the volume of solution before and after the neutralization reaction occurs. Student must calculate the change in volume for each solution to estimate the equivalence point of neutralization. Plot the volume change of solutions according to the volume of HCl or NaOH.

Table 1 A Pair list of volumes mixed with 2M HCl and 2M NaOH

Volume of HCl (mL)	0	10	20	30	40	50
Volume of NaOH (mL)	50	40	30	20	10	0

Ⅲ. Results and Discussion

The equivalence point was found from the plot of volume increments of solutions during HCl/NaOH titration experiment (Fig. 2). The volume increment of solution was at maximum when volumes of acid and base were same at 25 mL.

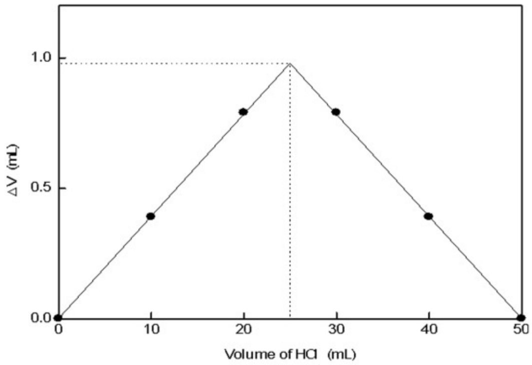

Fig. 2 Plot of the volume increment of solution by neutralization during HCl/NaOH titration

When I questioned Korean college students about why the reason of volume increment during HCl/NaOH titration, the ninety-nine percentages of students answered the formation of water during neutralization. I found they had misconception about volume during acid/base titration. Almost college students don't know about the volume contribution of NaCl by the partial molar volume.

I am going to calculate the partial molar volume of NaCl at equivalence point during HCl/NaOH tiration. In NaCl system like equation (1), total volume of a solution containing 1kg water is presented to the analytical expression: (Klotz, 1950; Lewis & Randall, 1961)

$$V = 1\,002.874 + 17.8213m - 0.87391m^{2} - 0.047225m^{2} \qquad (8)$$

where m is the molarity of NaCl. From equation (8), I can compute the partial molar volumes of NaCl($\overline{V}_B$):

$$\overline{V}_B = \left(\frac{\partial V}{\partial n_B}\right)_{n_A} = \frac{\partial V}{\partial m} = 17.8213 - 1.74782m - 0.141675m^{2} \qquad (9)$$

The partial molar volume of a solution containing 1kg(55.51 mol) of water and m mol of NaCl was plotted using equation (9) in Fig.3 (Bromberg, 1984).

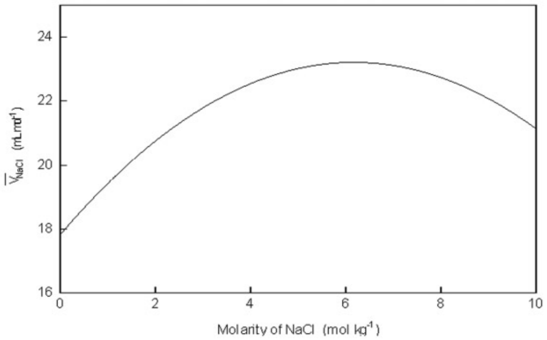

Fig. 3 Plot of the partial molar volume of NaCl in water as a function of concentration (m)

To explain the result of titration experiment, the quantity of NaCl by neutralization formed during HCl/NaOH titration can be calculated using equation (1). At equivalence point, a 25 mL of 2M HCl was perfectly combined with a 25 mL of 2M NaOH to form the water plus NaCl salt. Because both 0.05 mol of HCl and NaOH were reacted perfectly, the quantity of NaCl formed was a 0.05 mol by proportion from equation (1). Using equation (9), the partial molar volume of NaCl formed was about 0.97 mL mol^{-1} during HCl/NaOH neutralization. Because the volume increment from experiment was observed with about 0.99 mL at equivalence point during titration,the water formed by neutralization was actually about 0.02 mL during titration. Therefore the volume contribution of NaCl is more prevalent compared to water formation during neutralization. Here I can estimate the main factor of volume change to the partial molar volume of NaCl during HCl/NaOH titration.

Ⅳ. Implications

Students have misconception about the volume change of solution during HCl/NaOH titration experiment. They thought the reason of volume increment was due to the formation of water during neutralization. From calculation of the partial molar volume, I elucidated that the volume contribution of NaCl is more than the formation of water by neutralization during NCl/NaOH titration. Here I propose to introduce students to the concept of partial molar volume to reduce misconceptions of volume change during acid/base titration experiment.

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Abstract

I investigated Korean college students' conception about the volume change of solution when they detected the equivalence point during acid/base titration experiment using method of volume measurement. According to this study, most college students had a misconception that the volume increment was due to the formation of water by neutralization during acid/base titration. However, this is not enough to explain the volume change, neglecting contribution of a salt in solution. I calculated the partial molar volume of NaCl formed to explain the volume increment of solution during HCl/NaOH neutralization. Comparing the result of experiment with the calculation of partial molar volume, I elucidated that the main effect of volume increment was due to the partial molar volume of NaCl formed during HCl/NaOH neutralization. Here I propose to introduce college students to the concept of partial molar volume of the salt formed to reduce misconception about the volume change of solution during acid/base neutralization.

Key words: misconception, neutralization, volume change, partial molar volume