The Volume Change on Neutralization of a Strong Acid with a Strong Base[1]

By Akira TSUJIOKA

(Received November 23, 1958)

A method of calculation has been proposed by which we may evaluate the changes of volume on neutralization of various acids and bases at a constant temperature. The values of volume change fraction on neutralization of hydrochloric acid with sodium hydroxide solution at 20°C have been calculated. These calculated values have shown a good agreement with the observed ones. We have, on the other hand, shown that the volume change fraction of the reaction between a strong acid and a strong base of equal concentrations is represented by a simple function of the initial concentration.

It was noticed in an early period that there is an expansion on the neutralization of a strong acid with a strong base[2], but there are only a few data[3]. In particular, there are few data regarding the volume change on neutralization of an acid and a base of unequal concentrations. No investigation has as yet been made to correlate quantitatively the change of volume with concentration. Therefore we devised a method of calculation by which still more data can easily be provided, and then derived the relationship between the volume change on neutralization and the concentration of an acid or a base.

Now, if the density of a salt solution produced by neutralization is obtained, the volume change which occurs in this case can readily be evaluated. Then we have evaluated the density of the salt solution from the density table. That is, the weight per cent concentration of the resulting salt solution can be evaluated from the initial concentrations, so the density of this solution may be obtained by interpolation from the density table. The densities of electrolyte solutions have been fully known at intervals of one or two per cent concentration, so this interpolation does not cause any appreciable errors, as will be dealt with later.

The method mentioned above can be applied to the neutralization not only of a strong acid and a strong base, but also of both weak electrolytes or a strong electrolyte and a weak one.

Calculations

In considering the volume changes on neutralization of various acids and bases, we shall deal with both 1-1 strong electrolytes. In the other cases, we may deal with them in the manner described below.

If V_a ml. of a C_a mol./l. acid (the density, d_a) is neutralized with V_b ml. of a C_b mol./l. solution of a base (the density, d_b) at constant temperature, the volume change can be calculated as follows.

The weight per cent concentration of the resulting salt solution, denoted by a, is represented by the equation,

$$a = M_s/10(d_a/C_a + d_b/C_b) \tag{1}$$

where M_s is the molecular weight of the salt. If the density of this solution is denoted by d_s, the apparent molar volume of the acid by Φ_a, that of the base by Φ_b and that of the salt by Φ_s, these apparent molar volumes are defined by the following equations, respectively.

$$\Phi_a = \{1000 - (1000d_a - C_aM_a)/d_w\}/C_a \tag{2}$$

$$\Phi_b = \{1000 - (1000d_b - C_bM_b)/d_w\}/C_b \tag{3}$$

$$\Phi_s = 1000(d_a/C_a + d_b/C_b)(1/d_s - 1/d_w) + M_s/d_w \tag{4}$$

where d_w is the density of water, M_a, the molecular weight of the acid and M_b, that of the base.

Then it may be presumed that the volume change on neutralization is due to the change in the apparent molar volume of the solute, so that the volume change denoted by ΔV ml. is given by

---

[1] A part of this paper was presented at the 11th Annual Meeting of the Chemical Society of Japan, held in Tokyo in April, 1958.

[2] J. R. Partington, "An Advanced Treatise on Physical Chemistry", Vol. 2, 1st Ed., Longmans, Green and Co., London (1951), p. 33.

[3] J. D'Ans and E. Lax, "Taschenbuch für Chemiker und Physiker", 2nd Ed., Springer Verlag, Berlin (1949), p. 821; Landolt-Börnstein, "Physikalisch-Chemische Tabellen", Erg. B. II, Springer Verlag, Berlin (1931), p. 274.

$$\Delta V=(\Phi_s+\Phi_w-\Phi_a-\Phi_b)C_aV_a/1000 \qquad (5)$$

where Φ_w is the apparent molar volume of water, equal to M_w/d_w (M_w is the molecular weight of water). In Eq. 5, ΔV has been defined as a positive value when there is an expansion in total volume.

On the other hand, ΔV may be directly represented by means of the equation,

$$\Delta V=(d_aV_a+d_bV_b)/d_s-(V_a+V_b) \qquad (6)$$

We may choose between Eqs. 5 and 6 to evaluate ΔV, because substitution of Eqs. 2, 3 and 4 into Eq. 5 gives Eq. 6.

Neutralization at Equal Concentrations. —The equations by which we may evaluate the volume change on neutralization of a C mol./l. acid, which occupies a volume V ml., with a base of an equal concentration can be derived by replacing V_a and V_b in Eqs. 5 and 6 by V, and C_a and C_b in Eqs. 1—5 by C.

The weight per cent concentration of the resulting salt solution is obtained by

$$a^*=M_sC/10(d_a+d_b) \qquad (7)$$

Therefore, in the case of neutralization of an acid with a base of equal concentration, the increase in total volume is

$$\Delta V^*=(\Phi_s^*+\Phi_w-\Phi_a-\Phi_b)CV/1000 \qquad (8)$$

where

$$\Phi_s^*=1000(d_a+d_b)(1/d_s^*-1/d_w)/C+M_s/d_w$$

or by an alternative formula (using Eq. 6).

$$\Delta V^*=\{(d_a+d_b)/d_s^*-2\}V \qquad (9)$$

The subscripts refer to salt, water, acid and base, respectively, and the asterisk indicates that the salt concentration is a^* %.

Then replacing $(\Delta V^*/2V)\times10^3$ by Ψ in Eqs. 8 and 9, we have

$$\Psi=(\Phi_s^*+\Phi_w-\Phi_a-\Phi_b)C/2 \qquad (10)$$

$$\Psi=\{(d_a+d_b)/2d_s^*-1\}\times10^3 \qquad (11)$$

Now we will for convenience' sake call Ψ, which represents the rate of change of the volume upon neutralization, "Volume Change Fraction". The numerical value of Ψ represents the change in the total volume observed on mixing the acid, which amounts to 500 ml., with an equi-volume of the base, of which the concentration is equal to that of the acid. The value of Ψ has the same sign as ΔV^*, so it is positive when the total volume expands on mixing the two solutions.

Results and Discussion

The values of volume change fraction on neutralization of a hydrochloric acid with a sodium hydroxide solution of equal concentration at 20°C have been calculated by the method mentioned in the previous section.

The weight per cent concentration of the resulting sodium chloride solution has been evaluated by Eq. 7, so the density of this solution has been obtained by interpolation from the density data of the "International Critical Tables"[4].

Therefore, the value of Ψ has been calculated by Eq. 11. The results obtained here are shown in Table I. In this table the values of the fifth column are those observed by Saslawsky et al.[5] and those in the last column are those calculated by Eq. 24, which will be derived later.

In Table II are shown volume changes

TABLE I. VOLUME CHANGE FRACTIONS ON NEUTRALIZATION OF HYDROCHLORIC ACID WITH SODIUM HYDROXIDE AT 20°C

Initial concn.	Final concn.	Density of NaCl. aq.	Volume change fraction		
C (mol./l.)	a^* (%)	d_s^*	$\Psi_{calc.}$	$\Psi_{obs.}$	$\Psi_{eq.(24)}$
1	2.841	1.01849	10.02	9.8	9.9
2	5.530	1.03787	18.16	18.0	18.2
3	8.093	1.05658	25.37	25.1	25.5
4	10.544	1.07475	31.74	31.8	31.9
5	12.895	1.09246	37.42	37.6	37.7
6	15.159	1.10975	42.51	42.8	42.8
7	17.346	1.12677	46.91	47.2	47.3
8	19.459	1.14349	50.80	51.3	51.3
9	21.514	1.16002	54.14	54.6	54.8
10	23.504	1.17632	57.02	57.3	57.8
11	25.448	1.19254	59.35	59.0	60.4

---

[4] "International Critical Tables", Vol. III, McGraw-Hill Book Co., New York (1928), p. 79.

[5] J. J. Saslawsky aad E. G. Standel, *Z. anorg. Chem.*, **186**, 171 (1930).

TABLE II. VOLUME CHANGES ON NEUTRALIZATION OF HYDROCHLORIC ACID WITH SODIUM HYDROXIDE OF UNEQUAL CONCENTRATION AT 20°C

HCl		NaOH		NaCl		Vol. change	Vol. change
Concn. (mol./l.) C_a	Vol. (l.) V_a	Concn. (mol./l.) C_b	Vol. (l.) V_b	Concn. (%) a	Density d_s	ΔV ml.	per mole
1	1	2	0.5	3.756	1.02505	18.17	18.17
2	0.5	1	1	3.753	1.02503	19.68	19.68
2	1	4	0.5	7.266	1.05052	31.63	15.82
4	0.5	2	1	7.246	1.05038	35.93	17.97
4	1	8	0.5	13.725	1.09876	50.46	12.62
8	0.25	2	1	8.582	1.06019	34.97	17.49
8	0.5	4	1	13.628	1.09802	62.58	15.65
8	0.75	6	1	16.983	1.12392	84.88	14.15

on neutralization at unequal concentrations, which are calculated by Eqs. 1 and 6.

The Degree of Inaccuracy in Ψ.—Whether or not the values of Ψ in Table I and ΔV^* in Table II are nearly the same as those obtained by a strict experiment depends upon the extent to which an error is made in evaluating the density of the resulting solution by interpolation. Therefore, we will discuss the error in density caused by interpolation[6].

In the case of sodium chloride, the maximum error in density caused by interpolation at intervals of four per cent concentration is 0.007∼0.015 per cent in each range of concentration. It is proved by a mathematical calculation that the error in density caused by interpolation at intervals of two per cent concentration is less than one fourth of that at intervals of four per cent concentration, so that it would be rightly considered that the maximum of the errors which would be expected by interpolation at intervals of two per cent concentration is less than 0.004 per cent. If the density data are given at intervals of one per cent concentration, it is needless for us to consider the error in density caused by interpolation.

On the other hand, an error of 0.001 per cent in density would cause an inaccuracy of about 0.01 in Ψ. It is derived from Eq. 11 or deduced from the inaccuracy in Φ (cf. Eq. 10)[7]. Therefore, each of the calculated values of Ψ in Table I may be slightly less than the corresponding true value of Ψ, but the difference between the two does not exceed 0.04.

It is of course true that the above-mentioned discussion can be applied not only to Ψ in Table I, but also to ΔV^* in Table II.

Further, densities of the solutions of acids and bases at 20°C shown in Table III have been evaluated by the following equations, which have been suggested by Root[8].

$$d_{\mathrm{HCl}}=0.99823+0.01870\,C-0.00087\,C^{3/2} \quad (12)$$

$$d_{\mathrm{NaOH}}=0.99823+0.04744C-0.00454C^{3/2} \quad (13)$$

where C is the concentration in mol./l. of the electrolyte solution. These equations have been derived by using the values of Φ^0 and S_v for each electrolyte shown in Table IV.

TABLE III. DENSITIES OF HYDROCHLORIC ACIDS AND SODIUM HYDROXIDE SOLUTIONS AT 20°C

Concn. (mol./l.)	Density	
C	d_{HCl}	d_{NaOH}
1	1.01606	1.04113
2	1.03317	1.08027
3	1.04981	1.11696
4	1.06607	1.15167
5	1.08200	1.18467
6	1.09769	1.21615
7	1.11302	1.24623
8	1.12814	1.27502
9	1.14304	1.30261
10	1.15772	1.32906
11	1.17219	1.35444

TABLE IV. VALUES OF THE PARAMETERS OF EQS. 14, 15 AND 16 AT 20°C

Electrolyte	Φ^0	S_v
HCl	17.80	0.87
NaOH	−7.45	4.55
NaCl	15.82	2.32

---

[6] It has been fully discussed in "Changes of Volume of Mixing Electrolytic Solutions with Water", presented at the 10th Annual Meeting of the Chemical Society of Japan, held in Tokyo in April, 1957; A. Tsujioka, *Proc. of Faculty of Eng., Keio Univ.*, **10**, 47 (1957).

[7] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd Ed., Reinhold Publishing Co., New York (1950), p. 251.

[8] W. C. Root, *J. Am. Chem. Soc.*, **55**, 850 (1933).

At this point, therefore, the errors other than those caused by interpolation would be introduced in the values of Ψ and ΔV^* shown in Tables I and II, because they were evaluated by using the data in Table III. In conclusion, the values of Ψ and ΔV^* shown in Tables I and II appear to leave more or less room for doubt at 2 places of decimals. Nevertheless, the agreement between our data and Saslawsky's data has been found very satisfactory in Table I.

Relationships between the Volume Change Fraction and the Concentration.— Since the discovery by Masson[9] that the apparent molar volume of a dissolved salt is a linear function of the square root of the volume concentration, several investigators[10,11] have made extensive tests of the applicability of this relationship. It was found valid for a number of electrolytes over a surprisingly large concentration range. In the range of high dilution, however, the apparent molar volumes Φ_v of strong electrolytes in solution confirm the limiting law derived from the Debye-Hückel theory[12,13]. That is, the function $\Phi_v - S_v C^{1/2}$ is linearly related to the volume concentration C, where S_v is the universal limiting slope. (The experimental limiting slopes determined from the results above 0.25 N are specific[14].)

Therefore, the following Masson's linear relationships hold over a wide range of concentration except at high dilution.

$$\Phi_a = \Phi_a{}^0 + S_a\sqrt{C} \tag{14}$$

$$\Phi_b = \Phi_b{}^0 + S_b\sqrt{C} \tag{15}$$

$$\Phi_s{}^* = \Phi_s{}^0 + S_s\sqrt{C_s{}^*} \tag{16}$$

where $\Phi_a{}^0$, $\Phi_b{}^0$, $\Phi_s{}^0$, S_a, S_b and S_s are constants, and $C_s{}^*$ is the concentration in mol./l. of the salt solution, of which the concentration has been denoted by a^* % in the above section, obtained on neutralization of an acid with a base of equal concentration, C mol./l. Accordingly Eq. 10 for Ψ can be reduced to

$$\Psi = \{(\Phi_s{}^0 + \Phi_w - \Phi_a{}^0 - \Phi_b{}^0) + S_s\sqrt{C_s{}^*} - S_a\sqrt{C} - S_b\sqrt{C}\}C/2 \tag{17}$$

The resulting salt solution has a volume $(2V+\Delta V^*)$ ml., as has been indicated in the previous section. Hence the following equation:

$$C_s{}^* = C/2(1+10^{-3}\cdot\Psi) \tag{18}$$

Where Ψ, equal to $(\Delta V^*/2V)\times 10^3$, is the volume change fraction. Substituting Eq. 18 in Eq. 17 and then putting it in order by the binomial formula, we find the following equation.

$$\Psi = [(\Phi_s{}^0 + \Phi_w - \Phi_a{}^0 - \Phi_b{}^0) + (S_s\sqrt{2C}/2) \times \{1 + \sum_{r=1}^{\infty}\binom{-1/2}{r}(10^{-3}\cdot\Psi)^r\} - S_a\sqrt{C} - S_b\sqrt{C}\,]C/2 \tag{19}$$

In this equation, the terms $\sum_{r=1}^{\infty}\binom{-1/2}{r}(10^{-3}\cdot\Psi)^r$ are small and can usually be ignored[15], so that we may write,

$$\Psi = \{(\Phi_s{}^0 + \Phi_w - \Phi_a{}^0 - \Phi_b{}^0) + (S_s\sqrt{2C}/2)(1-\Psi/2000) - S_a\sqrt{C} - S_b\sqrt{C}\}C/2 \tag{20}$$

Solving this equation with respect to Ψ, we may readily derive the following equation.

$$\Psi = \{(\Phi_s{}^0 + \Phi_w - \Phi_a{}^0 - \Phi_b{}^0) + \sqrt{C}(\sqrt{2}\,S_s/2 - S_a - S_b)\}(1 - \sqrt{2}\,S_s C^{3/2}/8000)C/2 \tag{21}$$

Consequently we obtain the following equation for Ψ.

$$\Psi = K_1C + K_2C^{3/2} - K_3C^{5/2} - K_4C^3 \tag{22}$$

where
$$K_1 = (\Phi_s{}^0 + \Phi_w - \Phi_a{}^0 - \Phi_b{}^0)/2$$
$$K_2 = (\sqrt{2}\,S_s - 2S_a - 2S_b)/4$$
$$K_3 = (\sqrt{2}\,S_s/8000)K_1$$
$$K_4 = (\sqrt{2}\,S_s/8000)K_2$$

In most cases K_3 and K_4 are small and can be ignored, so that Eq. 22 is approximately represented by means of the following equaiion.

$$\Psi = K_1C + K_2C^{3/2} \tag{23}$$

As an example, we shall deal with the reaction between a hydrochloric acid and a sodium hydroxide solution. Values of the parameters of Eqs. 14, 15 and 16 at 20°C obtained by the present writer are shown in Table IV[16]. The limiting law of the apparent molar volume has been

---

[9] D. O. Masson, *Phil. Mag.*, **8**, 218 (1929).

[10] W. Geffcken and D. Price, *Z. physik. Chem.*, **B26**, 81 (1934).

[11] A. F. Scott, *J. Phys. Chem.*, **35**, 2315 (1931).

[12] B. B. Owen and S. R. Brinkley, Jr., *Ann. N. Y. Acad. Sci.*, **51**, 753 (1949).

[13] O. Redlich and J. Bigeleisen, *J. Am. Chem. Soc.*, **64**, 758 (1942).

[14] See Ref. 7, p. 523.

[15] The largest one of these terms, $\binom{-1/2}{2}(10^{-3}\cdot\Psi)^2$, is generally less than 0.001. So it would be rightly considered that the contribution of these terms to the value of Ψ does not exceed 0.1 per cent.

[16] These values were not evaluated from data at high dilution.

confirmed for aqueous solutions of sodium chloride up to 0.75 N and of hydrochloric acid up to 0.2 N[12,13]. Therefore the empirical equations, which will be derived below, should not be extrapolated to lower concentrations. Again for aqueous solutions of a few acids (i. e., perchloric acid and sulfuric acid) the apparent molar volume show an unusual dependence on the concentration[17-19].

It appears to be the same for aqueous solutions of hydrogen halides[20]. For hydrochloric acid, however, this deviation from Masson's rule is negligibly small[21,22], so we have not taken it into consideration.

By using the data in Table IV, the coefficients K_1, K_2, K_3 and K_4 in Eq. 22 have been calculated as follows.

$$K_1=11.76,\ K_2=-1.89,\ K_3=4.8\times10^{-3},$$
$$K_4=-7.7\times10^{-4}$$

In this case, therefore, we obtain

$$\Psi=11.76\,C-1.89\,C^{3/2} \qquad (24)$$

The correctness of this equation has been found very satisfactory in Fig. 1 and Table I. In Fig. 1, values of $2\Psi/C$ have been plotted against the square root of the concentration. The numerical value of $2\Psi/C$ represents the volume change in ml. on neutralization of an acid and a base of equal concentrations, C mol./l., which occupy the equal volume, v ml., where v is the volume of the solution, expressed in ml., containing one mole of the solute[23].

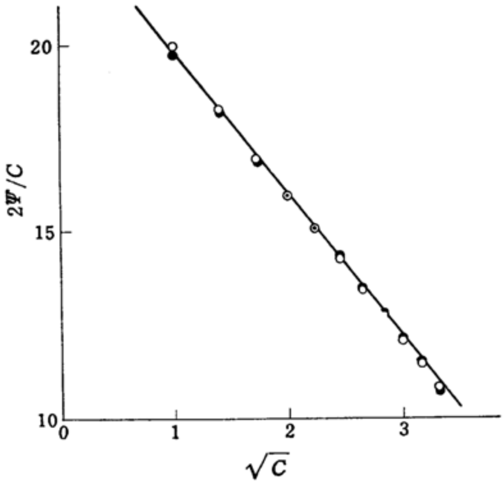

Fig. 1. Dependence of the volume change per mol., on neutralization of hydrochloric acid with sodium hydroxide of equal concn., upon concentration, at 20°C.
——, Calculated by Eq. 24, i. e., $2\Psi/C=23.52-3.78\sqrt{C}$;
○, Tsujioka's data; ●, Saslawsky's data

On the other hand, in the case of volume changes on neutralization of acids and bases of unequal concentrations, it has been shown in Table II that the expansion in total volume on neutralization gets larger as the range of concentration gets lower, and that the volume change which occurs when hydrochloric acid is more concentrated than sodium hydroxide is larger than that in the reverse case, and so on. These facts, together with the discussion of Eq. 24, may be explained by considering the volume change on dilution. It will be reported in this bulletin shortly.

The Chemical Laboratory, Keio University
Hiyoshi, Yokohama

---

[17] J. Bigeleisen, *J. Phys. and Colloid Chem.*, **51**, 1369 (1947).

[18] H. E. Wirth and F. N. Collier, Jr., *J. Am. Chem. Soc.*, **72**, 5292 (1950).

[19] I. M. Klotz and C. F. Eckert, ibid., **64**, 1878 (1942).

[20] A. Tsujioka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), in contribution.

[21] H. E. Wirth, *J. Am. Chem. Soc.*, **62**, 1128 (1940).

[22] T. F. Young and M. B. Smith, *J. Phys. Chem.*, **58**, 716 (1954).

[23] Then C is equal to $10^3/v$, and the volume change fraction Ψ is equal to $(\Delta v/2v)\times10^3$, as has been defined in the previous section, where Δv is the volume change in ml. on neutralization. Therefore it follows that $\Delta v=2\Psi/C$.