The Volume Change on Formation of Water from its Ions[1]

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The reaction between the hydrogen ion and the hydroxyl ion is given by

$$H^+ + OH^- = H_2O \qquad (1)$$

It was noticed by Geffcken et al.[2] that the volume change associated with this reaction in aqueous solution is about 23 cc. per mole at infinite dilution and at 25°C. But there has been no investigation to provide the data at various concentrations and to correlate quantitatively the volume change with concentration. Although the volume changes on formation of water are not susceptible of direct measurement, these values can be determined by using the data on changes of volume on neutralization of a strong acid with a strong base.

In the concentration range of high dilution, there is little or no difference between the volume change on neutralization of aqueous sodium hydroxide with hydrochloric acid and that with hydrobromic or hydroiodic acid[3]. The expansion

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[1] Presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

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

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

in total volume in such cases may be explained as mainly due to the disappearance of electrostriction of charged ions[4], which is caused by the fact that the hydrogen ion combines with the hydroxyl ion to form water. In the higher concentration range, however, the magnitudes of volume change per mole commonly decrease with three different series of reactions mentioned above and the differences among them becomes larger (see the second column in Table II). In order to explain these subjects, it is necessary to derive the relationship between the volume change on formation of water from its ions and the concentrations of acid and base.

With reference to the method employed by Rossini[5], who calculated the heat of ionization of water, i.e. the negative of the heat evolved in reaction 1 at infinite dilution, by combining the data on heats of neutralization and those on heats of dilution, the author has evaluated changes of volume on formation of water from its ions at constant temperature. On the other hand, the author has shown that the volume change on formation of one mole of water from its ions at moderate concentrations is represented by a linear function of the square root of the concentration of ions, by using the Masson-Geffcken relationship[2,6] on the apparent molar volume of electrolytes in solution. The relationship so obtained has been checked with the calculated data. The agreement of the results has been found very satisfactory.

In the present paper the author has utilized the data on changes of volume on neutralization recently obtained by the present author[7], and also the data of Saslawsky et al.[3,8]

Calculation and Results

In considering the volume changes on neutralization of various acids and bases, the author will deal with both uni-univalent strong electrolytes.

The reaction between a strong acid and a strong base at finite and equal concentrations, C mol./l., is given by

$$\mathrm{HB+MOH = MB+H_2O} \qquad (2)$$

This reaction represents the formation of one mole of water from its ions at the initial concentration C, and also the dilution of one mole each of M^+ and B^- ions from C to C', by which the concentration in moles per liter of the resulting salt solution is denoted.

The volume change for the process is

$$\varDelta V_{\mathrm{N}} = \varDelta V_{\mathrm{F}} + \varDelta V_{\mathrm{D}} \qquad (3)$$

where $\varDelta V_{\mathrm{N}}$ is the volume change on neutralization, $\varDelta V_{\mathrm{F}}$ is that on formation of water and $\varDelta V_{\mathrm{D}}$ is that on dilution. The value of $\varDelta V_{\mathrm{F}}$ can be obtained from that of $\varDelta V_{\mathrm{N}}$, which is directly measurable, if the corresponding value of $\varDelta V_{\mathrm{D}}$ is known. Then, it is assumed that the volume change on dilution of one mole each of M^+ and B^- ions from C to C' is equal to that on dilution of one mole of salt MB from C to C'. In other words, it is assumed that the sum of the apparent molar volumes of M^+ and B^- ions, in the basic and acid solutions respectively, is equal to the apparent molar volume of MB in the neutral salt solution. It will be permissible at the range of concentration here studied, because it would be rightly considered that the difference between B^- ion—H^+ ion interaction and B^- ion—M^+ ion interaction is small and can be ignored at low or moderate concentrations. Again, a similar assumption is made not only regarding M^+ ion, but also regarding H^+ and OH^- ions, respectively.

Thus, values of the volume change on formation of water from its ions at various concentrations at 20°C have been computed from those of the volume change, obtained by the present author[7], on neutralization of a hydrochloric acid with a sodium hydroxide solution of equal concentration. In computing these values

TABLE I. CHANGES OF VOLUME ON FORMATION OF WATER FROM ITS IONS AT 20°C[a]

Initial concn. C mol./l.	Vol. change on neutralization $\varDelta V_{\mathrm{N}}$ ml./mol.	Concn. of the resulting soln. a^* %	Vol. change on dilution ($C \to a^*$) $\varDelta V_{\mathrm{D}}$ ml./mol.	Vol. change on formation of water $\varDelta V_{\mathrm{F}}$ ml./mol.
1	20.04	2.841	−0.58	20.62
2	18.16	5.530	−1.00	19.16
3	16.91	8.093	−1.25	18.16
4	15.87	10.544	−1.45	17.32
5	14.97	12.895	−1.63	16.60

a) Calculated from values of the volume change, obtained by the present author[7], on neutralization of hydrochloric acid with sodium hydroxide solution.

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[4] I. Uhara, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **57**, 53 (1936).

[5] F. D. Rossini, *Bur. Standards J. Research*, **6**, 847 (1931).

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

[7] A. Tsujioka, This Bulletin, **32**, 685 (1959).

[8] J. J. Saslawsky and E. G. Standel, *Z. anorg. u. allgem. Chem.*, **186**, 171 (1930).

given in Table I, the author has taken ΔV_D as equivalent to the difference between the apparent molar volume of sodium chloride in the aqueous solution, of which the concentration is similar to the one of the acid or the basic solution, and that in the resulting solution, because both the density of the solution to be diluted and that of the resulting salt solution have been known[7,9].

TABLE II. VALUES OF ΔV_F CALCULATED FROM SASLAWSKY'S DATA[3,8] AT 20°C

(1) Calculated from values of ΔV_N on reaction: $HCl+NaOH=NaCl+H_2O$.

Initial concn. C mol./l.	Vol. change on neutralization ΔV_N ml./mol.	Concn. of the resulting soln. C^* ml./mol.	Vol. change on dilution $(C \rightarrow C^*)$ ΔV_D ml./mol.	Vol. change on formation of water ΔV_F ml./mol.
1	19.6	0.495	−0.7	20.3
2	18.0	0.982	−1.0	19.0
3	16.7	1.463	−1.2	17.9
4	15.9	1.938	−1.4	17.3
5	15.0	2.409	−1.6	16.6

(2) Calculated from values of ΔV_N on reaction: $HBr+NaOH=NaBr+H_2O$.

C	ΔV_N	C^*	ΔV_D	ΔV_F
1	20.0	0.495	−0.6	20.6
2	18.5	0.982	−0.9	19.4
3	17.5	1.462	−1.1	18.6
4	16.7	1.935	−1.2	17.9
5	15.9	2.405	−1.4	17.3

(3) Calculated from values of ΔV_N on reaction: $HI+NaOH=NaI+H_2O$.

C	ΔV_N	C^*	ΔV_D	ΔV_F
1	19.4	0.495	−0.5	19.9
2	18.4	0.982	−0.7	19.1
3	17.9	1.461	−0.9	18.8
4	17.1	1.934	−1.0	18.1
5	16.0	2.404	−1.1	17.1

Then, in Table II are shown values of ΔV_F, which have been calculated from the data, obtained by Saslawsky et al.[3,8], on changes of volume on three different series of reactions. In this calculation, the author has evaluated the concentration of the resulting salt solution from the value of ΔV_N, and computed the corresponding value of ΔV_D by the Masson-Geffcken relationship on the apparent molar volume of electrolyte*. Because the apparent molar volumes of these salts, i. e. sodium chloride, bromide and iodide, confirm satisfactorily this relationship over the range of concentration here treated[10,11].

In Tables I and II–1, the agreement of the results has been found very satisfactory. It is just as predicted from the fact that each of the values of volume change on neutralization obtained by the present author is in good agreement with the corresponding one by Saslawsky et al.[7] Furthermore, each of the values of ΔV_F shown in Tables II–2 and II-3 is in tolerable agreement with the corresponding one given in Table I or II–1, without an error greater than one or two per cent.

Discussion

The volume change per mole on reaction 2 is given by[7]

$$\Delta V_N = \Phi_s^* + \Phi_w + \Phi_a - \Phi_b \tag{4}$$

where Φ is the apparent molar volume of the solute. The subscripts refer to salt, water, acid and base, respectively, and the asterisk indicates that the salt concentration is C^* mol./l. As has been fully discussed in the previous section, this reaction represents the formation of one mole of water from its ions at the initial concentration, and also the dilution of one mole each of M^+ and B^- ions from the initial concentration C to the final one C'. Therefore, the changes of volume for these two processes are represented by means of the following equations, respectively.

$$\Delta V_F = \Phi_w - (\Phi_H + \Phi_{OH}) \tag{5}$$

$$\begin{aligned} \Delta V_D &= \Phi_s^* - (\Phi_M + \Phi_B) \\ &= \Phi_s^* - \Phi_s \end{aligned} \tag{6}$$

where Φ_H, Φ_{OH}, Φ_M and Φ_B are the apparent molar volumes of H^+, OH^-, M^+ and B^- ions at the initial concentration, respectively.

Substitution of Eqs. 4—6 into Eq. 3 gives the following equation.

$$\Phi_H + \Phi_{OH} = \Phi_a + \Phi_b - \Phi_s \tag{7}$$

If the apparent molar volumes of these three electrolytes confirm the Masson-Geffcken relationship, $\Phi = \Phi^\circ + S\sqrt{C}$, Eq. 7 can be reduced to

$$\Phi_H + \Phi_{OH} = (\Phi_a^\circ + \Phi_b^\circ - \Phi_s^\circ) + (S_a + S_b - S_s)\sqrt{C} \tag{8}$$

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9) A. Tsujioka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 467 (1959).

* The limiting slopes are $S_{(NaCl)}=2.32$, $S_{(NaBr)}=2.04$ and $S_{(NaI)}=1.64$ (cf. Ref. 10).

10) A. Tsujioka, *Proc. Faculty Eng., Keio Univ.*, **10**, 63 (1957).

11) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd Ed., Reinhold Publishing Co., New York (1950), p. 252.

where Φ° is the apparent molar volume of a solute at infinite dilution, and S is the limiting slope. Again it is the same as in Eq. 4 that the subscripts refer to acid, base and salt, respectively.

It has been found valid for most electrolytes that the Masson-Geffcken relationship holds over a wide range of concentration except on high dilution[2,12]. For aqueous solutions of some acids or lithium salts, however, the apparent molar volumes of the solutes show an unusual dependence on the concentration, especially at high concentrations[13,14]. Hydrogen iodide which has been treated in the present paper is one of these electrolytes, but its deviation from the Masson-Geffcken relationship would be rightly considered to be negligibly small at moderate concentrations[14].

At high dilution, on the other hand, the apparent molar volumes of strong electrolytes in solution confirm the limiting law derived from the Debye-Hückel theory[15,16]. That is, the apparent molar volumes, Φ, of strong electrolytes in solution at high dilution are represented by the following equation.

$$\Phi = \Phi^\circ + S_v\sqrt{C} + kC \qquad (9)$$

where Φ° is the apparent molar volume of a solute at infinite dilution, S_v is the universal limiting slope which is 1.86 at 25°C for 1—1 electrolyte[17], and k is constant and specific for each electrolyte. If the apparent molar volumes of acid, base and salt confirm Eq. 9**, Eq. 7 can be reduced to

$$\Phi_{\mathrm{H}} + \Phi_{\mathrm{OH}} = (\Phi_a^\circ + \Phi_b^\circ - \Phi_s^\circ) + S_v\sqrt{C} + (k_a + k_b - k_s)C \qquad (10)$$

where the subscripts refer to acid, base and salt. Therefore, the sum of the apparent molar volumes of H^+ and OH^- ions confirm the limiting Debye-Hückel law at high dilution as same as the 1—1 strong electrolytes.

Now, by using the values of the parameters*** of Masson-Geffcken equations for sodium chloride, hydrogen chloride and sodium hydroxide, Eq. 8 can be reduced to

$$\Phi_{\mathrm{H}} + \Phi_{\mathrm{OH}} = -5.47 + 3.10\sqrt{C} \qquad (11)$$

Using Eq. 5, therefore, one obtains the following equation:

$$\Delta V_{\mathrm{F}} = 23.52 - 3.10\sqrt{C} \qquad (12)$$

where ΔV_{F} is the volume change in ml./mol. which occurs on reaction 1, and C is the concentration in mol./l. of hydrogen and hydroxyl ions. This equation can be applied to moderate concentrations, i. e. 1~5 mol./l., at 20°C. Again, the numerical term in Eq. 12 does not refer to the value of volume change on formation of water from its ions at infinite dilution.

In Figs. 1 and 2, values of ΔV_{F} shown in Tables I and II, as well as those calculated by Eq. 12, have been plotted against the square root of the concentration. The agreement of the results has been found very satisfactory in Fig. 1. In Fig. 2, values of ΔV_{F} computed from values of the volume change on neutralization of hydroiodic acid with sodium hydroxide solution are considerably different from the corresponding ones computed from the data in other cases.

The apparent molar volume of hydrogen iodide, at concentrations above 1.5 N, deviate from the values predicted by the Masson-Geffcken relationship[18]. This behavior was attributed to incomplete ionization by Fajans[18], while to ion-ion and

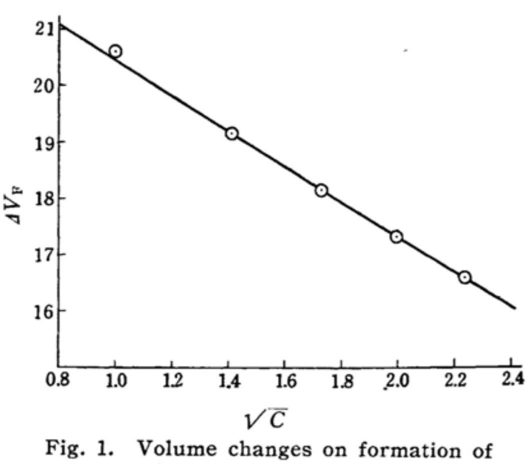

Fig. 1. Volume changes on formation of water, given in Table I, plotted against the square root of the concentration. (——, calculated by Eq. 12).

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

[13] J. Bigeleisen, *J. Phys. & Colloid Chem.*, **51**, 1369 (1947).

[14] K. Fajans and O. Johnson, *Trans. Electrochem. Soc.*, **82**, 273 (1942).

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

[16] O. Redlich and J. Bigeleisen, *Chem. Revs.*, **30**, 171 (1942).

** The limiting law of the molar volume has not been experimentally confirmed for sodium hydroxide. But the limiting slope appears to be the same for NaOH, HCl, NaCl and for other electrolytes of the 1—1 charge type. Because there is no reason to assume any anomaly in NaOH, in view of the theoretical derivation of Eq. 9.

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

*** $\Phi_{(\mathrm{NaCl})} = 15.82 + 2.32\sqrt{C}$; $\Phi_{(\mathrm{HCl})} = 17.80 + 0.87\sqrt{C}$; $\Phi_{(\mathrm{NaOH})} = -7.45 + 4.55\sqrt{C}$ (cf. Ref. 7).

[18] K. Fajans, *J. Chem. Phys.*, **9**, 281 (1941).

ion-solvent interactions by Bigeleisen[13]. But it appears to leave much room for discussions[19]. Nevertheless, it would be rightly considered that the less satisfactory linearity of HI, shown in Fig. 2, is due to a reason similar to the one to which its deviation from the Masson-Geffcken rule must be ascribed.

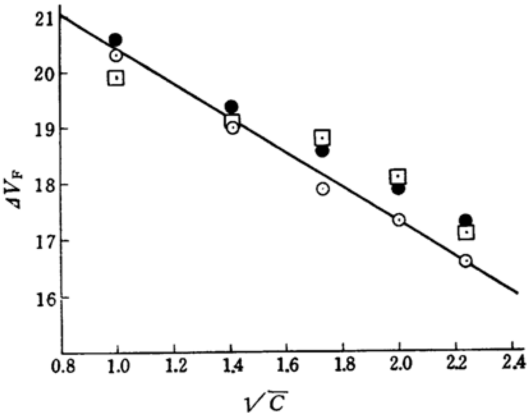

Fig. 2, Concentration dependence of ΔV_F, given in Table II.
(——, calculated by Eq. 12; ○, HCl+NaOH; ●, HBr+NaOH; □, HI+NaOH)

Thus, by using the results obtained in the present work, it is readily possible to predict changes of volume on neutralization of a strong acid with a strong base. The difference among values of the volume change, obtained in different series of reactions between acids and bases at the same conditions, is mainly due to that among the corresponding ones of ΔV_D. Values of ΔV_D are generally negative, so the expansion in total volume on neutralization gets smaller as the numerical value of ΔV_D gets larger. The diminution in total volume on dilution (ΔV_D) is proportional to the limiting slope of the salt[10] (cf. Eq. 6). Therefore, the larger the limiting slope for a salt, the smaller the expansion in volume on neutralization is. The correctness of this prediction has been found very satisfactory in Table II*.

Summary

Values of the changes of volume on formation of water from the hydrogen and hydroxyl ions in aqueous solutions, at various concentrations at 20°C, have been calculated, by combining the data of volume change on neutralization of a strong acid with a strong base and those on dilution of electrolyte solutions. Furthermore, the dependence of the volume change on the concentration has been derived and checked with the calculated data. The volme change on formation of water from its ions at moderate concentrations at 20°C is given by the equation: $\Delta V_F = 23.52 - 3.10\sqrt{C}$ ml. per mole, where C is the concentration of ions in mol./l.

Thus, the author has made it easy to analyze the volume changes on neutralizations of various acids and bases.

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