

## THE VOLUMES OF SOLUTE IN SOLUTION<sup>1,2</sup>

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Received March 5, 1955

The volumes of a solute in solution are found by a method which was used previously to compute the volumes of solutions under pressure. These solute volumes have the same values as those computed by another investigator from crystallographic data and from certain assumptions as to the solution state. The method developed here for finding the solute volumes is generally applicable and does not require crystallographic data.

The causes for the change of volume during solution have received the attention of a number of investigators. Some writers have attributed the change in volume during solution to the change in volume of one or the other component alone, while in some cases both the solvent and solute have been assumed to participate in the volume change. By experiment it is possible to observe only the resultant contractions and expansions during solution and it is understandable that the values for the purported volumes in solution depend on the theories assumed. In this article we show that the solute volumes in solution may be found by a method which was used previously to compute the volumes of solutions under pressure, and that the volumes thus found have been obtained from other assumptions on the mechanism of solution.

In a forthcoming article<sup>3</sup> we derived the equation

$$v_s = x_1 c^\alpha (v_w - b) + b x_1 + x_2 \psi_2 \quad (1)$$

where  $v_s$ ,  $v_w$  and  $\psi_2$  are, respectively, the specific volumes at atmospheric pressure<sup>4</sup> of the solution, water and the volume of the solute in solution.  $x_1$  and  $x_2$  are the weight fractions of water and solute;  $\alpha$  is the relative concentration of the solute and is the ratio of either the weight fraction of salt  $x_2$  or of the volume concentration  $x_2/v_s$ .<sup>5</sup> In this article we shall use  $\alpha = x_2/x_2^*$  (where the asterisk designates some arbitrary concentration) so that  $\alpha$  is 1 for the solution which contains  $x_2^*$  g. of solute and  $c$  is a constant corresponding to this concentration and depends on the amount the water is compressed due to the presence of the solute.  $b$  is the constant in the equation

$$P_0 - P = a \log_{10} \left( \frac{v_w(P_0) - b}{v_w(P) - b} \right) \quad (2)$$

which represents the variation of volumes of water with pressure.  $v_w(P_0)$  and  $v_w(P)$  are the specific volumes of water at the pressures  $P_0$  and  $P$  and the two parameters  $a$  and  $b$  may be determined by adapting the compressibility data of water to the equation.<sup>6</sup>

In eq. 1 only  $c$  and  $\psi_2$  are unknown (after  $\alpha$  is appropriately defined and the value of  $b$  assumed) and these may be found by writing this equation for each concentration and determining by the method of least squares their best values.

(1) Sponsored by the Office of Ordnance Research, U. S. Army.

(2) I am indebted to the Research Corporation for some assistance.

(3) J. S. Rosen, *J. Chem. Phys.*, in press (1956).

(4) In the original article eq. 1 is shown to hold for all pressures  $P$ ; the equation was used to compute the volumes of a number of salts in solution to 10,000 bars.

(5) It may be noted that other expressions for the concentration in  $\alpha$  might be used (e.g.,  $x_2/x_1$ , to correspond to molal concentration).

(6) The values of these parameters have been determined with the initial pressure  $P_0$  taken at atmospheric pressure.  $b$  does not remain constant as the pressure range  $P$  is increased; see Rosen, ref. 3.

In eq. 1,  $c^\alpha(v_w - b) + b$  represents the specific volume of water in solution, and from these terms it is evident that only a portion of the water is compressed (since  $c < 1$  for aqueous solutions of electrolytes). Thus  $b$  is the relatively incompressible portion of the volume of water, and because its value is not critically determined by eq. 2,<sup>6</sup> neither is  $\psi_2$ , the solute volume, in eq. 1.

Another condition is posed by eq. 1 before it describes the solution state: that is, that the exponent  $\alpha$ , which involves the concentration of the solution, must be adequately defined. We have not in previous work resolved this question of concentration and we have used both the weight fraction,  $x_2$ , or the volume concentration,  $x_2/v_s$ . Thus, it is apparent that the choice between these definitions (or others, for that matter) would again commit us to some particular theory on the mechanism of the solute state.

These considerations are made apparent in Fig. 1 where we show how  $\psi_2$ , the volume of the solute in sodium chloride solutions, varies with  $b$  and with the two definitions of concentrations indicated.

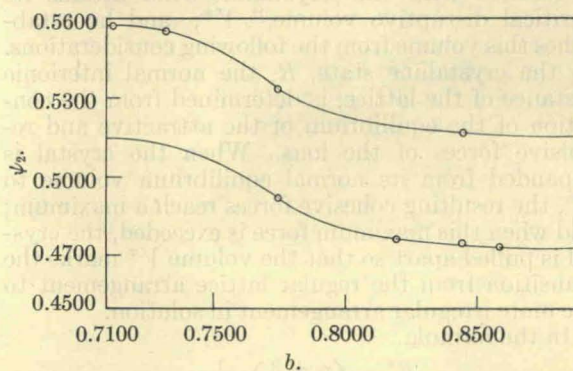


Fig. 1.—The variation of  $\psi_2$ , the volumes of the solute in sodium chloride solutions, with different values of  $b$ . In the upper curve  $\alpha$  is the ratio of the volume concentration  $x_2/v_s$ , and in the lower curve it is the ratio of the weight fraction of salt  $x_2$ .

In this article we give an interpretation of the volumes of solute,  $\psi_2$ , which result from eq. 1 for a particular choice of  $\alpha$  and  $b$ . If we take for the concentration of the solution its percentage by weight and set  $b = 0.8591$ ,<sup>7</sup> we find that the volumes of solute given by eq. 1 are remarkably close to those derived by Scott by a method so different that, both the methods and the results invite careful consideration.

(7) This is the value of  $b$  in eq. 2 for water with  $P_0 = 1$  and a pressure range of 1000 bars. See Tables I and II, Rosen, ref. 3. It should be apparent from Fig. 1 that  $\psi_2$  remains essentially constant around the value of  $b$  assumed here.

TABLE I  
THE MOLAL SOLUTE VOLUMES AND CRITICAL DISRUPTIVE VOLUMES OF THE ALKALI HALIDES AT 25°

Salt <sup>a</sup>	Max. $x_2$	$c^b$	Molal solute vol., $\phi^*$		Mol. vol. of solid <sup>a</sup>	Critical disruptive vol., $V^*$		Space-filling ratio, $\phi^*/V^*$	
			Scott <sup>c</sup>	Rosen <sup>d</sup>		Scott	Rosen	Scott	Rosen
LiCl	0.11	0.85880	25.3	27.09	20.5	32.4	21.75	0.78	1.246
LiBr	.20	.95873	30.0	30.00	25.1	39.1	38.33	.77	0.783
LiI	.19	.98325	39.2	39.19	33.0	51.2	51.95	.77	.755
NaCl	.25	.88968	26.9	27.65	27.05	41.6	36.63	.65	.755
NaBr	.40	.95313	31.5	31.53	32.13	49.0	48.04	.64	.657
NaI	.59	.97891	40.6	40.39	40.9	61.1	64.74	.66	.624
KCl	.22	.90803	36.3	38.11	37.5	56.6	40.31	.64	.945
KBr	.40	.95970	41.3	41.81	43.3	64.7	57.59	.64	.726
KI	.56	.97620	51.0	51.55	53.2	78.0	63.19	.65	.816
RbCl	.43	.95426	40.7	41.12	43.2	63.8	57.55	.64	.715
RbBr	.53	.97228	46.3	46.32	49.4	72.7	71.72	.64	.646
RbI	.41	.98422	55.9	55.94	59.8	86.7	81.47	.64	.687
CsCl	.66	.96831	48.0		42.3	62.4		.77	
CsBr	.53	.98113	53.4		47.9	70.4		.76	
CsI	.48	.98846	63.2		57.6	83.3		.76	
CsCl <sup>e</sup>	.66	.96831	47.2	47.49	42.3	73.4	67.82	.64	.700
CsBr <sup>e</sup>	.53	.98113	52.8	52.69	47.9	82.6	85.53	.64	.616
CsI <sup>e</sup>	.48	.98846	62.7	62.70	57.6	97.5	101.35	.64	.619

<sup>a</sup> The constants of eq. 1 were obtained from the volumes of the aqueous solutions of the alkali halides using the data of G. P. Baxter and C. C. Wallace, *J. Am. Chem. Soc.*, **38**, 96 (1916). <sup>b</sup> This is the value of  $c$  when  $x_2 = 0.1$ , so that for other concentrations  $\alpha = x_2/0.1$  in eq. 1. We have set  $b = 0.8591$  in this equation. <sup>c</sup> A. F. Scott, *THIS JOURNAL*, **35**, 3386 (1931). <sup>d</sup> Obtained from  $\psi_2$ , the specific volume of the solute, in eq. 1. <sup>e</sup> Hypothetical rock-salt type lattice structure.

Scott, in a series of papers,<sup>8</sup> has considered the problem of the volumes of solute in solution from a number of view points. We will outline briefly one of his methods for computing the solute volumes of the alkali halides in water and show in Table I that his results are essentially reproduced with our eq. 1.

Scott<sup>9</sup> postulates that the hypothetical upper limit to the concentration of the solute in solution<sup>10</sup> is reached when the crystalline solid attains its "critical disruptive volume,"  $V^*$ ; and he establishes this volume from the following considerations. In the crystalline state,  $R$ , the normal interionic distance of the lattice, is determined from the condition of the equilibrium of the attractive and repulsive forces of the ions. When the crystal is expanded from its normal equilibrium volume to  $V^*$ , the resulting cohesive forces reach a maximum; and when this maximum force is exceeded, the crystal is pulled apart so that the volume  $V^*$  marks the transition from the regular lattice arrangement to the more irregular arrangement in solution.

In the formula

$$\frac{R^*}{R} = \left( \frac{n+3}{m+3} \right)^{\frac{1}{n-m}} \quad (3)$$

derived by Joffe,<sup>11</sup>  $R^*$  is the interionic distance in the critical disruptive state,  $m$  is the attractive exponent (and is unity for the alkali halides), and  $n$  is the repulsive exponent for which the values given by Pauling<sup>12</sup> are used.

(8) (a) A. F. Scott, *THIS JOURNAL*, **35**, 2315 (1931); (b) **35**, 3379 (1931); (c) A. F. Scott and R. W. Wilson, *ibid.*, **38**, 951 (1934).

(9) See ref. 8a. A summary of Scott's work is also given in H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 257 ff.

(10) D. O. Masson had previously suggested that this hypothetical upper limit was reached when the concentration of the electrolyte became that of the pure crystalline salt. See *Phil. Mag.*, [7] **8**, 218 (1929).

(11) A. F. Joffe, "The Physics of Crystals," McGraw-Hill Book Co., New York, N. Y., 1928.

(12) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 341.

From the "critical disruptive volume,"  $V^*$ , calculated from  $R^*$ , the hypothetical upper limit to the concentration of the solute in solution is obtained and is  $1000/V^*$  (moles per 1000 cc. solution).

Scott then introduces Masson's empirical equation<sup>10</sup>

$$\phi = a\sqrt{m} + b \quad (4)$$

where  $\phi$  is the apparent molal volume of the solute,  $m$  the concentration (moles per 1000 cc. solution), and where  $a$  and  $b$  are constants characteristic of each salt.<sup>13</sup> Scott identifies the hypothetical maximum value of the apparent volume, given by

$$\phi^* = a\sqrt{1000/V^*} + b \quad (5)$$

with the molal volume of the solute in solution.

In Table I we give the constants of eq. 1 for the aqueous solutions of the alkali halides fitted to the same data<sup>14</sup> used by Scott to determine the constants of eq. 4 and 5. In Table I are shown also the volumes of the solute obtained by Scott and those given by eq. 1. The agreement of these results is remarkable, considering the dissimilar methods used in finding these volumes. It should, however, be noted that our solute volumes for the chlorides are consistently higher than those of Scott. In this table the "critical disruptive volumes,"  $V^*$ , are also compared<sup>15</sup>; the corresponding values in the two sets often differ considerably. This is due to the fact that in the two methods  $\phi^*$  (equated to the molal solute volume) and  $V^*$  are obtained in different order from eq. 5, and that in this equation a small change in  $\phi^*$  produces a large change in  $V^*$ .

For the interpretation of the molal solute volumes,  $\phi^*$ , the "disruptive critical volumes,"  $V^*$ ,

(13) These constants for the alkali halides are given in ref. 8a, p. 2317. See also Harned and Owen, ref. 9, p. 253.

(14) G. P. Baxter and C. C. Wallace, *J. Am. Chem. Soc.*, **38**, 96 (1916).

(15) Our "critical disruptive volume" was found by setting  $\phi^*$  in eq. 5 equal to our molal solute volume and solving for  $V^*$ ; the reverse order is necessary for finding these quantities by Scott's method.

and the space-filling ratio,  $\phi^*/V^*$ , the reader should consult the literature cited.<sup>8,9</sup>

If these solute volumes have any intrinsic meaning, some special merit in the method developed here (as well as the fact that it may throw addi-

tional light on the complex factors involved in the solution state), is that it requires only the specific volumes of the solutions and can be applied also where the crystallographic data used by Scott are lacking.