

The adiabatic compressibility, β_s , of the liquid was calculated from its density, d , and the sound velocity by the equation of Newton and Laplace:

$$\beta_s = -(\partial \ln V / \partial P)_s = 1/u^2 d. \quad (3)$$

Here V , P , and S , are volume, pressure, and entropy, respectively.

Results.—These are shown in Tables 1 and 2. Each molarity, c , is calculated from the weights of the components and the average of the measured densities (self-consistent to about 0.001%). The densities of the solutions are represented by cubic equations in $c^{1/2}$, fitted by the method of least squares:

$$d = d_1 + 4.2129 \times 10^{-2}c - 2.028 \times 10^{-3}c^{3/2} - 5.07 \times 10^{-5}c^2 \quad (\text{NaCl}), \quad (4)$$

$$d = d_1 + 4.7795 \times 10^{-2}c - 1.807 \times 10^{-3}c^{3/2} - 16.69 \times 10^{-5}c^2 \quad (\text{KCl}). \quad (5)$$

These give quadratic equations in $c^{1/2}$ for the apparent molar volume,

$$\Phi V_2 = v_1[M_2 - 10^3kc^{-1}(d - d_1)] \quad \text{cc mole}^{-1}, \quad (6)$$

when v_1 is the specific volume of solvent in gm cc^{-1} , M_2 the solute molecular weight, and $k = 1.000028 \text{ cc ml}^{-1}$. Our equations for d reproduce the classic results of Baxter and Wallace⁹ and later more precise work of Kruis,¹⁰ Geffken and Price,¹¹ and MacInnes and Dayhoff¹² as well as they do our own. Our values of ΦV_2° may be compared with those reported in the last three papers: 16.60 cc mole^{-1} for NaCl¹⁰ (corrected to current values of M_2 and d_1), and 26.81¹¹ and 26.50¹² cc mole^{-1} for KCl.

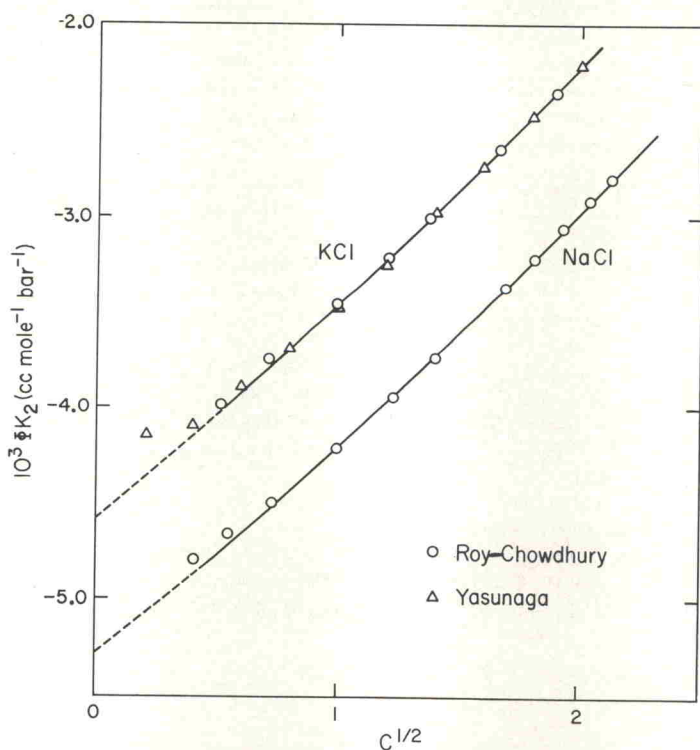


FIG. 3.—Apparent molar adiabatic compressibilities of NaCl and KCl.

The mean of our nine determinations of the velocity of sound in water at 25°C, $u_1 = 1496.55 \text{ m sec}^{-1}$ ($\sigma = 0.035 \text{ m sec}^{-1}$), agrees quite well with 1496.73 ($\sigma = 0.05$) m sec^{-1} found by Owen and Simons.¹³ The compressibilities of the solutions also are represented by cubic equations in $c^{1/2}$, fitted by the method of least squares.

$$\beta = \beta_1 - 6.0112 \times 10^{-6}c + 8.827 \times 10^{-7}c^{3/2} + 8.85 \times 10^{-8}c^2 \quad (\text{NaCl}), \quad (7)$$

$$\beta = \beta_1 - 5.7596 \times 10^{-6}c + 9.519 \times 10^{-7}c^{3/2} + 6.21 \times 10^{-8}c^2 \quad (\text{KCl}). \quad (8)$$

These yield quadratic equations for the apparent molar adiabatic compressibility,

$$\Phi K_2 = v_1[M_2\beta_1 - 10^3kc^{-1}(d\beta_1 - d_1\beta)] \quad \text{cc bar}^{-1} \text{ mole}^{-1}. \quad (9)$$

Plots of ΦK_2 for the two salts in Figure 3 include results for KCl obtained by Dr. Tatsuya Yasunaga of the University of Hiroshima with an earlier apparatus in our laboratory. He found $u_1 = 1496.92 \text{ m sec}^{-1}$, hence his values of u were multiplied by $(1496.55/1496.92)$ to put them on a common basis with our results. Since no systematic difference was found between the two series, his values of β and d were combined with ours to determine the coefficients of the empirical equations.

The Debye-Hückel limiting law predicts that ΦK_2 is a linear function of $c^{1/2}$ in very dilute solutions, with the same limiting slope for all salts of the same valence type. However, the theoretical slope depends upon pressure derivatives of the dielectric constant which are not known with sufficient accuracy, and we must rely upon extrapolation to zero concentration with empirical equations until the experimental limiting slope can be determined by more accurate measurements of sound velocities and densities now under way in our laboratory.

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¹ Boyle, R. W., and D. K. Froman, *Can. J. Res.*, **1**, 405-424 (1929).

² Graphite-bearing material made by the United States Graphite Co., Saginaw, Michigan.

³ Permatex No. 2 nonhardening gasket compound from the Permatex Co., Inc.

⁴ Ransom, F. A., *U.S. Nat. Bur. Standards Rept.*, No. 2083 (1952).

⁵ Gucker, F. T., Jr., and R. M. Haag, *J. Acoustical Soc. Am.*, **25**, 470-479 (1953).

⁶ Cameron, A. E., and E. Wickers, *J. Am. Chem. Soc.*, **84**, 4175-4197 (1962).

⁷ *International Critical Tables* (New York: McGraw-Hill Book Co., 1928), vol. III, p. 25.

⁸ Rossini, F. D., F. T. Gucker, Jr., H. L. Johnston, L. Pauling, and G. W. Vinal, *J. Am. Chem. Soc.*, **74**, 2699-2701 (1952).

⁹ Baxter, G. P., and C. C. Wallace, *J. Am. Chem. Soc.*, **38**, 70-105 (1916).

¹⁰ Kruis, A., *Z. phys. Chem.*, **B34**, 1-12 (1936).

¹¹ Geffken, W., and D. Price, *Z. Phys. Chem.*, **B26**, 81-99 (1936).

¹² MacInnes, D. A., and M. A. Dayhoff, *J. Am. Chem. Soc.*, **74**, 1017-1020 (1952).

¹³ Owen, B. B., and H. L. Simons, *J. Phys. Chem.*, **61**, 479-482 (1957).