Molal heat-content equations were derived by the method of Shomate.[9] Figures in parentheses give the temperature range of validity and the average degree of fit of the equation to the measured data.

Zr(α): $H_T - H_{298.16} = 6.83T + 0.56 \times 10^{-3}T^2 + 0.87 \times 10^5T^{-1} - 2378$; (298–1135°K., 0.2%)

Zr(β): $H_T - H_{298.16} = 7.27T - 1163$ (1135–1400°K., 0.3%)

ZrO_2(α): $H_T - H_{298.16} = 16.64T + 0.90 \times 10^{-3}T^2 + 3.36 \times 10^5T^{-1} - 6168$ (298–1478°K., 0.2%)

ZrO_2(β): $H_T - H_{298.16} = 17.80T - 4267$ (1478–1850°K., 0.2%)

ZrN(c): $H_T - H_{298.16} = 11.10T + 0.84 \times 10^{-3}T^2 + 1.72 \times 10^5T^{-1} - 3961$ (298–1700°K., 0.4%)

$ZrSiO_4$(c): $H_T - H_{298.16} = 31.48T + 1.96 \times 10^{-3}T^2 + 8.08 \times 10^5T^{-1} - 12{,}270$ (298–1800°K., 0.7%)

$ZrCl_4$(c): $H_T - H_{298.16} = 31.92T + 2.91 \times 10^5T^{-1} - 10493$ (298–550°K., 0.3%)

The corresponding heat-capacity equations are

Zr(α): $C_p = 6.83 + 1.12 \times 10^{-3}T - 0.87 \times 10^5T^{-2}$

Zr(β): $C_p = 7.27$

ZrO_2(α): $C_p = 16.64 + 1.80 \times 10^{-3}T - 3.36 \times 10^5T^{-2}$

ZrO_2(β): $C_p = 17.80$

ZrN(c): $C_p = 11.10 + 1.68 \times 10^{-3}T - 1.72 \times 10^5T^{-2}$

$ZrSiO_4$(c): $C_p = 31.48 + 3.92 \times 10^{-3}T - 8.08 \times 10^5T^{-2}$

$ZrCl_4$(c): $C_p = 31.92 - 2.91 \times 10^5T^{-2}$

Summary

Heat contents above 298.16°K. were measured for zirconium, zirconium oxide, zirconium nitride, zirconium silicate, and zirconium tetrachloride to the respective temperatures, 1370, 1841, 1672, 1823 and 567°K.

The heat of transition of zirconium metal is 920 cal. per mole. The temperature and heat of transition of zirconium oxide were found to be 1478°K. and 1420 cal. per mole, respectively.

A table of smooth values of heat-content and entropy increments above 298.16°K. was constructed, and representative heat-content and heat-capacity equations were derived.

BERKELEY, CALIFORNIA RECEIVED NOVEMBER 9, 1949

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[9] Shomate, THIS JOURNAL, **66**, 928 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficient of Potassium Chloride in Water at 4°

BY HERBERT S. HARNED AND CHARLES A. BLAKE

Accurate values of the diffusion coefficient of potassium chloride in dilute solutions at 20 and 30° and at concentrations between 0.001 and 0.55 molar at 25° have been the subject of recent communications from this Laboratory.[1,2,3,4] Owing to the interest of biological chemists in diffusion coefficients in the neighborhood of the freezing point of water, we have determined this quantity for potassium chloride at 4° over the concentration range between 0.01 and 0.6 molar.

Experimental Results

The technique and operation of the conductance method has been described in detail in the above communications. At 4° difficulty was encountered with the cells with larger electrodes due to the difference in the coefficients of expansion of the lucite and metal electrodes. As a result, our experiments were restricted to the cell with electrodes of 1 mm. diameter. These electrodes, which consisted of tapered rods of platinum screwed into the lucite, proved to be sufficiently tight and yielded satisfactory results. However, this type of cell cannot be relied upon to yield as accurate values in dilute solution as the cells with larger electrode surfaces. The accuracy of our mean values appears to be of the order of ±0.5%.

Table I contains the results. As before, five readings at two-hour intervals were made each day and this procedure was continued for five or six days. The values recorded in the table under column heading (1–2) are each the mean of five determinations according to the equation

$$\mathbf{D} = \frac{a^2}{\pi^2}\left[\frac{\Delta \ln (K_B - K_T)}{\Delta t}\right]_{\Delta t\, =\, 86{,}400 \text{ sec.}} \quad (1)$$

where $\Delta \ln (K_B - K_T)$ is the difference in the natural logarithm of the difference in the conductances at the bottom and top of the cell taken on the first and second days, Δt is the number of seconds in a day, and a is the depth of the cell. The results in the columns (2–3), (3–4), etc., refer to similar results taken from the second to the third days,

TABLE I

OBSERVED AND THEORETICAL DIFFUSION COEFFICIENTS OF POTASSIUM CHLORIDE IN WATER AT 4°

(1–2) (2–3) etc. are the values of $\mathbf{D} \times 10^5$ (cm.² sec.⁻¹) obtained from readings taken on first to second, second to third, etc., days.

c, mole l.⁻¹	(1–2)	(2–3)	(3–4)	(4–5)	(5–6)	D × 10⁵ (mean)	D × 10⁵ (theory)
0.0166	1.084	1.083	1.070	1.082	1.084	1.080	1.082
.168	...	1.034	1.045	1.035	...	1.038	1.039
.307	...	1.034	1.034	1.040	...	1.036	1.036
.379	1.030	1.040	1.037	1.041	...	1.037	1.036
.558	1.041	1.050	1.039	1.041	...	1.042	1.040

$T = 277.16°$ C.; $D = 86.43$; $\eta_0 = 15.676 \times 10^{-8}$; $\lambda°_K = 45.50$; $\lambda°_{Cl} = 46.17$; $A' = 1.170$; $\mathring{a} = 3.6$; $B = 0.014$; $S_{(f)} = 0.4913$; $d\,(4°) = 1.0000 + 0.05099c - 0.0031c^{3/2}$.

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[1] Harned and French, *Ann. N. Y. Acad. Sci.*, **46**, 267 (1945).

[2] Harned and Nuttall, *ibid.*, **51**, 781 (1949).

[3] Harned and Nuttall, THIS JOURNAL, **69**, 736 (1947).

[4] Harned and Nuttall, *ibid.*, **71**, 1460 (1949).

third to fourth days, etc. The seventh column in the table contains the mean value of these results.

Theoretical Considerations

The theoretical values[5] of the diffusion coefficient were computed by means of equations (1), (2), (3) and (4) of Harned and Nuttall.[4] The data required for this computation are compiled at the bottom of the Table I. The values of the dielectric constant, D, and the viscosity, η_0, were taken from Tables (5-1-3) and (5-3-1) of Harned and Owen.[6] The equivalent limiting conductances are those derived recently by Professor B. B. Owen from a comprehensive investigation of the conductances of the alkali halides. The activity coefficient function was computed from the activity coefficients of Harned and Cook.[7] The parameters A' and B were recalculated using a value of the limiting slope of the Debye and Hückel theory, $S_{(f)}$, computed by the universal constants of Birge.[8] The required density data were obtained from the computation of Scott.[9]

With these values, the theoretical equations for the diffusion coefficient of potassium chloride, **D**, at 4° become

$$\mathbf{D} = 4.609 \times 10^{13} \left(\frac{\overline{M}}{c}\right)\left[1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right] \qquad (2)$$

$$\frac{\overline{M}}{c} \times 10^{20} = 24.630 - 0.00049\,\frac{\sqrt{c}}{(1 + 1.170\sqrt{c})} + 10.34c\,\phi\,(1.170\,\sqrt{c}) \qquad (3)$$

$$\left[1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right] = 1 - \frac{0.5657\sqrt{c}}{(1 + 1.170\sqrt{c})^2} + 0.032\,c - c\psi(d) \qquad (4)$$

$$c\psi(d) = \frac{0.0125c - 0.0047c^{3/2}}{1.0000 + 0.0125c - 0.0031c^{3/2}} \qquad (5)$$

Comparison of the theoretical values, given in the last column of Table I, with the observed values shows agreement within the estimated experimental error up to the highest concentration. This behavior is identical with that found at 25°,[2,3,4] and is not very significant since one would not expect the theory to be valid at the higher concentrations. Dr. Louis J. Gosting has made one accurate determination of the diffusion coefficient of potassium chloride at 1° by the Gouy interference method[10,11,12] which he has kindly put at our disposal before publication. He obtained 0.954×10^{-5} at 0.300 molar for this quantity at 1°. After estimation of the temperature coefficient from the theoretical equations, we obtain 1.053×10^{-5} at 4°, a result which is about 1% higher than that obtained by the conductance method.

Summary

1. The diffusion coefficient of potassium chloride in water has been determined at 4° at concentrations between 0.01 and 0.6 molar.

2. Agreement with the theory of Onsager and Fuoss was found throughout the above range of concentrations. This result is in accord with previous observations at 25°.

NEW HAVEN, CONN. RECEIVED DECEMBER 7, 1949

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[5] Onsager and Fuoss, *J. Phys. Chem.*, **37**, 2689 (1932).

[6] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943.

[7] Harned and Cook, THIS JOURNAL, **59**, 1290 (1937) [see also ref. (6), p. 558].

[8] Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

[9] Scott, *J. Phys. Chem.*, **35**, 2315 (1931).

[10] Kegeles and Gosting, THIS JOURNAL, **69**, 2516 (1947).

[11] Gosting and Morris, *ibid.*, **71**, 1998 (1949).

[12] Gosting, Hanson, Kegeles and Morris, *Rev. Sci. Instr.*, **20**, 209 (1949).

[CONTRIBUTION FROM CARSON-NEWMAN COLLEGE]

Some Quaternary Salts of Hexamethylenetetramine[1]

BY CARL T. BAHNER, MADGE D. PICKENS, DONALD PICKENS AND WILLIAM K. EASLEY

The biological results obtained by Shear and associates[2] at the National Cancer Institute using quaternary salts derived from pyridine and its homologs and benzologs have led us to undertake the preparation of several series of similar quaternary salts containing other heterocyclic rings.[3] In a previous article[4] 23 salts containing the thiazole ring were reported, none of which has as yet given positive results in cancer chemotherapy screening tests. On the other hand, very dilute aqueous solutions of a number of members of a series of hexamethylenetetraminium salts have been found to have an effect of the same order of magnitude as nitrogen mustard in inhibiting the respiration of rabbit bone marrow cells in serum, in preliminary tests by Dr. C. E. Carter and associates, of Oak Ridge National Laboratories, and have been submitted to Dr. M. J. Shear and associates, of the National Cancer Institute, for screening tests against sarcomas in mice, results of which are to be reported elsewhere.

In 1915 Jacobs and Heidelberger[5] prepared an extensive series of quaternary salts of hexamethylenetetramine for other purposes. Several of their preparations have been repeated and in addition the salts listed in Table I have been prepared.

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[1] Presented in part at the Atlantic City meeting of the American Chemical Society, September, 1949.

[2] Shear, *et al.*, in "Approaches to Cancer Chemotherapy," American Association for the Advancement of Science, F. R. Moulton, Editor, Washington, D. C., 1947, p. 236 ff.; Hartwell and Kornberg, THIS JOURNAL, **68**, 1131 (1946).

[3] Bahner and Pickens, *J. Tenn. Acad. Sci.*, **23**, 104 (1948).

[4] Bahner, Pickens and Bales, THIS JOURNAL, **70**, 1652 (1948).

[5] Jacobs and Heidelberger, *J. Biol. Chem.*, **21**, 455 (1915).