elution. Application of eq. 12 shows that gradient elution actually separates them by 9.44 σ units. The large decrease in peak separation is therefore offset by peak sharpening. The calculated integral elution history curves are shown in Fig. 3.

Discussion

The equations presented here are subject to the same limitations as are those derived by Mayer and Tompkins, *viz.*, linear isotherms and near equilibrium column conditions. These authors have further indicated that the approximation of elution curves by Gaussian distribution curves becomes more accurate as P and C take on larger values. In the derivations used here, it has been necessary to apply this approximation both when the number of plates traversed by the adsorbate is small (at the beginning of a run) and when C is small (at the end of a run).

The peak shape equations involve still more approximations, and must therefore be used with more caution than the peak location equations. Of these, equation 12 appears to be the more exact. Because of the nature of the approximations involved, it would be expected to hold better in the region nearer the peak.

A more quantitative evaluation must await the present accumulation of experimental data.

With regard to the practical question of ease of computations based on eq. 12, consider the general case of a linearly decreasing C value

$$C = A - BV/V^*$$

for which eq. 12 becomes

$$t^2 = \frac{PC}{B}\,\frac{[\ln C/(A - B) + B]}{BC + 1 - C/(A - B) + B + \ln C/(A - B)}$$

In the example chosen it was found that the denominator could be represented by B^2C over the entire range of calculation at the sacrifice of only 3% accuracy. The equation then reduced to the very simple form

$$t = \frac{P^{\cdot/2}}{B}\,[B + \ln C/(A - B)]$$

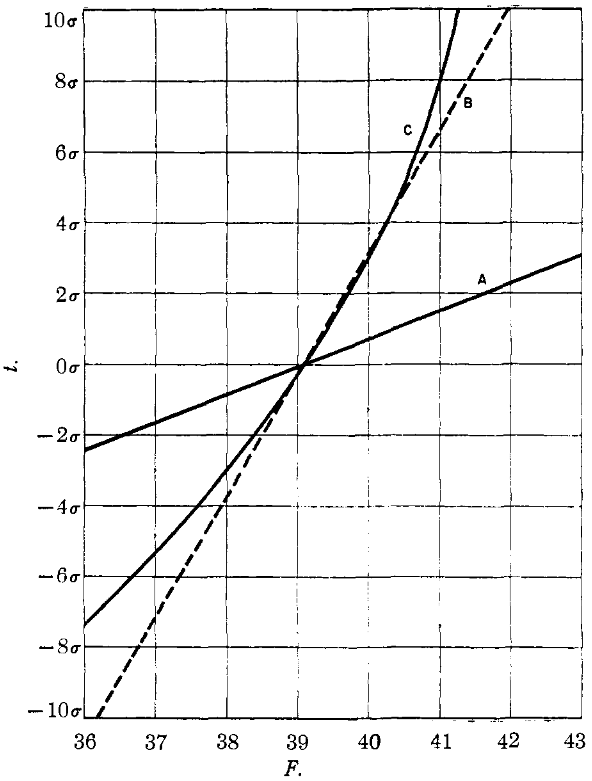

Fig. 3.—Integral elution history curves (calcd. from example in text): A, constant strength elution; B, gradient elution, approximate equation; C, gradient elution, exact equation.

It is quite likely that similar simplifications will be found in many of the cases to which eq. 12 is applied.

Acknowledgments.—The author is grateful to Dr. E. R. Tompkins for encouraging discussions, helpful suggestions and reviewing the manuscript, to Mr. Jarvis Todd for advice on the clarity of presentation.

SAN FRANCISCO, CALIF.

[CONTRIBUTION NO. 1269 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficients of Lithium and Potassium Perchlorates in Dilute Aqueous Solutions at 25°

BY HERBERT S. HARNED, HERMAN W. PARKER AND MILTON BLANDER

RECEIVED DECEMBER 15, 1954

The differential diffusion coefficients of lithium and potassium perchlorates have been determined at 25° by the conductometric method at concentrations between 0.001 and 0.01 molar. Theoretical considerations indicate that at low concentrations the activity coefficients of these electrolytes are nearly identical. This result differs from previous conclusions derived from freezing point data.

By employing the conductometric method devised in this Laboratory,[1] the diffusion coefficients of lithium and potassium perchlorates recorded in Table I have been determined at the concentrations designated.

Theoretical Considerations.—For 1–1 electrolytes, the theory of Onsager and Fuoss[2] is represented by the equation

$$\mathfrak{D} = 16.629 \times 10^{10}T(\overline{\mathfrak{M}}/c)\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) \quad (1)$$

---

(1) H. S. Harned and D. M. French, *Ann. N. Y. Acad. Sci.*, **46**, 267 (1945); H. S. Harned and R. L. Nuttall, THIS JOURNAL, **69**, 736 (1947).

(2) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

TABLE I

THE DIFFUSION COEFFICIENTS OF LITHIUM AND POTASSIUM PERCHLORATES AT 25°

	LiClO$_4$			KClO$_4$	
c	$\mathfrak{D} \times 10^5$ (obsd.)	$\mathfrak{D} \times 10^5$ (calcd.)	c	$\mathfrak{D} \times 10^5$ (obsd.)	$\mathfrak{D} \times 10^5$ (calcd.)^a
0.000	...	(1.309)	0.000	...	(1.873)
.0033	1.277	1.276	.0012	1.843	1.842
.0043	1.278	1.273	.0018	1.842	1.836
.00455	1.275	1.272	.0023	1.839	1.832
.0053	1.273	1.270	.0034	1.832	1.825
.0064	1.271	1.267	.0049	1.829	1.819
....			.0063	1.825	1.814
			.0075	1.813	1.811
			.0084	1.814	1.810
			.0097	1.792	1.807

^{a} Calculated upon assumption that the activity coefficient of potassium perchlorate is equal to that of lithium perchlorate in these dilute solutions.

where

$$(\overline{\mathfrak{M}}/c) \times 10^{20} = 1.0741\left(\frac{\lambda_1^0\lambda_2^0}{\Lambda^0}\right) - \frac{22.148}{\eta_0(DT)^{1/2}}\left(\frac{\lambda_1^0 - \lambda_2^0}{\Lambda^0}\right)^2 \frac{\sqrt{c}}{1 + A'\sqrt{c}} + \frac{9.304 \times 10^7}{\eta_0(DT)^2}\, c\phi(A'\sqrt{c}) \quad (2)$$

and

$$\left(1 + c\,\frac{\partial \ln y_\pm}{\epsilon c}\right) = 1 - \frac{1.1514\mathcal{S}_{(f)}\sqrt{c}}{(1 + A'\sqrt{c})^2} + 2.303Bc \quad (3)$$

The limiting law for the diffusion coefficient is

$$\mathfrak{D} = 17.872 \times 10^{-10}T\left(\frac{\lambda_1^0\lambda_2^0}{\Lambda^0}\right) - \mathcal{S}_{\mathfrak{D}}\sqrt{c} \quad (4)$$

where the first term on the right is the limiting value $\mathfrak{D}_0$ and the second term the limiting expression for the concentration dependence of $\mathfrak{D}$.[3] The symbols in these equations have been defined in earlier publications. It is advantageous to recall that $\mathfrak{D}$ is the differential diffusion coefficient in cm.^{2} sec.$^{-1}$, $A'\sqrt{c} = \kappa a$ where κ is the reciprocal radius of the theory, a the distance parameter and $\phi(\kappa a)$ the exponential integral function of the theory.

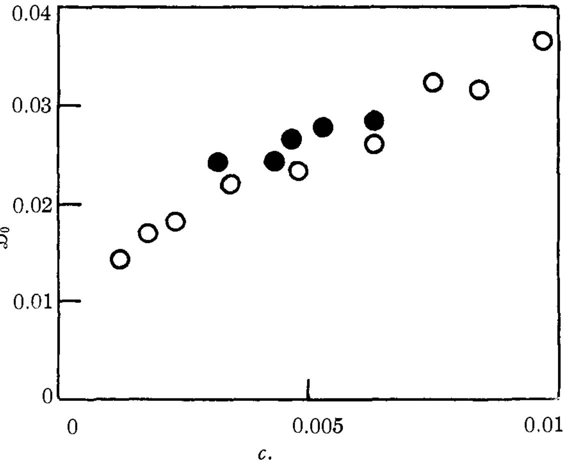

Fig. 1.—Values of the left side of equation 6 *versus* c.

Preliminary Considerations of the Data.—Since the algebraic sum of the second and third terms on the right of equation 2 which represent the mobility dependence upon concentration are about 0.5% of the magnitude of the first term at 0.01 molar concentration and less than this amount at the lower concentrations, equation 1 may be reduced to the approximate form

$$\mathfrak{D} \cong \mathfrak{D}_0\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) \quad (5)$$

and consequently

$$\frac{\mathfrak{D}_0 - \mathfrak{D}}{\mathfrak{D}_0} \cong -c\,\frac{\partial \ln y_\pm}{\partial c} \quad (6)$$

Figure 1 shows values of the quantity on the left of this equation computed from calculated values of $\mathfrak{D}_0$ and the observed results in Table I. It is apparent from this illustration that there is little if any difference between the values of $(\mathfrak{D}_0 - \mathfrak{D})/\mathfrak{D}_0$ for the two salts in the region of concentration 0.001 to 0.007 molar. If the experimental results are not in error, then according to equation 5, there should be little difference in the activity coefficients of the two salts in these dilute solutions.

Detailed Calculations.—The theoretical calculations have been carried by substituting in equation (2) 8.949 × 10^{-3}, 298.16 and 78.54 for the viscosity, temperature and dielectric constant, respectively, and 38.69,[3] 73.52[3] and 67.31 for the limiting equivalent conductances of the lithium ion, potassium ion and perchlorate ion. This latter quantity was derived from the conductance data of Jones.[4] The numerical equations which result from this substitution are

$$(\overline{\mathfrak{M}}/c) \times 10^{20} = 26.395 - \frac{1.172\sqrt{c}}{1 + A'\sqrt{c}} + 18.96c\phi(\kappa a) \quad (7)$$

for lithium perchlorate and

$$(\overline{\mathfrak{M}}/c) \times 10^{20} = 37.770 - \frac{0.0313\sqrt{c}}{1 + A'\sqrt{c}} + 18.96c\phi(\kappa a) \quad (8)$$

for potassium perchlorate.

The thermodynamic term represented by equation 3 has been estimated both from freezing point measurements[5] in dilute solutions and isopiestic vapor measurements at concentrations higher than 0.1 molal. The activity coefficient of lithium perchlorate 0.1 to 1 molal computed by Jones[6] is approximately equal to that of lithium iodide. We have assumed that at lower concentrations the activity coefficients for these two electrolytes are the same and have employed the values 5.05 Å. for a and 0.165 for B previously used for computing the activity coefficient of the iodide.[7] With these parameters, equation 3 reduces to

$$\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{0.5862\sqrt{c}}{(1 + 1.629\sqrt{c})^2} + 0.38c \quad (9)$$

Guggenheim[8] has computed the activity coefficients

---

[3] The complicated equation for $\mathcal{S}_{\mathfrak{D}}$ is given in Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 179. See also H. S. Harned, *Chem. Revs.*, **40**, 462 (1947), equation (187).

[4] J. H. Jones, THIS JOURNAL, **67**, 855 (1945).

[5] G. Scatchard and S. S. Prentiss, *ibid.*, **55**, 4355 (1933).

[6] J. H. Jones, *J. Phys. Chem.*, **51**, 516 (1947).

[7] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 381.

[8] R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Longmans, Green and Co., New York, N. Y., 1939, p. 418, 419.

from the freezing point data by using a simplified form of the equation for the activity coefficient in which $S_{(f)}$ equals 0.5 and A' equals unity for uniunivalent electrolytes. The individuality of the behaviors of the electrolytes was characterized by the magnitude of the linear parameter, B. For lithium perchlorate, Guggenheim obtained 0.33 for B which gives the equation

$$\left(1 + c\frac{\partial \ln y_{\pm}}{\partial c}\right) = 1 - \frac{0.578\sqrt{c}}{(1 + \sqrt{c})^2} + 0.76c \qquad (10)$$

Figure 2 illustrates the result of this calculation. The top curve represents values derived from equation 10 and the curve just under it was derived from equation 9. The lowest curve represents the limiting law which for lithium perchlorate is

$$\mathfrak{D} \times 10^5 = 1.309 - 0.776\sqrt{c} \qquad (11)$$

The results of this calculation are given in Table I and illustrated by Fig. 2 whence it is obvious that the calculated values are about 0.4% lower than the observed ones. The difference between the results computed by equations 9 and 10 is insignificant.

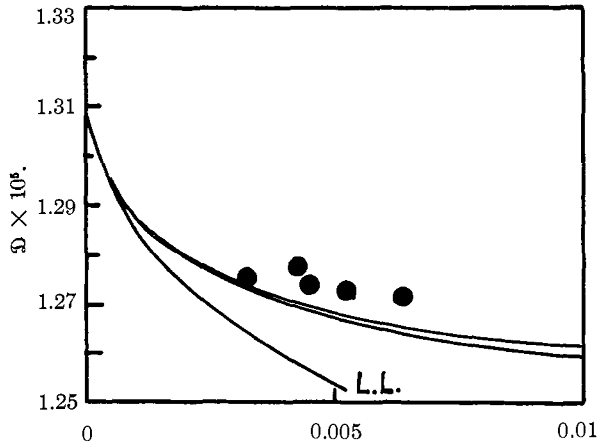

Fig. 2.—Calculated values and observed results for the diffusion coefficient of lithium perchlorate.

The computations of the diffusion coefficient of potassium perchlorate are represented in Fig. 3. The lower curve is the graph of the limiting law

$$\mathfrak{D} \times 10^5 = 1.873 - 1.1\sqrt{c} \qquad (12)$$

and the curve just above was computed by equation 3 using the value of -0.435 for B obtained by Guggenheim from the freezing point data. The upper curve represents the result of the calculation upon the assumption that in the region below 0.01, the activity coefficients of the lithium and potassium salts are the same or that the thermodynamic term is given by equation 10. Values derived from this graph are recorded in Table I. The agreement between the observed results and those represented by the upper curve in Fig. 3 is fairly satisfactory. On the other hand in these dilute solutions, the observed results are considerably higher than those estimated from the freezing point data.

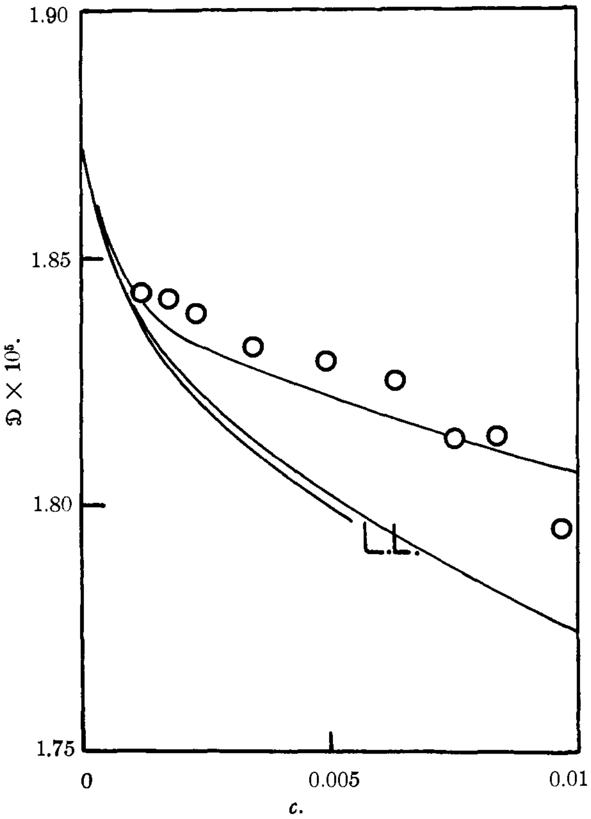

Fig. 3.—Calculated values and observed results for the diffusion coefficient of potassium perchlorate.

This investigation was supported in part by the Atomic Energy Commission under Contract AT-(30-1)-1375.

NEW HAVEN, CONN.