reaction a rate law identical to that of equation (8)

$$Cr^{+3} + SCN^- = CrSCN^{+2}$$

except for an additional term containing $(H^+)^2$ in the denominator. For the entropies of activation corresponding to the k_1 and k_2 terms of equation (8) they report +0.7 and +13 e.u., respectively, at an ionic strength of 0.08 M and at 25°. These values are within experimental error of those found here.

It would be of some interest to compare entropies of activated complexes with the entropies of similar stable complexes. We have considered the complexing reactions

$$Fe^{+++} + F^- = FeF^{++} \quad \Delta S_9 = 30 \text{ e.u.} \qquad (9)$$

$$FeF^{++} + F^- = FeF_2^+ \quad \Delta S_{10} = 23 \text{ e.u.} \qquad (10)$$

where the ΔS values refer to 25° and $\mu = 0.50$.[31]

The analogous entropies for the thiocyanate rates are

$$Fe(H_2O)_6^{+++} + SCN^- \xrightarrow{k_1} [Fe(H_2O)_6SCN^{++}] \quad \Delta S_1 = -5 \qquad (11)$$

$$Fe(H_2O)_5OH^{++} + SCN^- \xrightarrow{k_3} [Fe(H_2O)_5OHSCN^+] \quad \Delta S_3 = -7.6 \qquad (12)$$

The much more positive entropy changes for fluoride complexing are due to the smaller size of the fluoride ion and consequent greater release of water molecules from its field when the oppositely charged ions combine. The difference, however, between thiocyanate and fluoride should be largely eliminated if we subtract the entropies of reactions 11 and 12 and compare with the difference of reactions 9 and 10. The chief difference now is between the effects of fluoride and hydroxide on the entropies. The values $\Delta S_9 - \Delta S_{10} = 7$ e.u. and $\Delta S_1^{\ddagger} - \Delta S_3^{\ddagger} = 2.6$ e.u. lie within the experimental error of each other.

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BERKELEY, CALIF.

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[31] R. E. Connick, L. G. Hepler, Z. Z. Hugus, Jr., J. W. Kury, W. M. Latimer and Maak-Sang Tsao, THIS JOURNAL, **78**, 1827 (1956).

[CONTRIBUTION NO. 1481 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Activity Coefficients of Alkali Metal Nitrates and Perchlorates in Dilute Aqueous Solutions at 25° from Diffusion Coefficients

BY HERBERT S. HARNED AND JOSEPH A. SHROPSHIRE

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The diffusion coefficients of lithium and cesium nitrates have been measured at 25° over a concentration range from 0.003 to 0.015 molar. From these data, the activity coefficients of these electrolytes have been computed at low concentrations. Similar calculations have been carried out for lithium and potassium perchlorates and potassium nitrate solutions and the results tabulated.

The method for determining activity coefficients of univalent electrolytes from diffusion coefficients[1] has been employed by us[2] to determine the activity coefficient of sodium nitrate. Measurements of the diffusion coefficients of lithium and cesium nitrates recorded in this contribution and the earlier measurements of the diffusion coefficient of potassium nitrate[3] permit the evaluation of the activity coefficients of these nitrates in dilute solutions at 25° with a high degree of precision. In addition, the activity coefficients of lithium and potassium perchlorates from previously determined diffusion coefficients[4] have been computed and tabulated.

In brief, the method employs the integral

$$\log y_{\pm} = 0.8686 \int_0^c \frac{\mathfrak{D}'}{c^{1/2}}\, dc^{1/2} \qquad (1)$$

where the limiting value of $\mathfrak{D}'/c^{1/2}$ is fixed and equal to

$$\lim_{c=0} \left[\frac{\mathfrak{D}'}{c^{1/2}}\right] = -1.1513\, \mathcal{S}_{(f)} \qquad (2)$$

$\mathcal{S}_{(f)}$ is the theoretical Debye and Hückel slope of the logarithm of the activity coefficient. The quantity

TABLE I

COMPUTATION OF $\mathfrak{D}'/c^{1/2}$ USED FOR DETERMINING THE ACTIVITY COEFFICIENTS OF LITHIUM AND CESIUM NITRATES

c	$A'\sqrt{c}$	$\phi(A'\sqrt{c})$	$(\overline{\mathfrak{M}}'/c) \times 10^{20}$	$(\overline{\mathfrak{M}}''/c) \times 10^{20}$
0.00333	0.0664	1.584	0.077	0.100
.00585	.0880	1.343	.101	.149
.00923	.1105	1.155	.124	.202
.01000	.1150	1.123	.128	.213
.01287	.1305	1.027	.144	.250
.01533	.1424	0.962	.155	.280
$c^{1/2}$	$\mathfrak{D}$(obsd.) $\times 10^5$	$(\overline{\mathfrak{M}}/c) \times 10^{20}$	$-\mathfrak{D}'$	$-\mathfrak{D}'/c^{1/2}$
0.0577	1.295	26.998	0.03240	0.5615
.0765	1.287	27.023	.03967	.5186
.0961	1.275	27.053	.04945	.5147
.1000	1.278	27.060	.04766	.4766
.1135	1.273	27.081	.05224	.4603
.1238	1.268	27.100	.05606	.4528

$CsNO_3$

c	$\mathfrak{D}$(obsd.) $\times 10^{15}$	$(\overline{\mathfrak{M}}/c) \times^{5} 10^{20}$	$c^{1/2}$	$-\mathfrak{D}'/c^{1/2}$
0.00770	1.907	40.0715	0.0877	0.4554
.01378	1.886	40.1533	.1174	.4497
.01412	1.871	40.1577	.1188	.5093

For $LiNO_3$: $\lambda_+^0 = 38.69$; $\lambda_-^0 = 71.44$; $\Lambda^0 = 110.13$
$CsNO_3$: $\lambda_+^0 = 77.26$; $\lambda_-^0 = 71.44$; $\Lambda^0 = 148.70$
For both $LiNO_3$ and $CsNO_3$: $a = 3.5$ Å.; $D = 78.54$; $10^3\eta = 8.849$

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[1] H. S. Harned, *Proc. Nat. Acad. Sci.*, **40**, 551 (1954).

[2] H. S. Harned and J. A. Shropshire, THIS JOURNAL, **80**, 2618 (1958).

[3] H. S. Harned and R. M. Hudson, *ibid.*, **73**, 652 (1951).

[4] H. S. Harned, H. W. Parker and M. Blander, *ibid.*, **77**, 2071 (1955).

$\mathfrak{D}'$ in these equations is defined by

$$\mathfrak{D}' = \frac{\mathfrak{D}}{1000\nu\, RT(\overline{\mathfrak{M}}/c)} - 1 \qquad (3)$$

where $\mathfrak{D}$ is the diffusion coefficient and $(\overline{\mathfrak{M}}/c)$ is the mobility term.[5]

Table I contains details of the calculation of $(\overline{\mathfrak{M}}/c)$ and subsequently $\mathfrak{D}'/c^{1/2}$ for lithium nitrate and values for these quantities for cesium nitrate. The values of the limiting conductances and other quantities employed in the calculations are appended at the bottom of Table I.

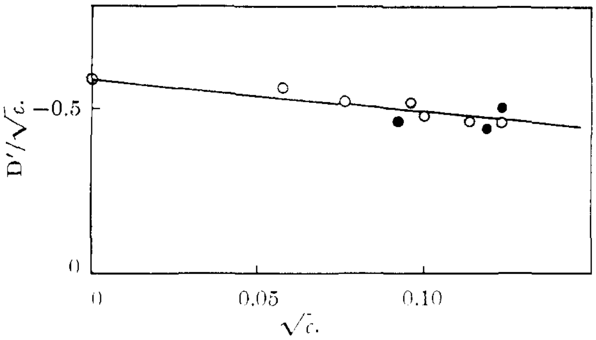

Fig. 1.—Plot for the computation of the activity coefficients of lithium and cesium nitrates at 25°: ○, lithium nitrate; ●, cesium nitrate.

The plot of $\mathfrak{D}'/c^{1/2}$ *vs.* $c^{1/2}$ used for the computation of the activity coefficients is shown in Fig. 1. Here the circles represent the results for lithium nitrate and the dots those for cesium nitrate. The graph is a straight line. Individual plots were used in evaluating the activity coefficients given in Table II from which it appeared that the activity of cesium nitrate is slightly less than lithium nitrate.

TABLE II

ACTIVITY COEFFICIENTS OF ALKALI METAL NITRATES IN DILUTE AQUEOUS SOLUTIONS AT 25°

	$\gamma_{\pm}$					
c (moles/l.)	$LiNO_3$	$NaNO_3$	KNO_3	$CsNO_3$	$LiClO_4$	$KClO_4$
0.0005	0.9746	0.9746	0.975	0.975	0.975	0.975
.001	.9646	.9646	.964	.964	.966	.966
.002	.9508	.9508	.950	.950	.954	.954
.005	.9251	.9251	.924	.924	.932	.934
.01	.8983	.8983	.896	.896	.913	.915
.015	.8793	.9793	...	...	...	...
.020	.8643	.8643	...	...	...	...

Similar calculation of the activity coefficients of lithium and potassium perchlorates leads to the results recorded in the last two columns of Table II. It is safe to conclude from these results that the activity coefficients of the perchlorate are greater than those of the nitrates. The result of this determination that potassium perchlorate appears to have a greater activity coefficient than the lithium salt at 0.005 and 0.01 seems unusual and may be due to experimental error.

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[5] The equations for computing $(\overline{\mathfrak{M}}/c)$ are given by H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., p. 121-122, equations (4-4-19), (4-4-20) and (4-4-21), Reinhold Publ. Corp., New York, N. Y., 1958. See also refs. 3 and 4.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Voltammetric Membrane Electrodes. I. Basic Theory and Characteristics of Thallous and Cadmium Reduction

BY RICHARD C. BOWERS AND ARTHUR M. WILSON[1]

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A new type of voltammetric mercury electrode is described. It is constructed in a manner such that linear finite diffusion of the reducible or oxidizable species takes place across a cellophane membrane. The theoretical equations for diffusion across the membrane are given and a method is outlined for the determination of diffusion coefficients in the membrane. Excellent agreement between theory and experiment is observed for diffusion currents due to the reduction of thallous ion. Adsorption in the membrane markedly affects the apparent diffusion characteristics of cadmium at low concentrations. The experimental results indicate a "homogeneous" phase rather than a porous structure for the cellophane membranes used.

Introduction

Clark, *et al.*,[2] have reported the use of a platinum electrode covered with a film of collodion or cellophane for the determination of oxygen in whole blood. These workers observed that the film prevented poisoning of the electrode while allowing oxygen access to the electrode. An electrode employing mercury as the electrode material and cellophane as an ion permeable diffusion layer has been described briefly by the authors.[3] In theory the membrane should act as a well defined diffusion layer when the electrode is placed in a stirred solution. Due to the finite thickness of the diffusion layer, a steady state is obtained.

The present investigation was initiated to evaluate theoretically the currents obtained with voltammetric membrane electrodes and to characterize more fully the behavior of this type of electrode.

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[1] Taken from the research by the junior author in partial fulfillment for the Ph.D. degree.

[2] L. C. Clark, R. Wolf, D. Granger and Z. Taylor, *J. Appl. Physiol.*, **6**, 189 (1953).

[3] R. C. Bowers and A. Wilson, "Third National Symposium on Instrumental Methods of Analysis," Chicago, Illinois, 1957.