[CONTRIBUTION OF DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Thermodynamic Quantities Associated with the Interaction between Ethylenediaminetetraacetate and Alkaline Earth Ions

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Thermodynamic equilibrium constants are reported for reactions between M^{+2}(aq) and V^{-4}(aq), where M^{+2} is an alkaline earth ion, and V^{-4} is the tetranegative anion of ethylenediaminetetraacetic acid. The calculations were carried out with e.m.f. data obtained from cells of the type Pt-H_2, $K^+(m_1)$, $M^{+2}(m_2)$, $Cl^-(m_3)$, $H_nV^{n-4}(m_4)$, AgCl-Ag at various temperatures and ionic strengths. For each temperature the data were extrapolated to infinite dilution with the aid of the Debye-Hückel activity coefficient relationship, and the thermodynamic chelate formation constant was evaluated. The thermodynamic quantities $\Delta F°$, $\Delta H°$ and $\Delta S°$ are calculated and discussed in the light of present theories of metal chelate formation in aqueous solution.

The reasons for abnormally high affinity of ethylenediaminetetraacetate and iminotriacetate anions for the alkaline earth ions have never been clarified in the light of the strongly-basic properties of these metal ions. Indeed, before the discovery of these complexing agents, the alkali and alkaline earth ions were considered to be examples of cations which did not form coördination compounds. Perhaps the most reasonable suggestion advanced to explain the high stability of chelates of this type is that of Calvin and Bailes.[1]

According to this theory, the entropy increase associated with the formation of chelate rings is considered to make a major contribution to the stability as measured by the equilibrium formation constant. This idea was more recently carried a step further and extended to the calcium ethylenediaminetetraacetate chelate.[2]

The purpose of this investigation is the determination of the experimental values of $\Delta F°$, $\Delta H°$ and $\Delta S°$ associated with chelate formation between the ethylenediaminetetraacetate ion and magnesium, calcium, strontium and barium ions. Information of this nature would be helpful in correlating the entropy effect with the formation of metal chelates of abnormally high stability.

With few exceptions, previous work on the stability of metal chelates has not resulted in the determination of thermodynamic constants, since most investigations were made in a supporting electrolyte having a concentration much higher than that of the chelate compound. The only thermodynamic chelate stability constants known to the authors of the present paper are that of Kety[3] for $lead^{II}$ and citrate ions, of Calvin and Zebroski[4] for thenoyltrifluoroacetone and $thorium^{IV}$ ions, and of Carini and Martell[5] for ethylenediaminetetraacetate and calcium ions. In the present paper the latter work is extended to other alkaline earth ions, and to measurements over a series of temperatures for the calculation of heats and entropies of chelate formation.

Experimental

The experimental method employed in this research has not been applied previously to the determination of metal chelate stability constants. In principle, it consists of the measurement of hydrogen ion activities in solutions containing an alkaline earth metal ion, ethylenediaminetetraacetic acid, and inert electrolyte, at equilibrium. This was accomplished by measurement of the e.m.f. of the cell

$$\text{Pt-H}_2,\ K^+(m_1),\ M^{+2}(m_2),\ Cl^-(m_3),\ H_nV^{n-4}(m_4),\ \text{AgCl-Ag} \qquad (I)$$

where M^{+2} represents an alkaline earth metal ion, V^{-4} is the ethylenediaminetetraacetate anion, and n may be varied from 0 to 2. The e.m.f. data thus obtained were extrapolated to infinite dilution, allowing the calculation of the standard free energy change, $\Delta F°$, for the reaction

$$M^{+2}(aq) + V^{-4}(aq) \longrightarrow MV^{-2}(aq)$$

Apparatus and Materials.—A Leeds and Northrup type K potentiometer was used with a cell similar to that described in a previous publication.[5] The platinum electrodes were prepared according to the directions given by Weissberger.[6] The silver-silver chloride electrodes were prepared by the method of Shedlovsky and MacInnes.[7]

The ethylenediaminetetraacetic acid, obtained through the courtesy of the Bersworth Chemical Company, Framingham, Massachusetts, was further purified by two successive recrystallizations from water. Carbon dioxide-free potassium hydroxide, prepared from silver oxide and potassium chloride by the method of Schwarzenbach and Biedermann,[8] was standardized against potassium acid phthalate as recommended by Kolthoff and Sandell.[9] The alkaline earth chloride solutions were standardized by the Volhard method.[10] All solutions made up in the course of this investigation were either prepared on or corrected to a molal basis.

Procedure and Experimental Data.—The e.m.f. of cell I was first measured for definite values of m_1, m_2, m_3 and m_4 at 25°. The cell was then cooled to approximately 0° and the initial reading was taken. The temperature was then raised by 5° increments, and e.m.f. readings were taken after equilibrium was established. In most cases, 5–10 hours was sufficient to obtain reproducible readings, which were then found to remain constant for as long as 3 or 4 days. At 25° a check was made for reproducibility of the initial reading. The solutions employed in cell I were made up so as to give a constant ratio of $(m_{M^{+2}})(m_{H_nV^{n-4}}):m_{MV^{-2}}:m_{Cl^-}$, as is required for the extrapolation method described below (equation 13). In the more dilute solutions there was a tendency for this ratio to be changed by greater dissociation of the metal chelate. Under these conditions the ratios were maintained by appropriate addition of potassium hydroxide. These ratios were kept constant for each temperature investigated.

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[1] M. Calvin and R. Bailes, THIS JOURNAL, **68**, 949 (1946).

[2] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 151.

[3] S. Kety, *J. Biol. Chem.*, **142**, 181 (1942).

[4] E. L. Zebroski, Thesis, University of California, 1947.

[5] F. Carini and A. E. Martell, THIS JOURNAL, **74**, 5745 (1952).

[6] A. Weissberger, "Physical Methods of Organic Chemistry," Second Edition, Vol. II, Interscience Publishers, Inc., New York, N. Y., 1949, p. 1722.

[7] T. Shedlovsky and D. A. MacInnes, THIS JOURNAL, **58**, 1970 (1936).

[8] G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 331 (1948).

[9] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Revised Edition, The Macmillan Co., New York, N. Y., 1948, p. 553.

[10] W. Scott, "Standard Methods of Chemical Analysis," Fifth Edition, Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 271.

TABLE I

t, °C.	Metal	$\mu_1{}^a$	$\mu_2{}^a$	E.m.f. (mv.) of cell I $\mu_3{}^a$	$\mu_4{}^a$	$\mu_5{}^a$	$\mu_6{}^a$
0	Mg	653.18	643.15	638.16	634.10	630.03	
	Ca	539.91	530.32	524.62	521.81	518.45	515.36
	Sr	628.95	624.02	616.00	613.56	610.74	606.08
	Ba	621.25	610.69	606.84	602.77	600.01	
5	Mg	657.29	647.13	642.17	637.97	633.83	
	Ca	542.06	532.29	526.50	523.41	520.26	517.22
	Sr	635.49	630.41	622.30	619.76	616.95	612.15
	Ba	624.78	614.19	610.21	606.02	603.37	
10	Mg	661.67	651.28	646.16	641.89	637.68	
	Ca	544.65	534.65	528.69	525.77	522.51	519.26
	Sr	640.77	635.55	627.29	624.53	621.84	617.29
	Ba	628.41	617.74	613.58	609.31	606.56	
15	Mg	665.67	654.97	649.89	645.54	641.20	
	Ca	546.92	536.86	530.74	527.83	524.51	521.25
	Sr	645.66	640.45	632.16	629.42	626.27	621.59
	Ba	631.93	621.19	616.73	612.50	609.75	
20	Mg	669.11	658.30	653.00	648.64	644.28	
	Ca	549.30	538.95	532.78	529.76	526.62	523.01
	Sr	650.74	645.27	636.83	633.93	630.90	626.07
	Ba	635.67	624.39	620.20	615.90	613.22	
25	Mg	673.06	662.00	656.62	652.18	647.75	
	Ca	551.26	540.79	534.46	531.45	527.96	524.64
	Sr	654.43	649.34	640.77	638.16	634.79	630.06
	Ba	639.05	627.63	623.26	619.00	615.92	
30	Mg	677.20	665.83	660.36	655.85	651.28	
	Ca	553.30	542.65	536.21	532.97	529.78	526.17
	Sr	658.37	652.96	644.18	642.01	638.46	633.65
	Ba	642.37	630.77	626.19	621.92	618.80	
				Molal concentration × 10^3			
Metal	Mg	6.534	10.890	14.001	17.112	21.06	
Acid		0.8572	1.3534	1.7084	2.0626	2.5132	
Metal	Ca	13.816	21.643	28.66	32.89	38.14	43.90
Acid		2.1957	3.249	4.214	4.481	5.096	5.711
Metal	Sr	7.283	9.153	13.246	14.978	17.021	20.39
Acid		1.1451	1.8306	2.061	2.320	2.629	3.141
Metal	Ba	13.342	22.32	27.29	33.02	37.49	
Acid		2.005	3.355	4.102	4.963	5.649	

[a] The values of μ_1, μ_2, μ_3, etc., differ for each e.m.f. measurement, and may be found as points in Fig. 1.

Sample e.m.f. data for cell I obtained at 0, 5, 10, 15, 20, 25 and 30° for each of the four alkaline earth ions at various ionic strengths are given in Table I. Because of space limitations only one value is given for each set of conditions, and all duplications and minor variations are omitted.

Calculations.—The e.m.f. of cell I is given by the equation

$$E = E^\circ - RT \ln a_{H^+} m_{Cl^-} \gamma_{Cl^-} \qquad (1)$$

where γ represents activity coefficient and the other terms have their usual meaning. The stability of the metal chelate is defined in terms of the chemical equilibrium

$$M^{+2} + V^{-4} \rightleftharpoons MV^{-2}$$

where M^{+2} represents an alkaline earth ion and V^{-4} represents the tetravalent anion of ethylenediaminetetraacetic acid. The corresponding stability constant expression is

$$K = \frac{a_{MV^{-2}}}{a_{M^{+2}} \times a_{V^{-4}}} \qquad (2)$$

At the pH employed in the experimental solutions for cell I, it is necessary to take into account the third and fourth acid dissociation equilibria of the amino acid

$$H_2V^{-2} \rightleftharpoons H^+ + HV^{-3}$$

$$HV^{-3} \rightleftharpoons H^+ + V^{-4}$$

The corresponding thermodynamic acid dissociation constants are defined by

$$k_3 = \frac{a_{H^+} \times a_{HV^{-3}}}{a_{H_2V^{-2}}} \qquad (3)$$

$$k_4 = \frac{a_{H^+} \times a_{V^{-4}}}{a_{HV^{-3}}} \qquad (4)$$

Rearrangement of equations (2), (3), and (4) gives

$$a_{H^+} = \left(\frac{a_{M^{+2}} \times a_{H_2V^{-2}}}{a_{MV^{-2}}} k_3k_4K\right)^{1/2} \qquad (5)$$

Combination of equations 1 and 5 results in the relationship

$$\frac{(E - E^0)F}{2.3RT} + \log m_{Cl^-} = -{}^1/_2 \log \left(\frac{a_{M^{+2}} \times a_{H_2V^{-2}}}{a_{MV^{-2}}} k_3k_4K\right) - \log \gamma_{Cl^-} \qquad (6)$$

Rearrangement of 6 with the substitution of $m_s\gamma_s$ for a_s and of p_wH for $(E - E°)F/2.3\ RT$ + log m_{Cl^-}, according to standard practice, results in the relationship

$$p_wH - {}^1/_2(pk_3 + pk_4) + {}^1/_2\log \frac{m_{M^{+2}} \times m_{H_2V^{-2}}}{m_{MV^{-2}}} = -{}^1/_2\log K - {}^1/_2\log \frac{\gamma_{M^{+2}} \times \gamma_{H_2V^{-2}} \times \gamma^2_{Cl^-}}{\gamma_{MV^{-2}}} \quad (7)$$

The activity coefficient term was defined as a function of ionics trength in terms of an arbitrary parameter, a^*, the "distance of closest approach" obtained from the Debye–Hückel relationship

$$-\log \gamma_i = \frac{AZ_i^2\sqrt{\mu}}{1 + Ba_i^*\sqrt{\mu}} + \beta m_i \quad (8)$$

where A, Z and B have their usual significance. The quantity β was evaluated by the method described by Hamer and Acree.[11] Since the properties of each ionic species present in the mixture are additive functions of those of the individual ions present, it follows that $\Sigma\beta m_i = \Sigma(1/n)\beta_i n\mu_i$. If the ionic strength contribution of each ion is some fraction of the total ionic strength (*i.e.*, μ_i = constant × μ where p, q and r are constants for a specified ratio of salts) and since $\mu_i = nm_i$ and $\mu = \Sigma\mu_i$, it follows that

$$\frac{1}{n_i}(p\beta_i n)\mu - \frac{1}{n_i}(q\beta_j n)\mu - \frac{1}{n_k}(r\beta_k n)\mu = \beta\mu \quad (9)$$

The relationship derived from equation 8 to fit the requirements for the extrapolation of the quantities of equation 7 to infinite dilution is

$$-{}^1/_2 \log \frac{\gamma_{M^{+2}} \times \gamma_{H_2V^{-2}} \times \gamma^2_{Cl^-}}{\gamma_{MV^{-2}}} = \frac{3A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} + \beta\mu \quad (10)$$

The values of β obtained by means of equation 9 and the values arbitrarily selected for the constant a^* so as to give a straight-line extrapolation of equation 7 with minimum slope were substituted into equation 10 to give values of log γ_r, equal to the quantity $-{}^1/_2 \log (\gamma_{M^{+2}} \times \gamma_{H_2V^{-2}} \times \gamma^2_{Cl^-}/\gamma_{MV^{-2}})$ for each temperature and each metal ion system. The values of log $m_{M^{+2}}(m_{H_2V^{-2}}/m_{MV^{-2}})$ were calculated and listed in Table II as log r, along with the values of a^* and β, determined as described above.

All the terms in the resulting relationship for equation 7 with the exception of K were placed on the left side of the equation and extrapolated as a function of ionic strength to infinite dilution. Thus, the thermodynamic constant K was evaluated for each temperature investigated. The graphical extrapolations to infinite dilution are given in Fig. 1. The values of pk_3 and pk_4 used in equation 7 were reported in an earlier publication.[12]

The standard thermodynamic quantities $\Delta F°$, $\Delta H°$ and $\Delta S°$ were calculated by means of the usual relationships

$$\Delta F^0 = -2.303\ RT \log K \quad (11)$$

$$\Delta H^0 = \frac{2.303\ RT_1T_2(\log k_2 - \log k_1)}{T_2 - T_1} \quad (12)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta F^0}{T} \quad (13)$$

TABLE II

EVALUATION OF ACTIVITY COEFFICIENTS

Metal ion	t, °C.	a^*	β	log r
Mg^{+2}	0	6.0	0.7	2.759
	5	6.0	.7	2.804
	10	6.0	.6	2.856
	15	6.1	.6	2.914
	20	6.1	.5	2.953
	25	6.2	.5	3.008
	30	6.2	.5	3.026
Ca^{+2}	0	10.3	1.0	1.025
	5	10.4	1.0	1.087
	10	10.4	0.9	1.156
	15	10.5	.9	1.235
	20	10.6	.9	1.309
	25	10.7	.9	1.380
	30	10.8	.9	1.446
Sr^{+2}	0	10.5	0.8	1.716
	5	10.6	.8	1.840
	10	10.7	.7	1.932
	15	10.8	.7	2.023
	20	10.9	.7	2.116
	25	11.0	.6	2.189
	30	11.0	.5	2.248
Ba^{+2}	0	6.0	0.6	0.811
	5	6.1	.6	.840
	10	6.2	.6	.879
	15	6.4	.6	.934
	20	6.5	.6	.983
	25	6.6	.6	1.029
	30	6.7	.6	1.069

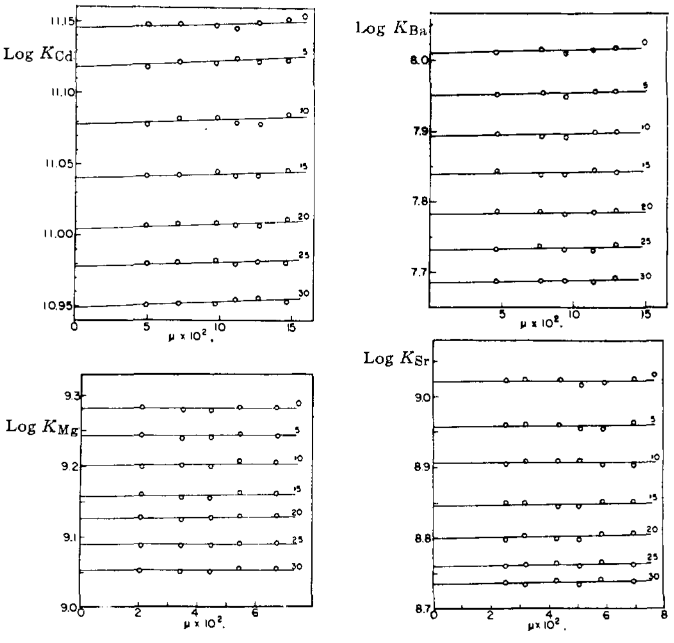

Fig. 1.—Extrapolation of potentiometric data to infinite dilution (see equation 7).

The equilibrium constants and thermodynamic constants calculated by means of equations 7, 11, 12 and 13 are given in Table III.

Discussion

From the equilibrium formation constants listed

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[11] W. Hamer and S. Acree, *J. Research Natl. Bur. Standards*, **35**, 381 (1945).

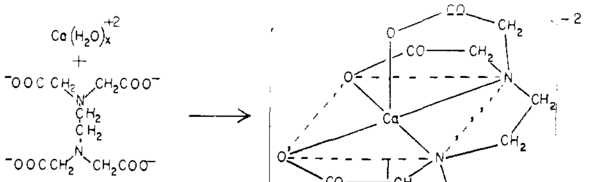
[12] F. F. Carini and A. E. Martell, THIS JOURNAL, **75**, 4810 (1953).

TABLE III

°C.	Mg	Ca	Sr	Ba
		log K		
0	9.28	11.14	9.02	8.01
5	9.24	11.12	8.96	7.95
10	9.20	11.08	8.91	7.89
15	9.16	11.04	8.85	7.84
20	9.12	11.00	8.80	7.78
25	9.09	10.98	8.76	7.73
30	9.05	10.95	8.74	7.68
		$-\Delta F^0$, kcal.		
0	11.60	13.92	11.33	10.01
5	11.77	14.15	11.44	10.12
10	11.92	14.35	11.54	10.22
15	12.08	14.55	11.66	10.33
20	12.24	14.76	11.80	10.44
25	12.40	14.97	11.90	10.54
30	12.56	15.18	12.11	10.66
		$-\Delta H^0$, kcal.		
0–30	2.9	2.5	4.1	4.1
		$+\Delta S^0$, e.u.		
0–30	32	42	26	22

in Table III, it is seen that the order of stability of the 1:1 alkaline earth chelates of ethylenediaminetetraacetic acid is: Mg(II) > Ca(II) > Sr(II) > Ba(II). This is the same order as was found by Schwarzenbach and Ackermann[13] on the basis of "concentration" constants in 0.1 M KCl at 20°, although the thermodynamic values of the present investigation are considerably higher, as expected. Although the stability as measured by the equilibrium constants decreases slightly with an increase in temperature, the values of $-\Delta F^\circ$ increase in magnitude as the temperature increases.

The enthalpies of formation of the metal chelates from the aqueous ions in their standard states are seen from the values of ΔH° in Table III to be all small, negative, and about the same magnitude. These values correspond to the breaking of the M–H_2O bonds of the hydrated ions and the formation of the metal–ligand bands in the chelates. Thus, if one neglects the slight amount of hydration of the ligand anion, the reactions involved in the calculated ΔH° values may be summarized by the equation



The heats of hydration of the alkaline earth metal ions are 448, 362, 334 and 288 kcal./mole for Mg(II), Ca(II), Sr(II) and Ba(II), respectively.[14] Since the value of ΔH° determined in this investigation is quite small compared to heats of hydration, it seems that the heats of formation of the metal chelate bonds are of approximately the same magnitude as the ion–dipole bonds of the hydrated ions.

The most significant result of this investigation is the fact that the high stability of the alkaline earth–ethylenediaminetetraacetate chelates is due primarily to the large entropy increase associated with complex formation. The entropy change accounts for from about two-thirds of the free energy increase for the barium chelate to about four-fifths for the calcium chelate. An entropy increase would be expected for a system such as this where the charge of the ions is decreased, where the ion formed is larger than the ions from which it is produced (to allow a more favorable distribution of charge), and where an increase in the number of particles occurs. From the equation given above it is readily seen that all three factors operate in this case. The latter effect, in which the highly polarized water molecules surrounding the metal ions are released to the body of the solution, is believed to be the most important of the three. The original suggestion of Calvin and Bailes[1] for the copper(II)–salicylaldehyde chelate attributed the greater part of the stability to the same type of entropy effect.

The fact that the reported entropy changes increase to a maximum with the calcium ion and then decrease again for the larger ions is interesting as a comparison of relative tendencies for chelate ring formation. It is probable that the coördination number of the magnesium ion is somewhat less than that of the other ions of the alkaline earth group. The release of fewer water molecules to the solvent in the case of the magnesium ion seems to correlate with the fact that the observed entropy change is less favorable than that of the calcium ion. The smaller magnitudes of the entropy increase for strontium and barium may be due to the introduction of strain in the chelate rings involving the larger ions.

The reasons for the high affinity of the ethylenediaminetetraacetate anion for alkaline earth ions has been a matter of speculation for some time. One of the chief difficulties is the fact that the highly basic alkaline earth ions are generally recognized as having little affinity for all complexing agents and most chelating agents. The formation of multiple chelate rings and the consequent entropy effect is in itself unsatisfactory, since other polydentate ligands, such as the polyamines, would otherwise form strong chelates with the alkaline earth ions. Therefore, it seems that a negative or very small positive value of ΔH° is also an essential requirement for a stable chelate. The formation of alkaline earth chelates of the polydentate polyamines would probably involve a favorable entropy increase but a highly unfavorable (*i.e.*, relatively large and positive) enthalpy change. Thus, the fact that the affinity of the donor groups in the ethylenediaminetetraacetate anion for calcium ion is at least as great as that of water molecules is fundamental to the attain-

[13] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

[14] A. Smekal, "Handbuch der Physik," 12th Ed., Vol. 24, part II, Julius Springer, Berlin, 1933, p. 1051.

ment of high stability in the resulting chelate.

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WORCESTER, MASS.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF TORONTO]

The Determination of the Adjusted Indicator Concentration behind a Moving Boundary in Dilute Solution; the System Potassium Chloride–Sodium Chloride in Water at 25°

BY D. R. MUIR, J. R. GRAHAM AND A. R. GORDON

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A method is described for determining the adjusted indicator concentration behind a moving boundary in dilute solutions. To test the procedure, the system KCl–NaCl was investigated. It is shown that the Kohlrausch ratio can be determined with a precision comparable with that obtainable in moving boundary determinations of transference numbers, and that the ratio, measured over a range of concentration, can be extrapolated unambiguously to zero concentration. From the limiting ratio and the limiting equivalent conductances of leading and indicator salts, limiting ionic conductances may be obtained at once. Thus limiting ionic conductances can be determined in any solvent in which precise conductance measurements are possible, without carrying out any transference measurements in the ordinary sense of the term. Possible applications of the method are discussed.

In 1934, Hartley, Drew and Collie[1] reported a method for measuring the transference number of a slow ion by determining the adjusted indicator concentration of that ion behind a boundary for which the transference number of the leading fast ion was known. The basis for the procedure was the familiar Kohlrausch[2] condition for a stable two salt boundary of the type MA/M_iA

$$C_i/C = t_i/t = r \qquad (1)$$

where C and C_i are the concentrations of the leading and indicator ions M and M_i, respectively, t and t_i are the corresponding transference numbers, and r is the Kohlrausch ratio. As originally developed, the method was not capable of high precision, but it did permit approximate determinations of the transference numbers of certain paraffin-chain salts.[3] Years later, and using modern techniques, analogous measurements were carried out by Longsworth[4] to test the Dole theory[5] of polysalt boundaries, but on the whole the possibility of obtaining reasonably precise transference data in this way has received little attention. In a recent paper[6] dealing with adjustment of indicator concentration during moving boundary measurements, it was shown that with the type of cell there employed, it was possible to determine the indicator concentration behind the boundary within a part in 500 or so; this suggested that if the precision of such measurements could be raised to a level comparable with that obtainable in the usual moving boundary determination, and that if the Kohlrausch ratio, measured over a range of concentrations, could be extrapolated to infinite dilution, the resulting limiting ratio could be combined with the corresponding limiting equivalent conductances to yield limiting ionic conductances. Since limiting ionic conductances provide information as to ion–dipole interaction unobtainable from the equivalent conductance data, and since the procedure outlined above would eliminate the need for transference measurements in the ordinary sense of the term, it seemed desirable to investigate this possibility.

The system chosen for investigation was KCl/NaCl in aqueous solution at 25°. The reasons for this choice were first, that for both salts the transference numbers were well established,[7–9] and second, that owing to the relatively rapid change of the transference number for NaCl with concentration as compared with that for KCl, this system provided a good test of any extrapolation procedure.

Experimental

A series of tests with the cells previously employed (see Fig. 2 of ref. 6) and with various modifications of them, showed that the desired precision in the measurement of the adjusted indicator concentration (0.02%) could not be attained, but partly by accident it was found that a much simpler technique could, with care, provide data of the accuracy desired. Essentially the cell is a conventional falling boundary cell of the type used for many years in this Laboratory with a type VIII shearing mechanism (see Fig. 1 of ref. 6). It differs only in that the channel is somewhat longer (approximately 30 cm.) than in earlier cells, and that there is an additional shearing stopcock at the base of the channel. As in earlier cells, the channel is 2.5 mm. internal diameter and cadmium and silver–silver chloride electrodes serve as anode and cathode. To fill, KCl solution is forced upward into the channel until it rises just above the top of the upper shearing stopcock, which is then closed. The reservoir above the stopcock is then repeatedly flushed with the NaCl solution; after filling, the cell is brought to temperature equilibrium in a bath regulated to ±0.01°, the junction is formed at the top of the channel, and the current is started. It should be noted that only an approximate knowledge of the current and the time of electrolysis is necessary. Fifteen or twenty minutes after the time calculated for the boundary to pass the lower stopcock, the current is stopped and both cocks closed, thus isolating a column of indicator solution. For a system for which the transference number of the leading ion was not known, a preliminary series of measurements would obviously be required to determine the length of electrolysis necessary for the concentration of the solution in the channel to become independent of further passage of current.

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[1] G. S. Hartley, E. Drew and B. Collie, *Trans. Faraday Soc.*, **30**, 648 (1934).

[2] F. Kohlrausch, *Ann. Physik. Chem.*, **62**, 209 (1897).

[3] G. S. Hartley, B. Collie and C. S. Samis, *Trans. Faraday Soc.*, **32**, 795 (1936).

[4] L. G. Longsworth, THIS JOURNAL, **67**, 1109 (1945).

[5] V. P. Dole, *ibid.*, **67**, 1119 (1945).

[6] A. R. Gordon and R. L. Kay, *J. Chem. Phys.*, **21**, 131 (1953).

[7] L. G. Longsworth, THIS JOURNAL, **54**, 2741 (1932).

[8] R. W. Allgood, D. J. LeRoy and A. R. Gordon, *J. Chem. Phys.*, **8**, 418 (1940).

[9] R. W. Allgood and A. R. Gordon, *ibid.*, **10**, 124 (1942).