[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# Applications of the Eastman Thermocell Equation.[1] I. Certain Absolute Ionic Entropies and Entropies of Transfer of Alkali Metal and Tetraalkylammonium Bromides and Hydroxides

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It has been shown by Eastman[3] that the e. m. f. of thermocells of the type exemplified by

$$\begin{array}{ccccc} \text{Ag,} & \text{AgBr,} & \text{KBr } (0.01\ M), & \text{AgBr,} & \text{Ag} \\ T_2 & T_2 & & T_1 & T_1 \end{array}$$

may be treated by classical thermodynamic methods. For a differential temperature between the two electrodes, Eastman has shown that $F\mathrm{d}E/\mathrm{d}T$ for such a thermocell in which the Soret effect is excluded is given by the equation

$$F\mathrm{d}E/\mathrm{d}T = \Delta S_{\mathrm{R}} + t_{\mathrm{C}}S_{\mathrm{C}}^* - t_{\mathrm{A}}S_{\mathrm{A}}^* \qquad (1)$$

where $\Delta S_{\mathrm{R}}$ is the entropy change in the electrode reaction occurring at the higher temperature when one equivalent of positive electricity flows through the cell from the hot to the cold electrode. The symbol, $F$, represents the faraday equivalent, $\mathrm{d}E/\mathrm{d}T$ is the electromotive force of the cell divided by the temperature difference, $t_{\mathrm{C}}$ and $t_{\mathrm{A}}$ are the transference numbers and $S_{\mathrm{C}}^*$ and $S_{\mathrm{A}}^*$ are the entropies of transfer of cation and anion, respectively. Equation (1) is referred to in this paper as the Eastman thermocell equation. The term on the left-hand side of equation (1) is obtained by direct measurement of the small but reproducible e. m. f. produced by appreciable temperature gradients.

Eastman[3] explored the possibility of using this equation for numerical calculations by the use of certain reasonable assumptions which lead to rough approximations of entropies of transfer of ions based upon fragmentary data then available. On the basis of his assumptions he calculated values of the entropy of transfer of certain positive ions, the values of which led to a tentative value for the absolute partial molal entropy of chloride ion. Eastman's original estimates of the values for entropies of transfer of ions have gone unchallenged up to the present time, as evidenced by the work of Bernhardt and Crockford,[4] who made use of these entropies of transfer in calculating a new value for the absolute partial molal entropy of chloride ion.

Fully aware of the tentative nature of his assumptions and the lack of satisfactory data, Eastman sponsored an extensive series of studies of all types of simple thermocells designed to yield data applicable to the solution of equation (1). The present paper is a record of a part of this work.

Theoretical implications discussed in connection with a study of the Soret effect[5] led to the speculation that large symmetrical ions would have low entropies of transfer, approaching zero with increasing size of the ion. A series of symmetrical quaternary ammonium ions should, according to speculation, satisfy these requirements. Extensive studies of thermocells involving dilute solutions of these ions led to confirmation of these implications and to entirely new values for the entropies of transfer of ions.

This paper is the first of a series designed to present the essential data and techniques evolved in Professor Eastman's Laboratory. No chronological order is attempted; instead, the following series of measurements were selected on the basis of their contribution to an orderly development of ideas leading to the new values of the entropies of transfer and of the absolute partial molal entropies of certain ions: (a) tetraalkylammonium, lithium, sodium and potassium hydroxides with mercury–mercuric oxide electrodes; (b) tetraalkylammonium, lithium, sodium, potassium and ammonium bromides with silver–silver bromide electrodes. The reduction of the data from these two series of salts leads to values for the entropies of transfer of the positive and the negative ions involved and to the absolute partial molal entropies of hydroxide and bromide ions.

## Selection of the Temperature Gradient and the Concentration Best Suited for Comparative Studies

The thermocells selected for investigation correspond to Eastman's Type II Cells.[3,6] Considerable exploratory work was done to determine suitable cell design and optimum concentrations and temperature differences. It was found that the lowest concentration that could be investigated with ease was 0.001 $m$ for a temperature difference of 10° (average temperature 25°). An appreciable quantity of data was obtained for concentrations of 0.1, 0.01 and 0.001 $m$. A study of the measured e. m. f. of the thermocells as a

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[1] Ermon Dwight Eastman, Professor of Chemistry at the University of California until his death in 1945 and beloved mentor of all of the authors of this paper, planned and directed the work leading to this publication. The war interrupted his plans for completing and publishing this work, and his untimely death deprived the present authors of his leadership in this undertaking. The data presented here are taken from the authors' doctorate theses deposited at the Library of the University of California.

[2] (a) Deceased. (b) College of Pharmacy, University of California, Medical Center, San Francisco 22. (c) The Brown Company, Berlin, New Hampshire. (d) Lieutenant, U. S. Navy, Bureau of Ships, Navy Department, Washington, D. C. (e) 726 Oak Avenue, Davis, California.

[3] Eastman, THIS JOURNAL, **50**, 292 (1928), and microfilm supplement of contributions by L. D. Tuck, R. G. Preston and M. B. Young showing that the entropy of electrons may be neglected, and giving the complete derivation of equation (1) as presented by Professor Eastman to his graduate students.

[4] Bernhardt and Crockford, *J. Phys. Chem.*, **46**, 473 (1942).

[5] Eastman, THIS JOURNAL, **50**, 283 (1928).

[6] Eastman, *ibid.*, **48**, 1482 (1926).

function of the log of the molality of the electrolyte showed only slight deviations from ideal behavior at a concentration of 0.01 *m*. Therefore, the standard concentration used throughout this research was 0.01 *m*. The standard temperature difference of 10° was similarly checked by measuring several thermocells at 5° intervals for an average temperature of 25°. Most of this preliminary work was done using the calomel electrode with the alkali metal chlorides and hydrochloric acid, and it was shown that the measured e. m. f. per degree C. was the same for both the 5 and 10° intervals (average temperature 25°). Table I sets forth the data upon which this conclusion was based. The effect of concentration was the subject of continuous investigation by all contributors to this work.

Table I

Dependence of E. m. f. of Calomel Thermocell upon Temperature Interval

| Electrolyte | Molality | E. m. f., millivolt/degree $\Delta T = 10°$ (20.0–30.0°) | E. m. f., millivolt/degree $\Delta T = 5°$ (22.5–27.5°) |
|---|---|---|---|
| HCl | 0.01005 | 0.636 | 0.638 |
| LiCl | .0999 | .823 | .824 |
| NaCl | .0962 | .780 | .780 |
| NaCl | .00965 | .966 | .966 |

In the early stages of the investigation it was discovered that apparent discrepancies in the e. m. f. measurements for identical silver–silver bromide cells were eliminated by reversing the cells in the temperature gradient. By reversal, two equilibrium e. m. f. values were obtained for each thermocell, the averages of which were found to be closely reproducible. Permanent differences in the silver–silver bromide electrodes, of the order of magnitude reported by Smith and Taylor,[7,8] were thus cancelled.

It was found that these differences did not occur with the mercury–mercuric oxide electrodes; therefore, reversal was omitted from the procedure for these electrodes. Most of the later and more accurate measurements with the silver–silver bromide electrodes were made by the method of reversal which is referred to as the "reversal technique." Another approach not involving the reversal of the thermocells in the temperature gradient is referred to as the "transfer technique" because pairs of electrodes were transferred successively from one thermocell to the next of a series maintained in the temperature gradient. The differences in e. m. f. produced by several different electrolytes were found to be the same by both methods within the experimental errors, and certain slightly larger deviations were attributed to failure to remove oxygen of the air in the application of the transfer technique.

Preliminary studies included several methods for preparing the different types of electrodes incorporated in the thermocells. Only those methods which were found to produce stable and reproducible electrodes are described in this paper. It was established beyond question that the Soret effect did not influence the results reported. Much longer periods of time than the three- to five-hour observation periods necessary for this work are required to produce a measurable Soret gradient in the systems described.

## Experimental

**Purification of the Salts.**—Several of the commercially available quaternary ammonium salts were purified by recrystallization from water or organic solvents. Those compounds not readily available were synthesized using standard methods. Iodides were sometimes converted to bromides through the hydroxide, using silver oxide followed by hydrobromic acid. All of the salts were obtained in the solid state by crystallization. The sodium and potassium bromides used in this work were obtained from reliable sources and were twice recrystallized from conductivity water and carefully dried before use. The lithium bromide was dried in a vacuum desiccator over phosphorus pentoxide after it was prepared from C. P. hydrobromic acid and C. P. lithium carbonate. A record of the methods of preparation and the significant properties of some of the salts are included in Table II.

Table II

| Salt | Preparation | M. p., °C. | % Bromide Calcd. | % Bromide Found |
|---|---|---|---|---|
| $(CH_4)_4NBr$ | Recrystallized salt | | | |
| $(C_2H_5)_4NBr$ | Recrystallized salt | 269.0–269.2 dec. | | |
| $(n\text{-}C_3H_7)_4NBr$ | From iodide by $Ag_2O + HBr$ | | 30.01 | 30.00 |
| $(n\text{-}C_4H_9)_4NBr$ | Menschutkin reaction | 101.0–101.6 | 24.79 | 24.78 |
| $(n\text{-}C_5H_{11})_4NBr$ | | 100.0–100.2 | 21.12 | 21.12 |
| $(n\text{-}C_7H_{15})_4NBr$[a] | Complete synthesis from $n\text{-}C_7H_{15}Br$[a] | 88.9–89.1 | 16.285 | 16.27 |

[a] Prepared by Dr. J. K. Holmes of this Laboratory.

**Preparation of Solutions.**—Solutions of all the bromides were prepared by weighing the solid salts and dissolving in weighed quantities of water. In some cases concentrations were redetermined by gravimetric analysis or by electrical conductivity methods for solutions of lithium, sodium and potassium bromides. The tetraalkylammonium hydroxide solutions were prepared from the corresponding bromides or iodides by the use of carbonate-free silver oxide which was freshly prepared and thoroughly washed. When possible the hydroxides were prepared from the corresponding amalgam. The hydroxide solutions were made at a concentration somewhat higher than required for use, and were filtered and diluted to the required concentration. The solutions were analyzed by titration using phenolphthalein as an indicator with 0.01 *M* hydrochloric acid. The usual precautions were taken to eliminate carbonate errors. Conductivity water was used throughout.

**Densities of Solutions.**—The densities of two of the solutions were determined at 25° by the use of a modified Shedlovsky U-tube type pycnometer[9] with graduated capillary stems. The graduated portion of the pycnometer was calibrated with mercury before sealing to the main portion of the U-tube which had a capacity of approximately 28 ml. The completed pycnometer was calibrated with distilled water; all readings of the graduated capillaries were made by means of a telescope. With these refinements, a precision well within five parts in 100,000 was obtained. The densities of solutions studied in this way are recorded in Table III.

**Conductance of Solutions.**—A modified Jones and Josephs bridge[10] was assembled from carefully calibrated resistances

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(7) Smith and Taylor, *J. Research Natl. Bur. Standards*, **20**, 837 (1938).

(8) Taylor and Smith, *ibid.*, **22**, 307 (1939).

(9) Shedlovsky and Brown, This Journal, **56**, 1066 (1934).

(10) Jones and Josephs, *ibid.*, **50**, 1049 (1928).

and was used with an electronic oscillator and amplifier to measure the resistance of a Jones and Bollinger type conductivity cell[11] at a frequency of approximately 1200 cycles per second. The cell constant of 12.492 cm.$^{-1}$ was based upon the 0.01 demal potassium chloride solution of Jones and Bradshaw.[12] The temperature of the solutions was maintained by an oil-bath held to a temperature of 25.000 ± 0.015°. The error introduced by the conductivity measurements was proved to be well below the limit of error of about 0.1% established by the analysis of the solutions studied. The more significant results of the conductivity measurements on the bromide solutions are presented in Table III.

TABLE III

DENSITIES AND EQUIVALENT CONDUCTANCES FOR 0.01 *m* SOLUTIONS AT 25°

| Compound | $d_4^{25}$ | Λ, mhos |
|---|---|---|
| $(CH_3)_4NBr$ | | 114.1 ± 0.2 |
| $(C_2H_5)_4NBr$ | | $101.1_2$ ± 0.1 |
| $(n\text{-}C_3H_7)_4NBr$ | $0.9973_3$ | $92.3_0$ ± 0.1 |
| $(n\text{-}C_4H_9)_4NBr$ | $.9973_2$ | $88.4_0$ ± 0.1 |
| $(n\text{-}C_5H_{11})_4NBr$ | | $86.3_8$ ± 0.1 |
| $(CH_3)_4NOH$ | | 233.6 ± 0.3 |
| $(C_2H_5)_4NOH$ | | 223.3 ± 0.5 |
| $(n\text{-}C_3H_7)_4NOH$ | | 211.7 (1 value) |
| $(n\text{-}C_4H_9)_4NOH$ | | 207.9 (1 value) |
| $(n\text{-}C_5H_{11})_4NOH$ | | 206.4 (1 value) |
| $(n\text{-}C_7H_{15})_4NOH$ | | $\left.\begin{matrix}205.4\\197.0\end{matrix}\right\}$ 2 values |

**Construction of Thermocells.**—Two different types of cells were used, one for the silver–silver halide electrodes and the other for the mercury–mercuric oxide electrode. Figure 1 illustrates the cell which was determined after considerable trial to be most suitable for the silver–silver bromide electrodes deposited on two pieces of platinum gauze (only one of these is shown in the drawing). The cell was constructed of Pyrex glass with two standard taper stoppers to which the electrodes were attached. $T_1$ and $T_2$ represent leads from a five-junction copper–constantan thermopile sealed through the bottom of the thermocell. The junctions were insulated one from another with bakelite varnish and the entire assembly held in place with solidified naphthalene. Tube O facilitated the introduction of the thermopile and was subsequently sealed off close to the bottom of the cell. G represents one of the squares of platinum gauze used to support the electrodes in close proximity to the thermopile junction. The other electrode (not shown) is similarly located in the other leg of the cell. Each gauze was sealed to no. 18 platinum wire which in turn at point Pt–Pt was sealed to no. 28 platinum wire to facilitate sealing through the long covered glass rod. Directly above the rod, no. 20 silver wire (E) was fused to the no. 28 platinum wire to complete the electrical connection to the potentiometer system. The location of this Pt–Ag junction at the same temperature as G served to eliminate an otherwise inherent thermocouple which would have contributed to the e. m. f. of the cell. DeKhotinsky cement was placed at this point to increase the efficiency of the platinum to glass seal. Short lengths of neoprene tubing (N) were used in filling the cells and in final sealing against the possibility of air leakage. The marked curvature in the connecting tube was incorporated to prevent convection currents which had been found to be a serious cause of error; the double hump also served for the purpose of facilitating permanent mounting of the cell in wooden blocks. The capillary extensions of the double hump were required in filling the cell and were equipped with neoprene tubes which were closed by means of pinch clamps. The portion of the thermopile extending outside of the glass tubing was housed in spaghetti insulation to prevent accidental bending of the wire of the thermocouple.

Figure 2 shows the construction of the cell for use with the mercury–mercuric oxide electrodes. Essentially, this cell is the same as the one previously described except for the inclusion of the thermopile in the removable electrode assemblies. Because of the necessity for keeping the platinum contact dry, the platinum lead was sheathed in glass below the level of the mercury. The use of a copper lead for the electrode introduced a copper–mercury thermocouple for which suitable correction was made to the reported e.m.f. values.

**Apparatus for Removal of Air from Solutions.**—It was necessary to remove oxygen from the tetraalkylammonium bromide solutions in order to obtain reproducible measurements, probably because of the formation of trialkylamine oxide from the reaction of oxygen with decomposition products of the tetraalkylammonium halide in aqueous solution,[13] which, it is presumed, interferes with the electrode mechanism. The solutions, before they were introduced into the cell, were freed of the oxygen by bubbling purified nitrogen through them. Tank nitrogen containing 0.5% of oxygen was purified by passing it over reduced hot copper and thoroughly washing it successively through 6 *N* sodium hydroxide, 6 *N* sulfuric acid, water, and an electrolyte of the same concentration as the solution. The solution undergoing oxygen removal was contained in a Brown and MacInnes flask[14] in series with the cell. By simple mechanical manipulation of this flask the solution was forced into the cell after bubbling nitrogen through the system for about forty-five minutes.

**Mercury–Mercuric Oxide Electrodes.**—Mercuric oxide, made from solutions of mercuric nitrate and carbonate-free sodium hydroxide, was thoroughly washed with distilled water by repeated decantation. The oxide was stored under distilled water and portions were withdrawn for treatment with the appropriate electrolyte several days before use. The first step in preparing the electrode was to allow the oxide to come to equilibrium with the electrolyte for a period of twenty-four hours followed by washing several times with additional portions of electrolyte. The decanted slurry was introduced into the cell over a layer of purified mercury carefully introduced so as to maintain dry platinum contacts. The mercury used for the preparation of the mercuric nitrate and also for filling the cell was distilled from well-washed virgin mercury. It was determined by experiment that ordinary red mercuric oxide was unsatisfactory for electrodes. The oxide used was yellow crystalline modification which was never allowed to become dry.

**Silver–Silver Bromide Electrodes.**—The silver–silver bromide electrodes were of the thermal type[8] and were prepared by the method of Keston.[15]

**Thermometry.**—The temperature difference existing between two electrodes of a thermocell is of primary importance, since the measured e. m. f. of a cell is proportional to this difference and is relatively insensitive to changes in the absolute value of the average of the two temperatures. For this reason, emphasis was placed on accurate determinations of temperature differences which were measured by means of five-junction copper–constantan thermopiles installed in the thermocells. Ample experimental evidence indicated that slight variations in temperatures were closely followed by proportional changes in thermopile and cell e. m. f. values. These temperature variations were produced by fluctuations of the order of magnitude of 0.01° in each of two constant temperature baths used to maintain a ten-degree temperature interval.

The two baths were oil-filled and separated by a one-inch kapok-insulated double-wall partition provided with slots to accommodate several wooden blocks. The thermocells were permanently mounted in wooden blocks interchangeable with those fitted into the slots in the parti-

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[11] Jones and Bollinger, THIS JOURNAL, **53**, 411 (1931).

[12] Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

[13] Kortum, *Ber.*, **71**, 695 (1938).

[14] Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935).

[15] Keston, *ibid.*, **57**, 1671 (1935).

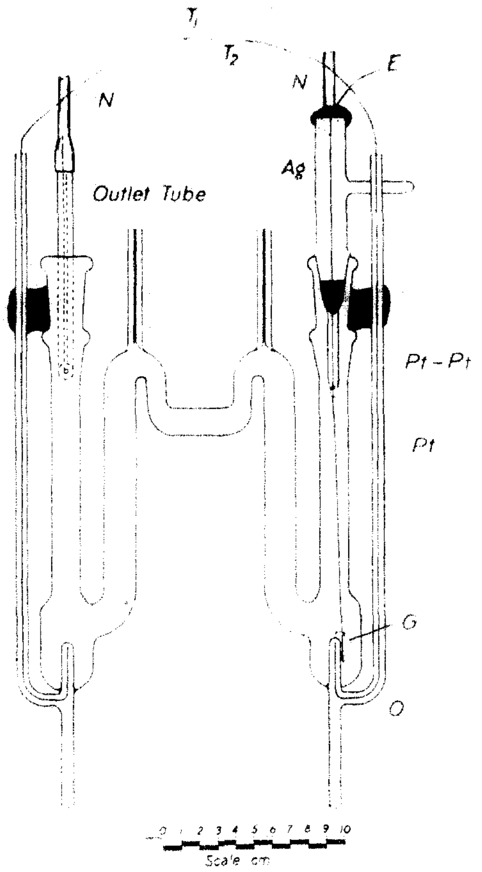

Fig. 1.—Cell for Ag–AgBr electrodes.

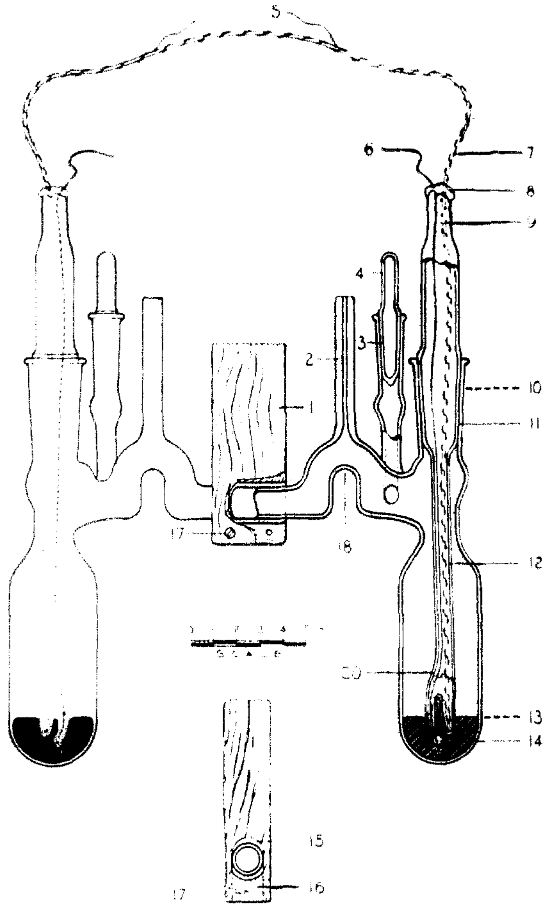

Fig. 2.—Cell for Hg–HgO electrodes: 1, wooden support; 2, capillary vent (3 mm.); 3, 4, ground glass joint (7/10); 5, 6, thermopile and electrode connections; 7, thermopile; 8, 9, de Khotinsky cement above a cotton plug; 10, level of thermostat oil; 11, ground glass joint (19/38); 12, glass tube; 13, 14, mercury; 15, plastic wood; 16, 17, details of support; 18, bend in connecting tube required to minimize convection within the cell; 20, upper level of solid naphthalene.

tion, and these slots were so situated that the thermocells shown in Figs. 1 and 2 were held in an upright position submerged in the two baths to the level of the lower portion of the ground glass stoppers. The temperatures of the two baths were maintained at 20 and 30°, respectively, by sensitive mercury-in-steel regulators, electric heaters controlled by magnetic and electronic relays, and continuous cooling of the 20° bath. Stirring was sufficiently rapid to maintain close regulation in the vicinity of the cells.

Individual copper–constantan thermopiles were embedded in solidified naphthalene and encased in thin-walled glass. They were calibrated against a similar secondary standard, the e. m. f. of which for a temperature difference of 10.00 ± 0.01° was determined by direct immersion in the two baths. The temperature difference was established and its error estimated by use of a resistance thermometer certified by the National Bureau of Standards. During the measurements, the resistance thermometer was used to read the temperature of the 20° bath; and a Beckmann thermometer, calibrated against the resistance thermometer, was used to read the temperature of the 30° bath. Earlier thermopile calibrations using certified mercury-in-glass thermometers were found to be in error by approximately 0.05° because of temperature gradients caused by insufficient circulation of the oil in the baths. Accordingly, all thermopile calibrations have been corrected to agree with the standard established by the resistance thermometer.

**Potentiometry.**—Two Leeds and Northrup Type K-1 potentiometers and one Rubicon Type B potentiometer were used with a high sensitivity Leeds and Northrup galvanometer. The potentiometers were compared one against the other, and usual care was exercised to provide reliable standard cells. Leads from the thermostats to the potentiometers were carefully insulated and shielded as proved by tests conducted to establish the adequacy of the electrical installation.

All e. m. f. measurements are recorded in Table IV with corrections for slight temperature deviation as indicated by thermopile readings. The final e. m. f. values included in this report also embody small corrections for deviation of concentration from the nominal value given. These corrections were made by using the ideal relationship between concentration and e. m. f. which was proved to be correct by measurements of the type reported as footnotes to Table IV.

## Results

**The Effect of Concentration.**—Equation (1) may be differentiated with respect to concentration if it may be assumed that the entropies of transfer and transference numbers remain con-

TABLE IV

$\Delta E/\Delta T$ (MV./10°) FOR 20–30° THERMOCELLS

| Cation | Mercury–mercuric oxide electrodes in 0.01 *m* solns. of different hydroxides | | | Silver–silver bromide electrodes in 0.01 *m* solns. of different bromides | | |
|---|---|---|---|---|---|---|
| | $\Delta E/\Delta T$, mv./10° | Av. dev., mv. | No. of cells | $\Delta E/\Delta T$, mv./10° | Av. dev., mv. | No. of cells |
| $Li^+$ | −7.071 | 0.017 | 7 | −8.313 | 0.007 | 4 |
| $Na^+$ | −6.610 | .013 | 8[a] | −7.888 | .008 | 6 |
| $K^+$ | −6.170 | .018 | 7 | −7.946 | .013 | 4 |
| $NH_4^+$ | | | | −8.282 | .005 | 4 |
| $(CH_3)_4N^+$ | −6.422 | .014 | 8 | −7.23 | .03 | 6[c] |
| $(C_2H_5)_4N^+$ | −6.512 | .017 | 8 | −6.961 | .008 | 7 |
| $(n\text{-}C_3H_7)_4N^+$ | −6.814 | .015 | 9 | −6.922 | .006 | 7 |
| $(n\text{-}C_4H_9)_4N^+$ | −6.918 | .007 | 7 | −6.927 | .004 | 9[d] |
| $(n\text{-}C_5H_{11})_4N^+$ | −6.983 | .005 | 4[b] | −6.935 | .009 | 5 |
| $(n\text{-}C_7H_{15})_4N^+$ | −7.05 | .01 | 4 | | | |

[a] Three cells with 0.003 *m* NaOH averaged −7.554 ± 0.003 mv./10° and eight cells with 0.001 *m* NaOH averaged −8.46 ± 0.05 mv./10°. [b] Five cells with 0.0035 *m* $(n\text{-}C_5H_{11})_4NOH$ averaged −7.82 ± 0.03 mv./10° and six cells with 0.001 *m* $(n\text{-}C_5H_{11})_4NOH$ averaged −8.85 ± 0.06 mv./10°. [c] Determined by the transfer technique referred to $(n\text{-}C_3H_7)_4NBr$ as a standard. [d] Two cells with 0.001 *m* $(n\text{-}C_4H_9)_4NBr$ averaged −8.88 ± 0.02 mv./10°.

stant. This treatment with the partial molal entropy of the ion involved in the electrode reaction as the only variable, leads to a theoretical slope of $2.303R/F$ for the curve representing variation of $dE/dT$ with the log of molality.

A linear relationship between $dE/dT$ and log *m*, as shown in Fig. 3, is indicative of how well the limiting slope of $2.303R/F$ is followed by sodium hydroxide and tetra-*n*-amylammonium hydroxide at concentrations between 0.001 and 0.01 *m*. Data for tetra-*n*-butylammonium bromide and other electrolytes (as yet unpublished) further confirm this linear relationship. It may be seen from the graphical representation of these data that the theoretical slope derived from the Eastman thermocell equation is reproduced as well as would be expected on the basis of perfect solution laws, and that further refinement of the calculations is not required for the purpose of the present extrapolations involving comparison of 0.01 *m* solutions. This graphical evidence also supports the assumption that the entropies of transfer may be treated as constant and additive for the purposes of these calculations.

**Transference numbers** required for the evaluation of the data presented in Table IV are presented in Table V together with the ionic mobilities from which they were computed. Even though additional conductance data were available for the hydroxide solutions, it was deemed advisable, in order to obtain self-consistent values, to base all of the calculations upon the equivalent ionic conductances calculated from data given by MacInnes[16] and Harned and Owen.[17]

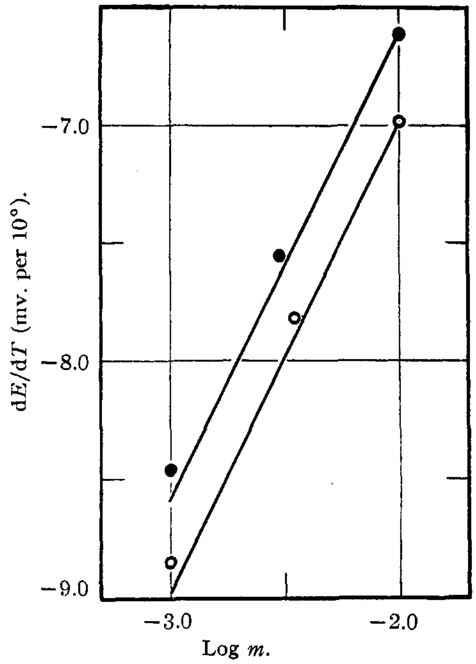

Fig. 3.—Plot of e. m. f. values of Hg–HgO thermocells as a function of the logarithm of molality of electrolyte: ●, NaOH; ○, $(n\text{-}C_5H_{11})_4NOH$; the straight lines represent the theoretical slope.

Ionic conductances not readily obtained from these sources were computed from Table III above, using 74.11 mhos as the equivalent conductance for bromide ion in 0.01 *M* solution. Transference numbers for the alkali metal hydroxide solutions are based upon a value of 191.5 mhos for 0.01 *M* hydroxide ion which was calculated from the data given by Harned and Owen.[17] However, a study of the conductivity measurements of the tetrasubstituted ammonium hydroxides suggests that the mobility of hydroxide ion is not constant for this series; therefore, transference numbers were computed by dividing the mobilities shown in Table V by the corresponding equivalent conductance values given in Table III.

TABLE V

CALCULATED IONIC CONDUCTANCES AND TRANSFERENCE NUMBERS FOR CATIONS IN 0.01 *m* SOLUTIONS AT 25°

| Ion | $\Lambda_C$, mhos | $t_C$ for hydroxides | $t_C$ for bromides |
|---|---|---|---|
| $Li^+$ | 35.30 | $0.155_6$ | $0.322_6$ |
| $Na^+$ | 46.46 | $.195_2$ | $.385_3$ |
| $K^+$ | 69.32 | $.265_8$ | $.483_3$ |
| $NH_4^+$ | 69.33 | .... | $.483_3$ |
| $(CH_3)_4N^+$ | $39.9_9$ | $.171_2$ | $.350_5$ |
| $(C_2H_5)_4N^+$ | $27.0_1$ | $.121_0$ | $.267_1$ |
| $(n\text{-}C_3H_7)_4N^+$ | $18.1_9$ | $.085_9$ | $.197_1$ |
| $(n\text{-}C_4H_9)_4N^+$ | $14.2_9$ | $.068_7$ | $.161_7$ |
| $(n\text{-}C_5H_{11})_4N^+$ | 12.27 | $.059_4$ | $.142_0$ |

**Calculation of Ionic Entropies of Transfer.**—The homologous series of tetraalkylammonium compounds reported in this paper were selected

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[16] MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, pp. 85, 337–340.

[17] Harned and Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, pp. 537–538.

for study in order to obtain d$E$/d$T$ values which could be meaningfully plotted against the transference numbers of the respective cations. Equation (1) may be written in the form

$$F\mathrm{d}E/\mathrm{d}T = (S_C^* + S_A^*)t_C + (\Delta S_R - S_A^*) \quad (2)$$

showing that the Eastman thermocell equation is linear in $F$d$E$/d$T$ and $t_C$ if $(S_C^* + S_A^*)$ and $(\Delta S_R - S_A^*)$ are constant terms. For each series, the latter term is known to be constant because each point is obtained from measurements made with one of a series of thermocells involving the same electrode reaction and the same anion. Therefore, the fact that the $F$d$E$/d$T$ values (as plotted in Fig. 4) fall on straight lines for the larger ions of each series is evidence that, for these larger ions, $S_C^*$ is a constant term. Experimental proof of a linear relationship of the same type in a series of normal amine hydrochlorides was also obtained during the course of this investigation,[18] and may be used to show that the entropies of transfer of non-symmetrical ions of large size may also approach some common value.

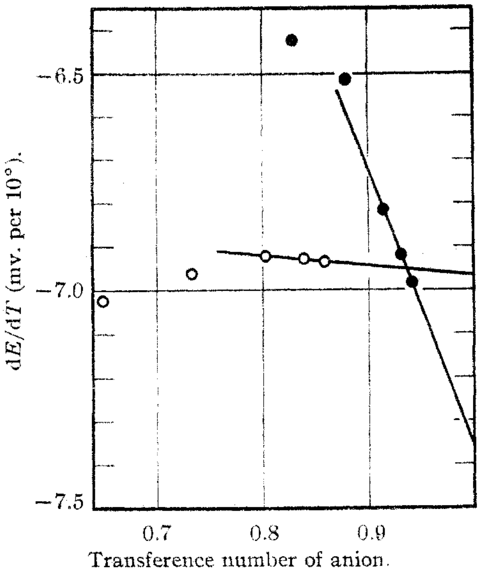

Fig. 4.—Plot of the e. m. f. values of thermocells as a function of anionic transference numbers: ●, hydroxide series; ○, bromide series.

It may be assumed for non-symmetrical ions that an active group is bound to solvent molecules in some way, and remains unmodified as the length of the hydrocarbon chain increases. However, this type of interaction with solvent would not be independent of the number of carbon atoms of the symmetrical tetraalkylammonium ions because an increase in the length of the hydrocarbon chains increases the effective radius of the ion, thereby changing the character of any interaction between active group and solvent. On the basis of this reasoning it must be assumed that the value for the entropy of transfer of any of these large ions falling on the straight lines must be nearly zero; in other words, $S_C^*$ for the large tetraalkylammonium ions may be assigned a value of zero within the limits of the experimental accuracy. Regardless of the absolute validity of this assumption, it is a convenient basis for presenting the experimental results in usable form, and is further supported by other non-thermodynamic considerations showing that large ions are characterized by the absence of solvation effects,[19,20,21] leaving for consideration only those effects which would presumably change considerably with changing ionic radii. No such changes are observed.

It is apparent from equation (2) that each of the two straight lines (Fig. 4) has a slope equal to the limiting value for $(S_C^* + S_A^*)$. From the foregoing discussion it is clear that $S_C^*$ may be neglected because, in this special case, it represents the entropy of transfer for any one of the large symmetrical tetraalkylammonium ions. Therefore each slope, multiplied by 2.307 to convert to calories per degree, is properly tabulated in Table VI as the entropy of transfer of the corresponding negative ion. The entropies of transfer of the positive ions presented in Table VI were obtained by substituting into equation (2) appropriate values for the term $(\Delta S_R - S_A^*)$ which were obtained by extrapolating the line for each series to the axis representing a zero value for $t_C$. Extrapolation performed analytically by the method of least squares without weighting gives, for the three points of the bromide series falling on the bromide line, a value of −6.966 mv./10° for the term, $(\Delta S_R - S_A^*)$. An extrapolation for the hydroxide series, based upon weighting each of the corresponding three points roughly as the precision of the e. m. f. measurements, yields a corresponding value of −7.361 mv./10°. These extrapolated values substituted into equation (2) proved a means for evaluating the term $(S_C^* + S_A^*)$ for each thermocell reported for which transference data are available. The values of $S_C^*$ shown in Table VI are obtained by

TABLE VI

CALCULATED MOLAL ENTROPIES OF TRANSFER, CALORIES PER DEGREE

| Ion | Calcd. from bromide series $(\Delta S_R - S_A^*) =$ −16.07 | Calcd. from hydroxide series $(\Delta S_R - S_A^*) =$ −16.98 |
|---|---|---|
| $Li^+$ | −10.15 | −10.5 |
| $Na^+$ | − 6.04 | − 5.9 |
| $K^+$ | − 5.20 | − 4.4 |
| $NH_4^+$ | − 6.80 | .... |
| $(CH_3)_4N^+$ | − 2.26 | − 2.1 |
| $(C_2H_5)_4N^+$ | − 0.48 | + 1.4 |
| $(n\text{-}C_3H_7)_4N^+$ | 0.00 | − 0.1 |
| $(n\text{-}C_4H_9)_4N^+$ | + 0.04 | + 0.1 |
| $(n\text{-}C_5H_{11})_4N^+$ | − 0.01 | − 0.1 |
| $Br^-$ | + 0.52 | .... |
| $OH^-$ | ..... | +148. |

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(18) Goodrich, Thesis, University of California, 1941.

(19) Lange, *Z. physik. Chem.*, **168A**, 147 (1934).

(20) Mead, Hughes and Hartley, *J. Chem. Soc.*, 1207 (1933).

(21) Remy, *Trans. Faraday Soc.*, **23**. 382 (1926).

subtracting the appropriate slope ($S^*_A$) from each calculated sum.

**The Absolute Partial Molal Entropy of Hydrogen Ion.**—Both the bromide data and the hydroxide data shown in Table VI may be used independently to calculate a value for the absolute entropy of the corresponding anion. The $\Delta S_R$ value of −2.2 e. u. of the electrode reaction, $^1/_2\text{Hg} + \text{OH}^- = {^1/_2}\text{HgO} + {^1/_2}\ \text{H}_2\text{O} + \text{e}^-$, is obtained from Table VI, and combined with established entropy values.[22] Neglecting the insignificant contribution of the electron, a value of 10.1 e. u. results from this calculation for 0.01 *m* hydroxide ion, or 0.9 e. u. for the hypothetical 1 *m* solution. Latimer's relative entropy value of −2.5 e. u. for hydroxide ion[22] differs from the absolute by 3.4 e. u.; thus establishing a value of −3.4 e. u. as the absolute entropy of hydrogen ion.

A similar calculation for the bromide series based upon −15.55 e. u. for the electrode reaction, and upon 21.8 e. u. for the hypothetical 1 *m* bromide ion, results in a comparable value of −2.1 e. u. for the partial molal entropy of hydrogen ion. This value must be regarded as more reliable than the value calculated from the hydroxide series. It will be noted from Fig. 4 that the extrapolation of the hydroxide data is much more sensitive to slight differences in transference numbers than the extrapolation of the nearly horizontal line of the bromide series, a fact demonstrated by one of the present authors[23] who applied approximations based upon the Gorin equation[24] to obtain from the hydroxide data a comparable value of −2.6 ± 0.8 e. u. for the entropy of hydrogen ion. Another of the present authors[25] obtained from the bromide data presented above an independent comparable value of −2.5 ± 0.4 e. u. for the entropy of hydrogen ion. Although this value was obtained by an independent extrapolation by a different method, it indicates that the final value of −2.1 ± 0.4 e. u. for the partial molal entropy of hydrogen ion is entirely reasonable. This value of −2.1 e. u. compares favorably with the value of −1.5 e. u. suggested by Latimer, Pitzer and Slansky,[26] for the absolute partial molal entropy of hydrogen ion, and may be used, together with the entropies of transfer from the bromide series given in Table VI, in subsequent papers for reducing thermocell data.

## Discussion

Table VI summarizes the results of considerable experimental work in terms of the Eastman thermocell equation. It is possible to read from this table the entropy of transfer of natural ion pairs within the limits of error of extrapolation without making use of the non-thermodynamic assumption required to state values for individual ions. For example, −10.15 + 0.52, or −9.63 e. u. is the entropy of transfer of lithium ion plus bromide ion in 0.01 *m* solutions, −5.52 would be read off for sodium bromide, −4.68 for potassium bromide. This property of Table VI follows from equation (2) which in turn is simply a statement of Eastman's original equation.

The validity of the Eastman equation is taken for granted in choosing the above method of tabulating results because the Eastman equations have not been seriously questioned since 1930 when Wagner[27] summarized a revision of his previous work[28] by the flat statement that his equation was in agreement with that of Eastman. Later workers[4] have accepted the Eastman thermocell equation, and recently Tyrrell and Hollis[29] have stated that their calculation of thermal diffusion potential by rate process theory is not in conflict with the thermodynamic treatment of Eastman and Wagner. However, Tyrrell and Hollis calculate a value of +3.6 e. u. for the entropy of transfer of bromide ion and do not predict high negative values for the entropy of transfer of any ion. One of Eastman's former students[30] has carried on the theoretical investigation by taking into account the irreversible entropy terms in a new derivation which leads to the original Eastman equation.

Only when values for the entropies of transfer of the individual ions are required, does a non-thermodynamic assumption become important. Thus the arguments given above in support of the selection of zero as a first approximation for the value of entropies of transfer of large tetraalkylammonium ions enter into the final conclusions and lead to the discovery of large negative entropies of transfer for the smaller cations. These negative values were not predicted by Eastman at the time he published his early speculations,[5] but they are not in conflict with modern thought. Frank and Evans[31] have shown that non-electrolytes and some ions dissolved in water produce an association of water molecules referred to as "icebergs," while most dissolved ions have the reverse effect of further breaking down normal water structure. Since heat of transfer is defined as heat adsorbed by a region from whence a mole of solute is diffusing, it follows that removal of non-electrolytes would cause the "icebergs" to melt and absorb heat (positive sign), while the opposite sign would be assigned to the heat or entropy of transfer of ions. The large tetraalkylammonium ions and some negative ions are known to fall in an intermediate classification, thereby accounting for values near zero. Hydrogen ion and hydroxide ion probably exert an entirely different influence.

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(22) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

(23) Morse, Thesis, University of California, 1940.

(24) Gorin, *J. Chem. Phys.*, **7**, 405 (1939).

(25) Preston, Thesis, University of California, 1941.

(26) Latimer, Pitzer and Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

(27) Wagner, *Ann. Physik*, **6**, 370 (1930).

(28) Wagner, *ibid.*, **3**, 629 (1929).

(29) Tyrrell and Hollis, *Trans. Faraday Soc.*, **45**, 411 (1949).

(30) Tuck, Thesis, University of California, 1948; *J. Chem. Phys.*, in press (1950).

(31) Frank and Evans, *J. Chem. Phys.*, **13**, 507 (1945).

## Summary

The usefulness and validity of the Eastman thermocell equation are demonstrated by calculations based upon thermocell e. m. f. measurements and conductance measurements which are reported for the first time. Entropies of transfer for $Li^+$, $Na^+$, $K^+$, $NH_4^+$, $Br^-$, $OH^-$ and a series of the first five symmetrical tetraalkylammonium ions are presented. The absolute partial molal entropy of hydrogen ion is calculated from the data and given as $-2.1 \pm 0.4$ e. u., based upon the absolute partial molal entropy of $Br^-$ determined by the Eastman equation with the assumption of zero entropy of transfer for large tetraalkylammonium ions. The tabulated ionic entropies of transfer are shown to be valid on a relative basis regardless of this assumption.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

# A Study of the Diffusion of Potassium Chloride in Water at 25° with the Gouy Interference Method

BY LOUIS J. GOSTING[1]

**Introduction.**—The object of this research was the determination, with the aid of the Gouy interference method, of the diffusion coefficients of potassium chloride for comparison with the results of Harned and Nuttall who used a conductance method. With the diffusion cells now available this optical procedure cannot be used with sufficiently dilute solutions to obtain a direct comparison with the Onsager–Fuoss theory. Fortunately, however, Harned and Nuttall have extended their initial measurements at low concentrations,[2] which are in excellent agreement with the theory, up to 0.5 $N$,[3] thereby making possible a direct comparison of the two experimental procedures. In this manner it is hoped to establish the validity of a precise optical procedure that, in contrast with the conductance method, is also applicable to the study of the diffusion of proteins and related substances.

In addition to the comparison with the conductometric results the measurements have been extended to concentrated solutions and the wave-length term in the theory of the Gouy method confirmed experimentally. Some improvements in experimental procedure are also reported.

**Experimental.**—The apparatus used in the present research is a modification of the electrophoresis equipment developed in this laboratory[4] in which the optical "lever arm," $b$, is 191.043 cm. The modifications are based on the experience gained in the construction of the diffusion equipment at the University of Wisconsin[5,6] and are as follows:

(1) In order to avoid excessive heating of the illuminated slit in the object plane of the schlieren lens and the resulting vertical movement of this slit as its ambient temperature rises during an experiment the H4 mercury vapor lamp was mounted separately and the arc focussed on the slit with the aid of a pair of condensing lenses of 40 mm. diameter and 85 mm. focal length. Heating of the slit was further reduced and possible distortion of the Gouy fringes from imperfections in the Wratten 77A filter was avoided by placing this filter between the condensing lens and the slit.

(2) As in the earlier work[6] a Tiselius cell, with the height of the top section increased to extend out of the thermostat liquid, was used as the diffusion cell, the technique of Kahn and Polson[7] being employed to sharpen the boundary after its displacement to the center of the channel. The support for this cell was provided with a masking arrangement that will be described below in connection with the photographic procedure. It was suspended in the water-bath with the aid of a steel frame bolted directly to the concrete block supporting this bath. Moreover, the optical bench was anchored to this block so that the position of the diffusion cell was fixed with respect to the other elements of the optical system.

(3) In order to minimize the movement of one optical element with respect to another the vertical steel plates carrying, respectively, the schlieren lens and bath window, the second thermostat window assembly, and the plate holder were braced with angle iron to the optical bench.

(4) The schlieren camera described in a previous communication[4] was replaced by the plate holder shown in perspective in Fig. 1. In this figure the hinged back, B, of the plate holder, P, is swung open and the dark slide, S, partially removed in order to show the gate, G, in the fixed plate, A, through which light reaches the emulsion. As is indicated at C the upper edge of A is bevelled and the plate P provided with a matching bevel so that gravity insures light-tight contact between the two plates as P is moved to each of the eight positions at which photographs can be made on a 6 × 9 cm. plate without overlapping of the images. Although not shown in the figure the rectangular box, E, that carries the plate A is carried, in turn, by a vertical plate from the optical bench. A flap shutter in this box is operated by the knob, K, while that, D, with the removable stop-pin, F, connects with a shaft in the box to which are attached, at 90° intervals, four masking vanes. Any one of these vanes may thus be swung into place in front of the gate G in bracketing, as will now be described, the diffusion channel fringes with those from a reference opening.

**Photographic Procedure.**—For the computation of the diffusion coefficient, $D$, by the Gouy procedure the number, $j_m$, of fringes in the pattern must be known in addition to the movement of these fringes as the boundary spreads. If $a$ is the dimension of the diffusion channel parallel to the optic axis and $\Delta n$ the difference of refractive index between solution and solvent, $j_m = a\Delta n/\lambda$, where $\lambda$ is the wave length of the light. In general $j_m$ is a compound number and a count of the fringes in the Gouy pattern gives only the integral part, $I$. If $D$ is to be obtained from patterns having as few as fifty fringes and is to be

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[1] National Research Council Fellow in Chemistry.

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

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

[4] Longsworth, *Ind. Eng. Chem., Anal. Ed.*, **18**, 219 (1946).

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

[6] Gosting and Morris, THIS JOURNAL, **71**, 1998 (1949).

[7] Kahn and Polson, *J. Phys. and Colloid Chem.*, **51**, 816 (1947).