The Determination of the Transference Numbers of Potassium Iodide from the Electromotive Force of Iodide-Iodine Gravity Cells

By S. W. Grinnell[1] and F. O. Koenig

Let a cell consisting of two chemically identical electrodes in contact with a uniform solution be brought into a gravitational field, understood in the general sense which includes inertial fields. Let the electrodes be relatively thin and so arranged that the gravitational potential may be taken as constant throughout each electrode. Such a cell almost instantaneously acquires an e. m. f. which is proportional to the difference of gravitational potential between the electrodes, and then constitutes what we shall refer to as a "gravity cell."

Gravity cells have been investigated experimentally and theoretically by Des Coudres[2,3,4] and by Tolman.[5] A partial summary of the experimental work of these authors has recently been given by MacInnes.[6] A systematic treatment of the thermodynamic theory of gravity cells and related systems has been published by us.[7]

Des Coudres in his experiments used both centrifugal fields[2] and the earth's field,[4] obtaining more accurate results with the latter. His experiments with the earth's field were of two types: in *type 1*, the cell consisted of a straight glass tube about 90 cm. long with the electrodes near the ends, and the effect observed was the change in e. m. f. produced by rotating the cell about a horizontal axis from one of its vertical positions to the other; this effect is evidently twice the e. m. f. of the gravity cell corresponding to either vertical position; in *type 2*, the cell consisted of two glass electrode vessels connected by a rubber tube 400 cm. long, and the effect observed was the change in e. m. f. produced by interchanging the levels of the two electrodes when one was initially about 370 cm. higher than the other; this effect is likewise twice the e. m. f. of the gravity cell corre-

sponding to the difference in level in question. It is important to note that any residual e. m. f. due to departure of the two electrodes from identity, provided it remains constant during the course of a measurement, automatically cancels out in both types of experiment. Des Coudres thus found the e. m. f.'s of gravity cells in the earth's field to be of the order of a few microvolts per meter.

Des Coudres furthermore derived approximate formulas[2,4] showing that the e. m. f. of a gravity cell is a function of the transference numbers of the components of the cell solution. Applying these formulas to his experimental results in the earth's field, he was able to calculate transference numbers which for most of the electrolytes investigated by him agree with transference numbers obtained by other methods to within 6% (exceptions: cadmium chloride and cadmium iodide). This result constitutes the first demonstration of the correctness of the formulas but can hardly be regarded as establishing Des Coudres' methods as useful, by modern standards, for the determination of transference numbers.

Tolman's experiments[5] were carried out entirely with a powerful centrifuge and with electrodes of a single type, namely, Pt, 1.0 molal I⁻ + 0.01 molal I_2. The iodides used were those of potassium, sodium, lithium and hydrogen. The maximum difference of gravitational potential produced in Tolman's apparatus was equal to that of about 1160 meters in the earth's field and was thus about 150 times as great as the maximum difference (2 × 370 cm.) employed by Des Coudres in the earth's field; the e. m. f.'s observed by Tolman were accordingly of the order of several millivolts. In the case of potassium iodide, the transference number calculated by Tolman from his measured values of e. m. f. agrees with the best modern values to well within 1% (see Table II), and for the other iodides the agreement, although not so good as this, is better than that obtained by Des Coudres. Tolman's result with potassium iodide indicates that the gravity cell in the centrifugal field constitutes a method for the determination of transference number which might be useful at least in certain cases.

(1) Taken from the thesis submitted by S. W. Grinnell in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Stanford University, 1938.

(2) T. Des Coudres, *Ann. Phys.*, **49**, 284 (1893).

(3) T. Des Coudres, *ibid.*, **55**, 213 (1895).

(4) T. Des Coudres, *ibid.*, **57**, 232 (1896).

(5) R. C. Tolman, *Proc. Am. Acad.*, **46**, 109 (1910); This Journal, **33**, 121 (1911).

(6) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, pp. 174–180.

(7) F. O. Koenig and S. W. Grinnell, *J. Phys. Chem.*, **44**, 463 (1940).

In the present paper we report experiments with the earth's field which are at least as accurate as those of Tolman with the centrifugal field. Our method is that described above as "type 1" of Des Coudres. Our electrode was the same as that with which Tolman obtained his best result, namely Pt, KI (excess) + I_2. In addition to the remarkable reproducibility and constancy of this electrode, the chief factors contributing to the increase in accuracy over that obtained by Des Coudres were better temperature control and more precise measurement of the extremely small e. m. f.'s.

For the gravity cell here studied the formula relating transference number and e. m. f. is

$$t_+ = \frac{\dfrac{FE^{\alpha\alpha'}}{\varphi^{\alpha'} - \varphi^{\alpha}} + \dfrac{1}{2}(M_{I_2} - \rho V_{I_2})}{M_{KI} - \rho V_{KI}} \qquad (1)$$

Here $E^{\alpha\alpha'}$ denotes the e. m. f. of either of the electrodes, α, with respect to the other, α' (so that $E^{\alpha\alpha'} > 0$ if α is the positive pole and $E^{\alpha\alpha'} < 0$ if α is the negative pole), φ^{α} and $\varphi^{\alpha'}$ denote the gravitational potentials at α and α', respectively, M_{I_2} and M_{KI} the molal weights of iodine and potassium iodide, V_{I_2} and V_{KI} the partial molal volumes of iodine and potassium iodide in the cell solution, ρ the density of the cell solution and t_+ the transference number of K^+ in the cell solution. This formula, which is of the general type first obtained by Des Coudres,[4] and was first derived by Tolman,[5] is not theoretically exact, but a good approximation resulting from neglect of (1) the variation of the transference numbers and of the partial molal volumes corresponding to the variation of pressure throughout the gravity cell, (2) the transference of iodine (and/or I_3^-) in comparison with that of I^-. Theoretically exact formulas from which eq. (1) is derivable are given in the paper[7] already mentioned.

Experimental Method

Temperature Control.—During measurement the cells were kept immersed in a water thermostat 80 cm. long, 40 cm. wide, 70 cm. deep. The water thermostat was kept covered and was surrounded by a well-stirred air thermostat. Measurements with a 25-junction thermocouple showed that the maximum difference of temperature between any two points of the water-bath did not exceed 0.0001° when the stirrer of the water-bath was operating at 200 r. p. m. It was found that more rapid stirring tended to make the temperature less uniform owing no doubt to local heating by friction of the moving water.

Mounting of the Cells.—The cells were mounted in the water thermostat on a horizontal shaft which was con-

nected by gearing to a crank on the outside of the air thermostat. By turning the crank the cell could be rotated through all angles of elevation. The positions of the crank corresponding to the two vertical positions of the cells were accurately marked.

Construction of the Cells.—Figure 1 shows the main features of the cells. The over-all length was about 58 cm., the distance between the platinum disk electrodes about 46 cm., the diameter 3 cm. The glass was Pyrex and the leads through the cell wall were tungsten. The tungsten was spot-welded on the outside to nickel leads and on the inside to sturdy platinum wires which in turn were welded to the platinum disks. The tungsten–platinum weld was covered with glass so that only platinum was exposed to the cell solutions. The nickel leads were soldered to leads of flexible stranded copper wire, rubber-insulated, which extended out of the water thermostat into the air thermostat and there were connected without solder to the annealed solid copper wire leads of the potentiometer circuit. That part of the leads which was under water was protected, as shown in Fig. 1, by gum rubber pressure tubing attached to the glass tubes at the ends of the cell. The two side arms were used in filling the cell as described below.
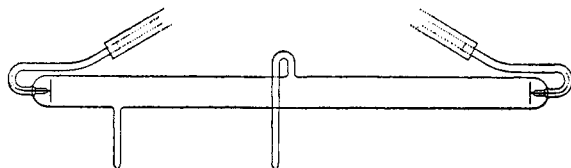

Fig. 1.—The cell.

Preparation of the Cell Solution and Filling of the Cells. —The cell solutions were prepared from conductivity water, c. p. potassium iodide, and iodine twice resublimed from potassium iodide. In filling the cell, oxygen was excluded by use of an all-Pyrex apparatus to which the two side arms of the cell were temporarily sealed. In a flask attached to this apparatus the cell solution was boiled for thirty minutes while there was bubbled through it a stream of tank nitrogen purified by passage through alkaline pyrogallol and hot copper gauze; the large excess of potassium iodide in the cell solution prevented appreciable loss of iodine in this process. At the same time oxygen was similarly removed from a portion of conductivity water in another flask likewise attached to the apparatus. The cell was thoroughly swept out with nitrogen and, after the solution in the flask had cooled, some of it was forced through the bent side arm (Fig. 1) into the cell by nitrogen pressure, the nitrogen in the cell escaping through the straight side arm. When the cell was thus almost filled, the stream of solution through the bent side arm was replaced by a stream of conductivity water in order to rinse this side arm preparatory to sealing it off. Then the conductivity water in the bent side arm was displaced by nitrogen and both side arms were sealed off. After shaking the cell to ensure perfect mixing, the bubble of nitrogen in the cell was maneuvered into the end of the bent side arm where it remained during the e. m. f. measurements. After completion of the e. m. f. measurements the composition and density of the cell solution were determined by chemical analysis and pycnometer, respectively.
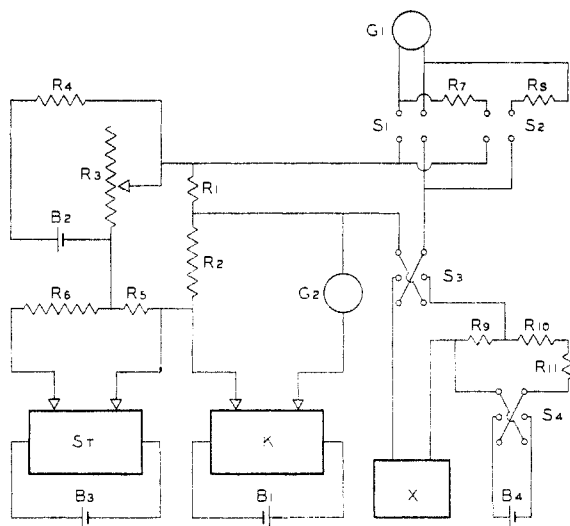
Fig. 2.—The potentiometer.

Potentiometer Circuit.—It has been pointed out by Brooks and Spinks[8] and by Teele and Schumann[9] that for the measurement of minute e. m. f.'s a potentiometer in which the balancing e. m. f. is produced by a variable current through a constant resistance is preferable to the more usual type in which a resistance carrying a constant current is variably tapped. Figure 2 shows the variable current potentiometer used in the present investigation. The rectangle X is the source of the e. m. f. to be measured. G_1, the null instrument, is an extremely sensitive moving magnet galvanometer of the Paschen type made by the Cambridge Instrument Co. R_1 and R_2 are Leeds and Northrup standard manganin resistances of 1 ohm and 1000 ohms, respectively, certified by the Bureau of Standards to be correct within 0.01%; R_1 and R_2 both carry the same variable current and the resulting e. m. f. across R_1 serves as the balancing e. m. f. K is a Leeds and Northrup Type K potentiometer which is operated by the storage battery, B_1, and which, in conjunction with the Leeds and Northrup Type HS galvanometer, G_2, serves to measure the e. m. f. across R_2; the reading of K divided by 1000 then gives the value of the balancing e. m. f. across R_1 exactly at any temperature. The coarse regulation of the variable current through R_1 and R_2 is accomplished by R_3, which is a Leeds and Northrup 3-dial resistance box of 999 ohms, in steps of 1 ohm, and is in series with the fixed manganin resistance R_4 of 300 ohms and the 2-volt storage battery, B_2. The fine regulation of the variable current is accomplished by the Leeds and Northrup Student Type potentiometer, St, in conjunction with the 2-volt storage battery, B_3, and the fixed manganin resistances R_5 and R_6 of 5 ohms and 2000 ohms, respectively. S_1, the master switch to the galvanometer G_1, is a double pole single throw knife switch with copper blades 6 inches long and a handle which is well insulated from the blades and covered with tin foil to prevent electrostatic effects. S_2 is a double-pole single-throw knife switch with 2-inch copper blades, and R_7, R_8 are protective resistances of

(8) H. B. Brooks and A. W. Spinks, *Nat. Bur. Stand. J. Res.*, **9**, 781 (1932).

(9) R. P. Teele and S. Schumann, *ibid.*, **22**, 431 (1939).

15,000 ohms each. The switches connecting G_2 to K are not shown in the figure since they are contained within the Type K instrument. S_3 is a double-pole double-throw reversing switch with 2-inch copper blades, used to take care of the change of polarity occurring with each inversion of the cell under measurement. R_9, R_{10}, R_{11} are resistances which in conjunction with the 2-volt storage battery, B_4, and the double-pole double-throw copper reversing switch, S_4, serve in the manner described below to measure the parasitic e. m. f. in the potentiometer circuit; R_9 is a 0.1 ohm resistance made of annealed copper wire; R_{10}, R_{11} are manganin resistances of 20,000 ohms each; and the value of the ratio R_9/R_{10} is known to 0.1% from separate measurements.

Range and Sensitivity of the Potentiometer.—The total range of the balancing e. m. f. across R_1 is about 1540 microvolts. Since the Type K potentiometer has two alternative ranges, from 0–1600 millivolts on a scale readable to 0.01 millivolt, and from 0–160 millivolts on a scale readable to 0.001 millivolt, the balancing e. m. f. can be read either (1) over the entire range from 0–1540 microvolts, to 0.01 microvolt, or (2) over the range from 0–160 microvolts, to 0.001 microvolt. The Paschen galvanometer, G_1, was adjusted to have a current sensitivity of 5×10^{-11} amp. per mm. at 1 meter, with an internal resistance of 190 ohms. Taking the smallest deflection of the light spot detectable with certainty by direct observation without photoelectric amplification to be 0.2 mm., the smallest deviations from potentiometric balance detectable by our apparatus are calculated to be as follows: for a cell resistance of

100 ohms:	0.003 microvolt
1,000 ohms:	0.01 microvolt
10,000 ohms:	0.1 microvolt
100,000 ohms:	1.0 microvolt

etc. This estimate of sensitivity is substantiated by the data reported below: the cells investigated had resistances of several hundred ohms and their e. m. f.'s. are seen to have been measurable to a few thousandths of a microvolt.

Parasitic E. m. f.—The following precautions are taken to reduce parasitic e. m. f. R_1 and R_2 are kept packed in wool inside a large Dewar vessel. R_9, R_{10} and R_{11} are kept in the air thermostat and therefore at a constant temperature very nearly equal to that of X, which is in the water thermostat. The contacts of the switches S_1, S_2, S_3, S_4 are kept well cleaned and covered with vaseline. The circuit between X and G_1 is made as symmetrical as possible. All the wiring is of annealed copper wire (no. 16) and bends are avoided as much as possible, especially near the points of entry into the air thermostat. All connections outside the water thermostat are made without solder by lapping the well cleaned parts together with fine copper wire. The parasitic e. m. f. remaining in the potentiometer circuit is measured as follows: X is disconnected from the potentiometer and the potentiometer leads are joined in the air thermostat. S_3 is closed in either direction, and then S_4 is closed in that direction which makes the polarity of the e. m. f. across R_9 such that this e. m. f. can be balanced by that across R_1; then the *apparent* value of the e. m. f. across R_9 (which is of the order of 5 microvolts) is measured. Immediately afterward the e. m. f. across R_{10} (which is of the order of 1 volt) is

measured directly by means of K and G_2 (the leads connecting R_{10} to K are omitted from Fig. 2 for simplicity). From the e. m. f. across R_{10} and the known value of the ratio R_9/R_{10}, the *true* value of the e. m. f. across R_9 is calculated, and this subtracted from the *apparent* value give the parasitic e. m. f. Then S_3 and S_4 are both reversed and the parasitic e. m. f. again determined in the same way. The values of the parasitic e. m. f. corresponding to the two positions of S_3 will be referred to as Δ_1 and Δ_2, respectively. Δ_1 and Δ_2 never differed from each other by more than 0.02 microvolt and their sum never exceeded 0.05 microvolt. Δ_1 and Δ_2 were furthermore found usually to remain constant over one or two hours.

Procedure in Measuring E. m. f.—It was found that in spite of the care taken to exclude oxygen, the e. m. f. of a cell in one of its vertical positions was not constant but always showed a slight change with time. In the cells here studied this change did not exceed 0.004 microvolt per minute. In order to keep error from this source as small as possible, the following procedure for obtaining the e. m. f. of the gravity cell was adopted: the cell was brought into one of its vertical positions, called "position 1," and the e. m. f. read as quickly as possible; then immediately it was inverted into its other vertical position, called "position 2," and the e. m. f. read as quickly as possible; then immediately it was inverted into position 1 and the e. m. f. read as quickly as possible, and so forth. The time required to set and read the potentiometer after attainment of a given vertical position was regularly about forty-five seconds, and the time between consecutive inversions about sixty seconds. The upper electrode was always the positive pole and the change in polarity on inversion was taken care of by means of S_3 in Fig. 2. The sum of a pair of consecutive e. m. f. readings is therefore equal to $2E^{\alpha\alpha'} + \Delta_1 + \Delta_2$ where $E^{\alpha\alpha'}$ is the e. m. f. of the gravity cell corresponding to either vertical position, α being the upper and α' the lower electrode, and Δ_1 and Δ_2 are the parasitic e. m. f.'s as explained above. Δ_1 and Δ_2 were measured at the beginning and the end of each series of measurements and were always found to have remained constant during the series. For example: in one series of eighteen inversions the mean value of $2E^{\alpha\alpha'} + \Delta_1 + \Delta_2$ was found to be 3.600 $\pm$ 0.003 microvolts with a maximum deviation of 0.006 microvolt; in this series $\Delta_1 + \Delta_2$ was found to be 0.0048 microvolt; hence $E^{\alpha\alpha'} = 3.552$ $\pm$ 0.003 microvolts.

Experimental Data and Calculation of Results

Data were obtained on two cells hereafter referred to as cells I and II, respectively. The composition of the cell solutions was

Cell I: 0.975 molal KI + 0.00531 molal I_2
Cell II: 0.712 molal KI + 0.00385 molal I_2

The results of all the e. m. f. measurements are summarized in Table I.

For purposes of comparison the data on each cell separately are reduced to microvolts per meter at 20° as follows. By comparing the values of $2E^{\alpha\alpha'}$ in Table II at the two lower temperatures

TABLE I
SUMMARY OF E. M. F. DATA

Cell	Temp., °C.	No. of inversions	$2E^{\alpha\alpha'}$, microvolts
I	19.20	18	3.552 $\pm$ 0.003
I	21.30	12	3.543 $\pm$ 0.009
I	29.28	14	3.523 $\pm$ 0.006
I	29.40	5	3.525 $\pm$ 0.006
II	19.20	19	3.569 $\pm$ 0.006
II	21.30	12	3.567 $\pm$ 0.005
II	29.28	10	3.527 $\pm$ 0.007
II	29.40	10	3.537 $\pm$ 0.004

with those at the two higher temperatures, the temperature coefficients, $2\partial E^{\alpha\alpha'}/\partial T$, are found to be, in microvolts per degree

Cell I	Cell II
-0.0029	-0.0042
$-.0026$	$-.0031$
$-.0025$	$-.0050$
$-.0022$	$-.0037$
Mean $-.0026$	$-.0040$

Although the disparity between these mean values of the temperature coefficients indicates a relatively large error, these values may be used safely for interpolation among the data from which they have been calculated; in this way one obtains from the four values on each cell in Table II the following values for $2E^{\alpha\alpha'}$ at 20°, in microvolts

Cell I	Cell II
3.550	3.566
3.546	3.572
3.547	3.564
3.549	3.575
Mean 3.548	3.569

The distance between the electrodes is 46.40 cm. for cell I and 46.60 cm. for cell II; hence one finds cell I, 3.823 microvolts per meter at 20°; cell II, 3.829. Values of t_+ at 20° are now readily calculated by substituting into equation (1) these e. m. f.'s per meter at 20° together with the accepted values of F, M_{KI}, M_{I_2} and the following data

$$\varphi^{\alpha'} - \varphi^{\alpha} = -97998 \text{ erg} \times g.^{-1}$$

$$\rho = \begin{cases} 1.1105 \text{ g.} \times \text{cm.}^{-3} \text{ in cell I} \\ 1.0814 \text{ g.} \times \text{cm.}^{-3} \text{ in cell II} \end{cases}$$

$$V_{KI} = \begin{cases} 47.08 \text{ cm.}^3 \times \text{mole}^{-1} \text{ in cell I} \\ 46.68 \text{ cm.}^3 \times \text{mole}^{-1} \text{ in cell II} \end{cases}$$

$$V_{I_2} = 60.30 \text{ cm.}^3 \times \text{mole}^{-1} \text{ in both cells}$$

The value of $\varphi^{\alpha'} - \varphi^{\alpha}$ of course follows from the local value of g, namely, 979.98 dyne $\times$ $g.^{-1}$. The values of ρ were found by pycnometric measurement at 20.00°. The values of V_{KI} were obtained, on the assumption that the effect of the small concentration of iodine (and/or I_3^-) on V_{KI}

KI concn.	Concentration of I_2	Temp., °C.	t_+	Method and author
0.975 m	0.00531 m	20	0.4900	Present investigation
0.712 m	0.00385 m	20	.4893	Present investigation
1.00 m	0.01 m	20	.486	Centrifugal field, Tolman[5]
0.500 m	0	25	.4878	Concentration cells, Gelbach[10]
0.01 N	0	25	.4884	Moving boundary, Longsworth[11]
0.02 N	0	25	.4883	Moving boundary, Longsworth[11]
0.05 N	0	25	.4882	Moving boundary, Longsworth[11]
0.1 N	0	25	.4883	Moving boundary, Longsworth[11]
0.2 N	0	25	.4887	Moving boundary, Longsworth[11]

is negligible, from a graph of V_{KI} in solutions of pure potassium iodide against the square root of the molality; this graph in turn was plotted from values calculated by us, using the Lewis and Randall method of intercepts, from the density of potassium iodide solutions at 20° given in the "International Critical Tables"; the values of V_{KI} are probably correct to within 0.1 cm.³ × mole⁻¹. The value of V_{I_2} is that determined by Tolman[5] for iodine in small concentration in the presence of a large excess of iodide, at 20°, and is also probably correct to within 0.1 cm.³ × mole⁻¹. The result of the calculation is cell I, $t_+ = 0.4900$; cell II, $t_+ = 0.4893$. In Table II these values are compared with values obtained by other methods.

The most accurate of these determinations are those of Longsworth; they are here cited *in extenso* because they show that at a concentration of 0.2 normal, where they break off, t_+ is slowly

(10) R. W. Gelbach, THIS JOURNAL, **55**, 4858 (1933).
(11) L. G. Longsworth, *ibid.*, **57**, 1185 (1935).

increasing with increasing concentration; this tends to diminish the gap between our results and those obtained by other methods. In any case the difference between the present results and the best modern ones would seem not to exceed 0.5%. The conclusion seems justified that the method here described might be useful for the determination of transference numbers in certain cases.

Summary

Precise measurements are described of the e. m. f. of gravity cells using the earth's field, with the electrode Pt, KI (excess) + I_2. The transference numbers of K^+ calculated from the measured values of the e. m. f. agree with the best modern values to within 0.5%. The potentiometer used in the measurement is described in detail; it has a range of 1540 microvolts in steps of 0.01 microvolt or of 160 microvolts in steps of 0.001 microvolt.

Copper(II) and Nickel(II) Complex Ions of Diethylenetriamine

BY HELMUT M. HAENDLER

In a recent publication, Vosburgh and Cooper[1] have extended the method of continuous variations originated by Job[2] to include reactions in which more than one complex ion is formed from a pair of components. Measurement of absorption at pre-selected wave lengths offers means of identifying the ions present, when both components are in solutions of equimolecular concentration.

Preliminary work on the preparation of metal complexes of diethylenetriamine, $H_2N(CH_2)_2NH$-

(1) Vosburgh and Cooper, THIS JOURNAL, **63**, 437 (1941).
(2) Job, *Ann. chim.*, [10] **9**, 113 (1928).

$(CH_2)_2NH_2$, (abbreviated dn) suggested the advisability of determining the probable composition of the ions formed in water solution by this amine and various metal ions. It was found that copper(II) and nickel(II) were the most satisfactory; other ions generally were precipitated as hydroxide.

Determination of composition was made exactly as described by Vosburgh and Cooper.[1] Maxima of curves obtained by plotting the amount of diethylenetriamine solution (x) against the difference (Y) between observed extinction and that calculated for no reaction give directly the com-