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THE NORMAL POTENTIAL OF THE IODINE–IODIDE ELECTRODE

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Historical Introduction

There is considerable confusion in the literature because of different definitions of the normal potential of the iodine–iodide electrode by various authors. In the following discussion we shall use the term normal potential of the iodine–iodide electrode to mean the potential of the cell Pt, I_2 (solid), I^- (activity = 1.0); 1.0 N KCl, HgCl, Hg containing a platinum electrode immersed in a solution which is in equilibrium with solid iodine and which has the iodide ion present at such a concentration that its activity is unity, measured against a normal (1 mole of KCl per liter) calomel electrode, and with corrections applied for liquid junction potentials. In accordance with the usual convention a positive sign of the potential would mean that the mercury is the positive pole of the cell and the platinum the negative pole. As a matter of fact, in this case the platinum is positive and the mercury negative, which is indicated by using a negative sign.

The other definition used by some authors postulates instead of solid iodine a solution in which the activity or concentration of the dissolved free iodine is unity. The concentration of free iodine (I_2) in water saturated with iodine at 25° is 0.00132.[1] Since this solution is dilute and free from ions the activity of iodine may be taken as equal to its concentration, 0.00132, and this figure may be used for any aqueous solution saturated with iodine. Therefore the difference between these two definitions at 25° is $(RT/2F)$ ln 1.0/0.00132 = 0.0851 volt.

At 0° the activity[2] is 0.000635 and therefore the difference between the two definitions is $(RT/2F)$ ln 1.0/0.000635 = 0.0866 volt. These corrections will be applied if necessary in the following discussion to make the results of the various authors comparable. In case the other authors referred to have omitted liquid junction corrections or defined the normal calomel electrode differently, no correction will be applied for this variation from the definition given above.

The work of Crotogino[3] and of Sammet[4] is similar in technique and the

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[1] W. C. Bray, THIS JOURNAL, **32**, 932 (1910); W. C. Bray and E. L. Connolly, *ibid.*, **33**, 1485 (1911).

[2] Grinnell Jones and B. B. Kaplan, *ibid.*, **50**, 1845 (1928).

[3] F. W. Küster and F. Crotogino, *Z. anorg. Chem.*, **23**, 87 (1900); F. Crotogino, *ibid.*, **24**, 247 (1900).

[4] V. Sammet, *Z. physik. Chem.*, **53**, 674 (1905).

results agree within one millivolt. They measured the potential of a platinum electrode immersed in solutions of potassium iodide varying from about 0.001 *N* to 1.0 *N* saturated with solid iodine against a calomel electrode. Crotogino did not attempt to compute a normal potential from his data. Sammet computes the normal potential on the assumption that exactly one-half of the iodide is converted into tri-iodide and that the concentration can be computed from the conductivity and applies no liquid junction corrections. It is now known that both of these assumptions are only approximately true. These results show an apparent shift in the normal potential with dilution from −0.256 volt in the more concentrated solutions to −0.278 in 0.001 *N* KI. He regards the value obtained with the more concentrated solutions as the more reliable, which would not be the modern interpretation.

Maitland[5] was the first to use solutions of potassium iodide containing less iodine than is required to saturate the solutions (about $^1/_3$ to $^1/_{30}$ saturated). The amount of free iodine was determined by distribution experiments using carbon tetrachloride. The concentration of the potassium iodide varied from 1.0 *N* to 0.1 *N*. The degree of ionization assumed was based on conductivity data. No liquid junction correction was applied. The results show a distinct systematic variation with the degree of saturation of iodine and with the concentration of the potassium iodide but Maitland averages all of the results, obtaining −0.2569 in good agreement with Sammet's result derived from 1.0 *N* KI saturated with iodine. Unfortunately Maitland's measurements did not extend below 0.1 *N*. All the earlier workers either made no measurements below 0.1 *N* or rejected their measurements in dilute solutions as unreliable.

Jones and Schumb[6] made measurements with saturated iodine electrodes with 0.1 *N*, 0.05 *N* and 0.02 *N* KI, interpreted by the use of data by Bray and MacKay[7] on the tri-iodide formation, obtaining −0.2558, −0.2558 and −0.2549 at these concentrations. They were the first to apply the liquid junction correction. All investigators agree that the more dilute the KI solution the greater is the difficulty in obtaining definite and reproducible experimental results; but the theoretical interpretation of the data on dilute solutions is more reliable. Jones and Schumb also made measurements at 0° which when recomputed with the definition given above give −0.2536, −0.2534 and −0.2528 with 0.1 *N*, 0.05 *N* and 0.02 *N* KI, respectively. The systematic variation of the results with concentration made it desirable to extend the measurements to still greater dilution but Jones and Schumb were unable to obtain definite results with 0.01 *N*

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[5] W. Maitland, *Z. Elektrochem.*, **12**, 263 (1906).

[6] Grinnell Jones and W. C. Schumb, *Proc. Am. Acad.*, **56**, 226 (1921).

[7] Bray and MacKay, THIS JOURNAL, **32**, 914 (1910); Grinnell Jones and M. L. Hartmann, *ibid.*, **37**, 241 (1915).

solution and therefore the results were averaged, giving −0.2555 at 25° and −0.2533 at 0°.

The measurements of Maitland have been recomputed by Lewis and Randall,[8] who were the first to reject the calculation of the concentration of the ions from the conductivity and substitute instead the activity of the iodide ion as determined from thermodynamic considerations. They also use a new conventional definition of the normal calomel electrode as the potential measured against 0.1 *N* KCl, 1 *N* KCl, HgCl, Hg, with no correction applied for the liquid junction potential between 0.1 *N* KCl and 1 *N* KCl. The usual formulas for the computation of liquid junction potentials give 0.0004 volt for this potential, the dilute solution being negative. Therefore to make this result comparable with results against 1 *N* KCl calomel electrode without the intervention of 0.1 *N* KCl, a correction of −0.0004 volt should be applied. Lewis and Randall used Maitland's results with 0.1 *N* KI only and assumed that the activity coefficient of the iodide ion in this solution is 0.794 (instead of assuming that the degree of dissociation is 0.86 as was done by Maitland), with the following results.

TABLE I

NORMAL POTENTIAL OF IODINE–IODIDE ELECTRODE COMPUTED BY LEWIS AND RANDALL AFTER MAITLAND

KI, KI_3	Degree of saturation	*E*
0.1 *N*	0.3127	−0.2530
.1 *N*	.0881	− .2541
.1 *N*	.0686	− .2542
.1 *N*	.0338	− .2539

The change in the method of calculation thus influences the result by more than 2 millivolts.

The results of a research by Lewis and Faragher (which so far as we know has not been published in detail) are also given by Lewis and Randall. In these experiments several mixtures of potassium chloride and potassium iodide were shaken with a standard solution of iodine in carbon tetrachloride to make them 0.1411 saturated with iodine. The normal potential is computed by the use of the activities of the ions from the tables of Lewis and Randall, giving −0.2539 volt.

By combining measurements by Gerke[9] of an iodine electrode against a lead–lead iodide electrode with measurements by Lewis and Brighton[10] of this lead–lead iodide electrode against a normal calomel electrode (as defined by Lewis and Randall) the result −0.2531 has been computed.

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[8] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, New York, **1923**, p. 428.

[9] R. H. Gerke, THIS JOURNAL, **44**, 1703 (1922).

[10] G. N. Lewis and T. B. Brighton, *ibid.*, **39**, 1906 (1917); G. N. Lewis and M. Randall, ref. 8, p. 430.

McKeown[11] has carried out experiments similar to those of Crotogino and of Sammet, using solutions saturated with iodine varying from 0.1 N to 0.001 N in potassium iodide. McKeown's results differ greatly from all others. He regards his data obtained with the 0.001 N solutions as the most reliable and concludes that -0.2454 is the normal potential of the iodine electrode. This value is nearly one centivolt different from the value obtained by all other investigators and since McKeown fails to point out any source of error in the earlier work this figure does not deserve serious consideration.

Murray[12] measured the potential of a cell Pt, $x\text{I}_2 + y\text{KI}$ 0.1 N KCl, HgCl, Hg in which x and y were much less than 0.1 N. The effect of tri-iodide formation was allowed for by computation. He determined the equilibrium constant 0.001390 by the distribution method for this purpose and uses Lewis and Randall's tables of activities. He gives 0.6204 against the hydrogen electrode for an assumed free iodine of unit activity. If this is reduced to the normal calomel electrode by applying the correction -0.2818 (see pages 2075–2076) and to saturated iodine by the correction -0.0851, it becomes -0.2535.

Experimental

The innovation of Lewis and Randall in using the activity of the iodide as determined thermodynamically is undoubtedly sound but the experimental basis for the values of the activity coefficients of the individual ions at the various concentrations[13] is yet meager and is not fully explained by them except in general terms. The values given in their table for the activity coefficient of the iodide ion at various concentrations are not supported by references to experimental data but are probably mainly based on the assumption that they are the same as the chloride ion at the corresponding concentration. They do not give references to experimental proof of this assumption but it wins some support from the measurements of Pearce and Fortsch.[14]

It therefore seemed desirable to check up the values for the activity coefficient of the iodide ion, f, as given in the table of Lewis and Randall. The change in activity coefficient of the iodide ion with dilution can be computed from measurements of the potential of concentration cells with transference, with silver–silver iodide electrodes. The relative activity coefficients at the two concentrations can then be computed by the well-known formula

$$E_2 - E_1 = -2t_K \frac{RT}{F} \ln \frac{c_2 f_2}{c_1 f_1}$$

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[11] A. McKeown, *Proc. Faraday Soc.*, **17**, 517 (1922).

[12] H. D. Murray, *J. Chem. Soc.*, **127**, 882 (1925).

[13] G. N. Lewis and M. Randall, ref. 8, p. 382.

[14] J. N. Pearce and A. R. Fortsch, THIS JOURNAL, **45**, 2852 (1923).

Fortunately in this case the mobility of the potassium ion (74.8) and of the iodide ion (76.5) are so nearly alike that the liquid junction potential is small. The factor $2t_K$ (twice the transference number of the potassium ion), which gives the effect of the unequal mobilities of the ions at the liquid junction on the measured potential, is $(2 \times 74.8)/(74.8 + 76.5) = 0.989$. Therefore the liquid junction potential is only 1.1% of the measured potential. We measured the potential of a silver–silver iodide electrode in 0.1 *N* KI against a similar electrode in various other concentrations of KI at 25°. The ground stopper type of cell was used. An electrostatic condenser was used to increase the sensitiveness as described by us in an earlier paper.[15] Constant and reproducible results were obtained using 0.05 *N* and 0.02 *N* KI measured against 0.1 *N* KI, but variable, non-reproducible, mostly abnormally high values were obtained with the more dilute solutions tried. Unfortunately the work had to be interrupted before the proper technique was developed to overcome this difficulty with the dilute solutions. Only the results which we believe to be reliable are published. The duplicate results given were obtained with

TABLE II

POTENTIALS OF CELLS OF THE TYPE AG, AGI, 0.1 *N* KI; $c_x N$ KI, AGI, AG

c_x	Volts	Log $\frac{f_1}{f_x}$
c_1 0.1 *N*	0.0000	
c_2 .05 *N*	.0160	
	.0159	
Mean	.01595	−0.0283
c_3 .02 *N*	.0376	
	.0377	
Mean	.03765	− .0552

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[15] Jones and Kaplan, THIS JOURNAL, **50**, 1853 (1928). After the publication of our earlier paper and while this paper was in proof the article by Beans and Oakes, THIS JOURNAL, **42**, 2116 (1920), first came to our attention. Beans and Oakes describe the use of a condenser and ballistic galvanometer to measure the voltage of a cell with high internal resistance. In their arrangement the total voltage of the cell is impressed on the condenser, then discharged through the galvanometer and the total voltage inferred from the scale reading of the calibrated galvanometer. An accuracy of 0.5 millivolt was obtained. In our arrangement the condenser and galvanometer are used as null instruments. Only the difference between the setting of potentiometer and the potential of the cell is impressed on the condenser and the potentiometer is adjusted until this difference becomes zero, so that the voltage of the cell is obtained from the setting of the potentiometer, which is an advantage. No calibration of the galvanometer is necessary. With our arrangement a senitiveness of 0.02 millivolt was obtained in measuring a cell having 1,600,000 ohms internal resistance. Moreover, our arrangement is superior to that of Beans and Oakes in avoiding errors due to leakage and dielectric absorption, since the potential impressed on the condenser need never exceed one millivolt.

new electrodes and solutions. The values given remained constant for many hours.

Brönsted[16] found empirically that the activity coefficient, f, varies with the concentration in accordance with the equation

$$\log f = -3\alpha\sqrt{c} + 2\beta c$$

where α and β are constants. This relationship has since been deduced from the Debye-Hückel theory.[17] We may therefore write

$$\log \frac{f_1}{f_2} = -3\alpha(\sqrt{c_1} - \sqrt{c_2}) + 2\beta(c_1 - c_2)$$

or

$$-0.0283 = -3\alpha(\sqrt{0.1} - \sqrt{0.05}) + 2\beta(0.1 - 0.05)$$

and similarly

$$-0.0552 = -3\alpha(\sqrt{0.1} - \sqrt{0.02}) + 2\beta(0.1 - 0.02)$$

From these equations the values of -3α and 2β have been computed and substituted in the general equations, giving

$$\log f = -0.373\sqrt{c} + 0.125\, c$$

From this equation the values of the activity coefficient, f, have been computed at various concentrations and the results are compared in Table III with the values given in the tables of Lewis and Randall and with the degree of dissociation as computed from the conductivity.

TABLE III

ACTIVITY COEFFICIENTS OF THE IODIDE ION AT VARIOUS CONCENTRATIONS AT 25°

c	f, calcd. from our equation	f, from Lewis and Randall	Dissoc. from conductivity
0.1	0.784	0.79	0.859
.05	.837	.84	.888
.02	.891	.89	.9205
.01	.920	.92	.940
.005	.943	.95	.955
.002	.963	.97	.970
.001	.973	.98	.978
.000	1.000	1.00	1.000

The agreement between our new results and the table of Lewis and Randall is good. The values of the degree of ionization computed in the conventional manner from the conductivity are unmistakably different.

The new equilibrator which we invented for this purpose and have described in a separate article[18] gives a means of avoiding the dilemma which has introduced some uncertainty in the earlier work on the iodine electrode. Some experimenters (Crotogino, Sammet, Jones and Schumb, McKeown) have used solutions saturated with iodine, thereby making

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[16] J. N. Brönsted, THIS JOURNAL, **44**, 938 (1922).

[17] E. Hückel, *Ergebnisse der exakten Wissenschaften*, **3**, 249 (1924); G. Scatchard, THIS JOURNAL, **47**, 648 (1925).

[18] Grinnell Jones and B. B. Kaplan, *ibid.*, **50**, 1600 (1928).

liquid junctions and osmotic corrections large and risking errors due to higher polyiodides. Others (Maitland, Lewis and Randall, Lewis and Faragher) have decreased these difficulties by using solutions unsaturated with iodine but have been obliged to fix the iodine concentration by shaking with carbon tetrachloride, thereby risking analytical errors due to emulsified carbon tetrachloride, or a change in the nature of the solvents due to solution of carbon tetrachloride in the water. With the new equilibrator we can use solutions containing only a little iodine and fix this concentration accurately without the use of any other medium. Furthermore, the improvement in potentiometer which we have described[19] has made it possible to work with 0.01 N solutions successfully.

In Table IV below, E_s is the measured potential of the cell Pt, I_2 (solid) xN KI; 0.1 N KCl, HgCl, Hg, taken from the measurements of Jones and Schumb for the 0.1 N, 0.05 N, and 0.02 N solutions. We made new measurements using 0.01 N KI against 0.1 N calomel electrodes, using the cell with liquid junction in a ground stopper. The measured difference between the decinormal and normal calomel electrode is -0.0529 according to Lewis, Brighton and Sebastian[20] and this figure has been exactly confirmed by Jones and Schumb. For the reason explained above the liquid junction of -0.0004 should be added giving -0.0533 as the value to be added to change from decinormal to normal calomel electrode. E_2 is the measured potential of the cell Pt, I_2 (unsat.) xN KI; xN KI, I_2 (solid), Pt, in which the composition of the unsaturated solution was determined by the equilibrator and is shown at the top of the column.[21] E_j is the liquid junction correction, which is the potential between 0.1 N KCl and the KI solution unsaturated with iodine shown at the top of the column. It should be noted that by the use of the equilibrator this correction is reduced to a small value. This reduction in magnitude is important because the calculation is relatively uncertain. $E_c = (RT/2F) \ln I_2 \text{ (unsat.)}/0.00132$ makes proper allowance for the unsaturation of the iodine. In order to obtain the potential in a solution of unit activity in iodide ion the quantity $-(RT/F) \ln fI$ must be added. For convenience in computation and analysis, this is split up into two terms $E_0 + E_f = -(RT/F) \ln \mathrm{I} - (RT/F) \ln f$. The values of the activity coefficient used are taken from Col. 2 of Table III.

These results show a gratifying concordance with no evidence of systematic variation with the concentration of either potassium iodide or of iodine. If the activity coefficients from the tables of Lewis and Randall are used, the following results will be obtained: 0.1 N KI, -0.25458; 0.05 N KI, -0.25447; 0.02 N KI, -0.25447; 0.01 N KI, -0.25434.

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[19] Jones and Kaplan, This Journal, **50**, 1853 (1928).

[20] G. N. Lewis, T. B. Brighton and R. L. Sebastian, *ibid.*, **39**, 2245 (1917).

[21] The method of using the equilibrator with these solutions is explained in more detail in our recent paper, *ibid.*, **50**, 1845 (1928).

These results show a slight systematic variation with concentration which disappears when our values for the activity coefficient are used. The difference between our value of the normal potential and the value of Lewis appears to be due chiefly to the fact that Lewis used the measured difference for the potential between decinormal and normal calomel electrode, -0.0529, ignoring the liquid junction potential between decinormal and normal potassium chloride. This potential, like all liquid junction potentials, is somewhat uncertain but it may be computed to be -0.0004 volt. If our data are computed with the Lewis convention, the result would be -0.2540 (compared with his result, -0.2539).

Table IVA

Normal Potential of Iodine–Iodide Electrode at 25°

	0.1 N KI		0.05 N KI			
ΣK, g. mol./l.	0.10000	0.10000	0.04994	0.04977	0.04998	0.05000
% sat. with I_2	9.4%	5.37%	33.4%	5.8%	2.4%	2.35%
I_2, g. mol./l.	.00012413	.000070864	.0004413	.00007647	.000031518	.00003111
ΣI_3, g. mol./l.	.0081219	.0047946	.012055	.0025935	.0011219	.0011053
ΣI, g. mol./l.	.091878	.095205	.037885	.047176	.048858	.048895
E_s: Pt, I_2 sat., D. E.	− .28040	− .28040	− .29760	− .29760	− .29760	− .29760
D. E.: N. E.	− .05330	− .05330	− .05330	− .05330	− .05330	− .05330
E_2: Pt, I_2 unsat., I_2 sat., Pt	+ .04240	+ .05030	+ .02250	+ .04950	+ .06160	+ .06180
E_j, volts	− .00030	− .00009	− .00054	+ .00062	+ .00079	+ .00078
E_c, volts	− .03037	− .03757	− .01407	− .03659	− .04798	− .04814
E_0, volts	+ .06133	+ .06042	+ .08409	+ .07834	+ .07756	+ .07754
E_f, volts	+ .00625	+ .00625	+ .00457	+ .00457	+ .00457	+ .00457
E	− .25439	− .25439	− .25435	− .25446	− .25436	− .254356
Averages	−0.25439		−0.25438			

Table IVB

Normal Potential of Iodine–Iodide Electrode at 25°

	0.02 N KI		0.01 N KI
ΣK, g. mol./l.	0.02000	0.02000	0.01000
% sat. with I_2	13.2%	6.3%	100%
I_2, g. mol./l.	.0001745	.00008353	.00132
ΣI_3, g. mol./l.	.0021923	.0011105	.004865
ΣI, g. mol./l.	.017808	.0188895	.005135
E_s: Pt, I_2 sat., D. E.	− .32000	− .32000	− .33740
D. E.: N. E.	− .05330	− .05330	− .05330
E_2: Pt, I_2 unsat., I_2 sat. Pt	+ .03710	+ .04830	0
E_j, volts	+ .00097	+ .00130	− .00121
E_c, volts	− .02599	− .03546	0
E_0, volts	+ .10349	+ .10197	+ .13543
E_f, volts	+ .00296	+ .00296	+ .00214
E	− .25477	− .25423	− .25434
Averages	−0.2545		− .25434

In similar fashion measurements are carried out at 0° and reported in Table V.

TABLE V

NORMAL POTENTIAL OF THE IODINE–IODIDE ELECTRODE AT 0°

ΣK, g. mol./l.	0.10017	0.10017	0.10017	0.10017
% sat. with I_2	14.7%	8.3%	4.2%	4.1%
I_2, g. mol./l.	0.00009328	0.00005241	0.000027008	0.00002624
ΣI_3, g. mol./l.	.011297	.0069116	.0036460	.0035358
ΣI, g. mol./l.	.088873	.093258	.096524	.096634
E_s: Pt, I_2 sat., D. E.	− .2753	− .2753	− .2753	− .2753
D. E., N. E.	− .0489	− .0489	− .0489	− .0489
E_2: Pt, I_2 unsat., I_2 sat., Pt	+ .0317	+ .0391	+ .0478	+ .0483
E_j, volts	.0000	+ .0002	+ .0004	+ .0004
E_c, volts	− .0226	− .0294	− .0372	− .0375
E_o, volts	+ .0570	+ .0559	+ .0551	+ .0550
E_f, volts	+ .0057	+ .0057	+ .0057	+ .0057
E: Pt, I_2 sat., I = 1.0, N. E.	− .2524	− .2527	− .2524	− .2523
Average			− .2524	

	0.05 N KI			0.02 N KI		0.01 N KI
ΣK, g. mol./l.	0.05000	0.05000	0.05000	0.02000	0.02000	0.01000
% sat.	4.8%	4.6%	4.3%	9.8%	2.8%	100%
I_2, g. mol./l.	.000030255	.00002935	.00002712	.000062015	.00001758	.000635
ΣI_3, g. mol./l.	.0019537	.0019746	.0017969	.0015885	.00048242	.004719
ΣI, g. mol./l.	.048046	.048025	.048203	.018412	.019518	.005277
E_s	− .2909	− .2909	− .2909	− .3114	− .3114	− .3275
D. E., N. E.	− .0489	− .0489	− .0489	− .0489	− .0489	− .0489
E_2	+ .0474	+ .0475	+ .0489	+ .0380	+ .0539	0
E_j	+ .0008	+ .0008	+ .0008	+ .0010	+ .0013	− .0015
E_c	− .0358	− .0362	− .0371	− .0274	− .0422	0
E_o	+ .0715	+ .0715	+ .0714	+ .0940	+ .0926	+ .1234
E_f	+ .0042	+ .0042	+ .0042	+ .0027	+ .0027	+ .0020
E	− .2517	− .2520	− .2516	− .2520	− .2520	− .2525
Averages		−0.2518		− .2520		− .2525

These results are not so concordant or reliable as the results for 25° for two reasons. (1) It is more troublesome to maintain a constant temperature at 0° in the equilibrator for the longer time necesssary to obtain equilibrium with iodine (unfortunately this work had to be done in June and July and there were several very hot nights so that the ice in the tub was nearly gone by morning). (2) Owing to unavoidable interruptions of the work, we have no direct measurements of the activity coefficient of the iodide ion at 0° but are compelled to assume provisionally that the activity coefficients are the same at 0° as at 25°.

The results on the normal potential of the iodine–iodide electrode are summarized in the following table. In this table the figures given by the authors have been changed if necessary to make them applicable to a saturated iodine electrode; but no corrections to the authors figures have been applied on account of liquid junction potential, variations in definition of normal calomel electrode, or to the use of activity instead of concentration.

TABLE VI

THE NORMAL POTENTIAL OF THE SATURATED IODINE–IODIDE ELECTRODE WITH IODIDE ION AT UNIT ACTIVITY AGAINST THE NORMAL CALOMEL ELECTRODE

Observer	Date	At 25°, volts	At 0°, volts
Crotogino	1900	−0.256	......
Sammet	1905	− .256	......
Maitland	1906	− .2569	......
Jones and Schumb	1921	− .2555	−0.2525
McKeown	1922	− .2454	......
Gerke	1922	− .2531	......
Lewis and Randall	1923	− .2539	......
Lewis and Faragher	1923	− .2539	......
Murray	1925	− .2535	......
Jones and Kaplan	1928	......	......
	From 0.1 *N* KI	− .25439	− .2524
	From 0.05 *N* KI	− .25438	− .2518
	From 0.02 *N* KI	− .2545	− .2520
	From 0.01 *N* KI	− .25434	− .2525
	Averages	− .2544	− .2522

It is of some interest to express the normal potential of the iodine–iodide electrode against the hydrogen electrode instead of against the calomel electrode. Unfortunately, there seems to be more uncertainty as to the difference between the hydrogen and calomel electrodes than between the iodine and calomel electrodes. In 1917 Lewis, Brighton and Sebastian found for Hg, HgCl, KCl (1 mole per liter), 0.1 *N* KCl, H^+ (activity 1.0), H_2, (g); $E = -0.2828$. In 1923 Lewis and Randall in their book on Thermodynamics, p. 407, changed this figure to −0.2822. The change is caused by revision of the activity coefficients used in the calculations. This value has come into common use. Very recently Randall and Young[22] have cast serious doubt on the reliability of this figure. They find that the presence of air influences the potential of the hydrochloric acid calomel electrodes but not the potassium chloride calomel electrode. They also redetermine the activity coefficients of hydrochloric acid solutions. From these experiments they conclude that the difference between the calomel and hydrogen standards is −0.2812, a value differing by 1 millivolt from the figure of Lewis and Randall. In a matter of this importance independent confirmation is desirable. Pending such confirmation and systematic recomputation on the hydrogen basis of all normal potentials determined by the aid of the calomel electrode, we shall provisionally use the older value of Lewis and Randall, −0.2822. This must be changed by 0.0004 volt on account of the different definitions of the calomel electrode used by Lewis and Randall and the definition adopted in this paper (see page 2066). The result will thus be on the same basis as most other recent values for normal potentials. We may therefore write

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[22] M. Randall and L. E. Young, THIS JOURNAL, **50**, 989 (1928).

Pt, I_2 sat., I^- ($\alpha = 1.0$), 1 N KCl, HgCl, Hg $E = -0.2544$
Hg, HgCl, 1 N KCl, 0.1 N KCl, H^+ ($\alpha = 1.0$) H_2 (g), Pt $E = -0.2822$
Liquid junction correction 1 N KCl, 0.1 N KCl $E = +0.0004$
Pt, I_2 sat., I^-($\alpha = 1.0$), H^+(α=1.0) H_2 (g) $E = -0.5362$

No attempt will be made at this time to compute the normal potential of the iodine–iodide electrode referred to the hydrogen electrode at 0°, owing to inadequate data on the difference between hydrogen and calomel electrodes at this temperature.

Summary

The normal potential of the iodine–iodide electrode has been redetermined, using solutions containing so little free iodine that the effect of formation of tri-iodide is minimized and can be accurately allowed for. The activity of the iodine has been determined by a new device. The activity coefficient of the iodide ion in solutions of potassium iodide has been determined by measurements of the potential of iodide concentration cells with transference containing silver–silver iodide electrodes. The results can be expressed by the formula of the form suggested by Brönsted: $\log f = -373 \sqrt{c} + 0.125\, c$. The normal potential of the iodine–iodide electrode against the normal calomel electrode at 25° is found to be −0.2544 volt; and at 0° is found to be −0.2522 volt.

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THE EXTRAPOLATION OF ELECTROMOTIVE FORCE MEASUREMENTS TO UNIT IONIC ACTIVITY

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The relation between the electromotive force, E, of a cell such as Ag, AgCl, HCl, H_2 and the mean activity coefficient, γ, of the ions of the electrolyte is given by the equation

$$E = E_0 - 2k \log m - 2k \log \gamma \tag{1}$$

Here m is the molality of the acid, k is $2.3026\, RT/NF$, and E_0 is the electromotive force which the cell would have if the mean activity of the ions, or the product $m\gamma$, were equal to unity. In order to calculate activity coefficients from electromotive force data alone, it is necessary to determine the value of E_0 by extrapolation. This has usually been done, following Lewis and Randall,[1] by plotting the quantity E_0', which is defined as $E + 2k \log m$, against $\sqrt{m}$. Since $\gamma = 1$ when $m = 0$, it follows from equation (1) that $E_0' = E_0$ when $m = 0$. Curves which have

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 335.