In conclusion, I wish to express my indebtedness to Mr. Earle A. Harding for his kind assistance in the preliminary work in connection with this investigation.

PRINCETON, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY.]

A STUDY OF THE TENTH-NORMAL HYDROCHLORIC ACID CALOMEL ELECTRODE.[1]

BY N. EDWARD LOOMIS AND MERLE R. MEACHAM.

Received August 8, 1916.

I. Purpose of the Investigation.

The purpose of this investigation was to carefully measure the electromotive force of the system

$$H_2\text{–}Pt\text{–}0.1\ N\ HCl\text{–}Hg_2Cl_2\text{–}Hg$$

at 25° with the view of comparing the value so obtained with that of the cell

$$H_2\text{–}Pt\text{–}0.1\ N\ HCl\ ||\ 0.1\ N\ KCl\text{–}Hg_2Cl_2\text{–}Hg,$$

from which the contact potential has been eliminated. From this comparison the relative potentials of the 0.1 N hydrochloric acid and the 0.1 N potassium chloride calomel electrodes can be determined and thereby the relative degrees of dissociation of the two electrolytes measured.

The degree of dissociation of an electrolyte, as commonly calculated from conductivity data, depends upon the assumption that the mobilities of the ions are independent of the concentration. This assumption was first questioned by Jahn[2] and considerable evidence against it has since been accumulated. The mobility of the hydrogen ion appears to increase with increasing concentration, and consequently the degrees of dissociation of the more concentrated solutions of hydrochloric acid, as determined by conductivity data, are probably too high.

In 1909 Lewis and Sargent[3] assumed that hydrochloric acid and potassium chloride are equally dissociated at equivalent concentrations, even though the apparent dissociation, as indicated by conductivity measurements, is considerably higher for the acid. If the two electrolytes are equally dissociated then the 0.1 N HCl calomel electrode should have the same potential as the 0.1 N KCl calomel electrode. This was assumed to be the case by Lewis and Sargent and their assumption has been adopted by several subsequent workers.

In 1912, however, Lewis[4] showed that the degree of dissociation of 0.1 N

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[1] An abstract of this paper was presented at the Urbana meeting of the American Chemical Society.

[2] *Z. physik. Chem.*, 33, 545 (1900); 35, 1 (1900).

[3] THIS JOURNAL, 31, 363 (1909).

[4] *Idem.*, 34, 1631 (1912).

HCl was in doubt several per cent., and in a later paper[1] he states that, whereas hydrochloric acid and potassium chloride are equally dissociated at 0.01 *N* concentrations, uncertainty exists in regard to the conditions at 0.1 *N*.

It was to throw light upon the uncertainty which has existed in regard to the relative dissociations of 0.1 *N* HCl and 0.1 *N* KCl that this investigation was undertaken.

II. Previous Work.

The system

$$H_2\text{–Pt–}0.1\ N\ \text{HCl–}0.1\ N\ \text{KCl–}Hg_2Cl_2\text{–Hg}$$

has been carefully studied by several workers. The results which have been obtained at 25°, after correction for the vapor tension of the solution surrounding the hydrogen electrode, and for the new value of the electromotive force of the Weston cell, are summed up in the following table:

Bjerrum[2]	0.4273
Loomis and Acree[3]	0.4269
Myers and Acree[4]	0.4273
Average,	0.4272

This value includes the contact potential existing between 0.1 *N* HCl and 0.1 *N* KCl. Lewis[5] calculates that this potential amounts to —0.0284 volt and as evidence for this value states that Sebastian has obtained for the system

$$\text{Hg–}Hg_2Cl_2\text{–}0.1\ N\ \text{HCl–}0.1\ N\ \text{KCl–}Hg_2Cl_2\text{–Hg},$$

a potential of 0.0284 volt, which represents the contact potential if it is assumed that the two electrolytes are equally dissociated. On the other hand Bjerrum[6] obtains as his best value for the contact potential of the above system —0.0278 and this is just the potential which Myers and Acree obtain by direct comparison of the two electrodes.

It follows then that the difference of potential between the 0.1 *N* HCl hydrogen electrode and the 0.1 *N* KCl calomel electrode lies between 0.3988 and 0.3994 volt, depending upon whether —0.0284 or —0.0278 is adopted for the contact potential. The lower figure 0.3988 is probably nearer the correct value.

At the time this investigation was begun the only figures which were at all reliable for the system

$$H_2\text{–Pt–}0.1\ N\ \text{HCl–}Hg_2Cl_2\text{–Hg}$$

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[1] THIS JOURNAL, **36**, 1969 (1914).

[2] *Z. physik. Chem.*, **53**, 430 (1905).

[3] *Am. Chem. J.*, **46**, 585 (1912).

[4] *Idem.*, **50**, 396 (1913).

[5] THIS JOURNAL, **36**, 1973 (1914).

[6] *Z. Elektrochem.*, **17**, 61 (1911).

at 25° had been obtained in the laboratories of Acree and Lewis. Loomis and Acree used only two calomel cells and their value for the electromotive force of the system 0.4004[1] can be considered as only a preliminary measurement. Later Myers and Acree studied this combination more thoroughly and found the difference in potential to be 0.4002.[2]

Lewis[3] states that he has obtained as a mean of several direct comparisons of the 0.1 *N* hydrochloric acid hydrogen electrode with the 0.1 *N* hydrochloric acid calomel electrode, 0.3987 volt, which when corrected for vapor tension and for the new value of the Weston cell becomes 0.3990. He states that more recently Sebastian, working in his laboratory, has obtained the same value. No details of these measurements of Lewis and Sebastian have been published so far as the authors are aware.

Since this investigation was begun there has appeared an article by Ellis[4] in which a careful study of the system

$$H_2\text{-}Pt\text{-}HCl\text{-}Hg_2Cl_2\text{-}Hg$$

has been made at different temperatures and concentrations. In the course of this study four simultaneous measurements with 0.09999 *N* HCl at 25° gave as a mean 0.39884 volt.

It is evident that the electromotive force of the system

$$H_2\text{-}Pt\text{-}0.1\ N\ HCl\text{-}Hg_2Cl_2\text{-}Hg$$

has been in doubt by more than 1.5 millivolts.

III. Experimental Procedure.

All measurements were carried out at 25° ± 0.01, using much the same apparatus and technique as previously described in the articles of Loomis and Acree. The calomel electrode used in the electromotive force measurements was compared before and after each experiment with the mean of several other calomel electrodes, which were assumed to be of standard potential, and any difference in potential was applied to the measured e. m. f. as a "calomel cell correction." This procedure is even more important in the use of hydrochloric acid calomel electrodes than with potassium chloride calomel electrodes.

Several different types of hydrogen electrodes were used, the most satisfactory form for these experiments being a modification of that described by Frary[5] in which a gauze electrode is substituted for his sheet platinum electrode.

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[1] The figure given in the original article is 0.4001. The above value is obtained by correcting for the vapor tension at the hydrogen electrode and for the present value of the Weston cell.

[2] To the value given in the original article 0.399803 is to be applied a correction of 0.0004 for the vapor tension at the hydrogen electrode.

[3] THIS JOURNAL, 36, 1973 (1914).

[4] *Idem.*, 38, 737 (1916).

[5] THIS JOURNAL, 37, 2260 (1915).

The system which was being studied involves only very small contact potentials. The only difference in the solutions upon the two sides of the cell is that the acid at the calomel electrode is saturated with calomel. This would produce only a very small contact potential. Consequently no precautions were taken to insure a fresh plane of contact between the two solutions. Care was always taken however to prevent the contamination of the solution about either electrode by that from the other. This was accomplished by keeping at least one stopcock in the system closed except momentarily during measurements.

All measurements were corrected (*a*) for variations in the potential of the comparison calomel cell, as already noted; (*b*) for the barometric pressure reduced to 0° and corrected for capillarity and latitude; and (*c*) for the vapor tension of the solution in the hydrogen electrode chamber. The barometric pressure corrections were calculated by the equation

$$e = -\frac{R.T}{2F}\log_e p = -0.02958 \log_{10} p,$$

in which e represents the desired correction and p is the corrected barometric pressure in atmospheres. The correction for the vapor tension of the solution is a constant value and equal to +0.00040 volt.

IV. Experimental Results.

The following table summarizes the results of the measurements which were carried out. The first column gives the number of the series. Measurements belonging to the same series were carried out with the same set of calomel cells. The second column gives the experiment number. The third column gives the date of the preparation of the calomel, *viz* the day on which it was set to soaking with the solution with which the calomel electrodes were later filled; the date of filling the calomel electrodes; and the date of measurement of the hydrogen electrode against the calomel electrode. The fourth column gives the measured e. m. f.; the fifth the correction to be applied to the calomel cell; the sixth the correction for the barometric pressure; the seventh the correction for the vapor tension; and the eighth column the final value of the corrected e. m. f.

The fourth series of measurements was brought to a close by the breaking of the comparison calomel electrode. An attempt was made to carry out Series V with only four standard calomel electrodes, but after April 15 the agreement of the electrodes among each other became worse and worse, and the measured differences of potential between the calomel electrodes and the hydrogen electrode became unusually low. It was suspected that the electrodes had become contaminated in some way and for that reason the last few measurements of this series are not included.

		Date.							
Series No.	Expt. No.	Prep. of calomel.	Prep. of cal. cells.	E. M. F. meas.	Meas. E. M. F. Volt.	Cal. cell correc. Millivolt.	Barom. correc. Millivolt.	Vap. T. correc. Millivolt.	Final E. M. F. Volt.
I	1	Dec. 20	Jan. 7	Jan. 12	0.39841	—0.16	+0.37	+0.40	0.39902
	2			Jan. 13	0.39877	—0.15	—0.02	+0.40	0.39900
	3			Jan. 14	0.39893	—0.21	—0.07	+0.40	0.39905
II	4	Feb. 21	Feb. 24	Feb. 26	0.39810	±0.00	+0.36	+0.40	0.39886
	5			Feb. 28	0.39824	+0.10	+0.24	+0.40	0.39898
	6			Feb. 28	0.39809	+0.21	+0.26	+0.40	0.39896
	7			Feb. 29	0.39807	+0.28	+0.22	+0.40	0.39897
	*8			Mar. 10	0.39770	+0.90	+0.22	+0.40	0.39922
III	9	Mar. 10	Mar. 13	Mar. 13	0.39761	+0.22	+0.38	+0.40	0.39861
	10			Mar. 14	0.39781	+0.09	+0.29	+0.40	0.39859
	11			Mar. 14	0.39781	+0.17	+0.25	+0.40	0.39863
	12			Mar. 15	0.39832	—0.03	+0.10	+0.40	0.39879
	13			Mar. 16	0.39804	+0.15	+0.10	+0.40	0.39869
	14			Mar. 17	0.39810	+0.12	+0.08	+0.40	0.39870
	15			Mar. 17	0.39809	+0.12	+0.02	+0.40	0.39863
IV	16	Mar. 24	Mar. 27	Mar. 28	0.39805	+0.07	+0.32	+0.40	0.39884
	17			Mar. 29	0.39788	+0.26	+0.20	+0.40	0.39874
	18			Mar. 29	0.39803	+0.10	+0.20	+0.40	0.39873
	19			Mar. 30	0.39817	+0.08	+0.17	+0.40	0.39882
	20			Mar. 31	0.39805	+0.18	+0.22	+0.40	0.39885
	21			Apr. 1	0.39802	+0.15	+0.27	+0.40	0.39884
	22			Apr. 2	0.39819	+0.04	+0.21	+0.40	0.39884
	23			Apr. 3	0.39812	+0.08	+0.27	+0.40	0.39887
	24			Apr. 4	0.39822	+0.13	+0.22	+0.40	0.39897
V	25	Apr. 6	Apr. 11	Apr. 12	0.39797	+0.12	+0.22	+0.40	0.39871
	26			Apr. 13	0.39795	+0.09	+0.26	+0.40	0.39870
	27			Apr. 14	0.39804	—0.02	+0.22	+0.40	0.39864
	28			Apr. 14	0.39809	±0.00	+0.21	+0.40	0.39870
	29			Apr. 15	0.39808	—0.05	+0.22	+0.40	0.39865

Of the twenty-nine measurements recorded in the table, No. 8 is considerably the highest and is omitted from the general average. This measurement was made ten days after the one preceding it and the potentials of the different electrodes had become so discordant that there was much doubt in regard to the proper value of the calomel cell correction. Of the remaining twenty-eight measurements the average value is 0.39879. The individual measurements range from 0.39905 to 0.39859, a total variation of 0.46 millivolt and a maximum variation from the mean of 0.26 millivolt. An instrument correction for the potentiometer reduces the average e. m. f. to 0.39876.

In the five sets of calomel electrodes changes were made in the mercury, calomel, and acid in order to eliminate any error due to possible faulty preparation. The variations in the electromotive force are larger than would seem warranted in the measurement of a system involving only very small contact potentials. The only regularity in these variations which could be detected was a general tendency for the potential of the calomel electrode to increase upon standing. This would be the result if the solution about the mercury electrode were slow in becoming saturated with calomel. It is not believed that such is the case. Ellis showed in the course of his work that hydrochloric acid calomel electrodes rapidly follow temperature changes, and such could not be the case unless saturation is quickly attained. It seems more probable that some chemical change occurs in the system, probably the change of the calomel to the bichloride as suggested by Clarke, Myers, and Acree.[1] These authors agree with us in regard to the 0.1 *N* hydrochloric acid calomel electrode that "its constancy continues over only a short period of time." Ellis finds that calomel electrodes made up with dilute solutions of hydrochloric acid are less satisfactory than those made up with more concentrated solutions, and that with acid of less than 0.03 *N* concentration are for some reason not at all reliable.

It appears then that the 0.1 *N* hydrochloric acid calomel electrode is not nearly as constant and reproducible as the 0.1 *N* potassium chloride calomel electrode. The age of the electrode is an important factor in determining its potential. This is probably the cause of the great variations in previous measurements of the system

$$H_2\text{–}Pt\text{–}0.1\ N\ HCl\text{–}Hg_2Cl_2\text{–}Hg$$

and is the cause of the smaller variations in the measurements which are recorded in this paper.

The average value obtained in the measurement of the hydrogen electrode against the 0.1 *N* hydrochloric acid calomel electrode is 0.39876. We have shown in the earlier part of this article that the most probable value of the potential of the hydrogen electrode against the 0.1 *N* potassium chloride calomel electrode, after allowance has been made for the contact potential, is 0.3988. Within the limits of experimental error we have the same electromotive force in each case, indicating that the 0.1 *N* hydrochloric acid calomel electrode has the same potential as the 0.1 *N* potassium chloride calomel electrode. This in turn implies that hydrochloric acid and potassium chloride are equally dissociated at 0.1 *N* concentration. A difference of 1% in the degree of dissociation of the two electrolytes would cause a difference of 0.3 millivolt in the relative potentials of the two electrodes. It follows from these results therefore that the two electrolytes are not more than 1% different in their degrees of ionization at 0.1 *N* concentration.[2]

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[1] *J. Phys. Chem.*, **20**, 264 (1916).

[2] Since this paper was placed in the hands of the editors there has appeared an article by Harned (THIS JOURNAL, **38**, 1986 (1916)) in which he arrives by a different method at the conclusion "that the activity of the ions in 0.1 *M* hydrochloric acid is greater than in 0.1 *M* potassium chloride but only slightly greater. If 0.0730 be ac-

V. Summary.

1. The potential of the system

$$H_2\text{-Pt-}0.1\ N\ \text{HCl-}Hg_2Cl_2\text{-Hg}$$

has been found to be 0.3988 $\pm$ 0.0002.

2. The variations in the electromotive force of this system are probably due to a chemical change in the calomel electrode by which the potential increases with time.

3. This series of experiments indicates that within the limits of experimental error, probably within 1%, hydrochloric acid and potassium chloride are equally dissociated at tenth-normal concentrations.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE SOLUBILITIES OF LIQUIDS IN LIQUIDS. THE PARTITION OF THE LOWER ALCOHOLS BETWEEN WATER AND COTTONSEED OIL.

BY B. B. WROTH AND E. EMMET REID.

Received September 13, 1916.

Introduction.

According to the commonly accepted partition law a solute C is partitioned between two immiscible solvents, in contact with each other,

$$\frac{C_a}{C_b} = r = \frac{S_a}{S_b}$$

in which C_a and C_b are the concentrations of C in the solvents A and B, respectively, r is a constant ratio, and S_a and S_b are the solubilities of the solute in the two solvents. It has frequently been shown that r is constant only when the solute C exists in the two solvents in the same molecular aggregation. The equality of $C_a/C_b = r = S_a/S_b$ has been proved for iodine partitioned between water and carbon disulfide, bromoform, and carbon tetrachloride by Jakowkin.[1] His results are as follows:

From solubilities in					From partition experiments.
A.	B.	S_a.		S_b.	
CS_2	H_2O	230	$\div$	0.3387 = 679	685
$CHBr_3$	H_2O	189.55	$\div$	0.3387 = 559	558.5
CCl_4	H_2O	30.33	$\div$	0.3387 = 89.6	89.7

cepted to represent the ion-activity of the salt, there is reason to assume that the ion-activity of the acid is 0.0755."

A possible explanation of the slight discrepancy between the conclusion of his article and this one may be found in the value which he adopted for the contact potential of 0.1 N HCl-0.1 N KCl. It will be noted that our conclusion is based upon the assumption that this contact potential is —0.0284 volt. If a lower value of this contact potential, such as found by Bjerrum, is correct, then the potential of the calomel electrode toward a solution of 0.1 N KCl is greater than that of a calomel electrode toward a solution of 0.1 N HCl. In other words, if such is the case, 0.1 N HCl is slightly more dissociated than 0.1 N KCl.

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[1] *Z. physik. Chem.*, 18, 390 (1895).