Since the values of K decrease with increasing concentration, it is evident that the anthracene associates in cinnamic acid, and for this reason a calculation of the latent heat of fusion is impossible. No record of previous work with cinnamic acid as solvent has been found.

Conclusions.

From the work here recorded it is evident that:

(1) The apparatus described has given much more accurate cryoscopic data for substances having considerably elevated melting points than any which has been used heretofore.

(2) The method is one which can be used for a large number of substances covering a wide range of melting points, since it is possible to secure the necessary adiabatic conditions by simply choosing a liquid having an appropriate boiling point for the mantling vapor.

(3) It can safely be concluded that the more serious sources of error usually found in such cryoscopic measurements, in particular the errors due to imperfect adiabatic conditions and to the sublimation of the solvent, have now been removed.

(4) The limit of accuracy of the method seems now to be limited to the accuracy with which temperatures can be read by the thermometer.

Further work along this same line, but with a platinum resistance thermometer capable of reading temperatures to 0.0001°, is contemplated.

MADISON, WISCONSIN.

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

THE APPLICABILITY OF THE ISOHYDRIC PRINCIPLE TO TENTH-NORMAL MIXTURES OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE.[1]

BY N. EDWARD LOOMIS, J. L. ESSEX, AND MERLE R. MEACHAM.

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In a previous paper[2] Loomis and Meacham showed that within the limits of our knowledge of the contact potential of the system

$$0.1\ N\ \mathrm{HCl}-0.1\ N\ \mathrm{KCl}$$

the potential of the 0.1 *N* hydrochloric acid calomel electrode is identical with that of the 0.1 *N* potassium chloride calomel electrode, thereby indicating that at 0.1 *N* concentration hydrochloric acid and potassium chloride have approximately equal degrees of dissociation.

In accordance with the isohydric principle, it follows that if 0.1 *N* potassium chloride and hydrochloric acid are equally dissociated, these solutions may be mixed in any proportion without changing their de-

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[1] Reports on sections of this work were submitted to Purdue University by J. L. Essex and Merle R. Meacham in partial fulfilment of the requirements for the degrees of Master of Science and Chemical Engineer, respectively.

[2] THIS JOURNAL, 38, 2310 (1916).

gree of dissociation and in such a mixture, either the hydrochloric acid or the potassium chloride will have the same degree of dissociation which it alone would have if present in the same volume in concentration equal to the total concentration of the mixture.. In other words, in any mixture of hydrochloric acid and potassium chloride in which the total concentration is kept at 0.1 N the degree of dissociation of each electrolyte is 86%, if 86% is the degree of dissociation for acid or salt alone at 0.1 N concentration. It should therefore be possible if hydrochloric acid and potassium chloride are equally dissociated at 0.1 N concentration and if the isohydric principle holds to predict the hydrogen-ion concentration of any mixture of the two in which the total concentration in kept at 0.1 N. If the mixture consists of xHCl + yKCl, where $x + y = 0.1$, the hydrogen-ion concentration will be x times that assumed for 0.1 N HCl. On the other hand, the chlorine-ion concentration will remain constant for the different mixtures.

It should therefore be possible to test the applicability of the isohydric principle to such mixtures of hydrochloric acid and potassium chloride by comparing the measured and calculated values for the electromotive force of the system

$$H_2\text{–Pt–}0.1\ N(\text{HCl} + \text{KCl})\text{–}Hg_2Cl_2\text{–Hg}.$$

If the isohydric principle applies the potential of the calomel electrode will remain constant for different mixtures, since the chlorine-ion concentration remains constant, and in every case will be the same as though made up with 0.1 N hydrochloric acid or potassium chloride. Any variations in the electromotive force of the above system with change in the proportions of the electrolytes must therefore be due to the change in the potential of the hydrogen electrode caused by the change in the hydrogen-ion concentration. Knowing the electromotive force of the system

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

to be 0.3988[1] and knowing the change in the hydrogen-ion concentration the electromotive force of

$$H_2 - \text{Pt} - 0.1\ N\ (\text{HCl} + \text{KCl}) - Hg_2Cl_2 - \text{Hg}$$

for any mixture can be readily calculated.

Agreement between the calculated and experimentally determined values for the electromotive force of the different systems would prove that hydrochloric acid and potassium chloride are dissociated to the same extent at 0.1 N concentration and that the isohydric principle applies exactly. It was realized when the work was undertaken that lack of agreement would be difficult of interpretation since it might be due to a difference in the degree of dissociation or to a lack of application of the isohydric principle, due perhaps to a salt effect.

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[1] See article by Loomis and Meacham, *loc. cit.*

After preliminary measurements of several mixtures had been made, an article by Harned[1] appeared in which he showed that the addition of potassium chloride to 0.1 *N* hydrochloric acid increased the hydrogen-ion concentration or activity markedly. Since Harned's method of attack was entirely different from ours and since he did not keep the total concentration at 0.1 *N* it seemed desirable to continue our measurements.

Experimental Measurements.

The apparatus used and the method followed were similar to those employed in the work of Loomis and Meacham. It will be observed that measurements of the system

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

involve no contact potential and hence little difficulty was anticipated or experienced due to diffusion. At the same time care was taken not to allow any calomel to come into contact with the platinum electrode and at no time was any gray deposit upon the platinum noticed. Two hydrogen electrodes, modified forms of the Frary type,[2] were used alternately during the measurements and the agreement of the results obtained warranted only very occasional replatinizing of the electrodes. Our usual custom was followed of correcting the measured electromotive force for changes in the potential of the comparison calomel electrode by checking it before and after each measurement against several other calomel electrodes kept as standards. All measurements were carried out at 25°.

Measurements were made with 0.1 *N* mixtures ranging from 0.09 *N* HCl + 0.01 *N* KCl to 0.01 *N* HCl + 0.09 *N* KCl. In all cases these mixtures were prepared by diluting the proper quantity of 0.1 *N* hydrochloric acid to a liter with 0.1 *N* potassium chloride solution. The solutions were carefully prepared from purified reagents.

The mercury and calomel were prepared and purified as in previous work.[3]

TABLE I.

Measurements of the System

$H_2\text{–Pt–}0.07\ N\ HCl + 0.03\ N\ KCl\text{–}Hg_2Cl_2\text{–}Hg$.

Meas. E. M. F. Volt.	Cal. cell correc. Millivolt.	Bar. correc. Millivolt.	Vap. tens. correc. Millivolt.	Corrected E. M. F. Volt.
0.40790	—0.12	+0.22	+0.40	0.40840
0.40796	—0.19	+0.19	+0.40	0.40836
0.40803	—0.21	+0.24	+0.40	0.40846
0.40807	—0.24	+0.21	+0.40	0.40844
0.40803	—0.28	+0.18	+0.40	0.40833
0.40808	—0.28	+0.17	+0.40	0.40837
			Average,	0.40839
			Corrected for potentiometer error =	0.40836

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[1] THIS JOURNAL, 38, 1986 (1916).

[2] *Ibid.*, 37, 2260 (1915); 38, 2312 (1916).

[3] Loomis and Acree, *Am. Chem. J.*, 46, 585 (1911).

It will not be necessary to give in detail all of the measurements obtained. Table I shows typical results with a mixture of 0.07 N HCl + 0.03 N KCl.

In this table the first column gives the measured values of the electromotive force; the second column gives the correction for the calomel cell obtained by comparing it with several other calomel electrodes; the third column gives the correction for the barometric pressure calculated by the equation

$$\pi = \frac{0.05915}{2} \log_{10} 1/p,$$

where p is the pressure in atmospheres.[1] The fourth column gives the correction for the vapor tension of water at the hydrogen electrode; and the last column the corrected electromotive force which would be given by a hydrogen electrode at whose surface the gaseous hydrogen had a pressure of 760 mm. at 25° when measured against an average calomel electrode.

TABLE II.

Summary of Electromotive-force Measurements of

H_2–Pt–0.1 N (HCl + KCl)–Hg_2Cl_2–Hg.

Comp. N HCl +	N KCl.	Series.	No. of meas.	Aver. correc. E. M. F. Volt.	Mean deviation Millivolt.	Calc. E. M. F. Volt.	Diff. Millivolt.	Most prob. diff.	Most prob. E. M. F.
0.09	0.01	I	6	0.40180	0.04	0.40151	+0.29	+0.14	0.40165
		II*	7	0.40166	0.02		+0.15		
0.08	0.02	I	3	0.40443	0.02	0.40453	−0.10	+0.28	0.40481
		II	8	0.40479	0.03		+0.26		
0.07	0.03	I	4	0.40813	0.03	0.40796	+0.17	+0.42	0.40838
		II	6	0.40836	0.03		+0.40		
0.06	0.04	I	6	0.41250	0.04	0.41192	+0.58	+0.56	0.41248
0.05	0.05	I	3	0.41722	0.04	0.41661	+0.61	+0.70	0.41731
		II	7	0.41710	0.11		+0.49		
		III*	2	0.41741	0.07		+0.81		
		IV	8	0.41738	0.04		+0.77		
0.04	0.06	I	8	0.42367	0.05	0.42234	+1.33	+0.85	0.42319
		II	5	0.42317	0.09		+0.83		
		III*	3	0.42324	0.03		+0.90		
0.03	0.07	I	4	0.43124	0.01	0.42973	+1.51	+0.99	0.43072
		II	6	0.43073	0.05		+1.00		
0.02	0.08	I	8	0.44156	0.03	0.44014	+1.42	+1.14	0.44128
		II	4	0.44090	0.03		+0.76		
0.01	0.09	I	4	0.45902	0.03	0.45795	+1.07	+1.28	0.45923
		II	8	0.45937	0.05		+1.42		

Table II summarizes the results which have been obtained with the different mixtures. The first column shows the composition of the mixtures; the second column gives the number of the series. In most cases more than one series of experiments was run with each mixture. In three

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[1] See Loomis and Acree, THIS JOURNAL, 38, 2391 (1916).

cases, those marked *, the new series uses the same set of calomel cells as the series immediately preceding, a new mixture of hydrochloric acid and potassium chloride being used only in the hydrogen electrode cell. In all other cases a new series means that a fresh mixture of the electrolytes was used throughout. The third column shows the number of measurements which were made in each series; and Col. 4 gives the average corrected electromotive force of the total number of measurements of the series. The fifth column gives the mean deviation of the various measurements of the series from the average. The sixth column gives the electromotive force calculated by the equation

$$E = 0.3988 + 0.05915 \log_{10} 0.1/x,$$

where x represents the concentration of the hydrochloric acid. 0.3988 is the electromotive force of the system

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

as determined by Loomis and Meacham. The second term of the equation gives the change in the potential of the hydrogen electrode caused by the decrease in the concentration of the hydrogen ions in the solution surrounding it. It will be observed that this calculation involves no assumption in regard to the degree of dissociation of 0.1 N hydrochloric acid, but only that the degree of dissociation of the acid in the mixture is the same as that of the 0.1 N hydrochloric acid solution. This value, whatever it may be, appears in both the numerator and denominator or of the fraction following the logarithm and is consequently canceled out. The seventh column gives the difference in millivolts between

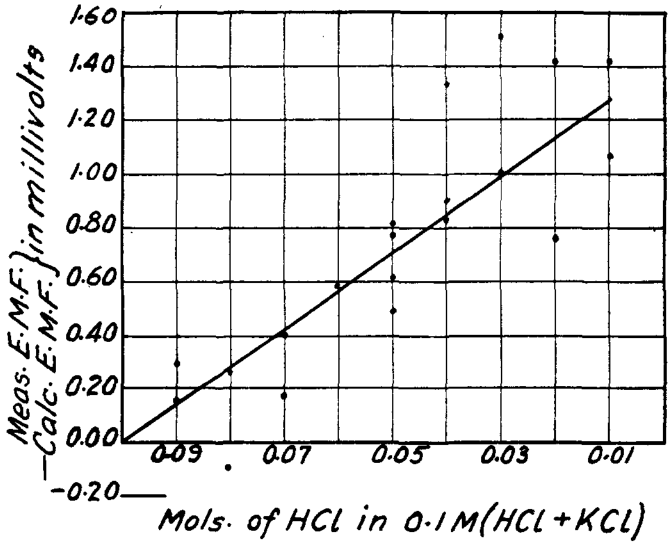

Fig. 1.

the values in Col. 4 and the corresponding ones in Col. 6. These differences are plotted in Fig. 1 and Col. 8 gives the most probable difference, read from the straight line of the graph. Col. 9 gives the most probable electromotive force of the mixture, obtained by adding to the calculated values of Col. 6 the most probable differences of Col. 8.

It will be observed that whereas the measurements in any one series are quite concordant, the mean deviation from the average being more than 0.5 millivolt in only three cases, the agreement of the averages of different series for the same mixture are in general much less concordant. It is believed that this is due to errors involved in the preparation of the mixtures. It is this belief which justifies the use of the graph of Fig. 1 for determining the most probable differences between the experimental and calculated voltages. In this way the average of a very large number of determinations can be used to eliminate the errors incident to any one measurement. As will be shown shortly such variations in the measured electromotive force correspond to very slight changes in the hydrogen- or chlorine-ion concentration.

The results of Table II show that in every case the most probable electromotive force is greater than the calculated electromotive force for a mixture. This fact means that the hydrogen-ion concentration about the hydrogen electrode is too low, or that the chlorine-ion concentration about the calomel electrode is too low, or that the deviations involve changes at both electrodes.

In the light of much previous work[1] on salt effects, especially in the light of Harned's results,[2] it seems improbable that the hydrogen-ion concentration of the mixtures is lower than that calculated from the isohydric principle. On the other hand, if the hydrogen-ion concentration or activity is increased in the presence of potassium chloride it is very probable that the chlorine-ion concentration of the mixture is decreased. This would explain the discrepancies which we note.

It is possible by a series of approximations to calculate closely what the change in the degree of ionization of the hydrochloric acid is. Considering the results for the mixture 0.01 *N* HCl + 0.09 *N* KCl, where there is a maximum discrepancy between the calculated and determined voltages, let us assume first that the total difference in the observed and calculated voltages is due to a decrease in the chlorine-ion concentration at the mercury electrode, and let us assume for the calculation that the chlorine-ion concentration in a 0.1 *N* hydrochloric acid calomel electrode is 0.086. A simple calculation shows that a difference of 1.28 millivolt

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[1] See Loomis and Acree, *Am. Chem. J.*, 46, 621 (1911); Loomis, *J. Phys. Chem.*, 19, 663 (1915), and references given in these two articles; Fales and Nelson, THIS JOURNAL, 37, 2769 (1915), and many others.

[2] *Loc. cit.*

corresponds to a decrease in chlorine-ion concentration from 0.086 to 0.08182. If, however, there is such a decrease in chlorine-ion concentration then there will be a corresponding increase in the hydrogen-ion concentration, from 0.0086 for 0.01 *N* HCl to 0.008659, when calculated from the standpoint of the influence of a common ion. If the hydrogen-ion concentration changes, however, then the potential of the hydrogen electrode does not remain constant as we assumed at the start but decreases in potential by 0.18 millivolt. Therefore the decrease in the chlorine-ion concentration must account not only for an increase of 1.28 millivolt in the potential of the calomel electrode but also for an additional increase of 0.18 millivolt to compensate for the change in the hydrogen electrode. A recalculation on this basis indicates a chlorine-ion concentration in the mixture of 0.08125 and a hydrogen-ion concentration of 0.008668.

The results of this series of electromotive-force measurements lead to the conclusion therefore that the isohydric principle does not apply strictly 0.1 *N* mixtures of hydrochloric acid and potassium chloride, but that there is a slight increase in the dissociation of the hydrochloric acid, amounting in the case of the 0.01 *N* HCl + 0.09 *N* KCl mixture to an increase from the theoretical 86% to 86.68%. In the other mixtures the increase would be less.

This increase in the dissociation of the hydrochloric acid might be accounted for by a lower degree of dissociation for 0.1 *N* potassium chloride than for 0.1 *N* hydrochloric acid; or it might be accounted for by an increase in dissociation due to a neutral salt effect. The exact cause cannot be determined from this series of measurements. If Harned's results are accepted both possible causes would be operative.

Summary.

1. Electromotive-force measurements have been carried out with the system

$$H_2\text{–Pt–}0.1\ N\ (\mathrm{HCl} + \mathrm{KCl})\text{–}Hg_2Cl_2\text{–Hg}$$

for mixtures ranging from 0.09 *N* HCl + 0.01 *N* KCl to 0.01 *N* HCl + 0.09 *N* KCl.

2. In every case it has been found that the electromotive force of the system is higher than the value calculated from the isohydric principle.

3. This result has been explained by the conclusion that the isohydric principle does not apply rigidly but that there is a slight increase in the dissociation of the hydrochloric acid with increasing proportions of potassium chloride. In the most extreme case, the mixture of 0.01 *N* HCl + 0.09 *N* KCl, the dissociation of the acid appears to have increased from 86% to 86.68%. The reason for this increase is not definitely indicated by this work.

LAFAYETTE, INDIANA.