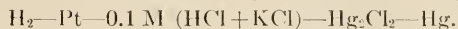


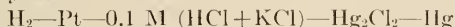
ELECTROMOTIVE FORCE MEASUREMENTS OF THE SYSTEM.



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For several years there has been great uncertainty in regard to the relative dissociations of 0.1 M HCl and 0.1 M KCl. It has been shown that the conductivity method indicates too high a degree of dissociation for hydrochloric acid because of increase in the mobility of the hydrogen ion with increasing concentration. Most authors in recent years have assumed that at 25° both solutions are 86% dissociated in accordance with the recommendation of Lewis and Sargent in 1909¹. Since 1912, however, Lewis has questioned his earlier view and the matter has again been left in doubt.

The writer has attempted to secure information upon the relative dissociations of 0.1 M HCl and 0.1 M KCl by studying the electromotive force of the system:



It is obvious that if 0.1 M HCl is dissociated to the same extent as 0.1 M KCl then the electromotive force of the system

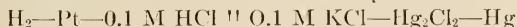


should be the same as that of

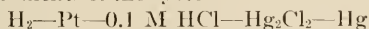


since the potential of the calomel electrode is a function only of the chlorine ion concentration of the surrounding solution.

Within the limits of experimental error this has been shown to be the case in an article recently published by the writer.³ The best measurements of the electromotive force of the system



at 25° give a value of 0.3988 or slightly greater depending upon the value of the contact potential used in the calculations. The mean of twenty-eight measurements of the system



gave 0.3988 ± 0.0002 . It is seen that the electromotive force of the two systems is identical within the limits of our knowledge of the contact potential of 0.1 M HCl—0.1 M KCl, and consequently 0.1 M HCl and 0.1 M KCl appear to be equally dissociated.

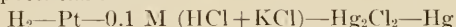
If 0.1 M HCl and 0.1 M KCl are equally dissociated then according to the isohydric principle it should be possible to mix the solutions in any proportion without changing the degree of dissociation of either. Consequently the potential of a calomel electrode surrounded by any mixture of 0.1 M HCl and 0.1 M KCl should be the same as that of a 0.1 M KCl calomel

¹ J. Am. Chem. Soc. 31, 363, (1909).

² The symbol (||) indicates that the contact potential has been eliminated.

³ J. Am. Chem. Soc. 38, 2310, (1916).

electrode or that of a 0.1 M HCl calomel electrode. Therefore any variations in the potential of



with change in the relative amounts of HCl and KCl would be due to the change in the potential of the hydrogen electrode, caused by the change in the hydrogen ion concentration. The change in hydrogen ion concentration corresponding to any change in the potential of the hydrogen electrode can be readily calculated and it is therefore possible to compare the experimentally determined hydrogen ion concentrations with those calculated on the isohydric principle. Agreement would further confirm the equal dissociation of the two solutions. Disagreement would indicate either a discrepancy in the degrees of dissociation or a failure in the application of the isohydric principle.

So far mixtures of the composition

0.08 M HCl+0.02 M KCl

0.05 M HCl+0.05 M KCl

0.03 M HCl+0.07 M KCl

0.01 M HCl+0.09 M KCl

have been studied and rough agreement between the calculated and experimental values is obtained. Variations of the order of 1% have not yet been explained and the study is being continued in order to account for these variations. At present it is thought that probably the variations are due to changes in the potential of the calomel electrodes upon standing, such as have been noted with 0.1 M HCl calomel electrodes.