

Electrometric Measurements with Hydrogen Electrodes in Mixtures of Acids and Bases with Salts

The Dissociation Constants of Water, Phosphoric Acid, Citric Acid, and Glycine.

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I. SURVEY

1. The investigations dealt with in the following report are mostly of an experimental nature. They consist of measurements of electromotive forces in cells which are built up in the following way:



One of us has already previously performed determinations of this kind¹. A comprehensive investigation was published by S. P. L. Sørensen² in 1909, and this investigation has later on been supplemented by a paper by S. P. L. Sørensen and K. Linderstrøm-Lang³. Similar measurements have also been carried out by many other investigators. Especially the investigations of Harned^{4,5} have yielded important experimental material.

The present study is mainly concerned with acids and bases which have already been investigated by Sørensen and Harned. In this renewed and extended investigation we have attached importance to measurements of the mixtures concerned at varying concentrations and temperatures.

2. In these measurements, hydrogen electrodes were combined with a *calomel electrode*. For this reason, part II of our paper consists of a careful investigation of various calomel electrodes with regard to reproducibility and durability. If

the instructions given here are followed, these electrodes are reproducible at 18° C within 0.1–0.2 millivolt and will keep for several months. At 25° C and 37° C they were less stable.

We have preferred to perform our measurements with a 0.1 *M* KCl-calomel electrode. In order to correlate measurements with this electrode and with other calomel electrodes, we have compared the differences in potential between calomel electrodes with 0.1 *M*, 1 *M*, 3.5 *M*, and saturated KCl solutions at temperatures of 0°, 18°, 25°, 37° C.

3. In the cells measured, the electromotive force is the sum of the electrode potentials and the liquid-junction potentials. If the liquid-junction potentials are calculated, it is possible from the potentials of the cells to calculate the pure electrode potentials. From the electrode potentials it is further possible to calculate the relative values of the activities of the hydrogen ions in the solutions investigated, by means of Nernst's formula.

The method which we have used in the calculation of the *liquid-junction potentials* is described in details in part III. The formula of Henderson was used in the calculation. It was assumed that the strong electrolytes present were completely dissociated. The interionic forces were taken into account, in as far as the mobilities of the ions in the solution in question were inserted in the equations.

4. The H^+ -activities obtained in this way need a more detailed explanation. It is impossible from a purely thermodynamic point of view to determine the individual activities of single ions from measurements of cells with or without liquid-junction potentials. This question is elucidated in the investigations by H. S. Harned⁵ and has been especially brought forward and discussed in detail by P. B. Taylor⁶ (compare also two papers in press by E. A. Guggenheim⁷). It is not possible to calculate thermodynamically the liquid-junction potentials in a cell without knowledge of the individual activity coefficients of the single ions, and vice versa we cannot calculate the individual coefficients without knowing the liquid-junction potentials.

Only when an assumption, not based in thermodynamics, is introduced is it possible to obtain definite individual ionic activity coefficients and liquid-junction potentials. Such an assumption can to some extent be made arbitrarily. Fundamentally it is permissible to consider the liquid-junction potentials of all other solutions in contact with a certain chosen solution as zero. We could for example stipulate that a 3.5 *M* KCl in water has the potential zero relative to all other solutions, or that the liquid-junction potential can be precisely eliminated by extrapolation from measurements with a 3.5 and a 1.75 *M* KCl solution. One of these assumptions will be sufficient to make possible the calculation of all other liquid-junction potentials and all individual ionic activity coefficients.

The coefficients of ionic activity obtained in this way will, however, be unpractical in one certain respect. The ions of potassium and chlorine in potassium chloride do not migrate at exactly the same rate. For this reason the individual ionic activities obtained will, with increasing dilution, show deviations from proportionality with the ionic concentration. We will not obtain activity coefficients converging towards a certain limiting value with increasing dilution. But if the liquid-junction potentials between 3.5 *M* KCl and the other solutions are calculated according to Henderson's formula in the way outlined above, this difficulty is avoided.*

Thus the activities and activity coefficients for single ions calculated in this paper are intimately connected with the method used in determining the liquid-junction potentials. Together they form a system, which, although arbitrary, is in itself consistent and unobjectionable from a thermodynamic point of view. All the values calculated by means of this system, but without the above mentioned arbitrarily chosen assumption (complete dissociation constants, concentration constants, mean ionic activity coefficients of electrolytes, E_o -values) are quite reliable. The arbitrariness of the system only affects those values, which cannot be subjected to a thermodynamic control (individual ionic activity coefficients, incomplete dissociation constants etc.)

5. The *scale used in measuring the activities* is as a rule defined in such a way that activity and concentration coincide at sufficiently large dilutions. In order to be able to convert our relative H^+ -activities to this scale, we have in part IV performed measurements of H^+ -activities in dilute hydrochloric acid with and without addition of alkali chlorides. These measurements were extended to very dilute solutions in order to approach as closely as possible the range in which activity and concentration become proportional to each other, so that only a small extrapolation is necessary to define the scale of activity.

In *measurements in very dilute solutions*, however, two difficulties are encountered. Firstly, the *cell potentials* in these solutions cannot be measured quite so accurately as in the more concentrated solutions. Secondly, the calculations of liquid-junction potentials in cells with strongly diluted solutions become to a considerable extent uncertain, since the transference number of the potassium ion in potassium chloride is not sufficiently well known. For these two reasons we have not succeeded in ranging the H^+ -activities as accurately within the adopted scale, as we had initially hoped.

In practice, this means that the potential (E_o) of the 0.1 *M* calomel electrode

* In solutions, in which the mean activity coefficients for the electrolytes present are all of the same magnitude, our individual ionic activity coefficients may, all the same, show deviations from this common value, due to differences in the ionic mobilities (E. A. Guggenheim⁷).

in combination with a normal hydrogen electrode could not be determined with as great a certainty as was originally hoped for.

In the extrapolation to infinite dilution we have assumed that (with increasing dilution) the activity coefficient of the hydrogen ion, $f_{\text{H}^+} = A_{\text{H}}/[\text{H}^+]$, approaches the limiting value 1 obeying Debye-Hückel's square root law, and in the calculation of the liquid-junction potentials we have reckoned with the transference number 0.497 for the potassium ion in potassium chloride. With these assumptions we obtain the following values for E_0 , the potential of a 0.1 M calomel electrode against a normal hydrogen electrode (hydrogen pressure 760 mm Hg, hydrogen-ion activity 1):

t	0°	18°	25°	37°
E_0	0.3351	0.3360	0.3360	0.3354

Had we introduced a transference number 0.005 lower, the values would have been about 1 millivolt smaller. Fortunately, this uncertainty, regrettable in itself, plays no important rôle in the subsequent calculation of dissociation constants. Since the measurements, from which these dissociation constants were calculated, are dealt with in the same way as the measurements in hydrochloric acid, the errors, if any, neutralize each other. If the measurements are performed in sufficiently dilute solutions (and with sufficient experimental accuracy) it is possible, in spite of the uncertainty present in the determination of E_0 , to obtain determinations of the dissociation constant with any required accuracy.

The H^+ -activities calculated on the basis of the values for E_0 given above are denoted by A_{H} and the corresponding H^+ -exponents by $-\log A_{\text{H}}$ or pA_{H} . By the symbol p_{H} we only denote the H^+ -exponents, which are calculated from the conventional values for E_0 , established by Sørensen and Clark. At the end of part IV, a survey of the values so far suggested for E_0 is given, and we shall there discuss in further detail the difference between pA_{H} and p_{H} .

6. On the basis of our measurements in HCl, in HCl + NaCl and in HCl + KCl we have calculated the expressions for the *individual hydrogen ion activity coefficients* in HCl, NaCl, and KCl. These expressions are valuable in the calculation of H^+ -concentrations in solutions with a known H^+ -activity or with measured hydrogen-electrode potentials.

7. In order to determine the dissociation constants of water, phosphoric acid, citric acid, and glycine, we have measured cells with alkaline solutions (part V), phosphate mixtures (part VI), with citrate mixtures (part VII), and with glycine mixtures (part VIII).

From these measurements were calculated, firstly the p_{H} values in the solutions investigated, secondly the dissociation constants, the ionic activity coefficients and heats of dissociation.

8. In the calculation of the dissociation constants, a distinction was made

between three different kinds of constants. Considering the dissociation of an acid HS, the dissociation constant K_0 can be defined as:

$$K_0 = \frac{A_H \cdot A_S}{A_{HS}} \quad (1)$$

(A_X = the activity of the molecules of kind X). According to its definition, the numerical value of this constant must be independent of the composition of the solution. This constant has been called the activity constant or the thermodynamic constant. We shall call it the *complete dissociation constant*.

The *concentration constant* is the quantity K_c defined by:

$$K_c = \frac{[H^+][S^-]}{[HS]} \quad (2)$$

($[X]$ = concentration (in mole per litre) of the molecules of kind X).

Finally, the *incomplete dissociation constant* K is defined by:

$$K = \frac{A_H \cdot [S^-]}{[HS]} \quad (3)$$

Hence, in the definition of the incomplete constant, the activity of the hydrogen ions and the molar concentrations of the other participants in the reaction are taken into account.

The concentration constant and the incomplete constant both change with the composition of the solution. By introducing the activity coefficient (f_x)

$$f_x = \frac{A_x}{[X]} \quad (4)$$

we get:

$$K_0 = K \frac{f_{S^-}}{f_{HS}} = K_c \frac{f_H f_{S^-}}{f_{HS}} \quad (5)$$

Since the activity coefficients, in accordance with the normally accepted definition of the activity scale, approach unity with increasing dilution, both K and K_c , according to equations 5, will approach K_0 with increasing dilution.

For the dissociation of water we define a complete dissociation constant by the equation:

$$K_0(H_2O) = \frac{A_H \cdot A_{OH^-}}{A_{H_2O}} \quad (6)$$

(A_{H_2O} = the activity of water in a scale, in which the activity of pure water is 1), a concentration constant by:

$$K_c(H_2O) = [H^+][OH^-] \quad (7)$$

and an incomplete dissociation constant by:

$$K(H_2O) = A_H[OH^-] \quad (8)$$

9. Table 1 comprises our values for the *complete dissociation constants*. As regards the expressions for the incomplete constants and for the concentration constants, we refer to the later chapters, in which we also give a comparison between our values and the results of other investigators.

Table 1. Values of $pK_0 = -\log K_0$. (K_0 = complete dissociation constant)

		0°	18°	25°	37°
Water		14.926	14.222	13.980	13.590
Phosphoric acid	1	—	2.120	2.161	2.232
—	2	—	7.227	7.207	7.165
—	3	—	12.465	12.325	12.180
Citric acid	1	—	3.087	3.057	3.042
—	2	—	4.769	4.759	4.747
—	3	—	6.398	6.400	6.424
Glycinium ion	{	1	2.420	2.347	2.332
(Amino acetic acid)		2	10.478	9.965	9.779
					2.276
					9.466

On the basis of these calculations, one obtains the following expressions for the dependence of pK_0 values upon temperature:

Water	$pK_0 = 14.926 - 0.0420t + 0.00016t^2$	(0° — 37°)
Phosphoric acid	$pK_0' = 2.120 + 0.0059(t - 18)$	(18° — 37°)
	$pK_0'' = 7.228 - 0.0033(t - 18)$	—
	$pK_0''' = 12.45 - 0.015(t - 18)$	—
Citric acid	$pK_0' = 3.081 - 0.0024(t - 18)$	—
	$pK_0'' = 4.769 - 0.0012(t - 18)$	—
	$pK_0''' = 6.395 + 0.0014(t - 18)$	—
Glycinium ion (Amino acetic acid)	$pK_0' = 2.420 - 0.0039t$	(0° — 37°)
	$pK_0'' = 10.478 - 0.0295t + 0.00006t^2$	—

11. The dependence of a dissociation constant upon the temperature permits the calculation of the corresponding *heat of dissociation* by means of the following equation:

$$Q = -RT^2 \frac{d \ln K}{dT} = 4.57 T^2 \frac{dpK}{dT} \quad (16)$$

If pK_0 values are inserted in this formula, one obtains heats of dissociation valid for infinitely dilute solutions. In this way the following values were found:

Table 4. Heats of dissociation in (infinitely) dilute solutions

Water	— 14.22 kcal	0° to 18°
—	— 13.73 -	18° to 37°
H ₃ PO ₄ 1. H ⁺	2.43 -	18° to 37°
— 2. H ⁺	— 1.35 -	—
— 3. H ⁺	— 6.20 -	—
Citric acid 1. H ⁺	— 1.02 -	18° to 37°
— 2. H ⁺	— 0.52 -	—
— 3. H ⁺	0.60 -	—
Glycinium ion 1. H ⁺	— 1.51 -	0° to 37°
— 2. H ⁺	— 10.57 -	—

If, however, the concentration constants are inserted in equations 16, one obtains the heats of dissociation for the salt solutions in question. In the case of water and phosphoric acid, the values calculated in this way can be compared with some figures obtained calorimetrically (comp. tables 5 and 6). It is, however, not permissible to identify the calculated and the experimental values, since the former represent differential, the latter integral values. On the other hand, these values can hardly be expected to deviate considerably from each other as long as both of them show only small deviations from the value which is valid for infinite dilution.

Table 5. Heats of neutralization in about 1/4 normal solution

	Observed by Wörmann	Calculated by Bj. and U.
9° NaOH + HCl	14.20 kcal	14.17 kcal
KOH + HCl	14.33 -	14.27 -
27.5° NaOH + HCl	13.19 -	13.58 -
KOH + HCl	13.41 -	13.53 -

Table 6. The three heats of dissociation of phosphoric acid in about 0.1 normal sodium phosphate buffer

	Calculated by Bj. and U. (18°—37°)	Thomsen's measurements (18°)
Q'	1.46 kcal	1.55 kcal
Q''	—1.11 -	—1.47 -
Q'''	—5.15 -	—4.27 -

12. Our measurements were completed a long time ago. The publication of the material has, however, been delayed by difficulties encountered in the theoretical treatment of the extensive material. During the period in which the measurements were performed, our knowledge of the properties of ionic activity has been greatly increased. Therefore, we have several times altered the form in which we wished to publish the experimental material, and at the present moment the circumstances are still such that we prefer to stress the experimental side of the investigation rather than the form of the theoretical interpretation of the results.

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