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THE DISSOCIATION CONSTANT  
OF THE ANILINIUM ION

BY

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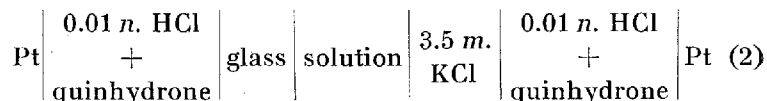
In this paper the dissociation constant of the anilinium ion

$$K = (\text{H}^+) (\text{An}) / (\text{AnH}^+), \quad (1)$$

where  $(\text{H}^+)$ ,  $(\text{An})$ , and  $(\text{AnH}^+)$  are the concentrations of hydrogen ions, aniline, and anilinium ions respectively, is measured electrometrically at different temperatures and salt concentrations.

Measurements were first attempted with the hydrogen electrode in aniline buffer solutions. Hydrogen was passed through a sintered glass filter into the solution, where it formed a large number of tiny bubbles. The e. m. f. was not, however, sufficiently reproducible. Changes as great as one millivolt were found when the current of hydrogen was made quicker or slower. Apparently a reaction takes place at the surface of the platinum electrode altering the composition of the solution in the neighbourhood of the electrode. It was therefore decided to use the glass electrode instead of the hydrogen electrode.

Cells of the following composition were measured



The "solution" is either hydrochloric acid of known hydrogen ion concentration or an aniline buffer solution.

The glass electrodes were of the type described by Mac INNES.<sup>1</sup> They consisted of a plane diaphragm of Corning glass no. 015 which formed the bottom of a piece of ordinary glass tubing whose upper part was covered with a layer of paraffin wax. Inside was a solution of quinhydrone in 0.01 normal hydrochloric acid into which dipped a bright platinum electrode.

As container for the solution under investigation a vessel was employed of the same kind as those used in this laboratory for calomel electrodes.<sup>2</sup> It was completely filled with the solution. Instead of the glass stopper, the glass electrode was placed in the opening, and fixed by means of a short piece of rubber tubing forming a belt round the tube of the glass electrode. The liquid-liquid junction was formed by sucking bridge solution half way up into the perpendicular part of the side tube. This is an easy way of obtaining a stable and reproducible diffusion potential.<sup>3</sup>

The other half cell, a quinhydrone electrode in 0.01 normal hydrochloric acid, was made in a vessel of the same kind as that used for the solution under investigation. The two vessels, and a test tube containing bridge solution into which they both dipped, were placed in an electrically regulated liquid paraffin thermostat.

As null instrument for the electrometric measurements a Lindemann electrometer was used. A sensitivity of 0.1 millivolt was obtained by carefully balancing the voltages

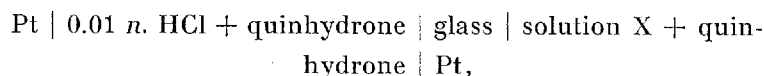
<sup>1</sup> MACINNES and DOLE, *J. Amer. Chem. Soc.* **52** (1930) 29. MACINNES and BELCHER, *J. Amer. Chem. Soc.* **53** (1931) 3315.

<sup>2</sup> LEWIS, BRIGHTON and SEBASTIAN, *J. Amer. Chem. Soc.* **39** (1917) 2245. J. K. GJALDBÆK, *Kgl. Danske Vid. Selsk., Math.-fys. Medd.* **5** (1924) no. 9.

<sup>3</sup> GUGGENHEIM, *J. Amer. Chem. Soc.* **52** (1930) 1315. UNMACK and GUGGENHEIM, *Kgl. Danske Vid. Selsk., Math.-fys. Medd.* **10** (1930) no. 8.

of the quadrants. The needle terminal of the electrometer was connected with the quinhydrone electrode inside the glass electrode. The potential of the other quinhydrone electrode was adjusted by means of a potentiometer until the needle showed no deflection when earthed. The accuracy of the measurements was  $\pm 0.1$  millivolt.

Before the actual measurements the glass electrode was tested by measuring the following combination

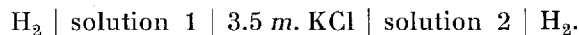


where solution X is 1) 0.01 normal hydrochloric acid, 2) a dilute acetate buffer solution of pH about 5, and 3) a dilute phosphate buffer solution of pH about 7. If we find that all the cells have the potential zero, we may conclude that the glass and quinhydrone electrodes have the same potential for all the solutions, that is, that the law of the reversible hydrogen electrode holds for the glass electrode in the interval examined. This was actually found to be the case with an accuracy of  $\pm 0.1$  millivolt, when a constant asymmetry potential of a few tenths of a millivolt was subtracted.

The aniline buffer solutions were freshly prepared for each day's measurements by mixing appropriate amounts of aniline and normal hydrochloric acid and diluting with water. These buffer solutions were in most cases further diluted with sodium chloride solution of the same ionic concentration. The aniline used was the middle fraction obtained by distillation *in vacuo* of KAHLBAUM's aniline for analytical purposes. Sodium chloride and hydrochloric acid for analytical purposes were used without further purifica-

ation. All the solutions were made from redistilled water. The quinhydrone solutions were renewed every day.

Cells of the type given in scheme 2 were measured at the three temperatures 14.8°, 25.0°, and 34.9°. The aniline buffer solution, which we may call solution 1, contained anilinium chloride and aniline (usually of nearly equal concentrations), and in addition sodium chloride. Within a series of measurements the concentrations of anilinium chloride and aniline were varied, while the total salt concentration  $s$  was kept constant by adding sodium chloride. A solution of known hydrogen ion concentration, which we may call solution 2, was always measured along with each series of aniline buffer solutions. Solution 2 was a mixture of hydrochloric acid (about 0.01 normal) and sodium chloride, generally of the same total salt concentration as solution 1. The difference  $E$  between the e. m. f. measured for solutions 1 and 2 does not contain the asymmetry potential of the glass electrode. We may consider  $E$  as the e. m. f. of the cell



According to the thermodynamic considerations of GUGGENHEIM<sup>1</sup> the e. m. f. of cells of this type may be written as a sum of three terms

$$E = E_{Ei} + E_D + E_S, \quad (4)$$

where  $E_{Ei}$  is the ideal electrode potential,  $E_D$  is the ideal diffusion potential, and  $E_S$  is the salt effect potential.  $E_S$  vanishes when both solution 1 and 2 are infinitely dilute.

If we use the abbreviation

<sup>1</sup> GUGGENHEIM, J. Phys. Chem, **34** (1930) 1758.

$$\varrho \equiv \frac{RT}{F \log e}, \quad (5)$$

the ideal electrode potential is

$$E_{El} = -\varrho \log \frac{(\text{H}^+)_1}{(\text{H}^+)_2}. \quad (6)$$

The ideal diffusion potential may be written

$$E_D = E_{1D} - E_{2D}, \quad (7)$$

where  $E_{1D}$  is the ideal diffusion potential of the junction solution 1 | 3.5 *m.* KCl, and  $E_{2D}$  that of the junction solution 2 | 3.5 *m.* KCl. For convenience we may write

$$E_{1D} \equiv \varrho \delta_1, \quad \text{and} \quad E_{2D} \equiv \varrho \delta_2. \quad (8)$$

The salt effect potential may be written

$$E_S = -\varrho \log \frac{f_1}{f_2}, \quad (9)$$

where  $f_1$  and  $f_2$  are characteristic of the combinations solution 1 | 3.5 *m.* KCl and solution 2 | 3.5 *m.* KCl respectively. They are generally called activity coefficients of the hydrogen ion, a misleading expression. Equation 9 defines only the relative values of  $f_1$  and  $f_2$ , not their absolute values. In the last part of this paper we shall discuss the question of an absolute definition.

From equations 4, 6, 7, 8, and 9 we obtain

$$-\log (\text{H}^+)_1 - \log \frac{f_1}{f_2} = \frac{E}{\varrho} - \delta_1 + \delta_2 - \log (\text{H}^+)_2.$$

If we introduce equation 1 we get

$$-\log K - \log \frac{f_1}{f_2} = \frac{E}{\varrho} - \delta_1 + \delta_2 - \log (\text{H}^+)_2 - \log \frac{(\text{An})}{(\text{AnH}^+)},$$

which equation may also be written as follows

$$-\log K - \log \frac{f_1}{f_{(\text{NaCl})_1}} = \frac{E}{\varrho} - \delta_1 + \delta_2 - \log (\text{H}^+)_2 - \log \frac{(\text{An})}{(\text{AnH}^+)} - \log \frac{f_2}{f_{(\text{NaCl})_1}}. \quad (10)$$

Here  $f_{(\text{NaCl})_1}$  is the value of  $f$  for a pure sodium chloride solution of the same ionic concentration as solution 1.

The ideal diffusion potential for the kind of junction used here may, according to GUGGENHEIM<sup>1</sup>, be calculated to a good degree of approximation from HENDERSON's formula.<sup>2</sup> Values of the ionic conductivities all corresponding to one and the same solution must be introduced into this formula.<sup>3</sup>

For the junction: electrode solution | 3.5 *m.* KCl, the formula may be written

$$\delta = \frac{3.5 (u_{\text{Cl}} - u_{\text{K}}) + \sum_{+} c_i u_i - \sum_{-} c_i u_i}{3.5 (u_{\text{Cl}} + u_{\text{K}}) - \sum_{+} c_i u_i - \sum_{-} c_i u_i} \log \frac{3.5 (u_{\text{Cl}} + u_{\text{K}})}{\sum_{+} c_i u_i + \sum_{-} c_i u_i}, \quad (11)$$

where  $c_i$  and  $u_i$  are respectively the concentration and conductivity of an ion  $i$ .  $\sum_{+}$  and  $\sum_{-}$  denote respectively summation over all positive and over all negative ions in the electrode solution.

In Table 1 values of  $\delta$  calculated from this formula are given for the junctions used in this paper. All the conductivities used for the calculation correspond to the electrode solution at 25°. If we make the sufficiently precise assumption that the ratio between the ionic conductivities

<sup>1</sup> GUGGENHEIM, J. Amer. Chem. Soc. **52** (1930) 1315.

<sup>2</sup> HENDERSON, Z. physik. Chem. **59** (1907) 118, **63** (1908) 325.

<sup>3</sup> GUGGENHEIM and UNMACK, Kgl. Danske Vid. Selsk., Math.-fys. Med. **10** (1931) no. 14, pag. 16.



is independent of the temperature from 15° to 35°, we may use the calculated values throughout the whole temperature interval. For hydrochloric acid and for solutions of sodium and potassium chloride we have used the conductivities given in the International Critical Tables, and the transference numbers determined by LONGSWORTH.<sup>1</sup> For mixtures of hydrochloric acid and sodium chloride we assume that the mixture law holds. For anilinium chloride we use the conductivities determined by SIDGWICK and WILSDON,<sup>2</sup> together with the assumption that the chloride ion has the same conductivity in equally concentrated solutions of anilinium chloride and potassium chloride.

The remaining term on the right hand side of equation 11, namely  $-\log \frac{f_2}{f_{(\text{NaCl})_i}}$ , is found from measurements with

Table 1.

Ideal diffusion correction  $\delta$  for the junction:  
solution of given composition | 3.5 *m.* KCl  
calculated from formula 11.

<i>c</i>	<i>c</i> molar AnHCl	<i>c</i> molar NaCl	0.001 <i>m.</i> HCl + ( <i>c</i> -0.001) <i>m.</i> NaCl	0.002 <i>m.</i> HCl + ( <i>c</i> -0.002) <i>m.</i> NaCl	0.005 <i>m.</i> HCl + ( <i>c</i> -0.005) <i>m.</i> NaCl	0.01 <i>m.</i> HCl + ( <i>c</i> -0.01) <i>m.</i> NaCl	<i>c</i> molar HCl
0.001	..	0.0688	..	..	..	..	0.0603
0.002	0.0637	0.0627	0.0580	..	..	..	0.0560
0.005	0.0562	0.0554	0.0539	0.0530	..	..	0.0524
0.01	0.0506	0.0501	0.0499	0.0489	0.0504	..	0.0525
0.02	0.0433	0.0436	0.0441	0.0446	0.0463	0.0492	0.0554
0.05	0.0317	0.0342	0.0350	0.0359	0.0383	0.0422	0.0691
0.10	0.0194	0.0250	0.0258	0.0267	0.0293	0.0334	0.0905
0.20	0.0025	0.0139	0.0148	0.0156	0.0180	0.0221	0.1265
0.21	..	..	0.0140	..	0.0172	0.0213	..
0.30	-0.0117	0.0057	..	..	..	0.0126	..

<sup>1</sup> LONGSWORTH, J. Amer. Chem. Soc. **54** (1932) 2741, **57** (1935) 1185.

<sup>2</sup> SIDGWICK and WILSDON, J. Chem. Soc. **99** (1911) 1118.

Table 2.  
 Electromotive force  $E$  at  $14.8^\circ$  of the cell  
 $\text{H}_2 \mid \text{solution 1} \mid 3.5 \text{ } m. \text{KCl} \mid \text{solution 2} \mid \text{H}_2$   
 measured by means of the glass electrode.

Solution 1			Solution 2		$E$ volts	$-\log \frac{f_2}{f_{(\text{NaCl})_2}}$	$-\log K - \log \frac{f_1}{f_{(\text{NaCl})_1}}$
(AnHCl)	(An)	(NaCl)	(HCl)	(NaCl)			
0.3025	0.3066	0.000	0.01025	0.290	0.1591	0.000	4.793
0.2017	0.2044	0.100	0.01025	0.290	0.1607	0.000	4.815
0.1008	0.1022	0.200	0.01025	0.290	0.1623	0.000	4.836
0.0504	0.0511	0.250	0.01025	0.290	0.1629	0.000	4.844
0.01891	0.01916	0.280	0.01025	0.290	0.1634	0.000	4.851
0.2513	0.0522	0.0505	0.01025	0.290	0.1215	0.000	4.819
0.0506	0.2530	0.2512	0.01025	0.290	0.2022	0.000	4.840
0.2017	0.2044	0.000	0.01025	0.190	0.1591	0.000	4.788
0.1008	0.1022	0.100	0.01025	0.190	0.1608	0.000	4.812
0.0390	0.0395	0.161	0.01025	0.190	0.1617	0.000	4.824
0.01833	0.01858	0.182	0.01025	0.190	0.1621	0.000	4.829
0.1012	0.1004	0.000	0.01025	0.090	0.1584	0.002	4.781
0.0506	0.0502	0.050	0.01025	0.090	0.1593	0.002	4.794
0.02024	0.02008	0.080	0.01025	0.090	0.1599	0.002	4.802
0.0506	0.0502	0.000	0.01025	0.040	0.1580	0.008	4.777
0.02024	0.02007	0.030	0.01025	0.040	0.1586	0.008	4.786
0.02024	0.02007	0.000	0.01024	0.010	0.1574	0.023	4.777
0.01012	0.01004	0.010	0.01024	0.010	0.1577	0.023	4.781
0.01012	0.01004	0.000	0.01024	0.010	0.1570	0.038	4.776
0.00405	0.00402	0.000	0.01024	0.010	0.1570	0.052	4.780

the hydrogen electrode in solutions of hydrochloric acid and sodium chloride, as described later in this paper.

We are now able to calculate  $-\log K - \log \frac{f_1}{f_{(\text{NaCl})_1}}$  from equation 10. The experimental data and the results of the calculation are given in the tables 2, 3, and 4. As can be seen from these tables  $-\log K - \log \frac{f_1}{f_{(\text{NaCl})_1}}$  varies even when

Table 3.  
 Electromotive force  $E$  at  $25.0^\circ$  of the cell  
 $\text{H}_2 \mid \text{solution 1} \mid 3.5 \text{ m. KCl} \mid \text{solution 2} \mid \text{H}_2$   
 measured by means of the glass electrode.

Solution 1			Solution 2		$E$ volts	$-\log \frac{f_2}{f_{(\text{NaCl})_h}}$	$-\log \frac{K}{f_1}$ $-\log f_{(\text{NaCl})_h}$
(AnHCl)	(An)	(NaCl)	(HCl)	(NaCl)			
0.3015	0.2965	0.000	0.01011	0.290	0.1522	0.000	4.600
0.2010	0.1977	0.100	0.01011	0.290	0.1537	0.000	4.619
0.1005	0.0988	0.200	0.01011	0.290	0.1554	0.000	4.642
0.0504	0.0496	0.250	0.01011	0.290	0.1561	0.000	4.651
0.01977	0.01944	0.280	0.01011	0.290	0.1566	0.000	4.657
0.2010	0.1977	0.000	0.01011	0.190	0.1524	0.000	4.598
0.1005	0.0988	0.100	0.01011	0.190	0.1540	0.000	4.620
0.0502	0.0494	0.150	0.01011	0.190	0.1548	0.000	4.630
0.01977	0.01944	0.180	0.01011	0.190	0.1553	0.000	4.636
0.1005	0.0988	0.000	0.01011	0.090	0.1522	0.002	4.592
0.1009	0.1026	0.000	0.01011	0.090	0.1532	0.002	4.594
0.1013	0.0995	0.000	0.01024	0.090	0.1526	0.002	4.590
0.0502	0.0494	0.050	0.01011	0.090	0.1531	0.002	4.604
0.05047	0.05133	0.050	0.01011	0.090	0.1541	0.002	4.606
0.05066	0.04974	0.050	0.01024	0.090	0.1535	0.002	4.605
0.01977	0.01944	0.080	0.01011	0.090	0.1538	0.002	4.613
0.02027	0.01990	0.080	0.01024	0.090	0.1540	0.002	4.611
0.08098	0.01974	0.0202	0.01011	0.090	0.1171	0.002	4.600
0.06751	0.03316	0.0337	0.01011	0.090	0.1354	0.002	4.606
0.05060	0.05000	0.0506	0.01011	0.090	0.1530	0.002	4.600
0.03371	0.06682	0.0675	0.01011	0.090	0.1711	0.002	4.603
0.02027	0.08021	0.0809	0.01011	0.090	0.1889	0.002	4.603
0.05047	0.05133	0.000	0.01011	0.040	0.1529	0.008	4.591
0.0506	0.0499	0.000	0.01011	0.040	0.1520	0.008	4.589
0.0506	0.0497	0.000	0.01025	0.040	0.1522	0.008	4.588
0.01990	0.02022	0.030	0.01011	0.040	0.1535	0.008	4.599
0.02020	0.01992	0.030	0.01011	0.040	0.1526	0.008	4.597
0.02027	0.01990	0.030	0.01025	0.040	0.1530	0.008	4.600
0.01990	0.02022	0.000	0.01011	0.010	0.1522	0.023	4.589
0.02020	0.01992	0.000	0.01011	0.010	0.1516	0.023	4.592
0.02021	0.01999	0.000	0.01011	0.010	0.1513	0.023	4.586

Table 3 (continued).

Solution 1			Solution 2		$E$ volts	$-\log \frac{f_2}{f_{(\text{NaCl})_2}}$	$-\log K$ $-\log \frac{f_1}{f_{(\text{NaCl})_1}}$
(AnHCl)	(An)	(NaCl)	(HCl)	(NaCl)			
0.02052	0.02012	0.000	0.01025	0.010	0.1516	0.023	4.586
0.00998	0.00984	0.010	0.01011	0.010	0.1520	0.023	4.598
0.01026	0.01006	0.010	0.01025	0.010	0.1521	0.023	4.593
0.00998	0.00984	0.000	0.01011	0.040	0.1509	0.044	4.586
0.01011	0.01000	0.000	0.01011	0.010	0.1512	0.038	4.591
0.01026	0.01006	0.000	0.01025	0.010	0.1513	0.038	4.590
0.00498	0.00493	0.000	0.01011	0.010	0.1511	0.049	4.592
0.00405	0.00399	0.000	0.01011	0.040	0.1513	0.058	4.596
0.00410	0.00402	0.000	0.01025	0.010	0.1512	0.052	4.592
0.00200	0.00200	0.000	0.01011	0.010	0.1516	0.060	4.591

the total salt concentration  $s$  is constant. Unfortunately, it is impossible to decide from measurements of this kind how the variation is distributed over the two terms. It is therefore in principle impossible to determine the dissociation constant  $K$  of an acid in its buffer solution by means of electrometric measurements of cells with liquid-liquid junctions without making an arbitrary assumption concerning the salt effect potential. However, it is possible, without making any such assumption, to find  $K$  for a sodium chloride solution containing only an infinitesimal amount of anilinium chloride and aniline. We plot  $-\log K - \log \frac{f_1}{f_{(\text{NaCl})_1}}$  against the concentration of anilinium chloride for the solutions in which (AnHCl) is approximately equal to (An). In Fig. 1 we have drawn straight lines through points corresponding to the same total salt concentration  $s$ . By means of the straight lines we extrapolate to (AnHCl) = 0, that is, to  $s$  molar sodium chloride solution. The ordinate is  $-\log K$  for the sodium chloride solution, because for this solution  $f_1 = f_{(\text{NaCl})_1}$ . This computation includes

Table 4.  
 Electromotive force  $E$  at  $34.9^\circ$  of the cell  
 $\text{H}_2$  | solution 1 | 3.5  $m.$  KCl | solution 2 |  $\text{H}_2$   
 measured by means of the glass electrode.

Solution 1			Solution 2		$E$ volts	$-\log \frac{f_2}{f_{(\text{NaCl})_1}}$	$-\log \frac{K}{f_1}$ $-\log f_{(\text{NaCl})_1}$
(AnHCl)	(An)	(NaCl)	(HCl)	(NaCl)			
0.3028	0.3034	0.000	0.01024	0.290	0.1477	0.000	4.430
0.2018	0.2022	0.100	0.01024	0.290	0.1492	0.000	4.449
0.1009	0.1011	0.200	0.01024	0.290	0.1508	0.000	4.469
0.0501	0.0502	0.250	0.01024	0.290	0.1516	0.000	4.478
0.01442	0.01444	0.286	0.01024	0.290	0.1521	0.000	4.484
0.2513	0.0522	0.0505	0.01024	0.290	0.1078	0.000	4.456
0.0506	0.2530	0.2512	0.01024	0.290	0.1936	0.000	4.468
0.2018	0.2022	0.000	0.01025	0.190	0.1479	0.000	4.428
0.1006	0.0991	0.101	0.01025	0.190	0.1492	0.000	4.451
0.0505	0.0498	0.150	0.01025	0.190	0.1500	0.000	4.460
0.0203	0.0200	0.180	0.01025	0.190	0.1505	0.000	4.466
0.1010	0.0996	0.000	0.01025	0.090	0.1470	0.003	4.418
0.0505	0.0498	0.050	0.01025	0.090	0.1481	0.003	4.432
0.0203	0.0200	0.080	0.01025	0.090	0.1488	0.003	4.442
0.08116	0.02110	0.0202	0.01024	0.090	0.1129	0.003	4.434
0.06750	0.03473	0.0337	0.01024	0.090	0.1306	0.003	4.429
0.05062	0.05158	0.0506	0.01024	0.090	0.1489	0.003	4.432
0.03375	0.06842	0.0675	0.01024	0.090	0.1670	0.003	4.428
0.02025	0.08189	0.0810	0.01024	0.090	0.1857	0.003	4.434
0.05050	0.04978	0.000	0.01025	0.040	0.1467	0.011	4.417
0.02020	0.01991	0.030	0.01025	0.040	0.1476	0.011	4.430
0.02050	0.01861	0.000	0.01025	0.010	0.1443	0.021	4.418
0.01025	0.00930	0.010	0.01025	0.010	0.1449	0.021	4.425
0.01025	0.01002	0.000	0.01025	0.010	0.1462	0.037	4.424
0.00512	0.00501	0.000	0.01025	0.010	0.1461	0.048	4.424
0.00202	0.00197	0.000	0.01025	0.010	0.1466	0.059	4.426

two extrapolations to pure sodium chloride solution, 1)  
 from mixtures of aniline buffer solution and sodium chlo-

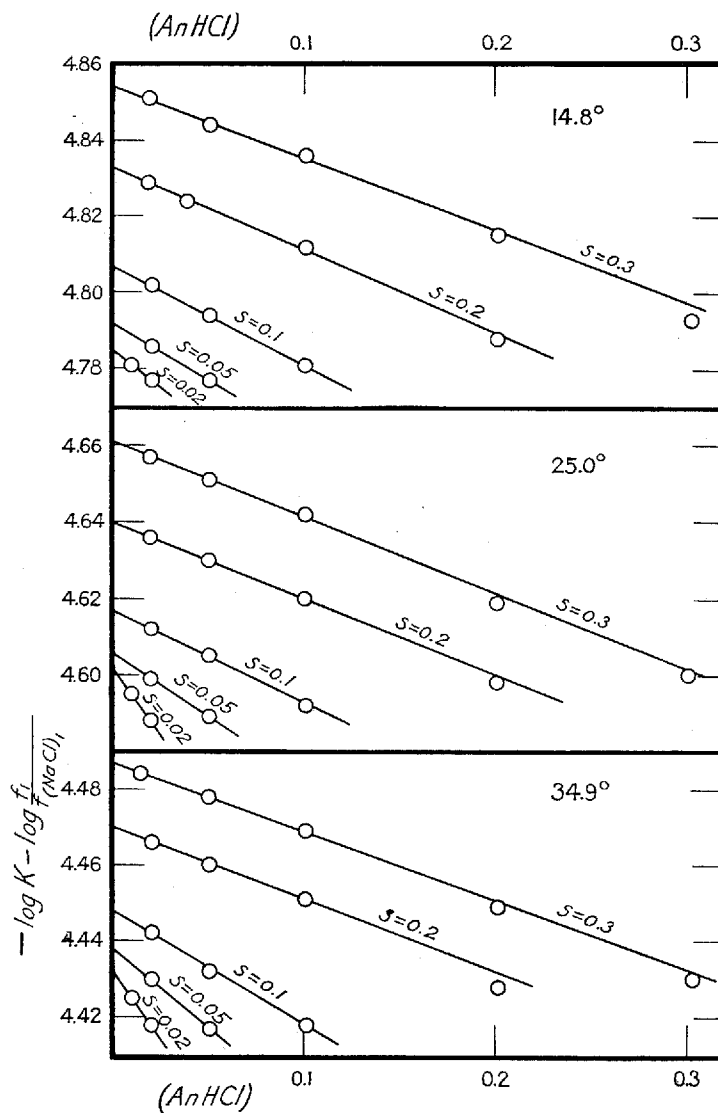
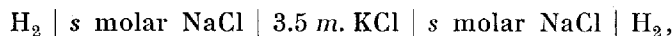


Fig. 1. The dissociation constant in mixtures of aniline buffer solution and sodium chloride of total salt concentration  $s$ . Extrapolation to pure sodium chloride solution.

ride solution, and 2) from mixtures of hydrochloric acid and sodium chloride solution (see later), that is, we have extrapolated to a cell of the composition



for which both  $E_D$  and  $E_S$  vanish. The dissociation constant of the anilinium ion in pure sodium chloride solutions found in this way is therefore independent, not only of the salt effect potential, but also of the special way in which we have corrected for the ideal diffusion potential.

If we wish to find  $K$  for finite concentrations of the buffer constituents we must, as already pointed out, make an assumption as to the way in which the variation of  $-\log K - \log \frac{f_1}{f_{(\text{NaCl})_s}}$ , within a series of buffer solutions of constant  $s$ , is distributed over the two terms. The simplest assumption is that either  $-\log K$  or  $-\log \frac{f_1}{f_{(\text{NaCl})_s}}$  is constant and has the same value as that of the pure  $s$  molar sodium chloride solution. We prefer the former alternative because the influence of salts on  $f_1$ , as will be seen in the last part of this paper, is of a very specific nature.

In Fig. 2 the values of  $-\log K$  for sodium chloride solutions are plotted against the concentration. For each temperature the points fall on a straight line corresponding to the following expressions for the dissociation constant  $K$  of the anilinium ion in an  $s$  molar sodium chloride solution ( $s < 0.3$ ):

$$\left. \begin{array}{l} \text{at } 34.9^\circ \quad -\log K = 4.428 + 0.20 s \\ \text{at } 25.0^\circ \quad -\log K = 4.596 + 0.22 s \\ \text{at } 14.8^\circ \quad -\log K = 4.780 + 0.26 s. \end{array} \right\} \quad (12)$$

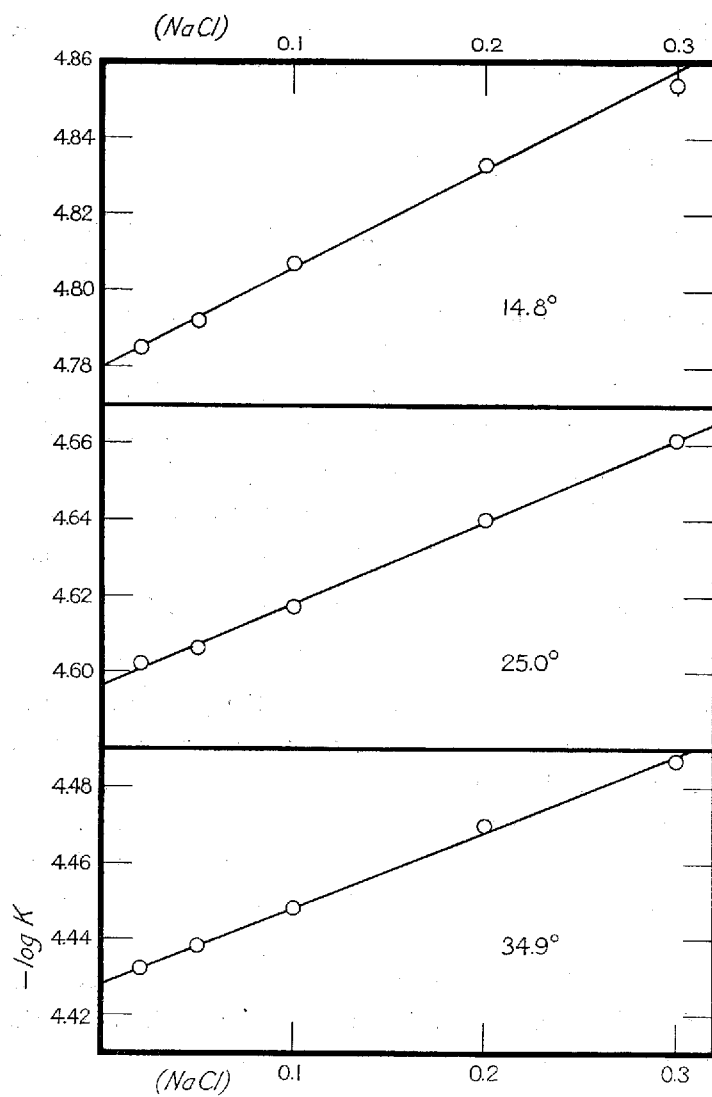


Fig. 2. The dissociation constant of the anilinium ion in sodium chloride solutions.



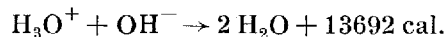
By setting  $s = 0$  we find  $K^0$ , the dissociation constant at infinite dilution. If we plot  $-\log K^0$  against  $\frac{1}{T}$ , the reciprocal of the absolute temperature, we get the points indicated by circles in Fig. 3. They fall on a straight line of equation

$$-\log K^0 = 1.553 \frac{10^3}{T} - 0.614. \quad (13)$$

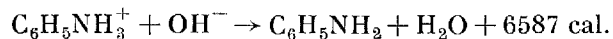
From the slope we find the heat of dissociation of the anilinium ion at infinite dilution



In order to find the heat of neutralization of the anilinium ion we combine this result with the heat of neutralization of the hydroxonium ion



found by HARNED and HAMER<sup>1</sup> for infinite dilution at 20° by electrometric measurements of cells without liquid-liquid junction. We thus find



We may compare this value with a calorimetric determination by THOMSEN.<sup>2</sup> He found that 6450 cal./equiv. are evolved when approximately 0.3 normal solutions of anilinium sulphate and sodium hydroxide are mixed at about 18°.

The dependence of  $K^0$  on the temperature may also be expressed by the following equation which is more convenient for interpolation than equation 13

<sup>1</sup> HARNED and HAMER, J. Amer. Chem. Soc. 55 (1933) 2194.

<sup>2</sup> THOMSEN, Thermochemische Untersuchungen I (1882) 408.

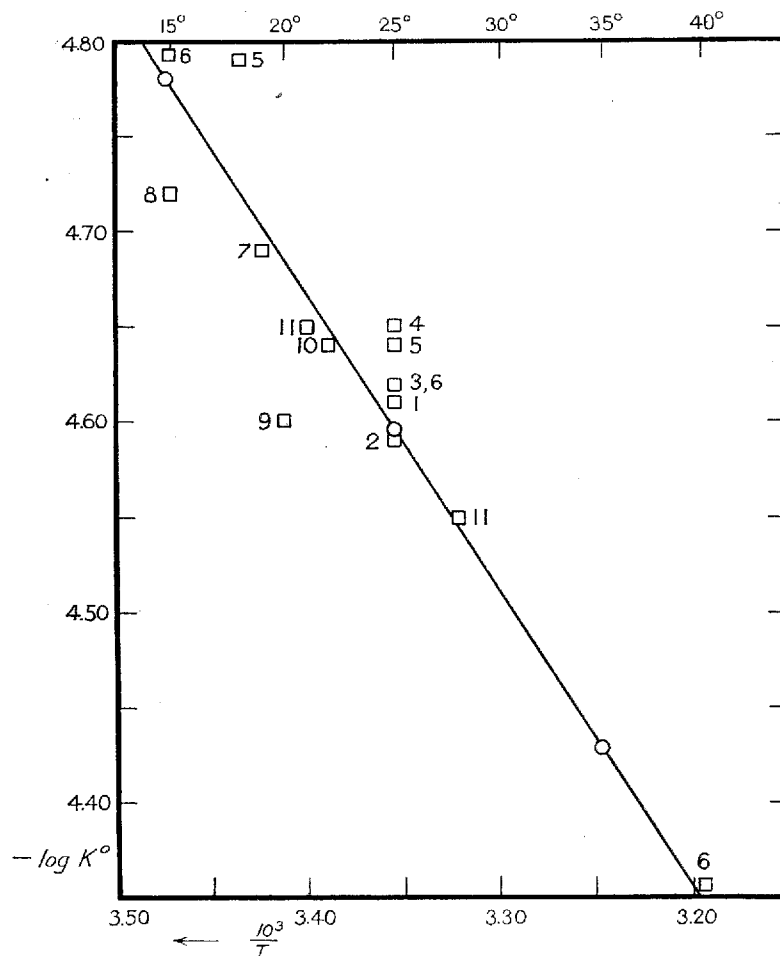


Fig. 3. The dissociation constant of the anilinium ion. Circles, this paper.  
Squares, other determinations.

<sup>1</sup> BREDIG, conductivity of anilinium chloride solutions. <sup>2, 8</sup> LÖWENHERZ, solubility of cinnamic acid (<sup>2</sup>) and of p-nitrobenzoic acid (<sup>8</sup>) in solutions of aniline, recalculated. <sup>4</sup> FARMER and WARTH, partition equilibria between benzene and aqueous solutions of anilinium chloride. <sup>5</sup> DENISON and STEELE, a special conductivity method. <sup>6</sup> LUNDÉN, conductivity of anilinium chloride solutions. <sup>7, 8</sup> BRØNSTED and DUUS, hydrogen electrode (<sup>7</sup>) and catalysis (<sup>8</sup>). <sup>9</sup> HAHN and KLOCKMANN, potentiometric titration, hydrogen electrode. <sup>10</sup> FLEXSER, HAMMETT and DINGWALL, ultraviolet spectrophotometry. <sup>11</sup> HALL and SPRINKLE, hydrogen electrode.

<sup>1</sup> Z. physik. Chem. 18 (1894) 322. <sup>2, 8</sup> *ibid.* 25 (1898) 394. <sup>4</sup> J. Chem. Soc. 85 (1904) 1713. <sup>5</sup> *ibid.* 89 (1906) 999. <sup>6</sup> Medd. från Vet.-Akad:s Nobelinstitut 1 (1907) no. 7. <sup>7, 8</sup> Z. physik. Chem. 117 (1925) 299. <sup>9</sup> *ibid.* A 146 (1930) 373. <sup>10</sup> J. Amer. Chem. Soc. 57 (1935) 2103. <sup>11</sup> *ibid.* 54 (1932) 3469.

$$-\log K^0 = 4.596 - 0.0175(t - 25) + 0.00005(t - 25)^2 \quad (14)$$

Here  $t$  is the temperature in degrees centigrade.

In Fig. 3 we have plotted both the determinations in this paper (circles) and those of other investigators (squares). The numbers refer to the list under the figure. The determinations of LÖWENHERZ have been recalculated (Table 5). He determined the solubility  $s$  at  $25^\circ$  of a sparingly soluble acid HS (dissociation constant  $K_1$ ) in  $b$  molar aniline. We assume that the concentration of the undissociated form of the sparingly soluble acid is the same ( $s_0$ ) in all the solutions.  $s_0$  is calculated from the solubility in pure water and  $K_1$ . The dissociation constant ratio is given by the equation

Table 5.

Recalculation of LÖWENHERZ's determination of the dissociation constant of the anilinium ion at  $25^\circ$ .

$b$	Cinnamic Acid $K_1^0 = 3.8 \times 10^{-5}$ * $s_0 = 0.00297$		p-Nitrobenzoic Acid $K_1^0 = 4.0 \times 10^{-4}$ ** $s_0 = 0.00100$	
	$s$	$-\log \frac{K^0}{K_1^0}$	$s$	$-\log \frac{K^0}{K_1^0}$
0.000	0.00331	..	0.00164	..
0.005	0.00610	0.175	..	..
0.010	0.00804	0.169	0.00841	1.226
0.020	0.01100	0.167	0.01379	1.239
0.040	0.01543	0.165	0.02172	1.201
0.080	0.0222	0.170	0.0347	1.204
	Mean... 0.169		Mean... 1.218	
	$-\log K^0 = 4.59$		$-\log K^0 = 4.62$	

\* LARSSON, Z. anorg. Chem. **155** (1926) 247.

\*\* OSTWALD, Z. physik. Chem. **3** (1889) 259.

$$\frac{K}{K_1} = \frac{(\text{An})(\text{HS})}{(\text{AnH}^+)(\text{S}^-)} = \frac{[b - (s - s_0) + (\text{H}^+)] s_0}{[s - s_0 - (\text{H}^+)] (s - s_0)}$$

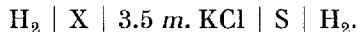
In Table 5 are given the values of

$$-\log \frac{K^0}{K_1^0} = -\log \frac{K}{K_1} - 2\alpha \sqrt{s - s_0},$$

where  $\alpha = 0.504$  is the Debye-Hückel coefficient. They are approximately constant for each of the two acids. From the average value and the value of  $K_1^0$  given at the top of the table we find the value of  $-\log K^0$  given at the bottom.

#### The activity coefficient of the hydrogen ion in solutions of hydrochloric acid and sodium chloride.

In order to find the last term of equation 10, cells of the following composition were measured with the hydrogen electrode



Here X denotes a solution containing hydrochloric acid and (in most cases) sodium chloride at known concentrations, while S is always 0.01011 normal hydrochloric acid. We calculate the ideal diffusion potential from HENDERSON'S formula (Table 1) and compute

$$-\log \frac{f_{(\text{X})}}{f_{(\text{S})}} = \frac{E}{\varrho} - \delta_{\text{X}} + \delta_{\text{S}} + \log (\text{H}^+)_{\text{X}} - \log 0.01011, \quad (15)$$

where  $f_{(\text{X})}$  and  $f_{(\text{S})}$  are the so called activity coefficients of the hydrogen ion characteristic of the combination X | 3.5 m. KCl and S | 3.5 m. KCl, respectively.

Table 6 contains the experimental data and the results of the computation. The composition of solution X is given in the two first columns. The next two columns give the e.m.f. measured at 25.0° and 34.9°, respectively. The values of  $-\log \frac{f_{(X)}}{f_{(S)}}$  calculated from the experimental data by means of equation (15) are given in last two columns. The dif-

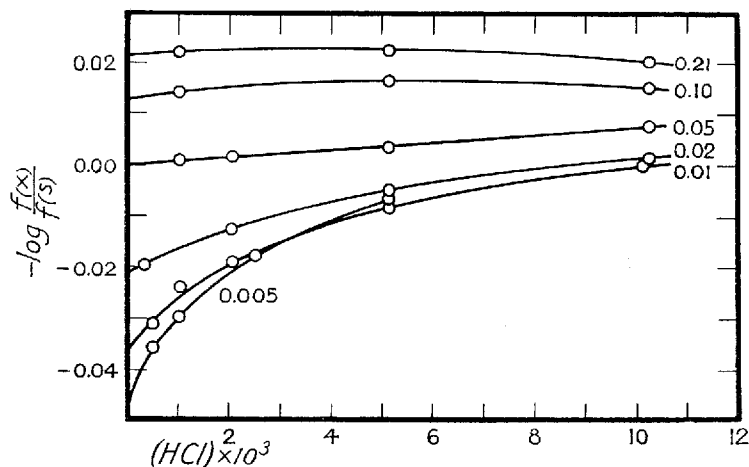


Fig. 4.  $-\log \frac{f_{(X)}}{f_{(S)}}$  in mixtures of hydrochloric acid and sodium chloride at 25°. The corresponding total salt concentrations are written beside the curves.

ference between the values at the two temperatures is hardly greater than the experimental error. In Fig. 4 and 5  $-\log \frac{f_{(X)}}{f_{(S)}}$  has been plotted against the concentration of hydrochloric acid, and curves drawn through points corresponding to the same total salt concentration  $s$ . In this way an attempt has been made to extrapolate to  $X =$  pure  $s$  molar sodium chloride solution. When  $s \geq 0.02$  the extrapolation seems safe. When  $s = 0.01$ , and even more so when  $s = 0.005$ , the extrapolation is less accurate owing

to the greater curvature. The values of  $-\log \frac{f(x)}{f(s)}$  for sodium chloride solutions found in this way are also given in Table 6.

The last term of equation 10 is now found from Table 6 by writing  $-\log \frac{f_2}{f_{(\text{NaCl})_1}} = -\log \frac{f_2}{f(s)} - \left( -\log \frac{f_{(\text{NaCl})_1}}{f(s)} \right)$ . At  $15^\circ$  we have used the values found for  $25^\circ$ .

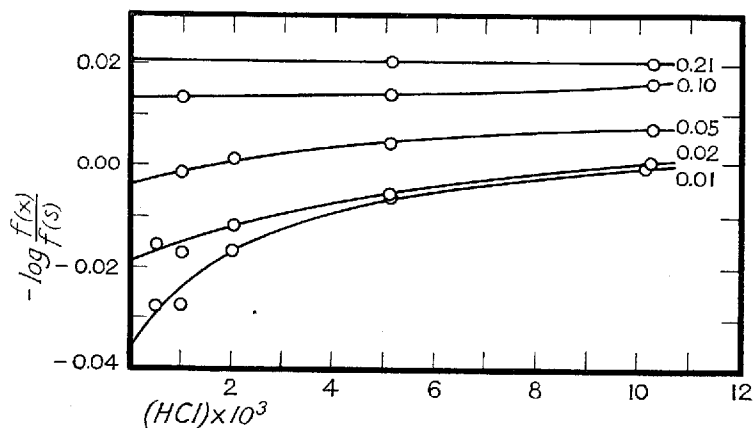


Fig. 5.  $-\log \frac{f(x)}{f(s)}$  in mixtures of hydrochloric acid and sodium chloride at  $35^\circ$ . The corresponding total salt concentrations are written beside the curves.

In this paper we have given only the ratios between values of  $f$  for different solutions. We have not followed the usual procedure of defining a standard state relative to which  $f$  is measured. From a theoretical point of view it is most natural to set  $f$  as unity for an infinitely dilute electrode solution. The practical availability of this definition depends on an extrapolation to infinite dilution, and here we meet difficulties. As pointed out by GUGGENHEIM<sup>1</sup>

<sup>1</sup> GUGGENHEIM, J. Phys. Chem. **34** (1930) 1758. UNMACK and GUGGENHEIM, Kgl. Danske Vid. Selsk., Math.-fys. Med. **10** (1930) no. 8.

Table 6.

Measurements of the cell

$\text{H}_2 \mid \text{Solution X} \mid 3.5 \text{ m. KCl} \mid \text{Solution S} \mid \text{H}_2$ ,  
 where Solution X has the composition given in  
 the table, while Solution S is always 0.01011  
 normal hydrochloric acid.

Solution X		$E \times 10^3$ 25.0°	$E \times 10^3$ 34.9°	$-\log \frac{f_{(X)}}{f_{(S)}}$ 25.0°	$-\log \frac{f_{(X)}}{f_{(S)}}$ 34.9°
(HCl)	(NaCl)				
0.01025	0.200	-0.97	-1.00	0.021	0.021
0.005125	0.205	16.72	17.15	0.023	0.021
0.001038	0.209	57.52	..	0.022	..
..	0.210	..	..	0.021*)	0.021**)
0.01025	0.090	-0.56	-0.53	0.015	0.016
0.005125	0.095	17.07	17.48	0.017	0.014
0.001030	0.099	57.94	59.80	0.014	0.013
..	0.100	..	..	0.013*)	0.013**)
0.01025	0.040	-0.50	-0.52	0.008	0.008
0.005125	0.045	16.83	17.45	0.004	0.005
0.002052	0.048	40.10	41.40	0.002	0.002
0.001029	0.049	57.7	59.50	0.001	-0.001
..	0.050	..	..	0.000*)	-0.003**)
0.01025	0.0102	-0.45	-0.48	0.002	0.001
0.005125	0.0152	16.80	17.32	-0.005	-0.005
0.002050	0.0182	39.78	41.14	-0.012	-0.012
0.001029	0.0191	..	59.10	..	-0.017
0.0005133	0.0197	..	77.64	..	-0.015
0.0003451	0.0202	85.1	..	-0.019	..
..	0.0203	..	..	-0.021*)	-0.019**)
0.01011	0.000	0	0	0.000	0.000
0.005055	0.0051	17.20	17.90	-0.008	-0.006
0.002022	0.0081	40.02	41.48	-0.019	-0.017
0.001016	0.0092	57.46	59.15	-0.024	-0.027
0.0005072	0.0096	74.90	77.60	-0.031	-0.027
..	0.0101	..	..	-0.036*)	-0.036**)

\*) By graphical extrapolation (Fig. 4).

\*\*) By graphical extrapolation (Fig. 5).

Table 6 (continued).

Solution X		$E \times 10^3$	$E \times 10^3$	$-\log \frac{f^{(X)}}{f^{(S)}}$	$-\log \frac{f^{(X)}}{f^{(S)}}$
(HCl)	(NaCl)	25.0°	34.9°	25.0°	34.9°
0.005055	0.0000	17.40	..	-0.007	..
0.002528	0.0025	34.60	..	-0.018	..
0.001016	0.0040	57.37	..	-0.029	..
0.000507	0.0045	74.88	..	-0.036	..
..	0.0050	..	..	-0.047*)	..
0.1010	..	-56.78	-58.61	0.002	0.002
0.05050	..	-39.72	-41.10	0.010	0.009
0.02030	..	-17.24	-17.88	0.008	0.007
0.01011	..	0	0	0.000	0.000
0.005055	..	17.40	17.88	-0.007	-0.008
0.002030	..	40.18	41.73	-0.021	-0.018
0.001020	..	57.75	60.27	-0.028	-0.018
0.000508	..	75.45	78.86	-0.040	-0.025

\*) By graphical extrapolation (Fig. 4).

$f$  is a function of the mean activity coefficients of all the salts and the transference numbers of all the ions in the electrode solution, throughout the transition layer and in the bridge solution. We have therefore no reason to believe that  $f$  follows the laws holding for the real activity coefficients of the salts. In spite of this, it is not unusual to extrapolate to infinite dilution by means of DEBYE-HÜCKEL'S law in the form  $-\log f = \alpha\sqrt{s} - \beta s$ , where  $s$  is the salt concentration,  $\alpha$  is the DEBYE-HÜCKEL coefficient (0.504 at 25° for a univalent ion), and  $\beta$  is a constant characteristic of the salt in the solution. From a treatment of the data in Table 6 we shall see that this procedure may give a meaningless result.

At the end of Table 6 are given the results of measurements in hydrochloric acid of different concentration. In



Fig. 6 we have plotted  $-\log \frac{f_{(X)}}{f_{(S)}} - 0.504\sqrt{s}$  against  $s$ , both for  $X =$  hydrochloric acid (open circles) and for  $X =$  sodium chloride solutions (solid circles). Only the results at  $25^\circ$  have been used. The straight lines drawn in the figure

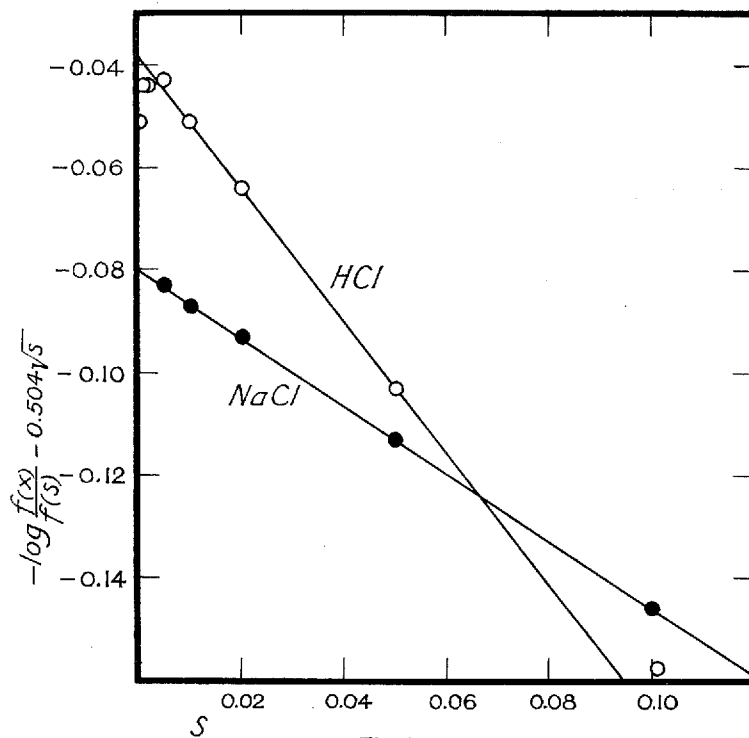


Fig. 6.

fit well to each set of points. Only for the most dilute solutions of hydrochloric acid are there considerable deviations, but here the experimental accuracy is smaller. If we determine  $-\log \frac{f_{(X)}}{f_{(S)}}$  at infinite dilution from the straight line through the points for hydrochloric acid we get  $-0.038$ , while we get  $-0.080$  when we extrapolate from the points for sodium chloride, that is, we find that  $-\log f$

for a 0.01 normal hydrochloric acid is 0.038, when we use the results for hydrochloric acid, and 0.080, when we use those for sodium chloride. Of course, the curves for sodium chloride and hydrochloric acid solutions must approach each other in more dilute solution. However, even for the most dilute solutions used here, where we might expect DEBYE-HÜCKEL's law to hold to a good approximation for the mean activity coefficients, the difference between the values of  $f$  in sodium chloride solution and hydrochloric acid is very considerable. According to GUGGENHEIM this individual effect is closely connected with the deviation from 0.5 of the transference numbers of sodium chloride and hydrochloric acid. For these electrolytes the transference numbers of the cations are respectively 0.396 and 0.821 at 25° and infinite dilution. The correct value for the extrapolation is therefore probably between those found in Fig. 6 for sodium chloride and hydrochloric acid, but nearer the former than the latter. However, for practical purposes it is of no use making an accurate extrapolation to infinite dilution. Instead of an infinitely dilute solution we may choose any other standard state. The determinations of  $f$  in the literature are all based on such conventional standard states, although they have always been chosen in such a way that  $f$  is about unity in infinitely dilute solution. A convention of this kind is included in SØRENSEN's<sup>1</sup> definition of  $\text{pH} = -\log [(\text{H}^+) f]$ . BJERRUM and UNMACK<sup>2</sup> use another convention, based partly on an extrapolation of the relative values for sodium chloride solutions in a similar way to that shown in Fig. 6.

<sup>1</sup> SØRENSEN, *Compt. rend. trav. lab. Carlsberg* 8 (1909) no. 1.

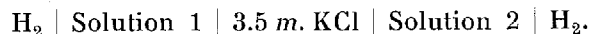
<sup>2</sup> BJERRUM and UNMACK, *Kgl. Danske Vid. Selsk., Math.-fys. Med.* 9 (1929) no. 1.

Finally GUGGENHEIM and SCHINDLER<sup>1</sup> have suggested a definition chosen in such a way that  $f$  agrees as well as possible with the mean activity coefficients of univalent electrolytes at concentrations generally used in experimental work.

I wish to express my thanks to the head of the laboratory, Professor NIELS BJERRUM, for his kind interest in my work.

### Summary.

By measurements with the glass electrode at 14.8°, 25.0°, and 34.9° we have determined the e. m. f. of cells of the composition



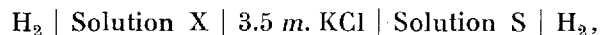
Solution 1 contains aniline, anilinium chloride and sodium chloride. Solution 2 contains hydrochloric acid and sodium chloride (Tables 2—4).

After subtraction of the ideal diffusion potential (calculated from HENDERSON'S formula), we compute  $-\log K - \log \frac{f_1}{f_2}$ , where  $K$  is the dissociation constant of the anilinium ion in solution 1, while  $f_1$  and  $f_2$  are the so called activity coefficients of the hydrogen ion in solutions 1 and 2. We eliminate  $-\log \frac{f_1}{f_2}$  by the following two extrapolations, 1) of solution 1 to an  $s$  molar sodium chloride solution containing a negligible amount of aniline buffer, and 2) of solution 2 to an  $s$  molar sodium chloride solution containing a negligible amount of hydrochloric acid. We thus find  $K$  for the anilinium ion in sodium chloride solutions (Fig. 2 and formulae 12). By linear extrapolation

<sup>1</sup> GUGGENHEIM and SCHINDLER, J. Phys. Chem. **38** (1934) 533.

to  $s = 0$  we find  $K^0$ , the dissociation constant of the anilinium ion at infinite dilution. From the variation with temperature (Fig. 3 and formulae 13 and 14) we find the heat of dissociation of the anilinium ion 7100 cal./mole.

In order to make the above extrapolation (2) we have measured cells of the following composition with the hydrogen electrode:



where X is a mixture of hydrochloric acid and sodium chloride solution, while S is 0.01011 *n.* HCl (Table 6). From the measurements we find  $-\log \frac{f_{(X)}}{f_{(S)}}$ , which we extrapolate to X = pure sodium chloride solution (Fig. 4 and 5).

In the last part of the paper we have discussed the definition of the single values of  $f$ . It has been shown from the measurements in this paper that the usual procedure of extrapolating to infinite dilution by means of DEBYE-HÜCKEL'S law for the real activity coefficients may give meaningless results.

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October 1936.