No correction was made for the small volume of the click-gage and capillary tubing which were out of the thermostat and at approximately room temperature. This volume was about one cubic centimeter and the correction due to this dead space would make a negligible difference in log K below 450°K. but may be as much as -1% at temperatures around 500°K.

When the results of the experiments are combined with specific heat data, the following expression for the standard change in heat content and free energy accompanying the reaction $2NO(g) + Br_2(g) = 2NOBr(g)$ are obtained

NO(g),[4] $C_p = 7.922 - 0.00441\,T + 6.30 \times 10^{-6}T^2$
Br_2(g),[5] $C_p = 7.710 + 0.00415\,T - 3.7 \times 10^{-6}T^2$
NOBr(g),[6] $C_p = 5.07 + 0.0163\,T - 12.9 \times 10^{-6}T^2$

Whence

$$\Delta C_p = -13.41 + 0.0372\,T - 34.7 \times 10^{-6}T^2$$
$$\Delta H^0 = -8780 - 13.14\,T + 0.0186T^2 - 11.6 \times 10^{-6}T^3$$
$$\Delta F^0 = -8780 + 30.88\,T \log_{10}T - 51.26T - 0.0186T^2 + 5.8 \times 10^{-6}T^3$$

These expressions are valid in the temperature range 250–600°K.

Directly from the experimental curve and independent of specific heat data, we obtain

$$\Delta H^0_{298.1} = -11{,}430 \pm 60 \text{ cal.}$$
$$\Delta F^0_{298.1} = -2790 \pm 30 \text{ cal.}$$
$$\Delta S^0_{298.1} = -29.0 \pm 0.3 \text{ cal./deg.}$$

This last value, combined with the known entropies of bromine[7] and nitric oxide,[4] gives for the standard virtual entropy of NOBr, $S^0_{298.1} = 65.2 \pm 0.3$ cal./deg. When the free energy change for the reaction studied is combined with that for the formation of nitric oxide, 20,650 cal.,[8] the standard free energy of formation of nitrosyl bromide gas from the elements in their standard states at 25° becomes 19,260 cal.

Summary

The equilibrium in the reaction $2NO(g) + Br_2(g) = NOBr(g)$ has been measured in the temperature range from 273.1 to 520°K. From the results of the measurements the following thermodynamic equations have been derived for the reaction

$$\Delta H^0 = -8780 - 13.41\,T + 0.0186\,T^2 - 11.6 \times 10^{-6}T^3$$
$$\Delta F^0 = -8780 + 30.88\,T \log_{10} T - 51.26\,T - 0.0186\,T^2 + 5.8 \times 10^{-6}T^3$$

At 25° the free energy of formation of NOBr(g) from the elements is 19,260 cal. The virtual entropy of NOBr(g) at 25° and one atmosphere is 65.2 ± 0.3 cal./deg.

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[4] Constructed from the data of Johnston and Chapman, THIS JOURNAL, **55**, 153 (1933).

[5] Constructed from the data of Gordon and Barnes, *J. Chem. Phys.*, **1**, 694 (1933).

[6] In the absence of experimental data for nitrosyl bromide the equation given by Eastman, Bureau of Mines, Technical Paper, 1929, for the specific heat of sulfur dioxide was used.

[7] Brown, *Phys. Rev.*, **42**, 355 (1932).

[8] Giauque and Clayton, THIS JOURNAL, **55**, 4875 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constants of Benzoic Acid and of the Three Monochlorobenzoic Acids, at 25°, from Conductance Measurements[1]

BY BLAIR SAXTON AND HARRY F. MEIER

The ionization constants were determined by the method and technique described in an earlier paper[2] except for the following changes.

All measurements were made with the bridge described by Dike.[3]

A "flask cell" similar to cell B but constructed entirely of silica with the exception of two small Jena G 20–silica graded seals, used in inserting the electrode supports, was used in measuring the conductances of the acids. Cell B was used in measuring the conductances of the sodium salts of the acids. Purified nitrogen, saturated with water vapor, was substituted for air in the removal of carbon dioxide. The water was from the Barnstead "Conductivity Water Still." When distilled directly into the silica cell and "aerated" with nitrogen its specific conductance was slightly lower than 1×10^{-7} mhos. Since a considerable amount of the work had been completed before the publication of the new measurements on potassium chloride by Jones and Bradshaw,[4] the results here reported are based upon the older measurements on the 0.01 demal solution given by Parker and Parker.[5] As pointed out in our previous paper,[4] both standards will give the same value of the ionization constant. The cell constant for the silica cell, C, is 1.0559.

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[1] This paper contains material which represents part of the dissertation submitted by Harry F. Meier to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1934.

[2] Saxton and Langer, THIS JOURNAL, **55**, 3638 (1933).

[3] Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[4] Jones and Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

[5] Parker and Parker, *ibid.*, **46**, 312 (1924).

Kahlbaum benzoic acid (from toluene) and Eastman No. 1694 *m*-chlorobenzoic acid were recrystallized twice from conductivity water. The crystals were dried in a bottle through which dry, purified air was passed. The purity of the benzoic acid was checked by a differential potentiometric titration with hydrogen electrodes against benzoic acid certified by the Bureau of Standards. Titration samples of each acid gave checks to one part in four thousand. Eastman No. 552 *o*-chlorobenzoic acid was recrystallized twice from benzene, then from conductivity water and dried in the manner just described. Eastman No. 627 *p*-chlorobenzoic acid was sublimed. Stock solutions of the acids were kept in a silica flask and were weighed into the cell by means of a silica weight buret.

Sodium salt solutions were made by weight of sodium carbonate (from the bicarbonate) and acid with the latter in excess by an amount calculated to bring the final solution to neutrality. Color comparison in the P_H 6.6–7.0 range, using brom thymol blue, usually gave a P_H of 6.9. Last traces of carbon dioxide were removed by treatment with nitrogen.

The measured equivalent conductances of the sodium salt solutions may be expressed by Shedlovsky's extension of Onsager's equation[7] and are given by

$$\mathrm{Na}^+ + \mathrm{Bz}^-;\quad \Lambda = 82.34 - 78.62\sqrt{c_i} + 99.9\, c_i\,(1 - 0.2276\sqrt{c_i}) \qquad (1)$$

$$\mathrm{Na}^+ + o\text{-}\mathrm{ClBz}^-;\quad \Lambda = 80.34 - 78.16\sqrt{c_i} + 111.0\, c_i\,(1 - 0.2276\sqrt{c_i}) \qquad (2)$$

$$\mathrm{Na}^+ + m\text{-}\mathrm{ClBz}^-;\quad \Lambda = 81.05 - 78.33\sqrt{c_i} + 109.0\, c_i\,(1 - 0.2276\sqrt{c_i}) \qquad (3)$$

The experimental results are given in Table I.

Combining these equations with the equation for $\Lambda_{(\mathrm{H}^+)} - \Lambda_{(\mathrm{Na}^+)}$ determined by us and cited in a previous paper,[2] the equations for the sums of the equivalent conductances of the ions of the weak acids as functions of their ionic concentrations, c_i, become

$$\mathrm{H}^+ + \mathrm{Bz}^-;\quad \Lambda = 381.96 - 146.81\sqrt{c_i} + 174.8\, c_i\,(1 - 0.2276\sqrt{c_i}) \qquad (4)$$

$$\mathrm{H}^+ + o\text{-}\mathrm{ClBz}^-;\quad \Lambda = 379.96 - 146.35\sqrt{c_i} + 185.9\, c_i\,(1 - 0.2276\sqrt{c_i}) \qquad (5)$$

$$\mathrm{H}^+ + m\text{-}\mathrm{ClBz}^-;\quad \Lambda = 380.67 - 146.52\sqrt{c_i} + 183.9\, c_i\,(1 - 0.2276\sqrt{c_i}) \qquad (6)$$

$$\mathrm{H}^+ + p\text{-}\mathrm{ClBz}^-;\quad \Lambda = 381.9 - 146\sqrt{c_i} \qquad (7)$$

The last equation is assumed from the values for benzoic acid and is sufficiently accurate, since, owing to its low solubility, we must deal with quite dilute solutions of *p*-chlorobenzoic acid and we know its concentration to only 0.3 per cent. From these equations and the measured equivalent conductances of the weak acids given in Table II, the remainder of the table was constructed. K' is the concentration (or dilution) constant and K is the ionization constant as calculated from K' by means of the limiting law of Debye and Hückel.[8]

If log K' of the first three acids be plotted against $\sqrt{c_i}$, the more dilute points fall on a straight line the slope of which is nearly equal to the value required by the limiting law of Debye and Hückel.[8] The equations of these lines are

TABLE I

			C_6H_5COONa			
$c \times 10^3$	1.1027	2.0304	3.4123	4.1147	4.5848	5.5335
Λ(obs.)	79.76	78.94	78.05	77.68	77.45	77.02
Λ(calcd.)	79.84	79.00	78.09	77.71	77.47	77.03
$c \times 10^3$	6.3888	7.8849	10.304	13.473	16.854	18.712
Λ(obs.)	76.68	76.14	75.39	74.54	73.77	73.40
Λ(calcd.)	76.68	76.13	75.37	74.53	73.77	73.40
			o-ClC_6H_4COONa			
$c \times 10^3$	0.18443	0.33293	0.76287	1.2491	1.8147	2.8455
Λ(obs.)	79.39	78.95	78.24	77.70	77.19	76.48
Λ(calcd.)	79.30	78.95	78.27	77.72	77.21	76.48
$c \times 10^3$	3.8959	4.8899	6.3421	7.6525	9.2587	10.706
Λ(obs.)	75.89	75.41	74.81	74.33	73.82	73.40
Λ(calcd.)	75.89	75.41	74.81	74.33	73.82.	73.41
			m-ClC_6H_4COONa			
$c \times 10^3$	0.19800	0.38783	0.83857	1.4388	2.1716	3.0028
Λ(obs.)	79.99	79.55	78.86	78.24	77.64	77.10
Λ(calcd.)	79.97	79.55	78.88	78.24	77.64	77.09
$c \times 10^3$	3.9377	5.1911	6.4408	7.8603	9.1132	10.973
Λ(obs.)	76.58	75.97	75.47	74.96	74.56	74.02
Λ(calcd.)	76.56	75.96	75.45	74.94	74.54	74.01

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[6] MacInnes and Cowperthwaite, THIS JOURNAL, **53**, 555 (1931).

[7] Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927); *Trans. Faraday Soc.*, **23**, 341 (1927); *J. Phys. Chem.*, **36**, 2689 (1932); Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

[8] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

$$C_6H_5COOH;\quad \log (K' \times 10^5) = \log (6.295 \times 10^5) + 0.980 \sqrt{c_i} \qquad (8)$$

$$o\text{-}ClC_6H_4COOH;\quad \log (K' \times 10^3) = \log (1.197 \times 10^3) + 1.004 \sqrt{c_i} \qquad (9)$$

$$m\text{-}ClC_6H_4COOH;\quad \log (K' \times 10^4) = \log (1.506 \times 10^4) + 1.028 \sqrt{c_i} \qquad (10)$$

TABLE II

BENZOIC ACID

Specific conductance of water = 0.82×10^{-7}

$c \times 10^3$	Λ	$c_i \times 10^3$	$K' \times 10^5$	$K \times 10^5$
0.084991	216.46	0.048292	6.355	6.253
.23404	153.97	.094689	6.434	6.290
.38559	127.026	.12879	6.459	6.290
.58234	107.40	.16454	6.480	6.289
.84368	91.828	.20393	6.501	6.288
1.15405	80.153	.24361	6.518	6.285
1.4753	71.910	.27951	6.533	6.283
2.0625	61.854	.33632	6.553	6.278
2.9144	52.808	.40600	6.571	6.270
3.9821	45.689	.48026	6.586	6.258
4.7210	42.187	.52593	6.593	6.250
6.1291	37.300	.60406	6.604	6.236
7.6934	33.477	.68091	6.612	6.221
8.9644	31.117	.73776	6.616	6.210
10.0035	29.518	.78118	6.617	6.199

o-CHLOROBENZOIC ACID

Specific conductivity of water = 1.1×10^{-7}

$c \times 10^3$	Λ	$c_i \times 10^3$	$K' \times 10^3$	$K \times 10^3$
0.69591	269.59	0.49795	1.253	1.189
.99373	248.02	.65493	1.266	1.193
1.4297	225.14	.85650	1.280	1.195
1.8230	209.73	1.0183	1.289	1.196
2.2824	195.60	1.1897	1.295	1.198
3.2904	173.25	1.5222	1.310	1.196
4.0788	160.64	1.7513	1.318	1.195
4.8698	150.61	1.9621	1.324	1.194
5.5098	143.85	2.1217	1.329	1.193
6.2617	137.03	2.2983	1.333	1.192

m-CHLOROBENZOIC ACID

Specific conductivity of water = 0.77×10^{-7}

$c \times 10^3$	Λ	$c_i \times 10^3$	$K' \times 10^4$	$K \times 10^4$
0.07979	274.17	0.05763	1.499	1.473
.15676	232.71	.09619	1.527	1.493
.29270	192.82	.14895	1.543	1.500
.58778	151.12	.23470	1.560	1.505
.87966	129.48	.30118	1.568	1.506
1.2793	111.37	.37702	1.575	1.506
1.6397	100.36	.43571	1.577	1.502
2.8228	79.17	.59241	1.573	1.487

p-CHLOROBENZOIC ACID

Specific conductivity of water = 1.5×10^{-7}

$c \times 10^3$	Λ	$c_i \times 10^3$	$K' \times 10^4$	$K \times 10^4$
0.1992	194.1	0.1016	1.058	1.033
.2396	183.5	.1156	1.078	1.051

At concentrations above 0.001 *N* benzoic acid behaves in the manner characteristic of weak acids in that the curve falls below the limiting slope. The values of *K* indicated by these equations were confirmed by a method briefly mentioned in a previous paper.[2] Log *K* was plotted against c_u, the concentration of the un-ionized acid, and the straight line was extrapolated to c_u equal to zero. The limiting values of *K* so obtained are 6.295×10^{-5}, 1.198×10^{-3} and 1.507×10^{-4} for benzoic acid, *o*-chlorobenzoic acid, and *m*-chlorobenzoic acid, respectively. The results on these three acids were further confirmed by measurements taken in the Jena G 20 glass cell, B, which gave the following values of *K* for the acids listed in the order just given: 6.295×10^{-5}, 1.198×10^{-4} and 1.512×10^{-4}. Owing to the low solubility of *p*-chlorobenzoic acid we have been able to obtain measurements at only two concentrations. The average value of *K* for this acid is 1.04×10^{-4}. Values of *K* for these acids are listed in the "International Critical Tables"[9] but only in one case, the *meta* acid, do these values agree with ours within one per cent.[10]

As in the cases of monochloroacetic acid and acetic acid,[2] c_i, the apparent ionic concentration, may be calculated from c, the total acid concentration, by using the relation

$$\log K' = \log K + a(K')^{1/4} c^{1/4} \qquad (11)$$

In the dilute region in which this equation is valid, the coefficient of $c^{1/4}$ is about 10% less than the fourth root of the average value of K' for acetic and monochloroacetic acids. Accordingly, we should expect it to be about 0.081, 0.171 and 0.101 for benzoic, *o*-chloro and *m*-chlorobenzoic acids, respectively. The equations found are

$$C_6H_5COOH;\quad \log (K' \times 10^5) = 0.7990 + 0.0817\, c^{1/4} \qquad (12)$$

$$o\text{-}ClC_6H_4COOH;\quad \log (K' \times 10^3) = 0.0781 + 0.1660\, c^{1/4} \qquad (13)$$

$$m\text{-}ClC_6H_4COOH;\quad \log (K' \times 10^4) = 0.1778 + 0.1010\, c^{1/4} \qquad (14)$$

As might be expected from the plot of log K' against $\sqrt{c_i}$, benzoic acid deviates from this linear relation above $c = 0.001$, behaving like acetic acid in that a pronounced medium effect is evident, and like acetic acid, obeying an equation of the above type to which a term in c is added. We thus obtain

$$\log (K' \times 10^5) = 0.7990 + 0.0855\, c^{1/4} - 0.515\, c \qquad (15)$$

from which c_i may be calculated up to the highest measured concentration.

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(9) "International Critical Tables," Vol. VI, pp. 278, 279.

(10) Since this paper was written, Brockman and Kilpatrick [THIS JOURNAL, **56**, 1483 (1934)] have reported measurements of the conductances of aqueous solutions of benzoic acid and its potassium salts. Combining these with Shedlovsky's [*ibid.*, **54**, 1411 (1932)] results of hydrochloric acid and potassium chloride, they obtain $K = 6.312 \times 10^{-5}$, which can be regarded as a virtual check.

At present there seems to be no adequate theoretical method for calculating the free energy of ionization of an organic acid,[11] hence methods which have been suggested for calculating or representing the effect of substituents upon the ionization constant of such an acid are approximate. While Smallwood[12] met with some success by attributing the change to the electric moment associated with the substituent, he obtained particularly bad results with the acids studied in this paper. MacInnes[13] has shown that log K for certain substituted acids, including the ones here studied, is nearly a linear function of d^{-1}, where d is taken as the distance between the polar bond joining the carboxyl group to the chain or ring and the polar bond connecting the substituent to the chain or ring. If the d's be taken as the ratios of the distances across a regular plane hexagon for the *ortho*, *meta* and *para* acids, namely, $1:\sqrt{3}:2$, these three acids give a straight line when log K is plotted against d^{-1} and the equation for the line is

$$\log K = -5.0471 + (2.1249/d) \qquad (16)$$

This equation reproduces the values of K to within $\pm 0.31\%$, but, as MacInnes has observed, the constant is not log K for the unsubstituted acid. This behavior of the substituted acids might be considered to point to a plane, regular, hexagonal structure for these substances, but, even if the relation used could be developed in a forthright way, the values of log K for the *meta* and *para* acids are so nearly equal that this indication should be given little weight. Our own attempts to develop an exact theory of the ionization of the weak electrolyte have been unsuccessful.

Summary

The conductances of aqueous solutions of benzoic acid, *o*-chlorobenzoic acid, *m*-chlorobenzoic acid, *p*-chlorobenzoic acid and the sodium salts of the first three acids have been measured at 25°.

From these results and our previous measurements on hydrochloric acid and its sodium salt the following ionization constants have been found

$C_6H_5COOH \quad K = 6.295 \times 10^{-5}$
$o\text{-}ClC_6H_4COOH \quad K = 1.197 \times 10^{-3}$
$m\text{-}ClC_6H_4COOH \quad K = 1.506 \times 10^{-4}$
$p\text{-}ClC_6H_4COOH \quad K = 1.04 \times 10^{-4}$

The results with the strong electrolytes again confirm Onsager's equation as a limiting law and Shedlovsky's extension of the equation to the moderately dilute solutions. The results with the weak acids again show that the theoretical constant of the limiting law of Debye and Hückel correctly represents the dependence of the activity coefficient of these acids upon their ionic concentrations.

At present, there is no adequate theoretical method of calculating the ionization of a weak electrolyte from its structure.

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[11] For a discussion of the several factors involved see Briegleb, *Z. physik. Chem.*, **10B**, 205 (1930).

[12] Smallwood, THIS JOURNAL, **54**, 3048 (1932).

[13] MacInnes, *ibid.*, **50**, 2587 (1928).

NOTES

Notes on the Movement of a Borax Bead on Platinum Wire

BY J. L. CULBERTSON

Anyone who has had occasion to use the borax bead on a platinum wire in the qualitative laboratory is familiar with the method by which the bead may be driven from one part of the wire to another by means of the flame. This is accomplished by heating one side of the bead on holding it in the edge of the flame. So heated the bead will recede from the hotter side and by drawing the wire through the flame as rapidly as the bead recedes the movement may be continued to the end of the wire. This phenomenon is exceedingly common and yet the writer has been unable to find in the literature any analysis of the situation based on a consideration of the surface tensions acting in the system. That such an analysis may be appropriate is suggested by the observation that the contact angle of the liquid bead on the surface of the platinum is much greater when at high temperatures than when at lower ones. No measurements of these contact angles have been made but the fact that the angle changes, as indicated, with temperature change is readily verified by even the most casual observation. This may be most readily accomplished by studying the form of a small globule of borax on a piece of platinum foil. When enveloped in a Bunsen