

The slowness of the reaction in glass vessels is to be attributed to the small absorption coefficient for wave lengths transmitted by glass.

Summary

It has been shown that the continuous absorption of hydriodic acid extends up to a wave length of 4000 Å. instead of terminating at 3340 Å. as reported by others. The absorption on the long wave length side of 3120 Å. has been interpreted as due to the dissociation of the molecule into normal atoms and that on the shorter wave length side as due to a dissociation with the iodine atom excited. The intensity distribution of the absorption has been discussed with reference to the potential energy curves for the normal and excited states of the molecule. The photochemical decomposition of hydriodic acid has been shown to be due to this absorption and the mechanism of the reaction has been discussed.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE ELECTROMETRIC AND CATALYTIC DETERMINATION OF HYDROGEN-ION CONCENTRATION. THE MEAN ACTIVITY COEFFICIENTS OF THE IONS OF BENZOIC ACID IN POTASSIUM CHLORIDE SOLUTIONS¹

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In connection with some work on the dissociation constants of indicators in aqueous salt solutions it became necessary to have buffer solutions of known hydrogen-ion concentration. Most buffer systems are standardized in terms of hydrogen-ion activity, the determination being based on certain non-thermodynamic assumptions regarding diffusion potentials. Where the classical dissociation constant is known in a given salt solution, the hydrogen-ion concentration can be calculated. However, accurate values of the dissociation constants are known for few acids except in very dilute solutions. The purpose of the present work is to determine the hydrogen-ion concentration of a series of benzoate-benzoic acid buffers in aqueous solutions of potassium chloride by two different methods. At the same time the mean activity coefficient $\sqrt{f_{H^+} f_{B^-}}$ will be obtained. The method of determining $f_{H^+} f_{B^-}$ the product of the activity coefficients, is as follows. The thermodynamic dissociation constant is equal to

¹ Paper Presented at the Indianapolis Meeting of the American Chemical Society, April, 1931.

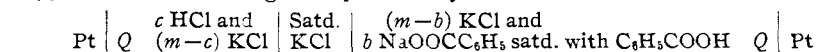
^{1a} Abstracted in part from the thesis of Elwyn F. Chase to be presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

$$K_a = \frac{a_{\text{H}^+} a_{\text{B}^-}}{a_{\text{HB}}} = \frac{C_{\text{H}^+} C_{\text{B}^-}}{a_{\text{HB}}} f_{\text{H}^+} f_{\text{B}^-}$$

If at constant temperature the solutions are always saturated in respect to benzoic acid, the activity of the molecular benzoic acid is constant in all solutions and its value can be obtained from the solubility in pure water taking into account only that part of the benzoic acid which is present as molecules. At 25° the ionic strength of the saturated benzoic acid solution is approximately 0.001 and the activity of the molecular benzoic acid can be set equal to its concentration within the limits of the error of measurement. The hydrogen-ion concentration is determined by the electrometric and catalytic methods, and the benzoate concentration is calculated from the stoichiometric composition of the buffer. The dissociation constant at zero electrolyte concentration can be determined from conductivity measurements. From these data we calculate the product $f_{\text{H}^+} f_{\text{B}^-}$.

The Electrometric Method

The method employed is the same as that used by Güntelberg and Schiödt² and is based on the principle of Brönsted³ which has been so useful in kinetic problems: "If a salt solution acts as a solvent for other salts, present in concentrations small compared with that of the solvent salt, the variation in the solute system keeping the medium or solvent salt unchanged will not, as in the case of pure water solutions, invalidate the ordinary gas laws and make the mass action law inapplicable." In other words, the activity coefficients of the substances present in small amount are independent of the small quantities of these substances and are determined solely by the salt present in large amount. Thus if we have a set of solutions of low hydrogen-ion concentration in potassium chloride solutions of relatively high concentration, we can assume that the activity coefficient of the hydrogen ion in these solutions of high constant potassium chloride concentration is constant. The assumption of practically complete ionization of the hydrochloric acid gives us a set of standards of known hydrogen-ion concentration. If the hydrogen-ion concentration in the above solutions is 0.01 molar, we do not have to take into account the possible alkalinity of the potassium chloride, which can be kept under $1 \times 10^{-4} M$. These standards at various potassium chloride concentrations from 0.01 to 3.0 M were compared with the benzoate-benzoic acid buffers by means of the quinhydrone electrode. The activity coefficient of the hydrogen ion was kept the same in both the standard and the unknown by keeping the ionic strength the same in each, where potassium chloride contributed from 90 to 99% of the ionic strength in practically all cases. The cell measured was



² Güntelberg and Schiödt. *Z. physik. Chem.*, 135, 393 (1928).

³ Brönsted, *Trans. Faraday Soc.*, 23, 430 (1927).

Under the conditions of the experiment the diffusion potential would be small.

Experimental Part

The buffers were prepared by adding potassium chloride and carbonate-free sodium hydroxide solutions to pure benzoic acid in glass bottles and rotating the mixture in a thermostat at $25.15 \pm 0.01^\circ$ until saturated with benzoic acid. It was found that Kahlbaum benzoic acid could be used without further purification. The acid was rotated in the bath for twenty-four hours, a sample of the saturated solution was removed and the acid concentration determined by titration with sodium hydroxide in an atmosphere free from carbon dioxide, using phenol red as indicator. The residue of benzoic acid was then rotated with more water and the solubility redetermined. This was repeated several times and in all cases the determinations agreed within 0.5%. To be certain that twenty-four hours of rotation was sufficient, determinations were made on samples rotated for varying lengths of time up to two hundred hours, without an appreciable change in solubility. Table I summarizes the results of these determinations and Table II gives the values obtained by other workers.

TABLE I
SOLUBILITY OF BENZOIC ACID IN WATER AT 25.15°

Sample	Hours rotated	C_6H_5COOH , moles per liter	Remarks
1	..	0.02773	
2	..	.02776	
3	24	.02783	Fresh sample
3	24	.02773	Fresh sample
4	96	.02781	Fresh sample
4	96	.02778	Fresh sample
5	166	.02780	Fresh sample
5	166	.02780	Fresh sample
6	217	.02784	Residue from 4
6	217	.02788	Residue from 4
7	72	.02778	Residue from 3
7	72	.02782	Residue from 3
8	71	.02790	Twice extracted residue
8	71	.02783	Twice extracted residue
	Av.	.02781	

TABLE II
SOME PREVIOUS DETERMINATIONS OF THE SOLUBILITY OF BENZOIC ACID IN WATER AT 25°

Solubility, moles per liter	Observer
0.028082	Paul, <i>Z. physik. Chem.</i> , 14 , 105 (1894).
.02793	Noyes and Chapin, <i>THIS JOURNAL</i> , 20 , 751 (1898).
.02796	Hoffmann and Langbeck, <i>Z. physik. Chem.</i> , 51 , 385 (1905).
.02799	Freundlich and Seal, <i>Kolloid Z.</i> , 11 , 257 (1912).
.02791	Rørdam, <i>Thesis, University of Copenhagen</i> , 1925.
.02781	Larsson, <i>Z. anorg. Chem.</i> , 155 , 247 (1926).

The potassium chloride was Kahlbaum "with certificate of guarantee" and the small quantities of alkali present could be neglected in the well-buffered solutions. The standard hydrochloric acid solutions were prepared from weighed amounts of potassium chloride and constant boiling hydrochloric acid made according to Hulett.

The cell as shown in Fig. 1 consisted of two cylindrical electrode vessels A and A' of Pyrex glass connected through stopcocks B and B' to the reservoir C for the saturated potassium chloride solution. The electrodes D and D' were pieces of bright platinum foil which were cleaned and heated to redness just before using. Constrictions at E and E' served to hold cotton plugs on which the quinhydrone was placed. Through the inlets F and F' nitrogen was passed into the solution to remove dissolved oxygen and to keep the solutions stirred, while the tubes G and G' served for adjusting the junctions H and H' and for emptying the vessels. The apparatus was set in a thermostat at $25.15 \pm 0.05^\circ$.

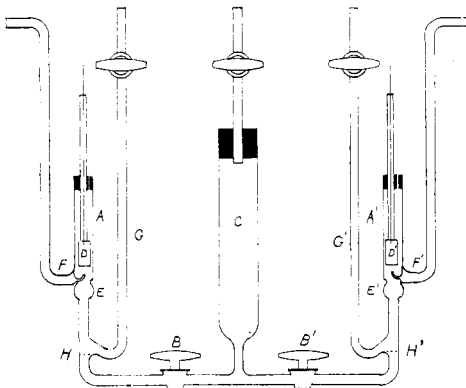
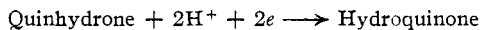


Fig. 1.—The quinhydrone cell.

The method of carrying out a determination was as follows. The standard hydrochloric acid solution in potassium chloride and the buffer solution were placed in A and A', respectively, and carbon dioxide-free nitrogen was bubbled through the solutions. By gentle suction at G and G' the junctions were made at H and H'. Quinhydrone was added from a spatula and the electrodes were set in place. The potential difference was measured by means of a Type K Leeds and Northrup potentiometer and a suitable galvanometer. The readings were usually constant to 0.0001 volt for the first fifteen minutes. Over the range studied 0.0001 volt represents approximately 0.3% in hydrogen-ion concentration. In general the results were reproducible to 1% in hydrogen-ion concentration.

The cell reaction is



and the potential is given by

$$E = E_0 + \frac{RT}{2F} \ln \frac{a_{\text{Hy}}}{a_{\text{Q}} a_{\text{H}}^2} = E - \frac{RT}{F} \ln a_{\text{H}} + \frac{RT}{2} \ln \frac{f_{\text{Hy}}}{f_{\text{Q}}}$$

since $C_{\text{Hy}} = C_{\text{Q}}$. The last term is the salt error which cancels out in our experiments because the activity coefficients in both solutions are equal. Since at constant potassium chloride concentration we may replace the

ratio of the activities of the hydrogen ion by the ratio of the concentrations and

$$\Delta E = \frac{RT}{F} \ln \frac{C'_{H^+}}{C_{H^+}} = 0.05914 \log \frac{C'_{H^+}}{C_{H^+}}$$

and

$$\log C'_H = \frac{\Delta E}{0.05914} + \log C_H$$

where C_{H^+} is the known concentration of the hydrogen ion in the standard solution of hydrochloric acid in potassium chloride and C'_{H^+} is the hydrogen-ion concentration of the buffer solution.

Table III gives the results of these determinations. The concentration of potassium chloride in each standard solution can be obtained by subtracting the hydrogen-ion concentration as given in Column 2 from the total electrolyte concentration as given in Column 1. Similarly the difference between Column 1 and the concentration of the sodium ion in Column 5 gives the concentration of potassium chloride for the buffer solutions.

TABLE III

THE ELECTROMETRIC DETERMINATION OF THE HYDROGEN-ION CONCENTRATION (25.15°)

Standard solution Electrolyte KCl + HCl, moles per liter	H ₂ O ⁺ , moles per liter × 10 ⁵	E. m. f., volts	H ₂ O ⁺ , moles per liter × 10 ⁵	Na ⁺ , moles per liter × 10 ⁵	Buffer C ₆ H ₅ COO ⁻ , moles per liter × 10 ⁵	C _{H⁺} C _{B⁻} × 10 ⁷	Av.
0.1000	1035	0.07859	48.5	480.9	529.4	25.6	
.1000	1035	.08869	32.8	734.5	767.3	25.6	
.1000	1035	.09553	25.1	1000	1025	25.8	
.1000	1035	.11188	13.3	1852	1865	24.9	
.1000	1035	.11187	13.3	1852	1865	24.9	25.5
.2000	933.1	.08479	34.3	727.3	761.6	26.1	
.2000	933.1	.10452	15.9	1647	1660	26.4	
.2000	933.1	.12289	7.79	3293	3301	25.7	26.1
.3000	878.5	.10343	15.6	1647	1663	25.9	
.3000	878.5	.10395	15.0	1729	1744	26.1	
.3000	878.5	.11364	10.5	2470	2481	26.0	
.3000	878.5	.12082	7.94	3293	3301	26.2	26.1
.4000	1050	.10811	15.6	1647	1663	25.9	
.4000	1050	.10911	15.0	1729	1744	26.1	
.4000	1050	.11888	10.2	2470	2480	25.3	
.4000	1050	.12581	7.82	3293	3302	25.8	25.8
.5000	1002	.06490	80.1	240.4	320.5	25.6	
.5000	1002	.11183	12.9	1976	1989	25.8	
.5000	1002	.13265	5.72	4323	4329	24.8	
.5000	1002	.13241	5.78	4323	4329	25.0	25.3
.6000	999.3	.10779	15.0	1647	1662	24.9	
.6000	999.3	.10905	14.3	1729	1743	24.9	
.6000	999.3	.11818	10.0	2470	2480	24.8	
.6000	999.3	.11837	9.94	2470	2480	24.6	24.8

TABLE III (Concluded)

Standard solution Electrolyte KCl + HCl, moles per liter	H ₂ O ⁺ , moles per liter × 10 ⁵	E. m. f., volts	H ₂ O ⁺ , moles per liter × 10 ⁵	Na ⁺ , moles per liter × 10 ⁵	Buffer C ₆ H ₅ COO ⁻ , moles per liter × 10 ⁵	C _H ⁺ C _B ⁻ × 10 ⁷	Av.
0.7000	1014	0.10944	14.3	1647	1661	23.7	
.7000	1014	.11953	9.64	2470	2480	23.9	
.7000	1014	.12742	7.09	3293	3300	23.4	
.7000	1014	.12761	7.04	3293	3300	23.2	23.6
.9000	1016	.11087	13.5	1647	1661	22.4	
.9000	1016	.12169	8.88	2470	2479	22.0	
.9000	1016	.12187	8.84	2470	2479	21.9	
.9000	1016	.12932	6.60	3293	3300	21.8	
.9000	1016	.12936	6.58	3293	3300	21.7	22.0
1.012	961.0	.09446	24.3	850	874.3	21.2	
1.012	961.0	.10551	15.8	1318	1334	21.1	
1.012	961.0	.11090	12.8	1647	1660	21.2	
1.012	961.0	.11606	10.5	1976	1987	20.8	
1.012	961.0	.13045	5.97	3293	3299	19.7	
1.012	961.0	.12885	6.36	3330	3336	21.2	
1.012	1067	.13950	4.66	4323	4328	20.2	
1.012	961.0	.13988	4.14	5000	5004	20.8	20.8
1.500	972.0	.07336	55.8	240.4	296.2	16.5	
1.500	972.0	.12026	8.98	1852	1861	16.7	
1.500	972.0	.12270	8.17	1976	1984	16.2	
1.500	972.0	.14387	3.58	4323	4327	15.5	
1.500	972.0	.14323	3.67	4323	4327	15.9	16.2
2.000	1122	.10201	18.3	617.5	635.8	11.6	
2.000	1122	.12106	10.1	1235	1245	12.6	
2.000	1122	.13213	6.53	1852	1859	12.1	
2.000	1122	.15408	2.78	4298	4301	12.0	
2.000	1122	.15380	2.81	4298	4301	12.1	12.1
2.500	996.5	.10815	14.8	617.5	632.3	9.35	
2.500	996.5	.12580	7.42	1235	1242	9.23	
2.500	996.5	.13884	4.47	1976	1980	8.86	
2.500	996.5	.13897	4.45	1976	1980	8.81	
2.500	996.5	.13842	4.54	1976	1981	8.99	9.05
3.000	1040	.11659	11.1	586.0	597.1	6.64	
3.000	1040	.12955	6.69	988	995	6.65	
3.000	966.1	.12792	6.63	988	995	6.60	6.63

The Catalytic Method

The catalytic method has been used for the determination of hydrogen-ion concentration in a number of cases but as in the case of the electro-metric and colorimetric methods a proper consideration of the electrolyte effect is necessary for accurate determinations. In addition, in choosing a suitable reaction we have to consider, as well as the effect of the hydrogen ion, possible catalytic effects of acids other than the hydrogen ion. Both

TABLE IV

THE ELECTROMETRIC DETERMINATION OF THE HYDROGEN-ION CONCENTRATION AT 20°

Standard solution Electrolyte KCl + HCl, moles per liter	H ₂ O ⁺ , moles per liter × 10 ⁴	E. m. f., volts	H ₂ O ⁺ , moles per liter × 10 ⁴	Na ⁺ , moles per liter × 10 ³	Buffer C ₂ H ₃ COO ⁻ , moles per liter × 10 ³	C _H ⁺ C _B ⁻ × 10 ⁷	Av.	G. + S. av.
1.000	200	.0292	62.8	200.0	262.8	16.5		
1.000	500	.06918	32.3	500.0	532.3	17.2	16.9	
2.000	500	.0828	18.7	500.0	518.7	9.81	9.81	
3.000	200	.0538	23.7	200.0	223.7	5.30		
3.000	500	.0977	10.5	500.0	510.5	5.36	5.33	5.16
NaCl								
1.000	200	.0299	61.3	200.0	261.3	16.0		
1.000	500	.0703	30.9	500.0	530.9	16.4	16.2	
2.000	200	.0425	37.1	200.0	237.1	8.43		
2.000	500	.0855	17.0	500.0	517.0	8.79	8.61	
3.000	200	.0600	18.6	200.0	218.6	4.07		
3.000	500	.1078	8.5	500.0	508.5	4.32	4.20	4.18
4.000	200	.0810	8.10	200.0	208.1	1.69		
4.000	500	.1249	3.60	500.0	503.6	1.81	1.76	1.82
5.000	200	.1015	4.57	200.0	203.6	0.733		
5.000	500	.1481	1.40	500.0	501.4	0.702	0.717	0.741

NOTE.—Table IV gives some measurements carried out by Mr. W. H. Berry at 20° which are given for comparison with the results of Güntelberg and Schiödt and to complete the values over the whole concentration range. They are not to be considered as accurate as the measurements of Güntelberg and Schiödt.

of these factors have been discussed in the recent paper of Brönsted and Grove.⁴

Brönsted and Wynne-Jones⁵ used the rate of hydrolysis of diethyl acetal to determine the hydrogen-ion concentration of formic acid buffer solutions at ionic strengths up to 0.05. They showed that this reaction was not catalyzed by acids weaker than the hydrogen ion (H₃O⁺) and Brönsted has calculated that in all cases the effect of acids stronger than the hydrogen ion (H₃O⁺), such as hydrochloric acid, will hardly be detectable in aqueous solution.⁶ In order to know the proportionality between the rate of reaction and the hydrogen-ion concentration for a given medium, Brönsted and Wynne-Jones determined the rate of reaction in a solution of hydrochloric acid in potassium nitrate and assumed that the same proportionality factor could be used for formic acid-sodium formate buffer solutions. A similar assumption has been used by previous workers.⁷ However, as further studies of primary salt effect have been made for these zero type reactions (a reaction between an ion and a non-electrolyte), it has been

⁴ Brönsted and Grove, *THIS JOURNAL*, **52**, 1394 (1930).

⁵ Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

⁶ Brönsted, *ibid.*, **24**, 630 (1928).

⁷ See Kilpatrick, *THIS JOURNAL*, **48**, 2091 (1926).

realized that although the effect is linear in conformity with the theory the magnitude of the effect between $\mu = 0.01$ and $\mu = 0.10$ for uni-univalent electrolytes is in many cases much greater than the 2 to 4% stated for the reactions studied previous to 1922.⁸ For the decomposition of nitroso-triacetonamine catalyzed by hydroxyl ion, the effect between $\mu = 0.01$ and $\mu = 0.10$ is 7% when sodium chloride is the solvent salt.⁷ For the hydration of ethylene oxide catalyzed by hydrogen ion it is 9% for the solvent salt sodium perchlorate over the same range of concentration.⁹ In the hydrolysis of diazoacetic ester catalyzed by hydrogen ion it is 14% for the same solvent salt and for the hydrolysis of diethyl acetal it is 11% for potassium chloride and approximately 13% for sodium chloride and potassium nitrate. The last two values are from Brönsted and Wynne-Jones⁵ and are doubtful in that the concentration of strong acid used was only 0.0008 *M*. Brönsted and Grove⁴ extended these studies to other acetals studied originally by Skrabal¹⁰ and found that the primary salt effect is large and varies with the individual salt to such an extent that one is confined to the determination of the hydrogen-ion concentrations of unbuffered solutions of weak acids where the electrolyte concentration is below $\mu = 0.01$.¹¹

Our problem was to determine the hydrogen-ion concentration of the benzoate buffers up to 3.0 molar concentration of potassium chloride. A search of the literature failed to reveal a suitable reaction with a small electrolyte effect, so the hydrolysis of diethyl acetal was used. As already pointed out, the primary salt effect cannot be studied at 25° because we must deal with such low concentrations of strong acids that the results are uncertain. Our method consisted of determining the electrolyte (salt) effect at 0° where the reaction is slow enough to permit the use of 0.01 to 0.005 molar hydrochloric acid. By determining accurately the temperature coefficient, which from previous experience would be expected to be independent of electrolyte concentration,^{12,7} the proportionality of the rate to the hydrogen-ion concentration for the various concentrations of solvent salt at 25.15° was calculated. Then by determining the rate of reaction with the benzoate-benzoic acid buffer solutions we obtained the hydrogen-ion concentration.

Experimental Method

The experiments at 0° were carried out in a dilatometer previously used for the determination of the rate of hydration of acetic anhydride.¹³ It was

⁸ Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

⁹ Brönsted, Kilpatrick and Kilpatrick, *THIS JOURNAL*, **51**, 420 (1929).

¹⁰ Skrabal, *Z. Electrochem.*, **33**, 322 (1927).

¹¹ Grove, *THIS JOURNAL*, **52**, 1404 (1930).

¹² Rice and Lemkin, *ibid.*, **45**, 1896 (1923).

¹³ Kilpatrick, *ibid.*, **50**, 2891 (1928).

found very convenient to have the whole apparatus in a refrigerator room which was kept a few degrees above the freezing point of water. Two samples of acetal were used and gave the same results. Preparation A boiled between 102 and 103° (760 mm.), while preparation B was very carefully fractionated and boiled at 103° (759 mm.). Preparation B was completely free from acidic impurities. Table V gives the results of the experiments in various concentrations of potassium chloride at 0°.

TABLE V
THE ELECTROLYTE EFFECT ($t = 0.0^\circ$)

KCl, moles per liter	HCl, moles per liter	μ , ionic strength	k_{observed}	$\frac{k_{\text{obs.}}}{C_{\text{HCl}}} = k_{\text{H}_3\text{O}^+}$
0.0	0.01315	0.013	0.0326	2.48 ^a
.087	.01315	.10	.0372	2.74
.20	.00933	.21	.0288 ₅	3.08
.40	.00933	.41	.0391	3.73 ^a
.60	.00395	.60	.0174	4.51 ^a
1.0	.01247	1.01	.0742	6.08
1.5	.00395	1.50	.03312	8.38
2.0	.00658	2.01	.0715	10.87
2.0	.00395	2.00	.0445	11.25

^a = acetal sample B

The salt effect from 0.01 to 0.10 molar is 10% and over the range studied changes from 2.48 to 11.25, a four-fold increase. Experiments at higher

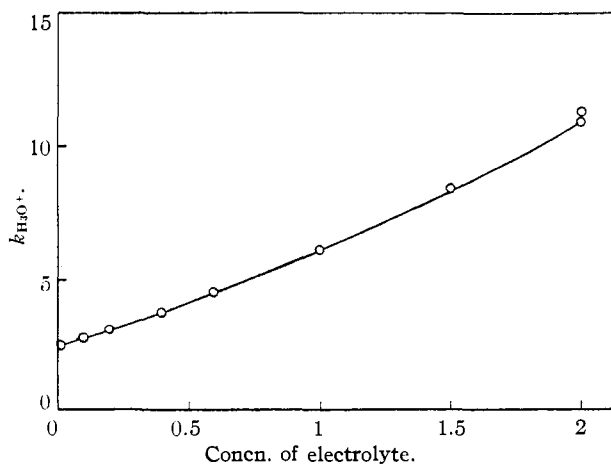


Fig. 2.—The electrolyte effect on $k_{\text{H}_3\text{O}^+}$.

concentrations of potassium chloride show an even greater effect between 2 and 3 molar but these results are more uncertain than the others, due to the lower hydrochloric acid concentrations, and are not given here. In Fig. 2 $k_{\text{H}_3\text{O}^+}$ is plotted against the electrolyte concentration. The electrolyte

effect is linear and for dilute solutions the experimental results can be expressed by the equation

$$k = 2.40 + 3.40 c$$

where c represents the total equivalent electrolyte concentration. To emphasize again the dependence of the effect upon the individual nature of the salt, $k_{\text{H}_3\text{O}^+}$ for a solution 0.75 M in potassium nitrate is 4.34 as against 5.04 for the corresponding potassium chloride solution.

The temperature coefficient was determined by the two-thermostat method.¹⁴ The reaction was followed dilatometrically, the reacting solutions being confined in two dilatometers similar in design to that used in the study of the hydration of ethylene oxide.¹⁵ The dilatometers were placed in thermostats regulated to $\pm 0.003^\circ$ and at temperatures exactly five degrees apart as determined by a calibrated resistance thermometer. Portions of a solution of suitable acid concentration were placed in the mixing chambers of the dilatometers and after thermal equilibrium was established with the baths, acetal was added. The velocity constants were determined in the usual way. Although the hydrogen-ion concentrations were too small to be known accurately they were the same in both cases and the temperature coefficient was obtained directly from the velocity constants. The results are given in Table VI, which also contains the heat of activation E calculated from the Arrhenius equation.

TABLE VI
THE TEMPERATURE COEFFICIENT

KCl, moles per liter.	0	0	0	0	1.0	2.0
$k_{25.00}/k_{20.00}$	1.870	1.893	1.887	1.894	1.923	1.944
E , cal. per degree.	21,720	22,150	22,000	22,160	22,690	23,070

The temperature coefficient seems to increase slightly with increasing salt concentration but this may be due to experimental error and we have given E an average value of 22,300 calories from which we calculated $k_{25.15}/k_0 = 32.19$. An error of 1% in k_{25}/k_{20} means about the same percentage error in E , which would mean a possible error of 3% in $k_{25.15}/k_0$. The velocity constant $k_{\text{H}_3\text{O}^+}$ for 25.15° is determined by multiplying $k_{\text{H}_3\text{O}^+}$ for 0° for each electrolyte concentration by 32.19.

Table VII gives the results of the determinations of hydrogen-ion concentration in the buffer solutions. In Column 6 are given the hydrogen-ion concentrations as determined by the electrometric method.

The agreement between the two methods is fairly good, the catalytic method giving slightly lower values above 1 molar concentration of electrolyte. At higher electrolyte concentrations the deviations obtained are greater, apparently exceeding the experimental error. These differences

¹⁴ Rice and Kilpatrick, THIS JOURNAL, 45, 1401 (1923).

¹⁵ Ref. 9, p. 428.

TABLE VII
THE CATALYTIC DETERMINATION OF THE HYDROGEN-ION CONCENTRATION

Total equivalent electrolyte, $\text{KCl} + \text{C}_6\text{H}_5\text{COO}^-$, moles per liter	Na^+ , moles per liter $\times 10^3$	k_{observed}	$k_{\text{H}_3\text{O}^+}$	$\frac{k_{\text{obs.}}}{k_{\text{H}_3\text{O}^+}} =$ moles per liter $\times 10^5$	E. m. f. method, H_3O^+ , moles per liter $\times 10^5$	$\text{C}_{\text{H}^+} + \text{C}_{\text{B}^-} \times 10^7$
0.0013 ^a	0.0	0.1017	77.4	131.6		17.0
.0998	734.5	.02960	88.3	33.6	32.8	25.8
.2000	741.0	.03510	99.2	35.4	35.5	27.4
.3000	1729	.01730	112.7	15.4	15.0	26.8
.4000	1729	.01856	120.1	15.5	15.0	26.9
.5000	1976	.01688	135.2	12.5	12.9	24.9
.6000	1729	.02036	145.2	14.0	14.3	24.4
.8000	1729	.02166	167.8	12.9	13.3	22.5
1.012	3293	.01143	195.7	5.84	5.97	19.3
1.500	1976	.02070	270	7.69	8.17	15.3
2.000	4298	.00993	362	2.74	2.78	11.8

^a Saturated solution of benzoic acid.

are being considered further in connection with the assumptions upon which both methods are based, in particular the assumption of practically complete ionization of the hydrochloric acid in potassium chloride solutions and the assumption that the reaction is a pure hydrogen-ion catalysis.

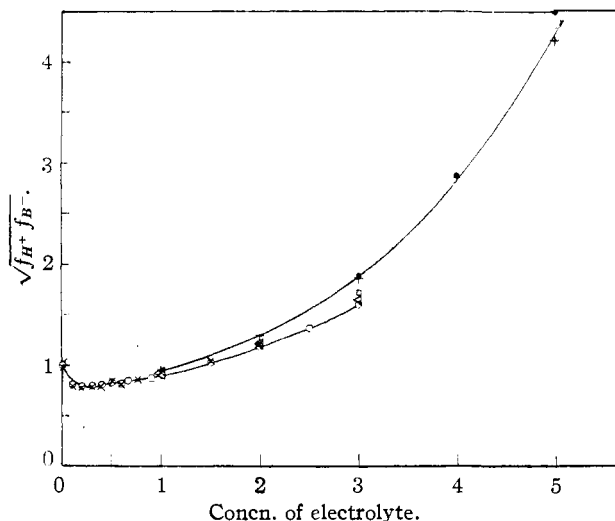
TABLE VIII
THE MEAN ACTIVITY COEFFICIENT OF THE IONS OF BENZOIC ACID

Total electrolyte concentration $\text{KCl} + \text{C}_6\text{H}_5\text{COONa}$	$\frac{25^\circ}{\sqrt{f_{\text{H}^+} f_{\text{B}^-}}}$ from e. m. f.	$\frac{25^\circ}{\sqrt{f_{\text{H}^+} f_{\text{B}^-}}}$ from catalysis	$\frac{20^\circ}{\sqrt{f_{\text{H}^+} f_{\text{B}^-}}}$ from e. m. f., Berry	$\frac{20^\circ}{\sqrt{f_{\text{H}^+} f_{\text{B}^-}}}$ G. + S.
0.001	..	0.98		
.1	0.81	.80 ₅		
.2	.80	.78		
.3	.80	.79		
.4	.80 ₅	.79		
.5	.81	.82		
.6	.82	.83		
.7	.84	..		
.8	..	.86		
.9	.87	..		
1.01	.90	.93	0.92	
1.5	1.02	1.04	..	
2.0	1.18	1.19	1.21	
2.5	1.36	
3.0	1.59	..	1.64	1.70
$\text{NaCl} + \text{C}_6\text{H}_5\text{COONa}$				
1.0			0.94	..
2.0			1.29	..
3.0			1.85	1.89
4.0			2.85	2.86
5.0			4.19	4.48

The values of the mean activity coefficients of the ions of benzoic acid can be calculated from the following equation

$$\sqrt{f_{H^+} f_{B^-}} = \sqrt{\frac{K_a a_{HB}}{C_{H^+} C_{B^-}}}$$

the product $C_{H^+} C_{B^-}$ being given in Tables III and VII. K_a is set equal to 6.31×10^{-5} .¹⁶ The value for the activity of the molecular benzoic acid is obtained from the solubility of benzoic acid in water by subtracting the small part present as ions, a_{HB} being set equal to 0.0265. Table VIII gives the values of $\sqrt{f_{H^+} f_{B^-}}$ from the electrometric and catalytic methods at the various concentrations of electrolyte (potassium chloride and benzoate). For comparison we have included the values of Berry and those of Güntelberg and Schiödt in sodium chloride solutions.



○, E. m. f., 25°; ×, catalytic, 25°; ◁, Berry, 20°; □, G. + S., 20° (in KCl); +, Berry, 20°; ●, G. + S., 20° (in NaCl); σ, Simons.

Fig. 3.—Mean activity coefficients of the ions of benzoic acid in KCl and NaCl solutions.

From Table VIII and Fig. 3 it is to be noted that the mean activity coefficient is higher in solutions of sodium chloride than in the corresponding solutions of potassium chloride in all cases. Güntelberg and Schiödt² interpret this as being due to the predominance of the "salting out" effect over that of interaction.

In another communication will be given the activity coefficients of the molecular acid determined from solubility measurements and K_c , the

¹⁶ This value has been determined by J. K. Simons by conductance measurements and will be the subject of another communication.

classical dissociation constant. At that time a comparison will be made of the activity coefficients of benzoic acid and those of other acids.

Summary

The hydrogen-ion concentrations of benzoic acid-benzoate buffers saturated with benzoic acid in potassium chloride solutions have been determined by two independent methods.

The results obtained by the catalytic method are in agreement with those determined by the quinhydrone electrode.

In both cases "electrolyte effects" have been considered.

The mean activity coefficients of the ions of benzoic acid have been determined in potassium and sodium chloride solutions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

THE SOLUBILITIES OF CERTAIN SLIGHTLY SOLUBLE ORGANIC COMPOUNDS IN WATER¹

By PAUL M. GROSS AND JOHN H. SAYLOR

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As part of a general investigation of solubility in relation to polar character, the solubilities of a number of slightly soluble organic compounds in water have been determined. Since the final interpretation of the data from this standpoint must await the completion of certain supplementary measurements now under way, it seemed advisable to publish the solubility data at this time since no reliable values for the solubilities of these substances are available in the literature.

Experimental

Method.—The saturated solutions of the substances were prepared by shaking in a thermostat and were analyzed by means of an interferometer. The instrument used was a combination liquid and gas interferometer made by Zeiss.

The procedure was a modification of that of Adams² and of Gross.³ The standard or reference solutions were made by dissolving weighed amounts of the substance under investigation in approximately 1000 g. of water. In the case of liquids, a vial containing a weighed amount of the substance was dropped into the weighed sample of water contained in a glass stoppered bottle. During the weighing, the vial was closed with a cork stopper and care was taken that the liquid did not come in contact with the stopper. The stopper of the vial was removed, the vial quickly

¹ Based upon a thesis submitted by John H. Saylor in partial fulfillment of the requirements for the Ph.D. degree at Duke University.

² Adams, *THIS JOURNAL*, 37, 1181 (1915).

³ Gross, *ibid.*, 51, 2362 (1929).