the results of previous measurements by similar methods. Divergences of variable magnitude that average about 15% exist between the remainder of the present results and the only data[8] available for further comparisons; these divergences appear explicable. An extrapolated maximum flame velocity of 320 cm. per sec. for the combustion of methane with pure oxygen is in fair agreement with the value 333 reported by Jahn[8]; this supports the previously unverified divergence between Jahn's value and the values obtained by Ubbelohde and Dommer[11] and by Stevens.[12]

Displacements.—In common with previous measurements by various methods, the present results show relatively small displacements for methane. However, the relations established between these displacements and the concentration of oxygen in the atmosphere used for combustion stand in marked contrast with previous results for methane as reviewed in the introduction to this paper, and complement analogous relations derived by the writers from data published for the combustion of hydrogen and of carbon monoxide. The continuous relation, showing a maximum, between the displacement and the oxygen content of the atmosphere used for combustion seems therefore to be a common characteristic for both types of ordinary combustible gases.

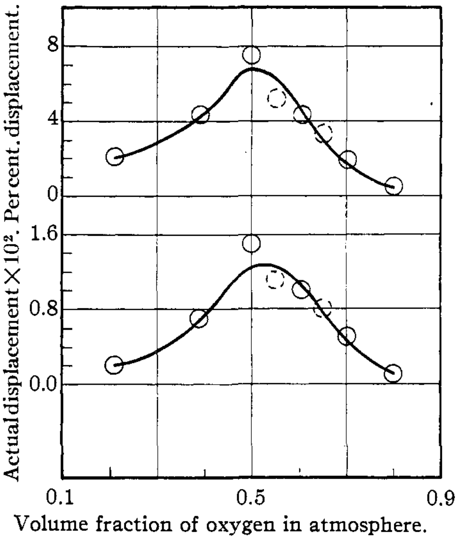

Fig. 2.—Relations between displacements of mixtures giving maximum flame velocities for methane and the composition of the atmosphere used for combustion.

V. Summary

Data showing effects of the oxygen content of atmospheres used for the combustion of methane on flame velocities and on displacements of mixtures giving maximum flame velocities are presented and discussed briefly. A new regularity between these displacements in the combustion of methane and the parameter cited has been adduced that contrasts with earlier indications for methane and complements relations derived by the writers from published data for other gases.

COLLEGE PARK, MARYLAND

RECEIVED APRIL 4, 1940

(11) L. Ubbelohde and O. Dommer, *J. Gasbeleucht.*, **57**, 757 (1914).

(12) F. W. Stevens, *Natl. Advisory Comm. Aeron. Repts.*, 305 (1929).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Acid–Base Equilibria in Methyl Alcohol[1]

BY MARTIN KILPATRICK AND WHITNEY H. MEARS

In a previous paper[2] it was shown that equilibrium constants between acids and bases could be determined by the colorimetric method, and the thermodynamic constants obtained by extrapolation. The present paper deals with the effect of ionic strength on the equilibrium

$$A_i^- + B^- = A^0 + B_i^{=}$$

in the solvent methyl alcohol. A_i^- represents the yellow form of brom phenol blue or brom cresol green, B^- represents benzoate ion or its monosubstituted derivative, A^0 represents the conjugate acid and $B_i^{=}$ the blue form of the indicator. Two methods of extrapolation to infinite dilution are considered and acid strengths relative to benzoic acid calculated from the data.

Experimental Part

Preparation of Compounds.—Commercial anhydrous methyl alcohol was purified by the method of Lund and Bjerrum.[3] A three-hour refluxing with anhydrous copper

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[1] Aided by a grant from the Penrose Fund of the American Philosophical Society.

[2] Minnick and Kilpatrick, *J. Phys. Chem.*, **43**, 259 (1939).

[3] Lund and Bjerrum, *Ber.*, **64B**, 210 (1931).

sulfate served to remove volatile alkalies. A density determination showed the samples to be 99.96% alcohol by weight if the impurity is assumed to be water.

All acids were recrystallized to constant melting point. The toluic acids were recrystallized three times from hot water. Other acids crystallized from hot water were *o*-bromo-, *o*-methoxy-, *p*-methoxy- and *p*-nitrobenzoic acids. In the case of *o*-iodo-, *m*-nitro-, *m*-bromo-, *m*-iodo-, *p*-iodo-, *p*-bromo- and *m*-hydroxybenzoic acids working in water involved inconveniently large volumes of liquid. Here the solvent pair, acetone–water, proved satisfactory. In the case of *p*-hydroxybenzoic acid, which forms a monohydrate,[4,5] the solvent pair acetone–toluene was used. An Abderhalden drying pistol served for final drying of the compounds.

The *m*- and *o*-fluorobenzoic acids[6] were prepared according to the method of Dippy and Williams.[7]

Brom phenol blue and brom cresol green, received from the Hynson, Westcott and Dunning Company, were used without further purification.

The experimental technique was that of Minnick and Kilpatrick.[2] However, the amplifier was one designed by F. H. Shepard, Jr.[8] A sample run is shown in Table I, where K_{A_iB} is defined by the equation

$$K_{A_iB} = \frac{C_A}{C_B}\frac{C_{B_i}}{C_{A_i}} \qquad (1)$$

where C_A, C_B, C_{A_i}, C_{B_i} refer to concentrations of the acid and basic forms of the acid and indicator respectively.

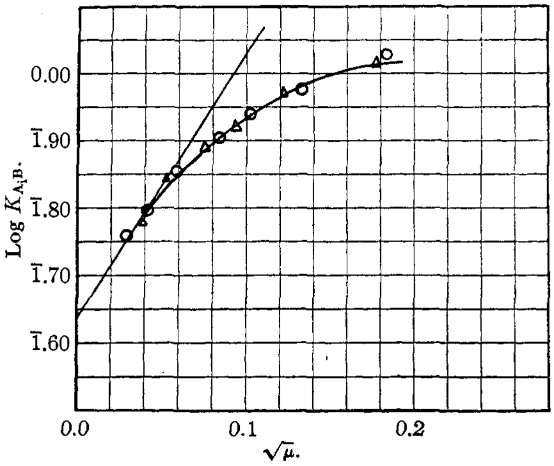

Fig. 1.—Extrapolation by equation (2): O, expt. 2; Δ, expt. 1.

TABLE I

Indicator + Benzoate = Benzoic Acid + Indicator
(acid form) (basic form)

Solvent, CH_3OH, purity 99.94% by density, dielectric, 32.1.
Acid, Kahlbaum, m. p. 122°, titrated purity 99.8%.
Indicator, brom cresol green, m. p. 220.5°.
$T = 21.5°$, $\lambda = 6300$, Debye slope = 3.99.
$C_{\text{ind.}} = 9.9 \times 10^{-6}\ M$, $C_A/C_B = 0.5002$.

C_B, moles/liter	C_{B_i}/C_{A_i}	log K_{A_iB}
0.02896	2.079	0.015
.01449	1.861	$\bar{1}.969$
.008689	1.687	$\bar{1}.926$
.005792	1.545	$\bar{1}.888$
.002896	1.400	$\bar{1}.845$
.001448	1.197	$\bar{1}.778$

log K_{A_iB} extrapolated $= \bar{1}.633$ by equation (2)
$\bar{1}.645$ by equation (3)
equation (3) log $K_{A_iB} = \bar{1}.645 + 3.99\sqrt{\mu} - 10.4\ \mu$

Table II gives the values of the equilibrium constant at various ionic strengths. The relation between the equilibrium constant and the thermodynamic equilibrium constant is given by the equation

$$\log K_{A_iB} = \log[K_{A_iB}]^0 + A(Z_{A_i} - Z_A)\sqrt{\mu} \qquad (2)$$

where

$$\frac{A}{2} = \frac{0.434\ \epsilon^3}{(DkT)^{3/2}}\sqrt{\frac{\pi N}{1000}}$$

and for $\epsilon = 4.80 \times 10^{-10}$ e. s. u.,[9] $D = 31.5$ at $T = 298.18$, A has a value of 4.02. Equation (2) is based upon the validity of the limiting law of Debye and Hückel in the solvent methyl alcohol. A typical extrapolation is shown in Fig. 1. This extrapolation is uncertain and can be avoided by the use of an indicator acid of the same charge type as the buffer acid, if a suitable indicator is available.[2] An extrapolation linear in the ionic concentration can also be made by the use of the empirical equation

$$\log K_{A_iB} - A(Z_{A_i} - Z_A)\sqrt{\mu} = \log[K_{A_iB}]^0 + B\mu \qquad (3)$$

The use of this equation is illustrated in Fig. 2. The equation for the line is

$$\log K_{A_iB} = \bar{1}.645 + 3.99\sqrt{\mu} - 10.4\ \mu$$

and the calculated values of log K_{A_iB} are given in column three of Table II. The intercept in Fig. 2 is $\bar{1}.645$ as compared with $\bar{1}.633$ by the extrapolation shown in Fig. 1. These values are in agreement with the value $\bar{1}.6$ from the data of Kolthoff and Guss[10] and the value $\bar{1}.610$ of Minnick and Kilpatrick.[2] This figure was obtained by extrapolation according to equation (2), but a value of $A = 4.22$ was used, based upon a dielectric constant of 30.3. The value of 31.5 at 25° is now

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[4] Stohmann, Kleber and Langbein, *J. prakt. Chem.*, [2] **40**, 130 (1889).

[5] Barth, *Ann.*, **152**, 95 (1869).

[6] We wish to express our thanks to Mr. Charles S. Miller who prepared the fluorobenzoic acids, and to Dr. W. C. Harden of Hynson, Westcott and Dunning Company for the two sulfonphthalein indicators.

[7] Dippy and Williams, *J. Chem. Soc.*, 1466 (1934).

[8] Keith Henney, "Electron Tubes in Industry," 2nd edition, McGraw-Hill Book Company, New York, N. Y., 1937, p. 437.

[9] Birge, *Phys. Rev.*, **52**, 241 (1937).

[10] Kolthoff and Guss, THIS JOURNAL, **60**, 2516 (1938).

adopted from the data of Åkerlöf,[11] since his data permit interpolation over a range of temperature. Equation (3) is to be preferred when the values of K_{A_iB} are known between $\mu = 0.02$ and $\mu = 0.004$. If the values are more reliable in dilute solution ($\mu < 0.004$) than at higher ionic strengths, extrapolation by equation (2) is advisable. The behavior of log K_{A_iB} at higher ionic strengths has been discussed by Kolthoff and Guss.[10]

TABLE II

THE EQUILIBRIUM CONSTANT

Brom Cresol Green (Yellow) + Benzoate = Benzoic Acid + Brom Cresol Green (Blue)

$\sqrt{\mu}$	log K_{A_iB} obsd.	log K_{A_iB} calcd.
Experiment 1		
Stoichiometric concentration of indicator, 1.0×10^{-5} M; $T = 21.5°$		
0.1790	0.015	0.056
.1204	$\bar{1}.969$	$\bar{1}.972$
.0935	$\bar{1}.926$	$\bar{1}.927$
.0762	$\bar{1}.888$	$\bar{1}.888$
.0532	$\bar{1}.845$	$\bar{1}.827$
.0396	$\bar{1}.778$	$\bar{1}.778$
Experiment 2		
Stoichiometric concentration of indicator = 6.7×10^{-6} M; $T = 22.8°$		
0.1814	0.030	0.002
.1324	$\bar{1}.977$	$\bar{1}.989$
.1027	$\bar{1}.941$	$\bar{1}.944$
.0837	$\bar{1}.906$	$\bar{1}.905$
.0592	$\bar{1}.856$	$\bar{1}.844$
.0418	$\bar{1}.795$	$\bar{1}.793$
.0286	$\bar{1}.766$	$\bar{1}.750$

TABLE III

EQUILIBRIUM CONSTANTS OF SUBSTITUTED BENZOIC ACIDS WITH BROM CRESOL GREEN

Substituent	Temp., °C.	log $[K_{A_iB}]^0$	A	$-B$	log $[K_{A_iB}]^0$ literature
.....	21.5	$\bar{1}.653$	3.987	11.6	$\bar{1}.610$[a]
.....	22.8	$\bar{1}.655$	3.995	12.0	$\bar{1}.6$[b]
.....	30.6	$\bar{1}.680$	4.084	10.5	
o-CH_3	23.0	$\bar{1}.562$	3.995	9.8	
o-CH_3	29.9	$\bar{1}.640$	4.082	12.0	
o-OCH_3	28.4	$\bar{1}.500$	4.064	13.0	
m-CH_3	23.0	$\bar{1}.750$	3.995	10.0	
m-OH	23.0	$\bar{1}.815$	3.997	11.0	
p-Cl	28.8	$\bar{1}.250$	4.063	11.5	
p-Cl	30.5	$\bar{1}.300$	4.084	9.0	
p-F	23.4	$\bar{1}.497$	4.000	14.7	
p-CH_3	22.5	$\bar{1}.865$	3.992	11.2	
p-OCH_3	29.2	$\bar{1}.990$	4.068	11.0	
p-OH	23.0	0.230	3.997	10.0	

[a] From the data of Minnick and Kilpatrick (ref. 2). [b] Results of Kolthoff and Guss, ref. 10.

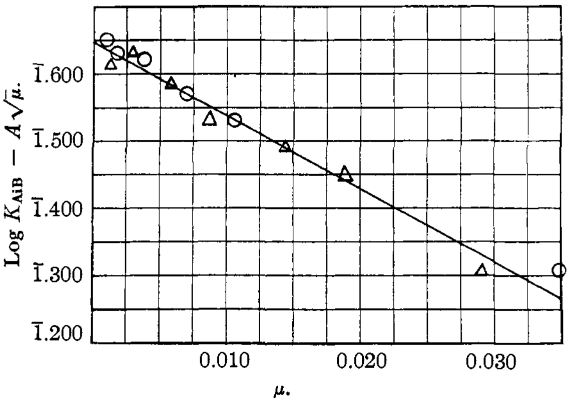

Fig. 2.—Extrapolation by equation (3): ○, expt. 2; △, expt. 1.

Tables III and IV summarize the results of similar expermients with substituted benzoic acids and the indicators brom cresol green and brom phenol blue. The constants A and B for equation (3) are given for each acid together with the intercepts determined by graphs similar to Fig. 2 The reproducibility of the experimental values of log

TABLE IV

EQUILIBRIUM CONSTANTS OF SUBSTITUTED BENZOIC ACIDS WITH BROM PHENOL BLUE

Substituent	Temp., °C.	log $[K_{A_iB}]^0$	A	$-B$	log $[K_{A_iB}]^0$ literature
....	22.0	0.575	3.980	11.5	0.6[b]
....	24.2	.580	4.010	14.0	0.490[a]
....	24.2	.620	4.010	12.0	
....	24.5	.615	4.015	11.0	
....	25.0	.615	4.020	12.0	
....	29.9	.585	4.076	12.5	
o-NO_2	22.2	$\bar{2}.720$	3.980	10.5	$\bar{2}.7$[b]
o-NO_2	29.2	$\bar{2}.795$	4.068	11.4	
o-I	23.4	$\bar{1}.410$	4.000	10.5	
o-Br	23.3	$\underline{1}.360$	3.995	10.3	
o-Br	27.4	$\bar{1}.345$	4.047	11.0	
o-Cl	28.5	$\bar{1}.385$	4.060	10.5	$\bar{1}.398$[a]
o-F	23.4	$\bar{1}.590$	4.000	11.5	
o-OH	26.4	1.067	4.036	10.5	
m-NO_2	22.2	$\bar{1}.547$	3.991	9.4	$\bar{1}.4$[b]
m-NO_2	27.8	$\bar{1}.540$	4.052	11.0	
m-I	23.4	0.060	4.000	9.0	
m-Br	22.5	.057	3.992	9.5	
m-Br	27.4	.000	4.047	12.0	
m-Cl	27.6	.033	4.050	11.5	$\bar{1}.930$[a]
m-Cl	28.5	.030	4.062	11.5	
m-F	26.2	.120	4.033	11.3	
p-NO_2	22.5	$\bar{1}.530$	3.993	8.3	$\bar{1}.5$[b]
p-NO_2	28.5	$\bar{1}.520$	4.061	10.0	
p-I	23.6	0.215	4.002	8.5	
p-Br	22.0	.197	3.978	10.7	
p-Br	29.3	.202	4.069	11.2	

[a] From data of Minnick and Kilpatrick. [b] Results of Kolthoff and Guss.

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[11] Åkerlöf, THIS JOURNAL, 54, 4125 (1932).

K_{A_iB} is ±0.01 log unit at $\mu = 0.005$, provided the same sample of indicator acid and solvent are used. The effect of temperature on the equilibrium constants is not large but the value of B determined over a short range of electrolyte concentration is sensitive to experimental error and to the value of A, which depends on the dielectric constant and temperature. B can be regarded as essentially the same for the various equilibria studied. This means that there are no appreciable specific salt effects in the range to $\mu = 0.02$ and the values of $K_{A_xB_0}$ given in Table V can be considered approximately independent of electrolyte concentration within the experimental error of the measurements.

TABLE V

RELATIVE ACID STRENGTHS

Substituent	$K_{A_xB_0}$ in water	Source	$K_{A_xB_0}$ in methyl alcohol	From literature for methyl alcohol	Source
o-NO_2	107	*b*	69.5	90, 99	*f, g*
o-Br	22.3	*d*	17.4		
o-I	21.9	*c*	15.4		
o-Cl	19.0	*a*	16.3	10.5	*g*
o-OH	15.9	*i*	34.0		
o-F	8.63	*c*	10.2		
p-NO_2	6.00	*c*	11.8	9, 20	*f, g*
m-NO_2	5.19	*c*	11.3	12, 24	*f, g*
m-Br	2.46	*c*	3.72		
m-Cl	2.39	*a*	3.68	3.0, 3.63	*g, h*
m-I	2.25	*c*	3.45		
m-F	2.18	*c*	3.01		
o-CH_3	1.97	*b*	1.16		
p-Br	1.71	*d*	2.50	2.4	*h*
p-Cl	1.66	*a*	2.45	2.5	*g*
p-I	...		2.42		
o-OCH_3	1.29	*b*	1.46		
m-OH	1.26	*i*	0.71		
p-F	1.15	*d*	1.47		
Benzoic acid					
m-CH_3	0.87	*c*	0.82		
p-CH_3	.68	*c*	.63	0.62	*h*
p-OCH_3	.54	*e*	.47		
p-OH	.44	*i*	.27		

[a] Saxton and Meier, THIS JOURNAL, **56**, 1918 (1934). [b] Dippy and Lewis, *J. Chem. Soc.*, 1426 (1937). [c] Dippy and Lewis, *ibid.*, 644 (1936). [d] Dippy, Williams and Lewis, *ibid.*, 343 (1935). [e] Dippy and Williams, *ibid.*, 1888 (1934). [f] Kolthoff and Guss, THIS JOURNAL, **61**, 330 (1939). [g] Bright and Briscoe, *J. Phys. Chem.*, **37**, 787 (1933). [h] Goodhue and Hixon, THIS JOURNAL, **56**, 1329 (1934). [i] Branch and Yabroff, *ibid.*, **56**, 2568 (1934).

Table V gives the ratios of the dissociation constants of substituted benzoic acids to benzoic acid, as computed from Tables III and IV. The values are the equilibrium constants for the reaction

$$A_x + B_0 \rightleftarrows A_0 + B_x \qquad (4)$$

where A_x represents the substituted acid, B_x the corresponding base, and A_0 and B_0 represent benzoic acid and benzoate. This equilibrium constant is designated $K_{A_xB_0}$. A comparison of column four with column two shows that the order of decreasing acid strength relative to benzoic acid is not the same in the solvent methyl alcohol as in water. On the quantitative side it is to be noted that the ratio of strength relative to benzoic acid increased in most cases of meta and para substitution on passing from water to methyl alcohol, while the reverse is true for the ortho acids. Various authors[12,13] have considered the electrostatic effect of substituents on the dissociation constants of acids and arrived at a relationship of the form

$$\log \frac{K_{A_x}}{K_{A_0}} = \frac{\epsilon \mu \cos \Theta}{2.303\, kT\, D_E\, r^2} \qquad (5)$$

where Θ is the angle between the radius vector r and the dipole lying along the C- substituent bond, μ the dipole moment of the substituent bond, r the distance between the dipole and the proton, and D_E the effective dielectric. In our case K_{A_x} and K_{A_0} are the dissociation constants of substituted and unsubstituted acids and the ratio K_{A_x}/K_{A_0} is equal to $K_{A_xB_0}$. The difficulty of applying such an equation is that the calculated value of $K_{A_xB_0}$ is very sensitive to the value chosen for r and that D_E must be evaluated. Westheimer and Kirkwood[14] have evaluated D_E by considering the ions and molecules involved as ellipsoidal cavities of low dielectric constant and Westheimer[15] has recently evaluated log $K_{A_xB_0}$ for the para substituted benzoic acids in aqueous solution. It is of interest to compare the experimental results in methyl alcohol with similar calculations for this solvent. These calculations are summarized in Table VI. The value of r is taken as 5.9 Å. in agreement with the value chosen by Westheimer[16] and the dipole moments of the correspondingly substituted benzenes are taken from the literature.

The agreement between the observed and calculated values is poorer in the solvent methyl alcohol than in water. In other words the Kirkwood–

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(12) Eucken, *Angew. Chem.*, **45**, 203 (1932).

(13) Schwarzenbach and Egli, *Helv. Chim. Acta*, **17**, 1183 (1934).

(14) Westheimer and Kirkwood, *J. Chem. Phys.*, **6**, 513 (1938).

(15) Westheimer, THIS JOURNAL, **61**, 1977 (1939).

(16) The authors take this opportunity to thank Dr. F. H. Westheimer for tables of the various functions employed in the calculation of d_E.

TABLE VI

COMPARISON OF CALCULATED AND OBSERVED VALUES OF $K_{A_xB_0}$

Substituent in para .position	Solvent water, DE 9.4		Solvent CH_3OH, 7.7	
	Calcd.	Obsd.	Calcd.	Obsd.
NO_2	4.1	6.0	5.5	12
I	1.6	...	1.7	2.4
Br	1.7	1.7	1.9	2.5
Cl	1.7	1.7	1.9	2.45
F	1.65	1.15	1.85	1.5
CH_3	0.87	0.68	0.85	0.62

Westheimer theory predicts that the relative acid strengths are less sensitive to the macro-dielectric constant of the solvent than experiment indicates. In the calculation of $K_{A_xB_0}$ the value of the partial molal volume was taken as approximately 180 Å^3. It is realized that the partial molal volume may be larger in methyl alcohol than in water,[17] and that slightly better agreement between experiment and theory can be obtained by the arbitrary choice of a larger value. A calculation of V (the partial molal volume) for a fixed value of r shows that V would have to be changed very considerably from its value in water to approximate the results in methyl alcohol. A calculation of V from equation (5), using the observed values of log $K_{A_xB_0}$, shows that V is far from constant in a given solvent.

Summary

1. The effect of ionic strength on the equilibrium constants for the reaction between sulfonpthalein indicators and monosubstituted benzoic acids has been investigated.

2. Two methods of extrapolation to infinite dilution have been compared.

3. The acid strength constants relative to benzoic acid have been calculated from the data.

PHILADELPHIA, PA. RECEIVED JULY 25, 1940

(17) Traube, *Saml. chem. chem.-tech. Vortr.*, **4**, 255 (1899).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AT THE UNIVERSITY OF PENNSYLVANIA]

Acid-Base Equilibria in Ethyl Alcohol*

BY MARTIN KILPATRICK AND WHITNEY H. MEARS

In the preceding paper[1] the equilibrium constants between the yellow-blue forms of brom cresol green and brom phenol blue, and the monosubstituted benzoic acid-benzoate buffers, were reported for the solvent methyl alcohol. This paper summarizes the results in ethyl alcohol and considers the significance of the results in both solvents.

Experimental Part

Ethyl alcohol was purified by the method of Lund and Bjerrum[2] and refluxed with anhydrous copper sulfate. The water content was determined by density measurements and found to be less than 0.04% by weight. The carboxylic acids and indicators were the same as those used in the solvent methyl alcohol. The experimental method was identical with that described in the previous paper.[1]

The extrapolation to infinite dilution is more difficult in ethyl alcohol than in methyl, since the dielectric constant is lower. For ethyl alcohol the dielectric constant[3] is given by the equation

$$\log D = 1.3979 - 0.00264(t - 20) \qquad (1)$$

Figure 1 shows an extrapolation by equation (2) of the previous paper

$$\log K_{A_iB} = \log [K_{A_iB}]^0 + A(Z_{A_i} - Z_A)\sqrt{\mu} \qquad (2)$$

and Fig. 2 gives the corresponding graph for equation (3)

$$\log K_{A_iB} - A(Z_{A_i} - Z_A)\sqrt{\mu} = \log[K_{A_iB}]^0 + B\mu \qquad (3)$$

The value for A at 25° is 5.94.

Table I summarizes the data for the equilibrium constants between brom cresol green and benzoic acid and the substituted benzoic acids. The reproducibility of the extrapolated values is indicated by the values in column three of Tables I and II, for the equilibrium between the indicator and benzoic acid. In general the results are reproducible to 0.02 log unit. The value of the constant B is uncertain to ±3 units and must be considered applicable only at low ionic strengths. If B were the same for all the acids studied we

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* Aided by a grant from the Penrose Fund of the American Philosophical Society.

(1) Kilpatrick and Mears, THIS JOURNAL, **62**, 3047 (1940).

(2) Lund and Bjerrum, *Ber.*, **64B**, 210 (1931).

(3) Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).