DISSOCIATION CONSTANTS OF *ORTHO-, META-* AND *PARA-* HYDROXY BENZOIC ACIDS, GALLIC ACID, CATECHOL, RESORCINOL, HYDROQUINONE, PYROGALLOL AND PHLOROGLUCINOL.

By C. T. Abichandani and S. K. K. Jatkar.

INTRODUCTION.

The concept underlying the polar effects of substituent groups in the benzene ring has been based partly on the dissociation constants of the substituted benzoic acids. The effect of OH substitution in benzoic acid and in phenols, has been studied by various methods. Kohlrausch and Stockmair (*Monatsch,* 1935, **66**, 316) while studying the Raman spectrum of hydroxy substituted benzoic acid esters, found that the presence of OH in *ortho-, meta-* and *para*-positions affects the CO frequency, and the order of influence is the same in which the substituent increases the dissociation constants of the acids. Recently Wulf and Liddel (*Jour. Amer. Chem. Soc.*, 1935, **57**, 1464) have measured infra-red spectra of mono, di- and tri-hydroxy benzenes, and observe that catechol and pyrogallol show double peaks, while the rest of the phenols show only single peaks. Pauling (*Ibid.,* 1936, **58**, 94) and later Wulf, Liddel and Hendricks (*Ibid.*, 1936, **58**, 2287) have explained these peaks on the assumption of *cis* and *trans* positions of two OH groups in catechol and pyrogallol. The other phenols have both the OH groups in *cis-cis* or *trans-trans* positions. The effect of substitution of various other groups on the infra-red spectra has been studied, but little attention has been paid to the mutual effect of hydroxyl and carboxyl groups in various positions in substituted phenols.

It has been known for a long time that the dissociation constants of carboxylic acids are influenced by the polar characters of the substituent groups. The extensive work of Ostwald has shown that the substituents may either increase or decrease the strength of carboxylic acids. Derik (*Ibid.*, 1911, **33**, 1152) has expressed the action of substituent groups as a logarithmic function of dissociation constants (log K) of the substituted acids. Walters (*Phil. Mag.*, 1929, **8**, 436) was the first to correlate the values of dissociation constants of a number of substituted benzonic acids X-C_6H_4COOH

with the dipole moment of the corresponding substituted benzene X-C_6H_5. He suggested that in the absence of the complications arising from factors such as electronic and steric effects, log K is a linear function of the dipole moment. Recently Nathan and Watson (*Jour. Chem. Soc.,* 1933, 893) have derived an equation connecting the dissociation constans of substituted acetic acids with the dipole moment of appropriate methane derivative X-CH_3. The possibility of a similar relationship in the aromatic acids was considered by Nathan and later by Dippy Williams and co-workers (*Jour. Chem. Soc.,* 1934, 161, 1888; 1935. 343, 346; 1936, 644; 1937, 1008) who found that, a straight line relationship exists between the dissociation constants of the substituted acids and the dipole moment of corresponding substituted benzene.

The first dissociation constants for the various acids and phenols have been obtained previously (Thiel and Roemer, *Z. Physik Chem.*, 1908, **63**, 731, 744) by the conductivity method, using Ostwald's classical formula for deducing the constants. It was necessary to obtain the value of the dissociation constants more acurately. In this investigation, the first and second thermo-dynamical dissociation constants of various *ortho-*, *meta-* and *para*-substituted hydroxy benzoic acids and di- and tri-hydroxy benzenes have been measured from the potentiometric titration data, making corrections for the interionic attraction, with the help of Debye-Hückel equation.

EXPERIMENTAL.

Titration cell used was the same as described previously (*This Journal,* 1938, **21A**, 345). It was kept in a water-bath maintained at a constant temperature at 30°. Pure *o*-hydroxy benzoic acid (m.p. 159°), *m*-hydroxy benzoic acid (m.p. 200.8°), *p*-hydroxy benzoic acid (m.p. 213°–7°), gallic acid (m.p. 239°), catechol (m.p. 105°), resorcinol (m.p. 110°), hydroquinone (m.p. 170.3°), pyrogallol (m.p. 132.9°–133.3) and phloroglucinol (m.p. 110°) were used.

Standard alkali solution was prepared from pure sodium taking all precautions to exclude carbon dioxide.

The pH was calculated from the observed E.M.F. by the use of the formula $\frac{E_{obs} - E_{cal.}}{\cdot 0601}$ at 30° C.; the junction potential being very small was neglected. (*Cf.* Abichandani and Jatkar, *This Journal,* 1938, **21A**, 373.)

CALCULATION OF DISSOCIATION CONSTANTS.

A dibasic acid dissociates in the following manner,

$$H_2An \leftrightarrows H^+ + HAn^-$$

$$HAn^- \leftrightarrows H^+ + An^{--}$$

and from the law of mass action the two dissociation constants are given by

$$K_1^a = \frac{a_H \, a_{HAn}}{a_{H_2An}} = \frac{c_H \cdot c_{HAn} \, f_H f_{HAn}}{c_{H_2An} \cdot f_{H_2An}} = K_1^c \frac{f_H \, f_{HAn}}{f_{H_2An}} \quad .. \quad (I)$$

$$K_2^a = \frac{a_H \, a_{An}}{a_{HAn}} = \frac{c_H \, c_{An} \, f_H \, f_{An}}{c_{HAn} \, f_{HAn}} = K_2^c \frac{f_H \, f_{An}}{f_{HAn}} \quad .. \quad (II)$$

The above equations involve the terms a the activity, f the practical activity coefficient and c the concentrations in moles per litre, while the Guldberg and Waage's original equation only involved the term c. Both experimental and theoretical observations have shown that mass law relation is given by activity rather than by concentration factors. The value of the activity coefficient f can be calculated from Debye and Hückel (*Phys. Z.*, 1923, **24**, 185, 305, 334) theory, which gives it as a function of concentration,

$$\log f = \frac{2 \cdot 954 \times 10^6}{2 \cdot 3026 \, (DT)^{1 \cdot 5}} Z_1 Z_2 \sqrt{\Sigma C_i Z_i^2}$$

$$= - A \, Z_i^2 \, \sqrt{\mu} \quad .. \quad .. \quad .. \quad (III)$$

where D is dielectric constant of solvent, T is absolute temperature, Z = ionic charge, 2.954×10^6 is the numerical product of Boltzman constant and the electronic charge, and D has the value 78.54. All these terms being constant, are grouped under one constant A. Guggenheim (*Jour. Phys. Chem.*, 1934, **38**, 533) has treated the electrolytes as though they have equal ionic parameters and modified the above equation; according to him

$$\log f = - A \; Z_i^2 \; \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \quad .. \quad (IV)$$

and for concentrated solutions

$$\log f = - A \, Z_i^2 \, \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + \beta\mu \quad .. \quad (V)$$

where term β is a constant called the 'salt coefficient' and arises from the repulsive forces between ions in concentrated solutions (Hückel, *Phys. Z.*, 1925, **26**, 93). In our case, however, the term involving β will be dropped, as the concentrations used are very low and the salt coefficient is very small. Upon substituting the equation (V) for activity coefficients in equations (I) and (II), taking f_{H_2An} and f_H (in very dilute solutions) as unity, we get

$$\log K_1^a = \log K_1^c - A \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \quad \cdots \quad (VI)$$

$$\log K_2^a = \log K_2^c - 4A \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + A \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \quad \cdots \quad (VII)$$

where K_1^a and K_2^a are thermodynamical dissociation constants in pure water.

For the calculation of dissociation constants, the various ionic concentrations have been calculated from their stoichiometrical concentrations. In Table I for each acid, the values of moles of NaOH per mole of acid and the stoichiometrical concentrations of added alkali (equivalent concentration of sodium salts = J), total acid, unneutralized acid, mono sodium salt and di-salt, are given. If M represents the stoichiometrical concentration and *c* the ionic concentrations, the following relationships hold good between the various quantities, throughout the titration. For the first half of titration,

$$\begin{aligned} C_{NaHAn} &= J + C_H - C_{OH} \\ C_{H_2An} &= M_{H_2An} - C_{NaHAn} \\ &= M_{H_2An} - J - C_H + C_{OH} \\ &= M_U - C_H + C_{OH} \end{aligned}$$

For the second half of titration

$$\begin{aligned} C_{Na_2An} &= J - M_{H_2An} + C_H - C_{OH} \\ &= M_{Na_2An} + C_H - C_{OH} \\ C_{NaHAn} &= 2M_{H_2An} - J - C_H + C_{OH} \\ &= M_{H_2An} - M_{Na_2An} - C_H + C_{OH} \\ &= M_{NaHAn} - C_H + C_{OH} \end{aligned}$$

These relations hold good for each acid group when treated independently of the dissociation of other acid groups. In the cases where overlapping of the two groups occur and both of them titrate simultaneously over a particular range, the above relations do not hold good.

It is seen from the results for phloroglucinol, and also from the dibasic acids studied by us previously (*This Journal,* **21A**, 373–84) that the range over which the overlapping of two groups occurs, depends on the ratio K_1/K_2, the range increasing with decreasing ratio and is shown by the fact that the calculated values for dissociation constants in this region vary enormously. This variation is due to the formation of di-salt before the first group is completely neutralized. To calculate the ionic concentration in this region, the value for each ion is solved by taking into account the formation of di-salt, (Burton, Hammer and Acree, *Jour. Bureau of Standards,* 1936, **16**, 575).

The equation $M_{NaOH} + C_H = C_{HAn} + 2C_{An}$ expresses the solution neutrality, and $C_{H_2An} + C_{An} + C_{HAn} = M_{H_2An}$ due to the conservation of mass. Solving these two simultaneously with equations (I) and (II), we get the ionic concentration of di-salt as

$$C_{An} = \frac{M_{H_2An}\, K_1^c\, K_2^c}{{C_H}^2 + C_H\, K_1^c + K_1^c\, K_2^c} \qquad \text{.. (VIII)}$$

The average values of K_1^c and K_2^c in the region where they are constant, are employed in the above equation. In phloroglucinol it is seen that the values go on changing rapidly from the very beginning, showing titration of both groups simultaneously. By taking the value of $K_1^c = 3.6 \times 10^{-9}$ and $K_2^c = 1{\cdot}6 \times 10^{-9}$ the ionic concentration of di-salt formed is calculated as given in Table III for this substance. The new values of K_1^c and K_2^c have been obtained by the method of successive approximation. The values of K_1^c and K_2^c are fairly concordant.

The ionic strength μ, corresponding to various ionic concentrations, is equal to one half the sum of each ion molality present in the solution, multiplied by the square of its valence (Lewis and Randall, *Thermodynamics,* 1923, pp. 373 and 428). In the first part of titration $\mu = (2J + 2\ CH)/2$ and for the second part $\mu = (4J - 2M_{H_2An} + 4CH)/2$. The values of μ calculated according to the equations are given in Table II for each acid.

Burton, Hammer and Acree (*Jour. Bureau of Standards,* 1936, **16**, 575) have taken the value of μ in the first half of the titration as $(2J + 3CH)/2$ and during the second half as $(4J - 2M_{H_2An} + 5CH)/2$. They have evidently taken the concentration of sodium ion as equal to $J + C_H$, which should be equal to J, the concentration of added alkali, since the salts are completely dissociated. The values of K_1^c, K_2^c and K_1^a, K_2^a calculated according to the method outlined, are given in Table II for each acid.

(1) ORTHO-HYDROXY BENZOIC ACID.

TABLE I. Stoichiometrical concentrations prevailing in the titration of 200 c.c. of 0·007130 M acid by 0·1057 N sodium hydroxide.

0·1057 N NaOH	Moles NaOH per mole acid	J = equiv. conc. of Na salts × 10^4	M_{H_2An} × 10^4	M_{H_2An} = U × 10^4	M_{NaHAn} × 10^4	M_{Na_2An} × 10^4
0·0	0·0000	0·00	71·30	71·30	0·00	..
1·0	·0741	5·26	70·94	65·68	5·26	..
2·0	·1482	10·47	70·50	60·12	10·47	..
3·0	·2224	15·62	70·23	54·61	15·62	..
4·0	·2965	20·73	69·87	49·14	20·73	..
5·0	·3706	25·78	69·52	43·74	25·78	..
6·0	·4448	30·79	69·23	38·44	30·79	..
7·0	·5189	35·74	58·80	33·06	35·74	..
8·0	·5930	40·65	68·52	27·87	40·65	..
9·0	·6671	45·52	68·16	22·64	45·52	..
10·0	·7412	50·33	67·88	17·55	50·33	..
11·0	·8154	55·10	67·52	12·42	55·10	..
12·0	·8895	59·83	67·24	7·41	59·83	..
13·0	·9636	64·51	66·88	2·37	64·51	..
14·0	1·0377	69·15	66·59	..	64·03	2·56
15·0	1·1119	73·74	66·31	..	58·87	7·43
16·0	1·1860	78·30	66·02	..	53·74	12·28
17·0	1·2601	82·81	65·67	..	48·53	17·14
18·0	1·3342	87·28	65·38	..	43·48	21·90
19·0	1·4083	91·70	65·10	..	38·50	26·60
20·0	1·4825	96·09	64·81	..	33·53	31·28
21·0	1·5566	100·44	64·53	..	28·62	35·91
22·0	1·6307	104·75	64·24	..	23·73	40·51
23·0	1·7048	109·02	63·96	..	18·90	45·06
24·0	1·7790	113·25	63·67	..	14·09	49·58
25·0	1·8531	117·44	63·39	..	9·34	54·05
26·0	1·9270	121·60	63·10	..	4·60	58·50
27·0	2·0013	125·72	62·82	..	..	62·90

TABLE II. Data for the titration.

First Equivalent of Sodium Hydroxide.

Calomel temp.	0·1057 N NaOH	E.M.F.	pH	$C_H \times 10^n$	n	$K_1^c \times 10^3$	$\mu \times 10^4$	$K_1^a \times 10^3$
28·0	0·0	0·3941	2·51	3·090	3	..	..	..
28·2	1·0	·3992	2·59	2·570	3	1·99	30·96	1·87
,,	2·0	·4021	2·64	2·291	3	2·06	33·38	1·93
,,	3·0	·4057	2·70	1·995	3	2·05	35·57	1·92
,,	4·0	·4101	2·77	1·698	3	1·99	37·71	1·86
28·3	5·0	·4145	2·85	1·413	3	1·90	39·91	1·77
,,	6·0	·4197	2·93	1·175	3	1·87	42·54	1·74
,,	7·0	·4252	3·03	9·333	4	1·77	45·07	1·65
28·4	8·0	·4316	3·14	7·244	4	1·68	47·89	1·56
,,	9·0	·4387	3·25	5·623	4	1·69	51·15	1·56
28·5	10·0	·4482	3·41	3·890	4	1·54	54·22	1·43
,,	11·0	·4602	3·61	2·455	4	1·42	57·56	..
,,	12·0	·4789	3·92	1·202	4	1·18	61·03	..
28·6	13·0	·5408	4·96	1·096	5	3·13	64·62	..
,,	13·2	·6342	..	..	..	..	..	..
28·8	*13·3*	·7623	..	..	..	..	..	..
								1·76

Second Equivalent of Sodium Hydroxide.

Calomel temp.	0·1057 N NaOH	E.M.F	pH	$C_H \times 10^n$	n	$K_2^c \times 10^{13}$	$\mu \times 10^4$	$K_2^a \times 10^{13}$
28·8	13·4	·8132	..	..	..	..	..	..
,,	14·0	·8525	10·14	7·244	11	..	69·14	..
,,	15·0	·8758	10·53	2·951	11	4·70	74·86	..
,,	16·0	·8803	10·61	2·455	11	18·77	82·99	..
28·9	17·0	·8972	10·89	1·288	11	5·50	85·50	4·10
,,	18·0	·9036	11·00	1·000	11	5·28	90·56	3·99
,,	19·0	·9085	11·08	8·318	12	5·63	95·91	4·13
,,	20·0	·9128	11·15	7·079	12	5·89	101·07	4·29
,,	21·0	·9165	11·21	6·166	12	5·99	106·15	4·33
28·8	22·0	·9193	11·26	5·495	12	6·13	111·18	4·38
,,	23·0	·9221	11·30	5·012	12	7·07	116·93	..
,,	24·0	·9245	11·34	4·571	12	7·37	122·09	..
28·7	25·0	·9260	11·37	4·266	12	8·37	127·84	..
,,	26·0	·9270	11·39	4·072	12	10·35	134·39	..
,,	27·0	·9299	11·43	3·715	12	..	..	..
								4·20

(2) META-HYDROXY BENZOIC ACID.

TABLE I. Stoichiometrical concentrations prevailing in the titration of 200 c.c. of 0·007268 M acid by 0·1017 N sodium hydroxide.

0·1017 N NaOH	Moles NaOH per mole acid	J = equiv. conc. of Na salts × 10^4	$M_{H_2An} \times 10^4$	$M_{H_2An} = U \times 10^4$	$M_{NaHAn} \times 10^4$	$M_{Na_2An} \times 10^4$
0·0	0·0000	0·00	72·68	72·68	0·00	..
2·0	·1399	10·07	71·95	61·88	10·07	..
3·0	·2099	15·03	71·59	56·56	15·03	..
4·1	·2869	20·43	71·15	50·72	20·43	..
5·0	·3498	24·80	70·86	46·06	24·80	..
6·0	·4198	29·62	70·57	40·95	29·62	..
7·0	·4897	34·39	70·14	35·75	34·39	..
8·0	·5597	39·12	69·85	30·73	39·12	..
9·0	·6297	43·79	69·48	25·69	43·79	..
10·0	·6996	48·43	69·19	20·76	48·43	..
11·0	·7696	53·02	68·83	15·81	53·02	..
12·0	·8396	57·57	68·54	10·97	57·57	..
13·0	·9095	62·07	68·17	6·10	62·07	..
14·0	·9795	66·53	67·88	1·35	66·53	..
15·0	1·0495	70·95	67·59	..	64·23	3·36
16·0	1·1194	75·33	67 30	..	59·27	8·03
17·0	1·1894	79·67	66·94	..	54·21	12·73
18·0	1·2594	83·98	66·65	..	49·32	17·33
19·0	1·3293	88·23	66·36	..	44·59	21·77
20·0	1·3993	92·45	66·07	..	39·69	26·38
21·0	1·4692	96·64	65·78	..	34·92	30·86
22·0	1·5392	100·78	65·48	..	30·18	35·30
23·0	1·6092	104·89	65·19	..	25·49	39·70
24·0	1·6791	108·96	64·90	..	20·84	44·06
25·0	1·7491	113·00	64·61	..	16·22	48·39
26·0	1·8191	117·00	64·32	..	11·64	52·68
27·0	1·8890	120·96	64·03	..	7·10	56·93
28·0	1·9590	124·89	63·74	..	2·59	61·15
29·0	2·0290	128·79	63·45	..	..	65·34

TABLE II. Data for the titration.

First Equivalent of Sodium Hydroxide.

Calomel temp.	0·1017 N NaOH	E.M.F.	pH	$C_H \times 10^n$	n	$K_1^c \times 10^4$	$\mu \times 10^4$	$K_1^a \times 10^4$
26·5	0·0	0·4269	3·03	9·333	4	..	..	..
,,	2·0	·4417	3·28	5·248	4	1·42	15·32	1·36
,,	3·0	·4493	3·41	3·890	4	1·40	18·92	1·33
,,	4·1	·4579	3·55	2·818	4	1·37	23·25	1·30
,,	5·0	·4645	3·66	2·188	4	1·35	26·99	1·28
26·6	6·0	·4715	3·77	1·698	4	1·35	31·32	1·27
,,	7·0	·4785	3·89	1·288	4	1·33	35·68	1·25
,,	8·0	·4853	4·00	1·000	4	1·35	40·12	1·26
,,	9·0	·4923	4·12	7·586	5	1·36	44·55	1·26
,,	10·0	·5006	4·26	5·495	5	1·33	48·98	1·23
26·8	11·0	·5110	4·44	3·631	5	1·25	53·38	1·16
,,	12·0	·5217	4·61	2·455	5	1·32	57·82	1·22
,,	13·0	·5393	4·91	1·230	5	1·28	62·19	1·20
,,	14·0	·5909	5·76	1·738	6	1·14	66·55	..
,,	14·2	·6252	..	..	..	..	..	..
,,	*14·3*	·6715	..	..	..	..	..	..
								1·25

Second Equivalent of Sodium Hydroxide.

						$K_2^c \times 10^{10}$		$K_2^a \times 10^{10}$
26·6	14·4	·7106	..	..	..	..	..	..
,,	*14·5*	*·7215*	..	..	..	..	..	..
,,	15·0	..	..	..	..	..	..	..
,,	16·0	·7736	8·80	1·585	9	2·11	83·24	..
,,	17·0	·7851	8·99	1·023	9	2·36	92·22	1·74
26·5	18·0	·7950	9·16	6·918	10	2·38	101·04	1·73
,,	19·0	·8041	9·31	4·898	10	2·33	109·62	1·68
,,	20·0	·8117	9·43	3·715	10	2·39	118·33	1·71
26·7	21·0	·8189	9·56	2·754	10	2·33	126·82	1·67
,,	22·0	·8262	9·68	2·089	10	2·31	135·19	1·62
,,	23·0	·8334	9·80	1·585	10	2·29	143·41	1·59
,,	24·0	·8402	9·91	1·230	10	2·34	151·51	1·61
,,	*25·0*	*·8479*	*10·04*	*9·120*	*11*	2·31	159·35	1·57
,,	26·0	·8555	10·17	6·761	11	2·35	166·93	1·59
,,	27·0	·8642	10·31	4·898	11	2·39	177·09	1·60
,,	28·0	·8725	..	..	..	..	..	..
,,	28·5	·8771	..	..	..	..	..	..
26·5	29·0	·8805	..	..	..	..	..	..
								1·65

(3) PARA-HYDROXY BENZOIC ACID.

TABLE I. Stoichiometrical concentrations prevailing in the titration of 200 c.c. of 0·006464 M acid by 0·1017 N sodium hydroxide.

0·1017 N NaOH	Moles NaOH per mole acid	J = equiv. conc. of Na salts $\times 10^4$	$M_{H_2An} \times 10^4$	$M_{H_2An} = U \times 10^4$	$M_{NaHAn} \times 10^4$	$M_{Na_2An} \times 10^4$
0·0	0·0000	0 00	64·64	64·64	0·00	..
2·0	·1573	10·07	63·99	53·92	10·07	..
3·0	·2360	15·03	63·67	48·64	15·03	..
4·0	·3147	19·94	63·35	43·41	19 94	..
5·0	·3933	24·80	63·02	38·22	24·80	..
6·0	·4720	29·62	62·77	33·15	29·62	..
7·0	·5507	34·39	62·38	27·99	34·39	..
8·0	62·93	39·12	62·12	23·00	39·12	..
9·0	·7080	43·79	61·80	18·01	43·79	..
10·0	·7867	48·43	61·54	13 11	48·43	..
11·0	·8653	53·02	61·21	8·19	53·02	..
12·0	·9440	57·57	60·96	3·39	57·57	..
13·0	1·0227	62·07	60·63	..	59·19	1·44
14·0	1·1013	66·53	60·37	..	54·21	6·16
15·0	1·1800	70·95	60·12	..	49·29	10·83
16·0	1·2587	75·33	59·86	..	44·39	15·47
17·0	1·3373	79·67	59·53	..	39·39	20·14
18·0	1·4160	83·98	59·27	..	34·56	24·71
19·0	1·4947	88·23	59·02	..	29·81	29·21
20·0	1·5733	92·45	58·76	..	25·07	33·69
21·0	1·6520	96·64	58·50	..	20·36	38·14
22·0	1·7307	100·78	58·24	..	15·70	42·54
23·0	1·8093	104·89	57·98	..	11·67	46·91
24·0	1·8880	108·96	57·72	..	6·48	51·24
25·0	1·9667	113·00	57·46	..	1·92	55·54

TABLE II. Data for the titration.

First Equivalent of Sodium Hydroxide.

Calomel temp.	0·1017 N NaOH	E.M.F.	pH	$C_H \times 10^n$	n	$K_1^c \times 10^5$	$\mu \times 10^4$	$K_1^a \times 10^5$
25·6	0·0	0·4376	3·20	6·310	4	..	..	..
25·7	2·0	·4632	3·63	2·344	4	5·64	12·41	5·42
,,	3·0	·4736	3·80	1·585	4	5·60	16·64	5·35
26·2	4·0	·4829	3·96	1·096	4	5·45	21·04	5·18
,,	5·0	·4911	4·10	7·943	5	5·43	25·59	5·13
26·0	6·0	·4994	4·23	5·888	5	5·46	30·21	5·14
26·1	7·0	·5078	4·37	4·266	5	5·39	34·82	5·05
26·0	8·0	·5155	4·50	3·162	5	5·51	39·47	5·14
,,	9·0	·5257	4·67	2·138	5	5·28	44·00	4·91
,,	10·0	·5359	4·84	1·445	5	5·41	48·57	5·02
,,	11·0	·5499	5·07	8·511	6	5·58	53·11	5·16
25·8	12·0	·5754	5·49	3·236	6	5·55	57·60	5·12
26·0	12·4	·5836	..	..	..	..	..	..
25·9	12·6	·6181	..	..	..	..	..	..
,,	12·7	·6358	..	..	..	..	..	..
25·7	12·8	·6578	..	..	..	..	..	5·15

Second Equivalent of Sodium Hydroxide.

Calomel temp.	0·1017N NaOH	E.M.F.	pH	$C_H \times 10^n$	n	$K_2^c \times 10^9$	$\mu \times 10^4$	$K_2^a \times 10^{10}$
25·7	13·0	·6806	7·24	5·623	8	..	..	..
25·8	14·0	·7265	8·01	9·772	9	..	..	..
25·9	15·0	·7446	8·31	4·898	9	1·07	81·74	8·01
26·0	16·0	·7566	8·51	3·090	9	1·07	90·74	7·89
,,	17·0	·7665	8·68	2·089	9	1·06	99·72	7·72
25·9	18·0	·7757	8·83	1·479	9	1·05	108·56	7·57
,,	19·0	·7838	8·96	1·096	9	1·06	117·24	7·55
,,	20·0	·7919	9·10	7·943	10	1·05	125·24	7·39
26·0	21·0	·8004	9·24	5·754	10	1·05	134·46	7·31
25·9	22·0	·8095	9·39	4·074	10	1·06	142·86	7·31
,,	23·0	·8193	9·55	2·818	10	1·11	151·14	7·48
,,	24·0	·8327	9·78	1·660	10	1·09	159·08	7·38
25·8	25·0	·8467	10·01	9·772	11	1·37	166·63	..
,,	25·2	·8505	..	..	..	..	..	..
,,	25·4	·8541	..	..	..	..	..	..
,,	25·6	·8568	..	..	..	..	..	..
,,	25·8	·8607	..	..	..	..	..	..
,,	26·0	·8635	..	..	..	..	..	..
								7·46

(4) GALLIC ACID.

TABLE I. Stoichiometrical concentrations prevailing in the titration of 200 c.c. of 0·004510 M acid by 0·0718 N sodium hydroxide.

0·0718 N NaOH	Moles NaOH per mole acid	J = equiv conc. of Na salts $\times 10^4$	$M_{H_2An} \times 10^4$	$M_{H_2An} = U \times 10^4$	$M_{NaHAn} \times 10^4$	$M_{Na_2An} \times 10^4$
0·0	0·0000	0·00	45·10	45·10	0·00	..
1·4	·1114	4·99	44·78	39·79	4·99	..
2·1	·1672	7·46	44·60	37·14	7·46	..
3·2	·2547	11·31	44·38	33 07	11·31	..
4·48	·3566	15·73	44·11	28·38	15·73	..
5·2	·4139	18·19	43·93	25·74	18·19	..
6·5	·5174	22·60	43·66	21·06	22·60	..
8·3	·6607	28·61	43·30	14·69	28·61	..
9·49	·7554	32·52	43·07	10·55	32·52	..
10·1	·8040	34·51	42·89	8·38	34·51	..
11·05	·8796	37·59	42·71	5·12	37·59	..
11·78	·9377	39·94	42·57	2·63	39·94	..
12·5	·9950	42·24	42·44	0·20	42·24	..
13·0	1·0348	43·82	42·35	..	40·88	1·47
13·5	1·0746	45·40	42·26	..	39·12	3·14
14·0	1·1144	46·98	42·12	..	37·26	4·86
14·5	1·1542	48·54	42·03	..	35·52	6·51
15·5	1·2338	51·64	41·85	..	32·06	9·79
16·5	1·3134	54·72	41·67	..	28·62	13·05
18·0	1·4328	59·28	41·36	..	23·44	17·92
20·1	1·6000	65·57	40·99	..	16·41	24·58
22·0	1·7512	71·15	40·63	..	10·11	30·52
23·0	1·8308	74·05	40·45	..	6·85	33·60
24·1	1·9184	77·12	40·23	..	3·34	36·89
25·2	2·0059	80·34	40·00	..	..	40·34

TABLE II. Data for the titration

First Equivalent of Sodium Hydroxide.

Calomel temp.	0·0718 N NaOH	E.M.F.	pH	$C_H \times 10^n$	n	$K_1^c \times 10^5$	$\mu \times 10^4$	$K_1^a \times 10^5$
28·1	0·0	0·4359	3·23	5·888	4	..	..	..
28·4	1·4	·4545	3·54	2·884	4	6·15	7·87	..
28·6	2·1	·4634	3·69	2·042	4	5·53	9·50	..
28·8	3·2	·4756	3·90	1·259	4	4·98	12·57	4·79
28·9	4·48	·4868	4·09	8·128	5	4·88	16·54	4·66
,,	5·2	·4926	4·19	6·457	5	4·85	18·84	4·62
29·0	6·5	·5033	4·36	4·365	5	4·88	23·04	4·63
,,	8·3	·5191	4·63	2·344	5	4·68	28 84	4·41
29·2	8·88	·5246	..	..	..	..	.	..
29·4	9·49	·5313	4·84	1·445	5	4·53	32·66	4·24
,,	10·1	·5392	4·97	1·072	5	4·49	34·62	4·22
29·5	11·05	·5561	5·25	5·623	6	4·18	37·65	..
29·6	11·37	·5638	..	..	..	..	..	..
,,	11·78	·5783	5·62	2·399	6	3·67	39·96	..
,,	12·2	·6034	..	..	..	..	..	..
29·7	12·5	·6387	6·65	2·239	7	..	..	..
,,	12·6	·6533	..	..	..	..	..	..
								4·63

Second Equivalent of Sodium Hydroxide.

						$K_2^c \times 10^9$		$K_2^a \times 10^9$
29·9	12·8	·6699	..	..	..	..	..	..
,,	13·0	·6829	7·37	4·266	8	1·53	45·29	..
,,	13·5	·7019	7·68	2·089	8	1·67	48·53	1·33
30·0	14·0	·7127	7·86	1·380	8	1·80	51·83	1·42
,,	14·5	·7218	8·01	9·772	9	1·73	54·84	1·36
,,	15·5	·7339	8·21	6·166	9	1·88	61·40	1·46
,,	16·5	·7446	8·39	4·074	9	1·85	67·72	1·42
30·2	18·0	·7574	8·61	2·455	9	1·86	77·12	1·41
,,	20·1	·7739	8·88	1·318	9	1·95	90·01	1·44
,,	22·0	·7904	9·16	6·918	10	2·02	101·42	1·49
,,	23·0	·8018	9·35	4·467	10	2·04	107·23	1·50
,,	24·1	·8172	9·58	2·630	10	..	..	..
,,	24·8	·8295	..	..	..	..	..	..
,,	25·0	·8328	..	..	..	..	..	..
,,	25·2	·8369	9·91	1·230	10	..	..	..
,,	25·6	·8435	..	..	..	..	..	..
								1·41

(5) CATECHOL.

TABLE I. Stoichiometrical concentrations prevailing in the titration of 200 c.c. of 0·008023 N catechol by 0·1017 M sodium hydroxide.

0·1017 N NaOH	Moles NaOH per mole catechol	J = equiv. conc of Na salts × 10^4	M_{H_2An} × 10^4	$M_{H_2An} = U$ × 10^4	M_{NaHAn} × 10^4	M_{Na_2An} × 10^4
0·0	0·0000	0·00	80·23	80·23	0·00	..
2·0	·1268	10·07	79·43	69·36	10·07	..
3·0	·1901	15·03	79·03	64·00	15·03	..
4·0	·2535	19·94	78·63	58·69	19·94	..
5·0	·3169	24·80	78·22	53·42	24·80	..
6·0	·3803	29·62	77·90	48·28	29·62	..
7·0	·4437	34·39	77·42	43·03	34·39	..
8·0	·5070	39·12	77·10	37·98	39·12	..
9·0	·5704	43·79	76·70	32·91	43·79	..
10·0	·6338	48·43	76·38	27·95	48·43	..
11·0	·6972	53·02	75·98	22·96	53·02	..
12·0	·7606	57·57	75·66	18·09	57·57	..
13·0	·8239	62·07	75·26	13·19	62·07	..
14·0	·8873	66·53	74·93	8·40	66·53	..
15·0	·9507	70·95	74·61	3·66	70·95	..
16·0	1·0141	75·33	74·29	..	73·25	1·04
17·0	1·0775	79·67	73·89	..	68·11	5·78
18·0	1·1408	83·98	73·57	..	63·16	10·41
19·0	1·2042	88·23	73·25	..	58·27	14·98
20·0	1·2676	92·45	72·93	..	53·41	19·52
21·0	1·3310	96·64	72·61	..	48·58	24·03
22·0	1·3944	100·78	72·29	..	43·80	28·49
23·0	1·4577	104·89	71·97	..	39·05	32·92
24·0	1·5211	108·96	71·65	..	34·34	37·31
25·0	1·5845	113·00	71·32	..	29·64	41·68
26·0	1·6479	117·00	71·00	..	25·00	46·00
27·0	1·7113	120·96	70·68	..	20·40	50·28
28·0	1·7746	124·89	70·36	..	15·83	54·53
29·0	1·8380	128·79	70·04	..	11·29	58·75
30·0	1·9014	132·65	69·72	..	6·79	62·93
31·0	1·9648	136·48	69·48	..	2·48	67·00

TABLE II. Data for the titration.

First Equivalent of Sodium Hydroxide.

Calomel temp.	0·1017 N NaOH	E.M.F.	pH	$C_H \times 10^n$	n	$K_1^c \times 10^{10}$	$\mu \times 10^4$	$K_1^a \times 10^{10}$
25·4	0·0	0·5475	5·03	9·333	6	..	..	..
,,	2·0	·7367	8·17	6·761	9	9·78	10·07	..
25·5	3·0	·7507	8·41	3·890	9	9·10	15·03	..
,,	4·0	·7624	8·60	2·512	9	8·48	19·94	8·08
,,	5·0	·7711	8·75	1·778	9	8·21	24·80	7·78
,,	6·0	·7789	8·88	1·318	9	8·02	29·62	7·56
25·6	7·0	·7855	8·99	1·023	9	8·10	34·39	7·61
,,	8·0	·7926	9·11	7·762	10	7·90	39·12	7·39
25·7	9·0	·7989	9·21	6·166	10	8·07	43·79	7·54
,,	10·0	·8057	9·33	4·677	10	7·92	48·43	7·36
,,	11·0	·8128	9·44	3·631	10	8·12	53·02	7·52
,,	12·0	·8201	9·57	2·692	10	8·15	57·57	7·52
,,	13·0	·8288	9·71	1·950	10	8·42	62·07	7·75
,,	14·0	·8387	..	..	..	..	..	..
,,	15·0	·8502	..	..	..	..	..	..
,,	15·2	·8524	..	..	..	..	..	..
,,	15·5	·8568	..	..	..	..	..	..
								7·50

Second Equivalent of Sodium Hydroxide.

Calomel temp.	0·1017 N NaOH	E.M.F.	pH	$C_H \times 10^n$	n	$K_2^c \times 10^{13}$	$\mu \times 10^4$	$K_2^a \times 10^{13}$
25·8	15·8	·8607	..	..	..	..	..	..
25·9	16·0	·8628	..	..	..	.	..	..
,,	17·0	·8746	10·47	3·388	11	1·33	79·96	..
,,	18·0	·8855	10·66	2·188	11	5·80	85·88	..
,,	19·0	·8926	10·77	1·698	11	9·86	92·25	7·31
26·0	20·0	·8996	10·89	1·288	11	9·64	97·53	7·10
,,	21·0	·9045	10·97	1·072	11	10·81	103·29	7·90
25·8	22·0	·9088	11·04	9·120	12	11·46	108·85	8·30
,,	23·0	·9124	11·10	7·943	12	12·05	114·34	8·67
,,	24·0	·9156	11·16	6·918	12	11·73	119·35	8·38
26·1	25·0	·9197	11·23	5·888	12	19·67	123·06	6·88
26·0	26·0	·9224	11·27	5·370	12	10·20	128·33	7·21
,,	27·0	·9247	11·31	4·898	12	10·28	133·22	7·22
,,	28·0	·9266	11·34	4·571	12	11·14	138·68	7·78
25·9	29·0	·9284	11·37	4·266	12	11·72	143·89	8·13
,,	30·0	·9305	..	..	..	..	..	..
25·8	31·0	·9328	..	..	..	..	..	..
,,	31·2	·9333	..	..	..	..	..	..
,,	31·4	·9342	..	..	..	..	..	..
,,	31·8	·9347	..	..	..	..	..	..
								8·37

(6) RESORCINOL.

TABLE I. Stoichiometrical concentrations prevailing in the titration of 200 c.c. of 0·006724 M resorcinol by 0·1057 N sodium hydroxide.

0·1057 N NaOH	Moles NaOH per mole resorcinol	J = equiv. conc. of Na salts $\times 10^4$	$M_{H_2An} \times 10^4$	$M_{H_2An} = U \times 10^4$	$M_{NaHAn} \times 10^4$	$M_{Na_2An} \times 10^4$
0·0	0·0000	0·00	67·24	67·24	0·00	..
1·0	·0786	5·26	66·90	61·64	5·26	..
2·0	·1572	10·47	66·57	56·10	10·47	..
3·0	·2358	15·62	66·23	50·61	16·52	..
4·0	·3144	20·73	65·90	45·17	20·73	..
5·0	·3930	25·78	65·56	39·78	25·78	..
6·0	·4716	30·79	65·29	34·50	30·79	..
7·0	·5502	35·74	64·89	29·15	35·74	..
8·0	·6288	40·65	64·62	23·97	40·65	..
9·0	·7074	45·52	64·28	18·76	45·52	..
10·0	·7860	50·33	64·01	13·68	50·33	..
11·0	·8646	55·10	63·48	8·58	55·10	..
12·0	·9432	59·83	63·41	3·58	59·83	..
13·0	1·0218	64·51	63·07	..	61·63	1·44
14·0	1·1004	69·15	62·80	..	56·45	6·35
15·0	1·1790	73·74	62·53	..	51·32	11·21
16·0	1·2576	78·30	62·26	..	46·22	16·04
17·0	1·3362	82·81	61·93	..	41·05	20·88
18·0	1·4148	87·28	61·66	..	36·04	25·62
19·0	1·4934	91·70	61·39	..	31·08	30·31
20·0	1·5720	96·09	61·12	..	26·15	34·97
21·0	1·6506	100·44	60·85	..	21·26	39·59
22·0	1·7292	104·75	60·58	..	16·41	44·17
23·0	1·8078	109·02	60·31	..	11·60	48·71
24·0	1·8864	113·25	60·05	..	6·85	53·20
25·0	1·9650	117·44	59·78	..	2·12	57·66

Table II. Data for the titration.

First Equivalent of Sodium Hydroxide.

Calomel temp.	0·1057 N NaOH	E.M.F.	pH	$C_H \times 10^n$	n	$K_1^c \times 10^{10}$	$\mu \times 10^4$	$K_1^a \times 10^{10}$
28·8	0·0	0·5223	4·65	2·239	5	..	.	..
28·9	1·0	·7059	7·71	1·950	8	16·61	5·26	..
,,	2·0	·7382	8·24	5·754	9	10·70	10·47	..
29·0	3·0	·7549	8·53	2·951	9	9·06	15·62	..
,,	4·0	·7695	8·77	1·698	9	7·73	20·73	7·36
,,	5·0	·7793	8·93	1·175	9	7·54	25·78	7·14
29·3	6·0	·7881	9·07	8·511	10	7·49	30·79	7·06
29·4	7·0	·7967	9·22	6·026	10	7·25	35·74	6·80
29·3	8·0	·8045	9·35	4·467	10	7·37	40·65	6·89
29·4	9·0	·8136	9·51	3·090	10	7·17	45·52	6·68
29·5	10·0	·8226	9·65	2·239	10	7·64	50·33	7·08
,,	11·0	·8322	9·82	1·514	10	8·30	55·10	7·67
,,	12·0	·8423	9·98	1·047	10	11·35	59·83	..
,,	12·4	·8464	..	..	..	..	..	..
29·7	12·6	·8479	..	.	.	.	..	..
29·8	12·8	·8506	.	..	..	..	..	..
								7·11

Second Equivalent of Sodium Hydroxide.

						$K_2^c \times 10^{12}$		$K_2^a \times 10^{12}$
29·8	13·0	·8533	10·18	6·607	11	..	..	..
..	14·0	..	.	..	..	..	..	..
29·3	15·0	·8677	10·40	3·981	11	4·64	80·17	..
,,	16·0	·8740	10·50	3·162	11	6·16	88·45	4·59
,,	17·0	·8807	10·62	2·399	11	6·45	95·93	4·75
29·5	18·0	8872	10·72	1·905	11	6·59	103·13	4·81
29·8	19·0	·8913	10·80	1·587	11	6·95	110·46	5·03
,,	20·0	·8956	10·87	1 349	11	7·15	117 26	5·12
,,	21·0	·8995	10·95	1·122	11	6·81	123·43	4·84
30·0	22·0	·9033	11·01	9·772	12	6·92	129·87	4·88
,,	23·0	·9063	11·06	8·710	12	7·22	136·35	5·06
,,	24·0	·9098	11·11	7·762	12	7·35	142·46	5·11
,,	25·0	·9121	11·15	7·079	12	7·81	148·80	..
,,	25·4	·9129	..	..	..	..	..	..
,,	25·6	·9145	..	..	..	..	..	..
,,	25·8	·9152	..	..	..	..	..	..
,,	26·0	·9155	..	..	..	..	..	..
								4·78

(7) HYDROQUINONE.

TABLE I. Stoichiometrical concentrations prevailing in the titration of 200 c.c. of 0·007522 M hydroquinone by 0·1057 N sodium hydroxide.

0·1057 N NaOH	Moles NaOH per mole hydroquinone	J = equiv. conc. of Na salts × 10^4	M_{H_2An} × 10^4	M_{H_2An} = U × 10^4	M_{NaHAn} × 10^4	M_{Na_2An} × 10^4
0·0	0·0000	0·00	75·22	75·22	0·00	..
1·0	·0703	5·26	74·84	69·58	5·26	..
2·0	·1405	10·47	74·47	64·00	10·47	..
3·0	·2108	15·62	74·09	58·47	15·62	..
4·0	·2810	20·73	73·72	52·99	20·73	..
5·0	·3513	25·78	73·34	47·56	25·78	..
6·0	·4216	30·79	73·04	42·25	30·79	..
7·0	·5918	35·74	72·59	36·85	35·74	..
8·0	5620	40·65	72·29	31·64	40·65	..
9·0	·6323	45·52	71·91	26·39	45·52	..
10·0	·7026	50·33	71·61	21·28	50·33	..
11·0	·7728	55·10	71·23	16·13	55·10	..
12·0	·8431	59·83	70·93	11·10	59·83	..
13·0	·9133	64·51	70·56	6·05	64·51	..
14·0	·9836	69·15	70·26	1·11	69·15	..
15·0	1·0538	73·74	69·95	..	66·16	3·79
16·0	1·1240	78·30	69·65	..	61·00	8·65
17·0	1·1943	82·81	69·28	..	55·75	13·53
18·0	1·2646	87·28	68·98	..	50·68	18·30
19·0	1·3348	91·70	68·68	..	45·66	23·02
20·0	1·4051	96·09	68·37	..	40·65	27·72
21·0	1·4754	100·44	68·07	..	35·70	32·37
22·0	1·5456	104·75	67·77	..	30·79	36·98
23·0	1·6158	109·02	67·47	..	25·92	41·55
24·0	1·6861	113·25	67·17	..	21·09	46·08
25·0	1·7564	117·44	66·87	..	16·30	50·57
26·0	1·8266	121·60	66·57	..	11·54	55·03
27·0	1·8969	125·72	66·27	..	6·82	59·84
28·0	1·9672	129·81	65·97	..	2·13	53·84

TABLE II. Data for the titration.
First Equivalent of Sodium Hydroxide.

Calomel temp.	0·1057 N NaOH	E.M.F.	pH	$C_H \times 10^n$	n	$K_I^c \times 10^{10}$	$\mu \times 10^4$	$K_I^a \times 10^{10}$
29·9	0·0	0·5935	5·84	1·445	6	..	..	..
30·0	1·0	·7659	8·72	1·905	9	1·41	5·26	1·37
,,	2·0	·7876	9·08	8·318	10	1·33	10·47	1·28
,,	3·0	·8013	9·30	5·012	10	1·30	15·62	1·26
,,	4·0	·9111	9·47	3·388	10	1·28	20·73	1·22
,,	5·0	·8199	9·61	2·455	10	1·27	25·75	1·20
,,	6·0	·8273	9·75	1·778	10	1·22	30·79	1·15
,,	7·0	·8337	9·85	1·413	10	1·27	35·74	1·19
,,	8·0	·8400	9·95	1·122	10	1·31	40·65	1·22
,,	9·0	·8462	10·07	8·511	11	1·29	45·52	1·20
30·1	10·0	·8526	10·16	6·918	11	1·37	50·33	1·27
,,	11·0	·8588	10·26	5·495	11	1·46	55·10	1·35
30·2	12·0	·8650	10·37	4·266	11	1·53	59·83	1·44
,,	13·0	·8714	10·48	3·311	11	1·67	64·51	..
,,	14·0	·8770	10·58	2·630	11	1·99	69·15	..
,,	14·1	·8780	..	..	..	..	..	..
,,	14·2	·8793	..	..	..	..	..	..
								1·22

Second Equivalent of Sodium Hydroxide.

Calomel temp.	0·1075 N NaOH	E.M.F.	pH	$C_H \times 10^n$	n	$K_2^c \times 10^{13}$	$\mu \times 10^4$	$K_2^a \times 10^{13}$
30·2	14·4	·8806	..	..	..	..	..	..
30·3	15·0	·8839	10·68	2·089	11	..	..	..
30·4	16·0	·8893	10·78	1·660	11	..	..	..
30·8	17·0	·8941	10·86	1·380	11	0·08	82·85	..
31·0	18·0	·8990	10·95	1·122	11	2·84	88·98	..
30·9	19·0	·9027	11·00	1·000	11	6·85	96·10	..
30·6	20·0	·9061	11·06	8·710	12	8·90	102·43	..
,,	21·0	·9096	11·12	7·586	12	9·85	108·26	..
30·4	22·0	·9126	11·16	6·918	12	12·06	114·81	8·70
30·5	23·0	·9154	11·21	6·166	12	12·47	120·37	8·92
,,	24·0	·9180	11·25	5·623	12	13·46	126·22	9·55
30·8	25·0	·9205	11·30	5·012	12	12·58	130·86	8·88
,,	26·0	·9226	11·33	4·677	12	13·86	136·82	9·73
,,	27·0	·9249	11·37	4·266	12	13·36	141·52	9·33
,,	28·0	·9271	11·41	3·890	12	12·43	145·79	8·59
,,	28·2	·9276	..	..	..	..	..	..
,,	28·4	·9280	..	..	..	..	..	..
								9·18

(8) PYROGALLOL.

TABLE I. Stoichiometrical concentrations prevailing in the titration of 200 c.c. of 0·005441 M pyrogallol by 0·1057 N sodium hydroxide.

0·1057 N NaOH	Moles NaOH per mole pyrogallol	J = equiv. conc. of Na salts $\times 10^4$	$M_{H_2An} \times 10^4$	$M_{H_2An} = U \times 10^4$	$M_{NaHAn} \times 10^4$	$M_{Na_2An} \times 10^4$
0·0	0·0000	0·00	54·41	54·41	0·00	..
1·0	·0971	5·26	54·14	48·88	5·26	..
2·0	·1943	10·47	53·87	43·40	10·47	..
3·0	·2914	15·62	53·59	37·97	15·62	..
4·0	·3885	20·73	53·32	32·59	20·73	..
5·0	·4857	25·78	53·05	27·27	25·78	..
6·0	·5828	30·79	52·83	22·04	30·79	..
7·0	·6799	35·74	52·51	16·77	35·74	..
8·0	·7770	40·65	52·29	11·64	40·65	..
9·0	·8742	45·52	52·02	6·50	45·52	..
10·0	·9713	50·33	51·80	1·47	50·33	..
11·0	1·0684	55·10	51·53	..	48·06	3·47
12·0	1·1656	59·83	51·31	..	42·79	8·52
13·0	1·2627	64·51	51·04	..	37·57	13·47
14·0	1·3598	69·15	50·82	..	32·49	18·33
15·0	1·4570	73·74	50·60	..	27·46	23·14
16·0	1·5541	78·30	50·38	..	22·46	27·92
17·0	1·6512	82·81	50·11	..	17·41	32·70
18·0	1·7483	87·28	49·89	..	12·50	37·39
19·0	1·8455	91·70	49·68	..	7·66	42·02
20·0	1·9426	96·09	49·46	..	2·83	46·63
21·0	2·0397	100·44	49·24	..	..	51·20

TABLE II. Data for the titration.

First Equivalent of Sodium Hydroxide.

Calomel temp.	0·1057 N NaOH	E.M.F.	pH	$C_H \times 10^n$	n	$K_1^c \times 10^9$	$u \times 10^4$	$K_1^a \times 10^{10}$
31·1	0·0	0·5930	5·85	1·413	6	..	..	.
,,	1·0	·7203	7·97	1·072	8	1·15	5·26	11·20
31·0	2·0	·7431	8·35	4·467	9	1·07	10·47	10·30
31·1	3·0	·7574	8·59	2·570	9	1·05	15·62	10·10
31·2	4·0	·7693	8·80	1·585	9	1·00	20·73	9·53
31·3	5·0	·7797	8·96	1·096	9	1·02	25·78	9·66
,,	6·0	·7897	9·12	7·586	10	1·04	30·79	9·80
,,	7·0	·8005	9·30	5·012	10	1·03	35·74	9·66
31·4	8·0	·8118	9·50	3·162	10	1·04	40·65	9·71
,,	9·0	·8258	9·74	1·820	10	1·08	45·52	10·1
31·5	10·0	·8399	9·97	1·072	10	1·62	50·33	15·0
,,	10·2	·8435	..	..	..	..	..	..
31·1	10·3	·8469	..	..	..	..	..	..
								9·67

Second Equivalent of Sodium Hydroxide.

						$K_2^c \times 10^{12}$		$K_2^a \times 10^{12}$
31·3	10·4	·8486	..	..	..	..	..	..
31·5	10·5	·8504	..	..	..	..	..	.
,,	11·0	·8580	10·27	5·370	11	..	..	..
31·7	12·0	·8707	10·48	3·311	11	1·98	62·73	..
,,	13·0	·8803	10·64	2·291	11	2·68	69·85	..
,,	14·0	·8876	10·76	1·738	11	3·06	76·76	2·33
,,	15·0	·8940	10·87	1·349	11	3·05	83·08	2·29
,,	16·0	·8993	10·96	1·096	11	3·04	89·24	2·27
,,	17·0	·9037	11·03	9·333	12	3·19	95·56	2·35
31·5	18·0	·9078	11·10	7·943	12	3·08	101·23	2·25
,,	19·0	·9112	11·15	7·079	12	3·28	107·42	2·38
31·7	20·0	·9144	11·21	6·166	12	3·07	112·52	2·21
,,	20·4	·9156	..	..	..	..	..	..
,,	20·6	·9162	..	..	..	..	..	..
31·6	20·8	·9168	..	..	..	..	..	..
31·7	21·0	·9173	11·2	5·495	..	..	..	..
								2·30

(9) PHLOROGLUCINOL.

TABLE I. Stoichiometrical concentrations prevailing in the titration of 200 c c. of 0·004352 N phloroglucinol by 0·1017 N NaOH.

0·1017 N NaOH	Moles NaOH per mole phloro-glucinol	J = equiv. conc. of Na salts $\times 10^4$	$M_{H_2An} \times 10^4$	$M_{H_2An} = U \times 10^4$	$M_{NaHAn} \times 10^4$	$M_{Na_2An} \times 10^4$
0·0	0·0000	0·00	43·52	43·52	0·00	..
1·0	·1168	5·06	43·30	38·24	5·06	..
2·0	·2337	10·07	43·08	33·01	10·07	..
3·0	·3505	15·03	42·87	27·84	15·03	..
4·0	·4674	19·94	42·65	22·71	19·94	..
5·0	·5842	24·80	42·43	17·63	24·80	..
6·0	·7011	29·62	42·26	12·64	29·62	..
7·0	·8199	34·39	42·00	7·61	34·39	..
8·0	·9347	39·12	41·82	2·70	39·12	..
9·0	1·0516	43·79	41·60	..	39·41	2·19
10·0	1·1684	48·43	41·43	..	34·43	7·00
11·0	1·2853	53·02	41·21	..	29·40	11·81
12·0	1·4021	57·57	41·04	..	24·51	16·53
13·0	1·5190	62·07	40·82	..	19·57	21·25
14·0	1·6358	66·53	40·65	..	14·77	25·88
15·0	1·7526	70·95	40·47	..	9·99	30·48
16·0	1·8695	75·33	40·30	..	5·27	35·03
17·0	1·9863	79·67	40·08	..	0·49	39·59

TABLE II. Data for the titration.

First Equivalent of Sodium Hydroxide.

Calomel temp.	0·1017 N NaOH	E.M.F.	pH	$C_H \times 10^n$	n	$K_1^c \times 10^9$
25·2	0·0	0·5736	5·46	3·467	6	..
25·4	1·0	·6950	7·48	3·311	8	4·38
,,	2·0	·7152	7·82	1·154	8	4·61
,,	3·0	·7266	8·01	9·772	9	5·26
,,	4·0	·7353	8·15	7·079	9	6·20
,,	5·0	·7422	8·27	5·370	9	7·53
,,	6·0	·7483	8·37	4·266	9	9·95
25·5	7·0	·7540	8·46	3·467	9	15·54
,,	8·0	·7591	8·55	2·818	9	39·73
Second Equivalent of Sodium Hydroxide.						
25·5						$K_2^c \times 10^9$
,,	9·0	·7647	8·64	2·291	9	0·12
,,	10·0	·7701	8·73	1·862	9	0·37
,,	11·0	·7755	8·82	1·514	9	0·60
25·6	12·0	·7817	8·92	1·202	9	0·80
,,	13·0	·7880	9·03	9·333	10	0·99
25·8	14·0	·7963	9·17	6·761	10	1·15
,,	15·0	·8065	9·34	4·571	10	1·32
,,	16·0	·8221	9·60	2·512	10	1·33
25·7	17·0	·8460	10·00	1·000	10	1·61

TABLE III. Data for titration of 0·004352 M phloroglucinol as a dibasic acid.

0·1017 N NaOH	$C_{Na_2An} \times 10^4$	$C_{NaHAn} \times 10^4$	$C_{H_2An} \times 10^4$	$K_1^c \times 10^9$	$K_2^c \times 10^9$	$\mu \times 10^4$	$K_1^a \times 10^9$	$K_2^a \times 10^9$
3·0	1·87	11·29	29·71	3·71	1·62	16·90	3·55	1·42
4·0	3·10	13·74	25·81	3·77	1·60	23·09	3·58	1·37
5·0	4·64	15·52	22·27	3·74	1·61	29·44	3·53	1·35
6·0	6·35	16·92	18·99	*3·80*	*1·60*	35·97	3·56	1·32
							3·56	1·32

DISCUSSION.

In Figs. 1 to 4 the E.M.F. titration curves of various acids are shown along with the change of mole fraction of mono sodium salt. Due to the strong hydrolysis after the carboxyl group is neutralized, the change in the composition of the acid during the second half of the titration does not strictly follow the curve given in the figures.

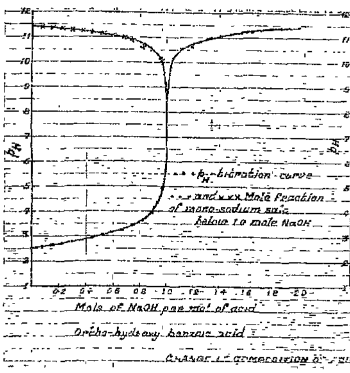


Fig. 1.

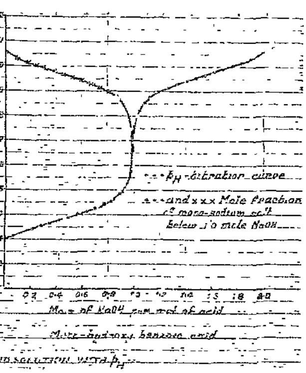


Fig. 2.

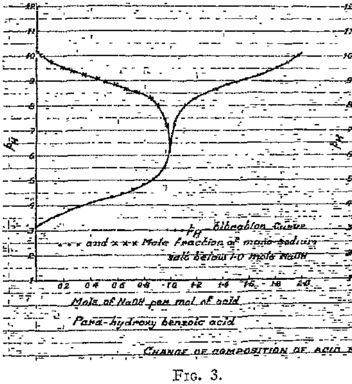


Fig. 3.

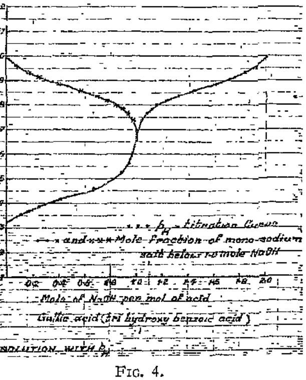


Fig. 4.

It is seen from the results of dissociation constants that the values of K_1^a remain constant from 0.1 mole to 0.85 moles of added alkali and the small variations show that the value of the 'salt coefficient' β is practically zero. The larger variations in the value of K_2^a are due to the large concentrations of salts, to the presence of two salts with unlike valence and to the strong hydrolysis in these regions.

The previous values of the dissociation consonants of the various phenols and the acids, along with those obtained in the present investigation, are given in the following table:—

Acid	K_1^a	K_2^a	Temp	Method	Author
Benzoic acid .	$6{\cdot}3 \times 10^{-5}$	..	25°	Conductivity	(1)
o-Hydroxy benzoic acid	$1{\cdot}76 \times 10^{-3}$	$4{\cdot}20 \times 10^{-13}$	30°	pH titration curve	(2)
	$1{\cdot}06 \times 10^{-3}$	..	25°	Conductivity	(3)
	$3{\cdot}8 \times 10^{-4}$	..	100°	Distill.	(4)
m-Hydroxy benzoic acid	$1{\cdot}25 \times 10^{-4}$	$1{\cdot}65 \times 10^{-10}$	30°	pH titration curve	(2)
	$8{\cdot}7 \times 10^{-5}$	..	25°	Conductivity	
	$6{\cdot}9 \times 10^{-5}$	..	25°	,,	(5)
p-Hydroxy benzoic acid	$5{\cdot}15 \times 10^{-5}$	$7{\cdot}46 \times 10^{-10}$	30°	pH titration curve	(2)
	$2{\cdot}86 \times 10^{-5}$	..	25°	Conductivity	(3)
Gallic acid ..	$4{\cdot}63 \times 10^{-5}$	$1{\cdot}41 \times 10^{-9}$	28·5°	pH titration curve	(2)
	$4{\cdot}0 \times 10^{-5}$	..	25°	Conductivity	(3)
	$3{\cdot}8 \times 10^{-5}$	..	,,	,,	(5)
	$4{\cdot}6 \times 10^{-5}$				
	$4{\cdot}6 \times 10^{-5}$	$2{\cdot}57 \times 10^{-9}$	28·5°	pH titration curve	(9)
Phenol	$1{\cdot}28 \times 10^{-10}$	..	25°	,,	(6)
	$1{\cdot}05 \times 10^{-10}$				
	$1{\cdot}30 \times 10^{-10}$	..	,,	Conductivity	(8)
Catechol	$7{\cdot}5 \times 10^{-10}$	$8{\cdot}37 \times 10^{-13}$	30°	pH titration curve	(2)
	$3{\cdot}3 \times 10^{-10}$	..	18°	Conductivity	(7)
Resorcinol	$7{\cdot}11 \times 10^{-10}$	$4{\cdot}78 \times 10^{-12}$	30°	pH titration curve	(2)
	$6{\cdot}4 \times 10^{-9}$	..	25°	Conductivity	(3)
	$3{\cdot}6 \times 10^{-10}$	..	18°	Do.	(7)
Hydroquinone ..	$1{\cdot}22 \times 10^{-10}$	$9{\cdot}18 \times 10^{-13}$	30°	pH titration curve	(2)
	$1{\cdot}10 \times 10^{-10}$	..	18°	Conductivity	(7)
Pyrogallol	$9{\cdot}67 \times 10^{-10}$	$2{\cdot}30 \times 10^{-12}$	30°	pH titration curve	(2)
Phloroglucinol ..	$3{\cdot}56 \times 10^{-9}$	$1{\cdot}32 \times 10^{-9}$	,,	Do.	(2)

(1) Brockman and Kilpatrick (*Jour. Amer. Chem. Soc.*, 1934, **56**, 1483).
(2) Abichandani and Jatkar (1938).
(3) Thiel and Roemer (*Z. Physikal Chem.*, 1908, **63**, 731, 744).
(4) Jaulmes (*Jour. Chim. Physics*, 1933, **30**, 556).
(5) Smith and Jones (*Amer. Chem. Jour.*, 1913, **39**, 50).
(6) Hahn and Klockman (*Z. Physikal Chem.*, (A), 1931, **157**, 206).
(7) Euler and Bolin (*Z. Physikal Chem.*, 1909, **66**, 71).
(8) Walker (*Ibid.*, 1900, **32**, 137).
(9) Sunthankar and Jatkar (*This Journal*, 1938, **21 A**, 209).

Most of the authors have measured only the first dissociation constant of the carboxylic acids and of di- and tri-hydroxy benzenes, although the nature and influence of the second OH dissociation in phenols and acids has been discussed by Thiel and Roemer from the conductometric titration curves. The values of K_i^c obtained by various authors do not agree. The differences are mainly due to the neglect of interionic attraction corrections, and the assumption that the sodium salts of these acids are not completely dissociated and possess the same equivalent conductance at equivalent concentrations as do the sodium salts of other dibasic and monobasic acids. The values of Thiel and Roemer are quite divergent from the values obtained in the present paper although the change observed in the order

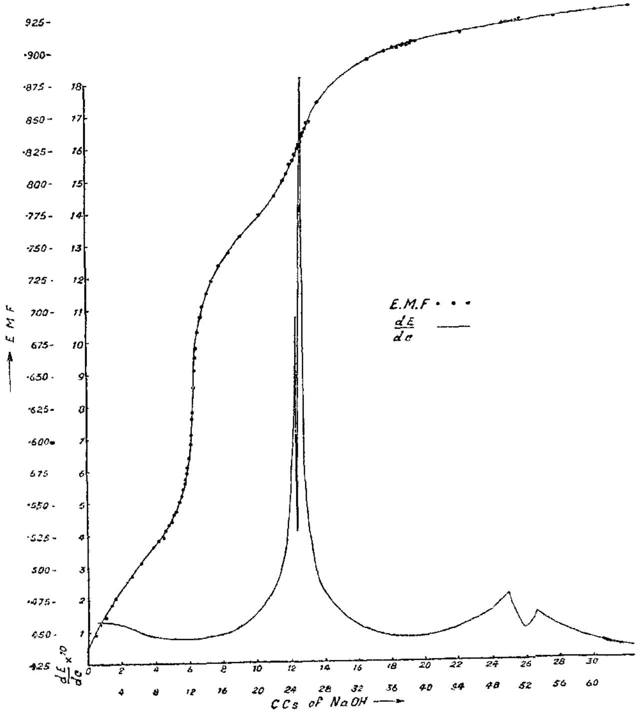
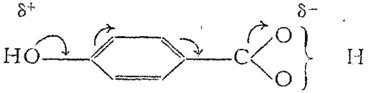


FIG. 5.

of dissociation constants due to OH substitution in various positions, is in the same direction.

Fig. 5 shows the E.M.F., c.c. and *dE/dc*, c.c. curves for the titration of gallic acid. The first dissociation constant calculated is in fair agreement with the values of previous workers. The value of the second dissociation constant obtained by Sunthankar and Jatkar (*loc. cit.*) is too high, as they did not apply the corrections for hydrolysis. The differential curve shows the double inflection for both the first and the second dissociation constants. The distances between the peaks increase at the second stage of titration, which is still more pronounced at the third and the fourth stage, which are not shown in the curve. This phenomena of the double peaks in the differential titration curves has been shown by us to be due partly to hydrolysis and partly to the formation of di-salt, whenever the difference between the two dissociation constants become small (*cf. This Journal*, 1938, **21A**, 363).

Comparing the dissociation constants of hydroxy substituted benzoic acids with that of benzoic acid itself, it is observed that the introduction of OH group in various *ortho-*, *meta-* and *para-*positions increases the strength of the acid in the order ortho > meta > H > para. Dippy and Williams (*Jour. Chem. Soc.*, 1934, 1888) have also observed the same order in methoxy substituted benzoic acids. The resonance between the quinonoid and ordinary structure, which will be expressed by the structure



will tend to reduce the strength of the *para*-substituted acids (*cf.* Ingold, *Jour. Chem. Soc.*, 1933, 1120). In *ortho-* and *meta*-acids, there being no possibility of a quinonoid structure, the dissociation constants are affected by the dipole effects, which increase the acidity, the influence being maximum in *ortho*-positions. The increased acidity of the *ortho*-substituted acid, can also be due to the special proximity of the sustituent group to the functional group, to such an extent that there is a diminished free rotation of the latter as pointed out by Smallwood (*Jour. Amer. Chem. Soc.*, 1932, **54**, 3048) and Walde (*J. Phys. Chem.*, 1935, **39**, 885).

The effect of OH substitution in various positions on the CO frequency in Raman effect has been studied by Kohlrausch (*loc. cit.*).

	CO frequency	K_1
Benzoic acid .	1715	$6 \cdot 31 \times 10^{-5}$
Ortho	1670	$1 \cdot 76 \times 10^{-3}$
Meta	1686	$1 \cdot 25 \times 10^{-4}$
Para	1680	$5 \cdot 15 \times 10^{-5}$

It is observed that a decrease in C=O frequency in *ortho-* and *meta*-positions corresponds to an increase in the dissociation constants. The influence in *para*-position is apparently affected by the resonating structure of the acid.

The character of the OH dissociation in these acids is also interesting. This group is of weakly acidic nature in *ortho*-position, while it is strong in *meta-* and *para*-position, the dissociation constants being in the order, gallic acid > para > meta > ortho. This behaviour can be explained on the consideration of the proximity of the two ionising groups, which tend to depress the ionisation of the second group, because of the negative charge developed on the anion. The strong acid nature of hydroxyl group in gallic acid is due to the promoting effect of the adjacent hydroxyl group.

In phenols, all the OH groups are similar but situated in different positions. The order of K_1^c in phenols is, phloroglucinol > pyrogallol > catechol > resorcinol > hydroquinone > phenol. The influence due to proximity of OH groups is thus very marked, except in phloroglucinol in which both OH groups titrate simultaneously as already shown. The second dissociation constants of these phenols follow the order: phloroglucinol > resorcinol > pyrogallol > hydroquinone > catechol. The mutual influence of OH group in various positions can be very well seen from the ratio K_1^c / K_2^c which decreases from catechol to hydroquinone owing to increasing distance of the two groups.

Pauling (*loc. cit.*) has pointed out, that in catechol, the attraction of partially shielded proton (hydrogen atom with some positive charge) by a negative atom, stabilizes the configuration, so that O-H axis is directed towards the attracting atom with consequent weakening of the hydrogen bond. This weak character of the hydrogen bond in catechol is also evident from its dissociation constant which is more than that of phenol. Pyrogallol also shows a weak O-H bond, because of its resemblance in configuration to catechol (Wulf, Liddel and Hendricks, *Ibid.*, 1936, 58, 2287). An attempt was made to find out if there was any relationship between the log K_1^a / K_2^a and the molal adsorption coefficient in the infra-red at 6970 cm.$^{-1}$ – 7060 cm.$^{-1}$ for these compounds given by Wulf and Liddel (*loc. cit.*). The results are given below:—

	K_1^a/K_2^a	log K_1/K_2	Infra red cm.$^{-1}$	Molal adsorption coefficient
Phloroglucinol ..	2·7	0·4313	..	..
Catechol	896	2·9523	6970	2·3
Pyrogallol	420	2·6232	6980	3·9
Resorcinol	149	2·1732	7050	5·6
Hydroquinone .	133	2·1239	7060	5·7

The adsorption band at 7100 cm.$^{-1}$ has been identified by Wulf and Liddel to be a harmonic of OH frequency, the fundamental of which occurs at 3500 cm.$^{-1}$ It has been shown by these authors that the formation of a strong hydrogen bond leads to the extinction of the absorption in 7000 cm.$^{-1}$ region, thus this extinction providing an important evidence of strong hydrogen bond.

It may however be pointed out that the disappearance of absorption peak at 7050 cm.$^{-1}$ in catechol and pyrogallol is accompanied by the appearance of a peak at 6970 cm.$^{-1}$ which is due to the weakness of the OH bond in these compounds and which is responsible for the higher values of the first dissociation constants.

If log K_1^a / K_2^a is plotted against the absorption coefficient of the prominent absorption frequency, a straight line relationship is obtained. From this it can be said that the height of the infra-red absorption peak is a function of the distance and dipole effects of two hydroxyl groups which are directly measured by the ratio of the two dissociation constants. If this relationship is taken into account, the infra-red molal absorption coefficient for phloroglucinol ought to be very high in the region, 7000 cm.$^{-1}$ The absorption data for phloroglucinol is however not available.

SUMMARY.

The potentiometric titrations of *ortho-*, *meta-* and *para-*hydroxy benzoic acids, gallic acid and various di- and tri-hydroxy benzenes by 0.1 N sodium hydroxide have been carried out at 30° and the primary and secondary dissociation constants calculated. Correction

for interionic attractions have been applied with the help of Debye-Hückel theory. The values of the first dissociation constants for some of the phenols are of the same order as obtained by Euler and Bolin. The second dissociation constants for all the substances have been determined for the first time. In the case of phloroglucinol both the OH groups titrate simultaneously, as the two dissociation constants are of the same order. The first and second dissociation constants of pyrogallol and phloroglucinol have been determined for the first time.

The effect of distance between the two ionising groups on the dissociation constants is shown, not only by the marked changes in the first dissociation constants but also more prominently by the ratio K_1^a / K_2^a. The order of the first dissociation constants is $o > m > H > p$ in the benzoic acids, and phloroglucinol > pyrogallol > catechol > resorcinol > hydroquinone in hydroxy benzenes. The order of the second dissociation constants of the benzoic acids is the reverse of that of the first dissociation constants.

A straight line relationship has been shown to exist between the $\log K_1^a / K_2^a$ and the molal absorption coefficient in the infra-red region at 7000 cm.$^{-1}$, for phenols. In catechol and pyrogallol the extinction of the band at 7050 cm.$^{-1}$ is accompanied by the appearance of a decreased frequency at 6970 cm.$^{-1}$ which is due to the weak OH bond responsible for the increased first dissociation constant.

Department of General Chemistry,
Indian Institute of Science,
Bangalore (India).

[Received, 19-10-1938.]

1772-38—Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent