

IX.—On the Relationship between Concentration and Electrolytic Conductivity in Concentrated Aqueous Solutions. By Professor John Gibson.

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Although great advances have been made during the last thirty years in our knowledge of dilute solutions, there has been no corresponding advance in respect of concentrated solutions. This is primarily due to the fact that hitherto no simple and general relationship has been discovered between the conductivity and the concentration of concentrated solutions of electrolytes. OSTWALD'S law of dilution holds only for dilute solutions of weak electrolytes, and the formulæ of RUDOLPHI and VAN THOFF are applicable only to dilute solutions of good electrolytes. It seems therefore important to inquire whether the difficulty may not be to some extent overcome by an alteration in the mode of representing the facts.

Our knowledge of the facts is mainly derived from the classical researches of KOHLRAUSCH. The following discussion is based throughout on the data given by KOHLRAUSCH and HOLBORN in Table I. of their invaluable compilation entitled *Leitvermögen der Electrolyte*.

The units adopted by KOHLRAUSCH are :—

- κ = Specific conductivity in $\text{ohm}^{-1} \text{ c.m.}^{-1}$.
- η = Concentration in gram equivalents per c.c.
- m = 1000 η or gram equivalents per litre.
- $\Lambda = \frac{\kappa}{\eta}$ = equivalent conductivity.
- s = Specific gravity.

Formerly the concentration was expressed in percentages, but the advantage gained by expressing the concentration in terms of gram equivalents is obvious. This advantage is, however, not dependent upon the adoption of the unit of volume (c.c. or litre). On the contrary, by expressing the concentration of a concentrated solution in terms of the number of gram equivalents of the solute per unit *volume* of the solution, the relationship between the concentration and the mass of a concentrated solution is necessarily masked, because the solution of electrolytes in water is accompanied by changes in volume differing with each electrolyte and by no means negligible in concentrated solutions.

Let the following units be taken :—

- κ = Specific conductivity in $\text{ohm}^{-1} \text{ c.m.}^{-1}$.
- γ = Concentration in gram equivalents per gram of solution.
- Γ = 1000 γ .
- $\Lambda_{\kappa} = \frac{\kappa}{\gamma}$ (corresponding to $\Lambda = \frac{\kappa}{\eta}$).

For concentrated aqueous solutions of good electrolytes the relationship between Λ_m and Γ expressed in these units is, over wide ranges of concentration, accurately expressed by the equation

$$\Lambda_m = a + b\Gamma \quad (1)$$

where a and b are constants for each electrolyte.

To avoid confusion, the units adopted by KOHLRAUSCH will be referred to as volume units and the units here proposed as mass units.

If the data for concentrated solutions of good electrolytes given by KOHLRAUSCH and HOLBORN be translated from volume units into mass units, and Λ_m be plotted against Γ , straight lines are obtained in almost every case. Fig. 1 shows the graphs obtained in this way for HNO_3 , H_2SO_4 , KOH , NaCl , and for comparison the corresponding graphs in volume units. The graphs obtained by using volume units are in thin lines and those obtained by using mass units in thick lines. It is important to notice that $\gamma = \frac{\eta}{s}$ and $\Lambda_m = \Lambda s$, so that the adoption of mass units instead of volume units does not affect the numerical statement of the relationships which have been established for dilute solutions: for when $s = 1$, as is practically the case in solutions more dilute than 0.1 normal, γ coincides with η and Λ_m with Λ . In such dilute solutions, whether we refer to unit volume of the solution or to unit volume of the solvent, or to unit mass of the solution or to unit mass of the solvent, the numerical expression of the experimental values is practically the same.

But in concentrated solutions the difference between the volume of a given solution and the sum of the volumes of the solvent and the solute taken separately often represents a very high internal pressure, and moreover this internal pressure varies greatly from one electrolyte to the other, so that, by taking equivalent quantities in equal volumes, we by no means establish comparable conditions. Even in an ideal case of a solution of a binary electrolyte without any such internal pressure, the concentration must be of the order of $\frac{1}{20}$ normal or less, if the condition of the solute in the solution is to be at all comparable with that of a gas at ordinary pressure. There appears therefore no logical reason in favour of volume units as against mass units, and, as stated above, the expression for the relationship between the concentration and conductivity becomes at once more simple and more useful when the mass units are adopted instead of volume units.

In order to test the applicability of equation (1) as closely as possible, the data given by KOHLRAUSCH and HOLBORN for concentrated solutions of good electrolytes, in so far as they are sufficient for the purpose, were translated from volume units into mass units, and from the new data thus obtained the constants a and b of equation (1) were calculated by the method of least squares. The results of these calculations are given in Table A, along with the data from which they are derived.

The several columns are as follows:—

- I. The formula of the electrolyte and also the values for the constants of equation (1).
- II. The percentages, *i.e.* the number of parts by weight of the electrolyte in 100 parts of the solution.
Interpolated points are indicated in this column by parentheses. Experimental numbers excluded from the calculation of the constants are marked †. Older values to which KOHLRAUSCH attributes less exactness are marked.*
- III. m , *i.e.* gramme equivalents per litre ($m=1000 \eta$).
- IV. κ , *i.e.* specific conductivity in ohms⁻¹ c.m.⁻¹.
- V. $\Lambda = \frac{\kappa}{\eta}$, *i.e.* equivalent conductivity.
- VI. Γ , *i.e.* gramme equivalents of electrolyte per kilogramme of the solution ($\Gamma=1000 \gamma$).
- VII. $\Lambda_M = \frac{\kappa}{\gamma}$, *i.e.* specific conductivity divided by the number of equivalents per gramme of the solution.
- VIII. As in column VII., but calculated from equation (1).
- IX. Percentage differences between Λ_M observed and Λ_M calculated.
- X. As in column IX., but for points outside the range within which equation (1) applies.
- XI. As in column IX., but for interpolated points.

This arrangement of the percentage differences in three columns facilitates a review of the evidence for or against the applicability of equation (1).

TABLE A.

I.	II. P	III. 1000 η (m ; $1/v$)	IV. $10^4 \kappa$	V. $\Lambda = \frac{\kappa}{\eta}$	VI. 1000 γ (Γ)	VII. Λ_M obs.	VIII. Λ_M calc.	IX. X. XI. Percentage Differences. Λ_M calc. - Λ_M obs.		
KCl $a=102.6$ $b=-1.067$	5	0.691	690	99.9	0.671	103.0	101.9	...	-1.1	...
	10	1.427	1359	95.2	1.342	101.3	101.2	-0.1
	15	2.208	2020	91.5	2.011	100.4	100.5	+0.1
	20	3.039	2677	88.1 ¹	2.681	99.7	99.7	± 0.0
	21	3.213	2810	87.5	2.816	99.8	99.6	-0.2
NH ₄ Cl $a=101.0$ $b=-3.094$	5	0.948	918	96.8	0.934	98.2	98.1	-0.1
	10	1.923	1776	92.4	1.869	95.1	95.2	+0.1
	15	2.924	2586	88.4	2.803	92.2	92.3	+0.1
	20	3.952	3365	85.0	3.738	90.0	89.4	-0.7
	25	5.003	4025	80.5	4.671	86.2	86.5	+0.4
NaCl $a=85.5$ $b=-8.34$	5	0.884	672	76.0	0.855	78.6	78.4	-0.3
	10	1.830	1211	66.2	1.709	70.9	71.2	+0.4
	15	2.843	1642	57.8	2.564	64.1	64.1	± 0.0
	20	3.924	1957	49.9	3.419	57.3	57.0	-0.5
	25	5.085	2135	42.0	4.274	50.0	49.9	-0.2
	26	5.325	2151	40.4	4.444	48.4	48.4	± 0.0
	26.4	5.421	2156	39.8	4.512	47.8	47.9	+0.2

¹ In KOHLRAUSCH and HOLBORN stated as 88.9. The calculation of the values for Γ and Λ_M involved the recalculation of the corresponding values for m and Λ . Only three errors of calculation were thus incidentally discovered.

TABLE A—continued.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX. X. XI.		
	P	1000 η (m ; $1/v$)	$10^4 \kappa_{18}$	$\Delta = \frac{\kappa}{\eta}$	1000 γ (Γ)	Δ_M obs.	Δ_M calc.	Percentage Differences. Δ_M calc. - Δ_M obs.		
LiCl $\alpha = 67.7$ $b = -6.79$	%									
	5†	1.209	733	60.6	1.177	62.3	59.7	...	-4.1	...
	10	2.487	1218	49.0	2.354	51.8	51.7	-0.2
	20*	5.249	1676	31.9	4.708	35.6	35.7	+0.3
	30*	8.340	1399	16.78	7.062	19.8	19.7	-0.5
	40*†	11.820	844	7.14	9.418	8.96	3.75	...	-58.0	...
BaCl ₂ $\alpha = 84.4$ $b = -7.84$	5	0.501	389	77.7	0.480	81.2	80.6	-0.7
	10	1.050	733	69.8	0.960	76.4	76.8	+0.5
	15	1.652	1051	63.6	1.440	73.0	73.1	+0.1
	(20)	2.314	1331	57.5	1.921	69.3	69.3	± 0.0
	24	2.894	1534	53.0	2.304	66.6	66.3	-0.5
SrCl ₂ $\alpha = 82.0$ $b = -9.04$	5	0.659	483	73.3	0.631	76.6	76.3	-0.4
	10	1.379	886	64.3	1.261	70.3	70.6	+0.4
	15	2.168	1231	56.8	1.892	65.1	64.9	-0.3
	(20)	3.034	1495	49.3	2.523	59.3	59.2	-0.3
	22	3.403	1583	46.5	2.775	57.0	56.9	-0.2
CaCl ₂ $\alpha = 79.3$ $b = -8.78$	5	0.938	643	68.6	0.901	71.4	71.4	± 0.0
	10	1.957	1141	58.3	1.803	63.3	63.5	+0.3
	(15)	3.059	1505	49.2	2.704	55.7	55.6	-0.2
	20	4.253	1728	40.6	3.605	47.9	47.7	-0.4
	25	5.545	1781	32.12	4.507	39.5	39.7	+0.5
	30†	6.945	1658	23.87	5.408	30.7	31.8	...	+1.1	...
	35†	8.468	1366	16.13	6.309	21.7	23.9	...	+10.1	...
MgCl ₂ $\alpha = 75.2$ $b = -9.99$	5	1.094	683	62.4	1.050	65.0	64.7	-0.4
	10	2.281	1128	49.5	2.100	53.8	54.2	+0.7
	20	4.942	1402	28.37	4.200	33.4	33.3	-0.3
	30†	6.052	1061	13.18	6.301	16.84	12.26	...	-27.1	...
	34†	9.434	768	8.14	7.142	10.75	3.86	...	-64.1	...
MnCl ₂ (Long, 1880) $\alpha = 69.8$ $b = -10.61$	5†	0.831	526	63.3	0.795	66.2	61.4	...	-7.3	...
	10	1.731	844	48.8	1.590	53.2	52.9	-0.6
	15	2.712	1055	38.9	2.383	44.3	44.6	+0.7
	20	3.784	1134	30.0	3.179	35.7	36.1	+1.1
	25	4.954	1090	22.00	3.972	27.43	27.70	+1.0
	28	5.707	1016	17.80	4.448	22.83	22.65	-0.8
KBr (Kohlrausch, 1879) $\alpha = 109.2$ $b = +2.396$	5	0.435	465	106.9	0.420	110.7	110.2	-0.5
	10	0.902	928	102.9	0.840	110.5	111.2	+0.6
	20	1.945	1907	98.1	1.679	113.6	113.2	-0.4
	30	3.162	2923	92.4	2.518	116.0	115.2	-0.7
	36	3.990	3507	87.9	3.023	116.0	116.4	+0.3
KI $\alpha = 108.5$ $b = +9.79$	5	0.312	338	108.3	0.301	112.3	111.5	-0.7
	10	0.648	680	104.9	0.602	112.9	114.4	+1.3
	20*	1.407	1455	103.4	1.204	120.8	120.3	-0.4
	30*	2.301	2303	100.1	1.808	127.4	126.2	-0.9
	40*	3.366	3168	94.1	2.410	131.4	132.1	+0.5
	55*†	5.401	4226	78.2	3.313	127.6	140.9	...	-10.4	...

TABLE A—continued.

I.	II. P	III. 1000η (m ; $1/v$)	IV. $10^4 \kappa_{18}$	V. $\Lambda = \frac{\kappa}{\eta}$	VI. 1000γ (r)	VII. Λ_M obs.	VIII. Λ_M calc.	IX. X. XI. Percentage Differences.		
								Λ_M calc. - Λ_M obs.		
NH_4I^* $a = 110.7$ $b = +3.259$	%									
	10	0.735	772	105.1	0.690	112.0	112.9	+0.8
	20	1.573	1599	101.7	1.380	115.9	115.2	-0.6
	(30)	2.538	2482	97.8	2.070	119.9	117.4	-2.1
	(40)	3.660	3393	92.7	2.760	122.9	119.7	-2.6
	50	4.973	4200	84.5	3.450	121.8	121.9	+0.1
NaI^* $a = 90.6$ $b = -4.165$	5	0.346	298	86.1	0.334	89.3	89.2	-0.1
	10	0.721	581	80.6	0.667	87.1	87.8	+0.8
	20	1.566	1144	73.1	1.334	85.8	85.0	-0.9
	(30)	2.569	1653	64.3	2.001	82.5	82.2	-0.4
	40	3.778	2111	55.9	2.674	79.0	79.4	+0.5
LiI^* $a = 80.7$ $b = -4.667$	5	0.387	296	76.5	0.373	79.3	79.0	-0.4
	10	0.803	573	71.4	0.747	76.8	77.3	+0.7
	(15)	1.252	838	66.9	1.120	74.8	75.5	+0.9
	20	1.739	1094	62.9	1.493	73.2	73.8	+0.8
	25	2.266	1346	59.4	1.867	72.1	72.0	-0.1
KF^* $a = 81.5$ $b = -6.53$	5	0.894	652	72.9	0.859	75.9	75.9	± 0.0
	10	1.862	1209	64.9	1.718	70.4	70.3	-0.1
	(20)	4.040	2080	51.5	3.435	60.6	59.1	-2.4
	(30)	6.554	2561	39.1	5.153	49.7	47.9	-3.6
	40	9.468	2522	26.6	6.870	36.7	36.7	± 0.0
AgNO_3 $a = 81.2$ $b = -6.18$	10†	0.641	476	74.3	0.588	80.9	77.6	...	-4.1	...
	20	1.407	872	62.0	1.177	74.1	74.0	-0.2
	(25)	1.847	1058	57.3	1.471	71.9	72.1	+0.3
	(30)	2.332	1239	53.1	1.765	70.2	70.3	-0.2
	(35)	2.872	1406	49.0	2.059	68.3	68.5	+0.3
	40	3.477	1565	45.0	2.353	66.5	66.7	+0.3
	(45)	4.158	1716	41.3	2.648	64.9	64.9	± 0.0
	(50)	4.926	1856	37.7	2.942	63.1	63.1	± 0.0
	(55)	5.791	1984	34.3	3.236	61.4	61.2	-0.3
	60	6.764	2101	31.1	3.530	59.6	59.4	-0.3
KNO_3 $a = 92.8$ $b = -8.38$	5†	0.509	454	89.2	0.494	91.9	88.6	...	-3.6	...
	10	1.051	839	79.8	0.988	84.8	84.5	-0.4
	15	1.626	1186	72.9	1.482	80.0	80.4	+0.5
	20	2.240	1505	67.2	1.977	76.1	76.2	+0.1
	22	2.496	1625	65.1	2.174	74.7	74.6	-0.1
NaNO_3 $a = 76.9$ $b = -8.95$	5†	0.607	436	71.8	0.588	74.2	71.6	...	-3.5	...
	10	1.255	782	62.3	1.175	66.5	66.3	-0.3
	20	2.688	1303	48.5	2.351	55.5	55.8	+0.6
	30	4.329	1606	37.1	3.526	45.6	45.3	-0.5
$\text{Mg}(\text{NO}_3)_2$ $a = 71.6$ $b = -10.45$	5	0.699	438	62.7	0.674	65.1	64.6	-0.8
	10	1.451	770	53.1	1.348	57.2	57.6	+0.7
	(15)	2.260	1021	45.2	2.021	50.5	50.5	± 0.0
	17	2.605	1102	42.3	2.290	48.1	47.7	-0.8

TABLE A—continued.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
	P	1000 η (m ; $1/v$)	$10^4 \kappa_{18}$	$\Lambda = \frac{\kappa}{\eta}$	1000 γ (r)	Λ_M obs.	Λ_M calc.	Percentage Differences. Λ_M calc. - Λ_M obs.		
Cu(NO ₃) ₂ (Long, 1880) $a = 72.5$ $b = -11.83$	%									
	5†	0.556	365	65.6	0.533	68.4	66.2	...	-3.2	...
	10	1.161	635	54.7	1.066	59.6	59.9	+0.5
	15	1.820	858	47.1	1.600	53.6	53.6	± 0.0
	20	2.543	1018	40.0	2.131	47.7	47.4	-0.6
	25	3.325	1089	32.8	2.664	40.9	41.1	+0.2
Sr(NO ₃) ₂ $a = 65.1$ $b = -11.89$	35	5.136	1062	20.7	3.730	28.5	28.4	-0.4
	10†	1.026	527	51.4	.945	55.8	53.9	...	-3.4	...
	15	1.604	690	43.0	1.417	48.7	48.2	-1.0
	20	2.233	802	35.9	1.890	42.4	42.6	+0.5
	25	2.920	866	29.66	2.361	36.7	37.0	+0.8
	35	4.478	861	19.23	3.310	26.0	25.7	-1.2
Pb(NO ₃) ₂ $a = 54.9$ $b = -10.00$	15†	1.039	429	41.4	0.906	47.5	45.8	...	-3.4	...
	20	1.455	521	35.8	1.208	43.1	42.8	-0.7
	25	1.916	600	31.3	1.511	39.7	39.8	+0.3
	30	2.422	668	27.6	1.813	36.9	36.8	-0.3
	10†	0.921	513	55.7	0.847	60.5	59.5	...	-1.7	...
	(15)	1.444	688	47.6	1.270	54.1	54.1	± 0.0
Cd(NO ₃) ₂ (Grottrian, 1883) $a = 70.3$ $b = -12.75$	20	2.017	827	41.0	1.694	48.8	48.7	-0.2
	(25)	2.647	919	34.7	2.117	43.4	43.3	-0.2
	30	3.336	956	28.7	2.540	37.7	37.9	+0.5
	(35)	4.092	948	23.17	2.964	32.0	32.5	+1.6
	40	4.937 ¹	903	18.29 ²	3.384	26.68	27.10	+1.1
	(45)	5.882	822	13.98	3.811	21.57	21.69	+0.5
KC ₂ H ₃ O ₂ $a = 76.0$ $b = -11.08$	48	6.497	755	11.62	4.065	18.57	18.45	-0.5
	4.67†	0.486	347	71.4	0.473	73.4	70.8	...	-3.5	...
	9.33	0.995	625	62.8	0.951	65.7	65.5	-0.3
	28.00	3.276	1256	38.3	2.853	44.0	44.4	+0.9
	46.67	5.985	1122	18.75	4.753	23.61	23.38	-0.9
	65.33†	9.128	479	5.25	6.656	7.20	2.30	...	-68.0	...
K ₂ SO ₄ $a = 84.9$ $b = -8.70$...	0.5	391	78.2	0.484	80.8	80.7	-0.1
	5	0.596	458	76.8	0.573	79.8	79.9	+0.1
	...	1.0	718	71.8	0.938	76.6	76.7	+0.1
	10	1.240	860	69.4	1.147	75.0	74.9	-0.1
Na ₂ SO ₄ $a = 67.7$ $b = -13.71$...	0.5	298	59.6	0.485	61.4	61.0	-0.7
	5	0.735	409	55.6	0.703	58.1	58.1	± 0.0
	...	1.0	508	50.8	0.943	53.9	54.7	+1.5
	10	1.536	687	44.7	1.407	48.8	48.4	-0.8
	...	2.0	800	40.0	1.789	44.7	43.3	-1.0
	15†	2.411	886	36.7	2.110	41.9	38.7	...	-7.6	...
(NH ₄) ₂ SO ₄ (Kohlrausch) $a = 75.1$ $b = -5.41$	5†	0.778	552	71.0	0.756	73.1	71.0	...	-2.9	...
	10	1.601	1010	63.1	1.513	66.8	66.9	+0.1
	20	3.377	1779	52.7	3.026	58.8	58.7	-0.2
	30	5.322	2292	43.1	4.537	50.6	50.5	-0.2
	31	5.528	2321	42.0	4.690	49.5	49.7	+0.4

¹ In KOHLRAUSCH and HOLBORN stated as 4.922.² In KOHLRAUSCH and HOLBORN stated as 18.35.

TABLE A—continued.

I.	II. P	III. 1000η (m ; $1/v$)	IV. $10^4 \kappa_{18}$	V. $\Lambda = \frac{\kappa}{\eta}$	VI. 1000γ (Γ)	VII. Λ_M obs.	VIII. Λ_M calc.	IX. X. XI. Percentage Differences.		
								Λ_M calc. - Λ_M obs.		
$(\text{NH}_4)_2\text{SO}_4$ (Klein, 1886) $a = 73.0$ $b = -4.860$...	1.0	681	68.1	0.965	70.6	68.3	...	-3.2	...
	...	1.5	941	62.7	1.425	66.0	66.1	+0.1
	...	2.0	1201	60.0	1.869	64.2	63.9	-0.5
	...	2.5	1414	56.6	2.303	61.4	61.8	+0.7
	...	3.0	1630	54.3	2.720	59.9	59.8	-0.2
MgSO_4 $a = 33.63$ $b = -5.71$	5†	0.873	263	30.1	0.831	31.6	28.9	...	-8.5	...
	10†	1.836	414	22.55	1.661	24.92	24.14	...	-3.1	...
	...	2.0	436	21.5	1.798	23.92	23.37	...	-2.3	...
	...	2.5	467	18.68	2.194	21.29	21.10	-0.9
	15	2.891	480	16.60	2.491	19.26	19.41	+0.8
	...	3.423	493	14.40	2.884	17.09	17.16	+0.4
	(20)	4.054	476	11.74	3.322	14.32	14.66	+2.2
	...	4.108	483	11.76	3.362	14.37	14.43	+0.4
ZnSO_4 $a = 32.79$ $b = -5.59$	25	5.342	415	7.77	4.153	9.99	9.92	-0.7
	5	0.651	191	29.3	0.620	30.80	29.32	...	-4.8	...
	10	1.371	321	23.42	1.239	25.90	25.86	-0.2
	15	2.169	415	19.13	1.858	22.34	22.40	+0.3
	(20)	3.053	468	15.33	2.478	18.90	18.93	+0.2
	25	4.040	480	11.88	3.097	15.50	15.47	-0.2
CuSO_4 $a = 31.83$ $b = -4.996$	(30)	5.124	444	8.66	3.717	11.95	12.01	+0.5
	5†	0.658	189	28.7	0.626	30.2	28.7	...	-5.0	...
	10	1.387	320	23.1	1.253	25.6	25.6	± 0.0
	15	2.194	421	19.19	1.880	22.40	22.44	+0.2
	17.5	2.631	458	17.41	2.192	20.90	20.88	-0.1
MnSO_4 (Klein, 1886) $a = 29.88$ $b = -5.12$...	1.476	315	21.34	1.344	23.44	23.00	...	-1.9	...
	...	2.034	372	18.29	1.793	20.75	20.71	-0.2
	...	3.231	433	13.40	2.668	16.23	16.23	± 0.0
	...	4.257	425	9.98	3.337	12.74	12.81	+0.5
	...	5.321	383	7.20	3.971	9.65	9.56	-0.9
	...	6.639	300	4.52	4.680	6.41	5.92	...	-7.6	...
CdSO_4 (Grotrian, 1883) $a = 30.91$ $b = -5.42$	5†	0.504	146	29.0	0.481	30.4	28.3	...	-6.9	...
	10	1.060	247	23.3	0.961	25.7	25.7	± 0.0
	(15)	1.674	325	19.42	1.442	22.54	23.10	+2.5
	(20)	2.354	388	16.48	1.922	20.18	20.50	+1.5
	25	3.112	430	13.82	2.403	17.90	17.90	± 0.0
	(30)	3.958	436	11.02	2.884	15.12	15.30	+1.1
	(35)	4.902	424	8.65	3.363	12.61	12.70	+0.7
FeSO_4 (Klein, 1886) $a = 31.37$ $b = -5.20$	36	5.102	421	8.25	3.460	12.16	12.17	+0.1
	...	1	258	25.8	0.935	27.6	26.5	...	-4.0	...
	...	2	390	19.5	1.758	22.2	22.2	± 0.0
	...	3	461	15.37	2.496	18.47	18.39	-0.4
	...	3.56	470	13.21	2.880	16.32	16.39	+0.4
NiSO_4 $a = 32.51$ $b = -5.85$...	0.5	153	30.6	0.482	31.8	29.7	...	-6.6	...
	...	1.0	254	25.4	0.929	27.3	27.1	-0.7
	...	2.0	385	19.25	1.738	22.14	22.35	+1.0
	...	3.0	452	15.07	2.455	18.41	18.15	-1.4

TABLE A—continued.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX. X. XI.		
	P	1000η ($m; 1/v$)	$10^4 \kappa_{18}$	$\Delta = \frac{\kappa}{\eta}$	1000γ (r)	Δ_M obs.	Δ_M calc.	Percentage Differences. Δ_M calc. - Δ_M obs.		
K_2CO_3 $a = 82.5$ $b = -7.15$	%									
	5	0.756	561	74.2	0.723	77.5	77.4	-0.1
	10	1.579	1038	65.7	1.446	71.7	72.2	+0.7
	20	3.448	1806	52.4	2.892	62.5	61.9	-1.0
	30	5.641	2222	39.4	4.338	51.2	51.5	+0.6
	40†	8.198	2168	26.45	5.784	37.48	41.16	...	+9.8	...
$KHSO_4$ $a = 229.5$ $b = -28.52$	50†	11.157	1469	13.16	7.230	20.30	30.81	...	+51.8	...
	5†	0.380	821	...	0.367	223.7	219.0	...	-2.1	...
	10	0.787	1528	...	0.734	208.2	208.6	+0.2
	(15)	1.224	2178	...	1.101	197.8	198.1	+0.2
	20	1.691	2769	...	1.468	188.6	187.6	-0.5
	(25)	2.188	3256	...	1.835	177.4	177.2	-0.1
$ZnCl_2$ (Long, 1880) $a = 62.4$ $b = -9.711$	27	2.400	3419	...	1.982	172.5	173.0	+0.3
	10	1.606	727	45.3	1.467	49.6	48.1	...	-3.0	...
	20	3.493	912	26.1	2.934	31.1	33.9	...	+9.0	...
$CdCl_2$ (Grotrian, 1883) $a = 17.52$ $b = -2.775$	30	5.720	926	16.19	4.404	21.0	19.6	...	-6.7	...
	20†	2.626	299	11.39	2.187	13.68	11.45	...	-16.3	...
	30	4.365	282	6.47	3.281	8.60	8.42	...	-2.1	...
	40	6.508	221	3.40	4.374	5.06	5.38	...	+6.3	...
$CdBr_2$ (Grotrian, 1883) $a = 23.05$ $b = -4.719$	50	9.185	137	1.49	5.468	2.50	2.35	...	-6.0	...
	10†	0.802	164	20.4	0.735	22.3	19.6	...	-12.1	...
	20	1.764	236	13.4	1.471	16.1	16.1	± 0.0
	30	2.934	273	9.30	2.206	12.4	12.6	+1.6
CdI_2 (Grotrian, 1883) $a = 20.08$ $b = -2.819$	43	4.892	261	5.34	3.162	8.26	8.13	-1.5
	10†	0.595	103.9	17.5	0.547	19.0	18.5	...	-2.6	...
	15	0.934	146	15.6	0.820	17.8	17.8	± 0.0
	20	1.306	186	14.2	1.093	17.0	17.0	± 0.0
	(25)	1.716	222	12.9	1.367	16.2	16.2	± 0.0
	30	2.170	254	11.7	1.640	15.5	15.5	± 0.0
	(35)	2.680	282	10.5	1.914	14.7	14.7	± 0.0
	40	3.241	303	9.35	2.187	13.9	13.9	± 0.0
KHS (Bock, 1887) $a = 127.4$ $b = -10.00$	45†	3.874	314	8.11	2.460	12.8	13.2	...	+3.1	...
	15.08†	2.274	1928	84.8	2.088	92.3	106.5	...	+13.3	...
	33.43	5.780	3749	64.7	4.630	81.0	81.1	+0.1
	39.22	6.748	3982	59.0	5.432	73.3	73.1	-0.3
K_2S (Bock, 1887) $a = 177.9$ $b = -17.22$	51.22	9.381	4003	42.7	7.094	56.4	56.5	+0.2
	24.64†	5.444	4401	80.8	4.467	98.5	101.0	...	+2.5	...
	29.97	6.889	4563	66.2	5.436	83.9	84.3	+0.5
	38.08	9.319	4106	44.1	6.902	59.5	59.1	-0.7
Na_2S (Bock, 1887) $a = 125.5$ $b = -17.05$	47.26	12.504	2579	20.63	8.566	30.1	30.4	+1.0
	2.02	0.529	612	115.7	0.518	118.2	116.7	-1.3
	5.03	1.359	1321	97.2	1.287	102.6	103.6	+1.0
	9.64	2.736	2017	73.7	2.464	81.8	83.5	+2.1
	14.02	4.163	2359	56.7	3.594	65.7	64.3	-2.1
	16.12	4.873	2243	46.0	4.126	54.3	55.2	+1.6
	18.15	5.647	2184	38.7	4.645	47.1	46.4	-1.4

TABLE A—continued.

Hydrates.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
	P	1000η (m ; $1/v$)	$10^4 \kappa_{18}$	$\Lambda = \frac{\kappa}{\eta}$	1000γ (r)	Λ_M obs.	Λ_M calc.	Percentage Differences.		
								Λ_M calc. - Λ_M obs.		
KOH $a = 214.6$ $b = -21.14$	%									
	4.2†	0.777	1464	188.4	0.748	195.6	198.8	...	+1.6	...
	8.4	1.612	2723	168.9	1.496	182.0	183.0	+0.5
	16.8	3.467	4558	131.5	2.992	152.4	151.3	-0.7
	25.2	5.583	5403	96.8	4.488	120.4	119.7	-0.2
	33.6	7.978	5221	65.4	5.984	87.2	88.1	+1.0
	42.0	10.695	4212	39.4	7.480	56.3	56.5	+0.4
NaOH $a = 190.5$ $b = -26.22$	2.5	0.641	1087	169.6	0.624	174.3	174.2	-0.1
	5.0	1.319	1969	149.3	1.248	157.8	157.8	± 0.0
	10.0	2.779	3124	112.4	2.496	125.1	125.1	± 0.0
	(15)	4.381	3463	79.0	3.744	92.4	92.4	± 0.0
	20.0†	6.122	3270	53.4	4.992	65.5	59.6	...	-10.5	...
LiOH* $a = 156.1$ $b = -19.23$	1.25†	0.527	781	148.2	0.520	150.2	146.1	...	-2.7	...
	2.5	1.069	1416	132.5	1.040	136.2	136.1	-0.1
	5.0	2.194	2396	109.2	2.080	115.2	116.2	+0.9
	7.5	3.371	2999	89.0	3.120	96.2	96.2	± 0.0
Acids.										
HNO ₃ $a = 356.0$ $b = -40.40$	6.2	1.017	3123	307.1	0.983	317.5	316.3	-0.4
	12.4	2.108	5418	257.0	1.967	275.4	276.5	+0.4
	(18.6)	3.276	6901	210.7	2.950	233.9	236.8	+1.2
	24.8	4.533	7676	169.3	3.935	195.1	197.0	+1.0
	31.0	5.873	7819	133.1	4.917	159.0	157.4	-1.0
$\frac{1}{2}$ H ₂ SO ₄ $a = 235.5$ $b = -18.70$	10	2.176	3915	179.9	2.039	192.0	197.4	...	+2.8	...
	15	3.376	5432	160.9	3.059	177.6	178.3	+0.4
	20	4.655	6527	140.2	4.077	160.1	159.3	-0.5
	25	6.019	7171	119.2	5.096	140.7	140.2	-0.4
	30	7.468	7388	98.9	6.116	120.7	121.1	+0.5
	35	9.011	7243	80.4	7.137	101.5	102.0	+0.5
	40	10.649	6800	63.8	8.155	83.4	83.0	-0.5
	(45)	12.396	6164	49.7	9.177	67.2	63.9	-4.9
	50	14.258	5405	39.9	10.195	50.8	44.9	...	-11.6	...
$\frac{1}{3}$ H ₃ PO ₄ $a = 19.08$ $b = -0.1406$	10	3.228	566	17.54	3.060	18.50	18.65	+0.8
	(15)	4.976	850	17.08	4.590	18.52	18.43	-0.5
	20	6.824	1129	16.56	6.120	18.45	18.22	-1.2	...	-
	(25)	8.776	1402	15.98	7.650	18.32	18.00	-1.7
	30	10.840	1654	15.26	9.182	18.01	17.79	-1.2
	35	13.023	1858	14.27	10.710	17.35	17.57	+1.3

(Constant a .)

[illegible]

(Constant b .)

[illegible]

DISCUSSION OF RESULTS.

For a number of electrolytes sufficient data are not available. Sufficiently concentrated solutions are not attainable for sparingly soluble salts such as $\text{Ba}(\text{NO}_3)_2$, KClO_3 , LiCO_3 , etc., at least not for a temperature so low as 18°C . In other cases the deficiency of data is due to the fact that the concentrations were originally expressed in percentages. Thus for HCl there are determinations for 5 per cent., 10 per cent., 20 per cent., 30 per cent., and 40 per cent., but the corresponding equivalent concentrations are 1.405, 2.877, 6.034, 9.482.

Now the range within which equation (1) applies to HNO_3 is in equivalents per litre 1.017 to 5.873, and within this range there are only two points for HCl , so that further determinations are required to settle the question. Similar remarks apply to the data for NH_4NO_3 , $\text{Ca}(\text{NO}_3)_2$, and $\text{NaC}_2\text{H}_3\text{O}_2$.

If equation (1) applies at all to solutions of weak electrolytes such as the organic acids and bases, the range of applicability is certainly small. Here also further data are required.

Data for forty-nine electrolytes are given in Table A. These include all the salts, strong acids, and strong bases for which sufficient data are given by KOHLRAUSCH and HOLBORN.

ZnCl_2 and CdCl_2 stand out as marked exceptions. They are inserted along with CdBr_2 and CdI_2 , in order to draw attention to the remarkable transition from CdCl_2 , which is a decided exception through CdBr_2 with a very slightly curved graph, to CdI_2 which shows a perfect agreement between the observed and the calculated values for concentrations between 0.934 and 3.241 normal.

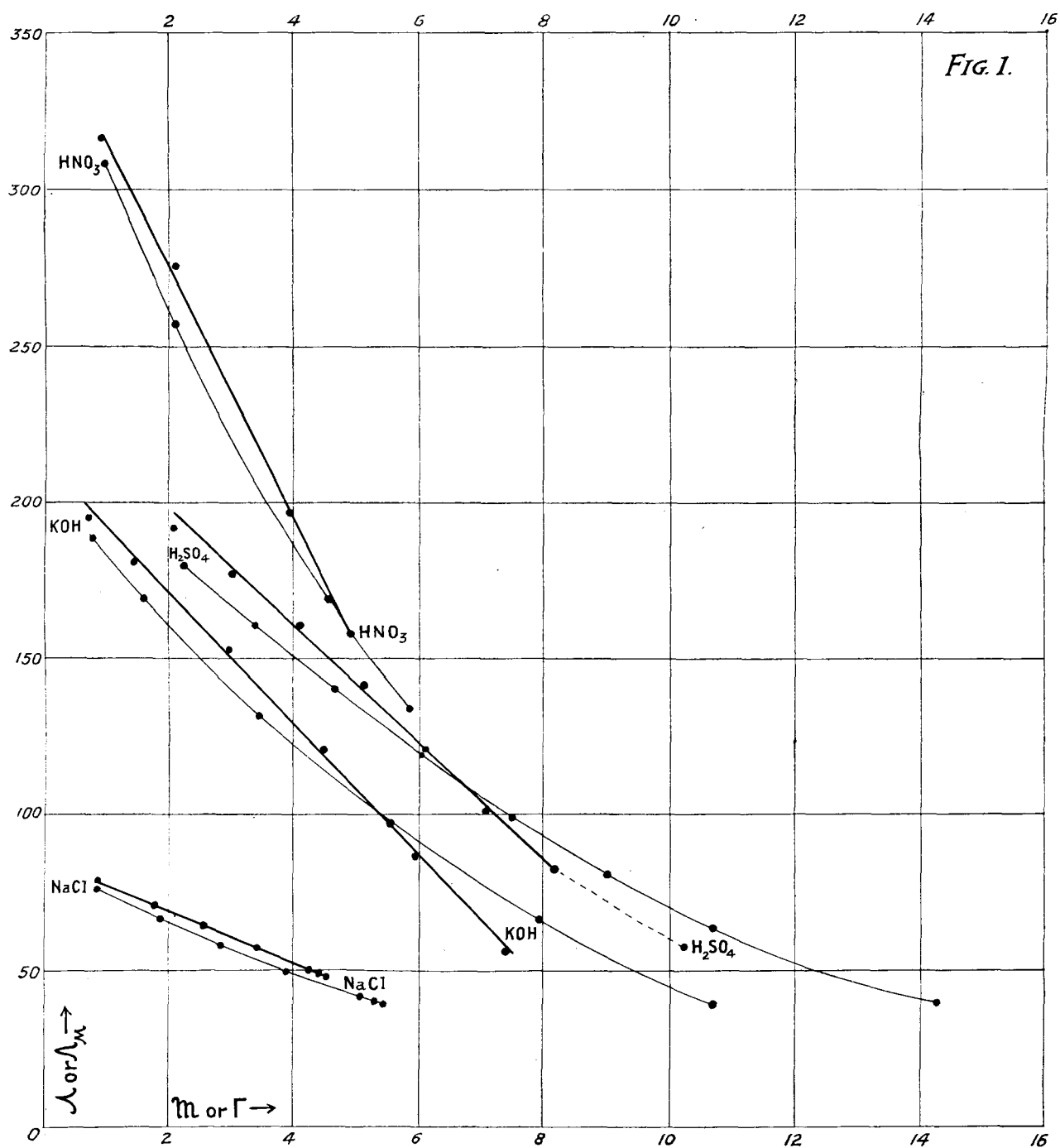
For the remaining 46 electrolytes the differences between the observed and the calculated values for Λ_m are given in column IX. Of these 185 differences, only 16 exceed 1 per cent., and none exceed 2.1 per cent. Of the 16 differences which exceed 1 per cent., 5 belong to Na_2S , and these five moreover include the only differences which exceed 1.7 per cent.

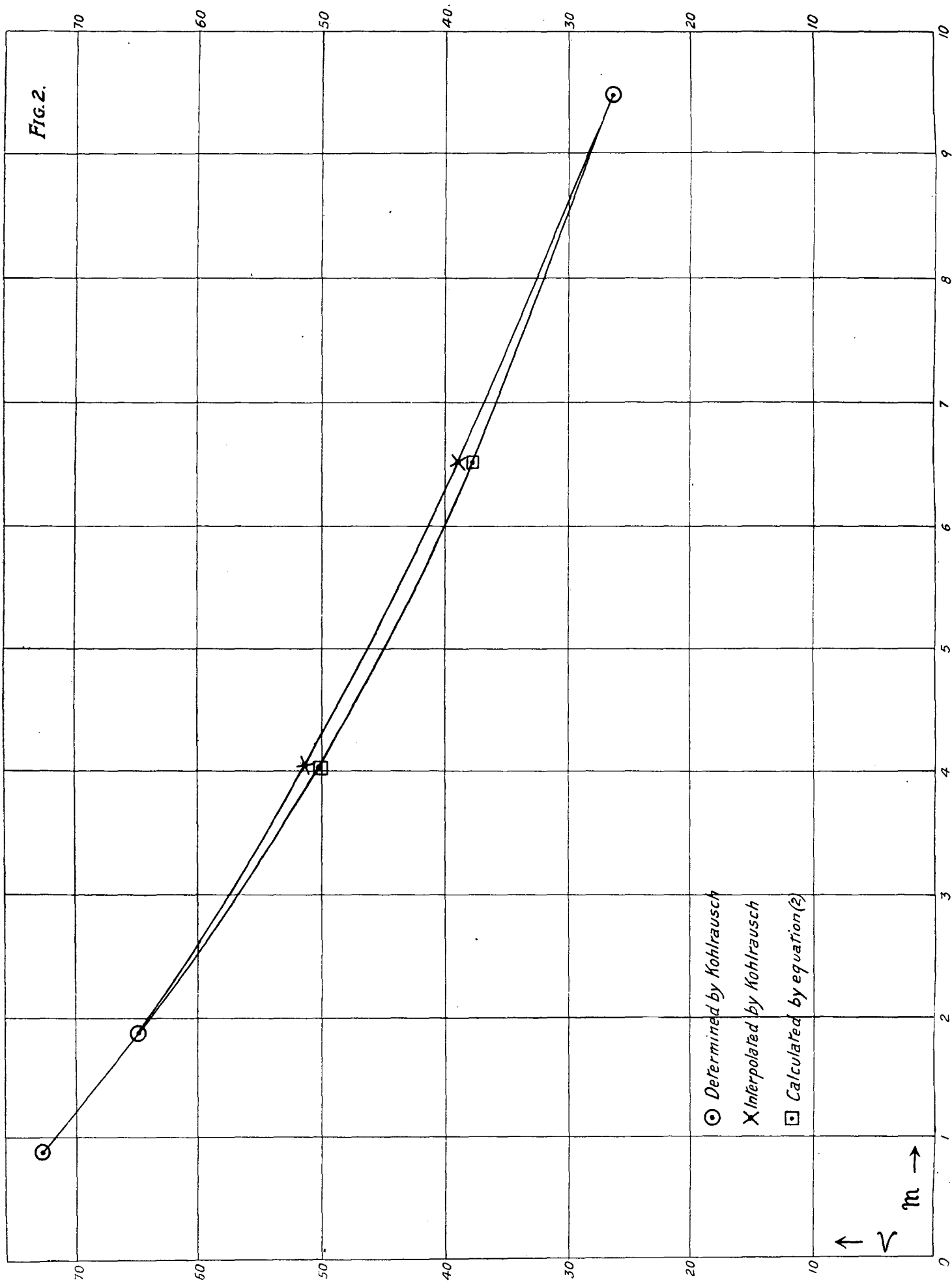
It is not easy to fix a criterion by which the applicability of equation (1) can be judged, or to say how close the agreement ought to be, for it is difficult to come to a definite conclusion as to the limits of error of the original determinations. KOHLRAUSCH and MALTBY, in discussing the errors affecting such determinations, make the following statement: "Immerhin kann man ziemlich sicher schliessen dass Fehler von 1 per cent. nicht selten vorkommen, was auch von vornherein wahrscheinlich wird sobald man die Fehlerquellen betrachtet." They also suggest a comparison between the results obtained by different observers as one means of throwing light on the question.

Now for K_2SO_4 , Na_2SO_4 , MgSO_4 , and $(\text{NH}_4)_2\text{SO}_4$ two sets of determinations are given by KOHLRAUSCH and HOLBORN, the one set by KOHLRAUSCH and the other by KLEIN.

In the case of the first three salts the number of the respective determinations is

Fig. 2 shows the graph for KF in volume units with KOHLRAUSCH's interpolations,





and for comparison the graph as interpolated by means of equation (2). Greater certainty in interpolation is clearly one of the advantages gained.

The Salts.

The graphs for a number of the salts given in Table A are shown in fig. 3. As in fig. 1 and fig. 4, the lines were calculated by equation (1), while the points indicate the experimental values. The agreement is, generally speaking, most satisfactory. As a rule the constant b is negative, so that Λ_m increases with the dilution. It is remarkable that in the case of KCl the constant b is only -1.067 , so that Λ_m varies very slightly with varying concentration. In the case of KBr, KI, and NH_4I the constant b is positive, that is, Λ_m decreases with dilution until a concentration of about 0.5 normal is reached. In solutions of these and of all the other electrolytes Λ_m rapidly increases on further dilution, and from about 0.1 normal down to infinite dilution the graphs practically coincide with those obtained by using the volume units. At a concentration of about 0.3–0.5 normal the values for Λ , for the salts generally, approximate very closely to the values for the constant a of equation (1).

The Hydrates.

The graphs for LiOH, NaOH, and KOH are shown in fig. 4.

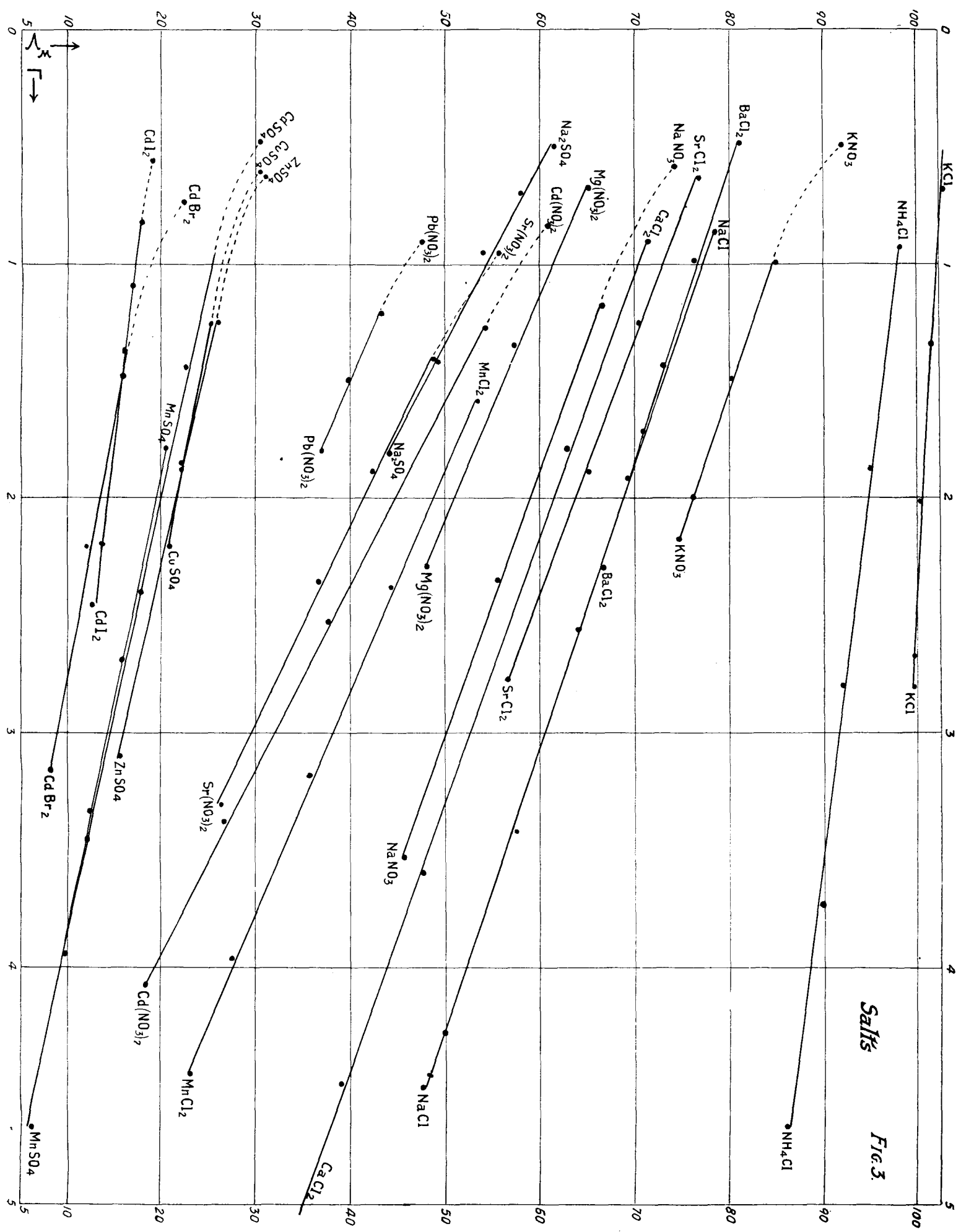
The data for LiOH and for NaOH are barely sufficient, but so far as they go, they point to a similar regularity. The graph for KOH is rectilinear over a very wide range of concentration, viz. from 1.612 normal to 10.695 normal, and the differences between the observed and calculated values for the five points given within this range in no case exceed 1 per cent., while for a concentration of 0.777 normal the difference is only +1.6 per cent. In the case of NaOH the agreement between the experimental and the calculated values for Λ_m is perfect for the three points from 0.641 to 2.779 normal and also for the interpolated point 4.381 normal.

The only other point of higher concentration given, viz. that for 6.122 normal, is 10.5 per cent. out, so that the graph evidently becomes curved between 4.381 and 6.122 normal.

The Strong Acids.

The data for the halogen acids HCl, HBr, and HI are altogether insufficient.

An investigation into the conductivity of these acids will be published shortly. Meantime it may be stated provisionally that the determinations so far made show that equation (1) applies over considerable ranges of concentration to HBr and HI, and probably applies also in the case of HCl. The graphs for HNO_3 , $\frac{1}{2}\text{H}_2\text{SO}_4$, and $\frac{1}{3}\text{H}_3\text{PO}_4$ are shown in fig. 4. The graph for $\frac{1}{3}\text{H}_3\text{PO}_4$ is remarkable for the very small variation in Λ_m over a wide range of concentration.



For nitric acid there are only four points given between 1 and 5.9 normal, but for these the greatest difference between the calculated and observed values is only + 1.1 per cent. At higher concentration the graph ceases to be even approximately linear.

The data for sulphuric acid are more complete. Six points, from 3-8 normal, show differences which do not exceed 0.5 per cent. As there is no indication of a trend in these differences, it is clear that equation (1) is applicable within this range. As in the case of nitric acid the graph ceases to be even approximately rectilinear at higher concentration. The data given are calculated for $\frac{1}{2}\text{H}_2\text{SO}_4$. Obviously they might have been calculated for $\text{H}(\text{HSO}_4)$. The advantages of this latter mode of representing the facts will be discussed in connection with the new data relating to the halogen acids.

The Constants of Equation (1).

Tables B and C show the manner in which anions and cations are grouped together according to the value of the constants a and b .

Certain groupings are clearly marked. The constants a for the chlorides, bromides, and iodides of potassium and ammonium agree closely. The isomorphous sulphates of Mg, Mn, Zn, Cd, Cu, and Fe show values for a and b which lie within narrow limits, viz., 30 to 34 for a , and 5.0 to 5.9 for b . In the case of the chlorides of Mg, Ca, Sr, and Ba the values for a rise in order from 75 for Mg to 83 for Ba, while conversely the values for b fall from -10 for Mg to -7.31 for Ba. These tables show clearly how much remains to be done before these relationships can be adequately discussed, but the data, though incomplete, justify the expectation that useful and general relationships will ultimately be established between the conductivity of concentrated solutions of good electrolytes and the character of their ions.

Some progress has been made towards filling up the gaps indicated by Tables B and C, but further discussion of these relationships must be postponed until some at least of these gaps have been filled up.

In a paper communicated to the Society in 1897, attention was drawn to increase in electrical conductivity as a characteristic of photo-chemical action, and in a second communication in December of the same year the following statement was made: "It would appear that the chemical behaviour of the acids just mentioned (HNO_3 , HCl , H_2SO_4) depends in many of their reactions on whether their concentration is above or below that corresponding to their maximum electrolytic conductivity."*

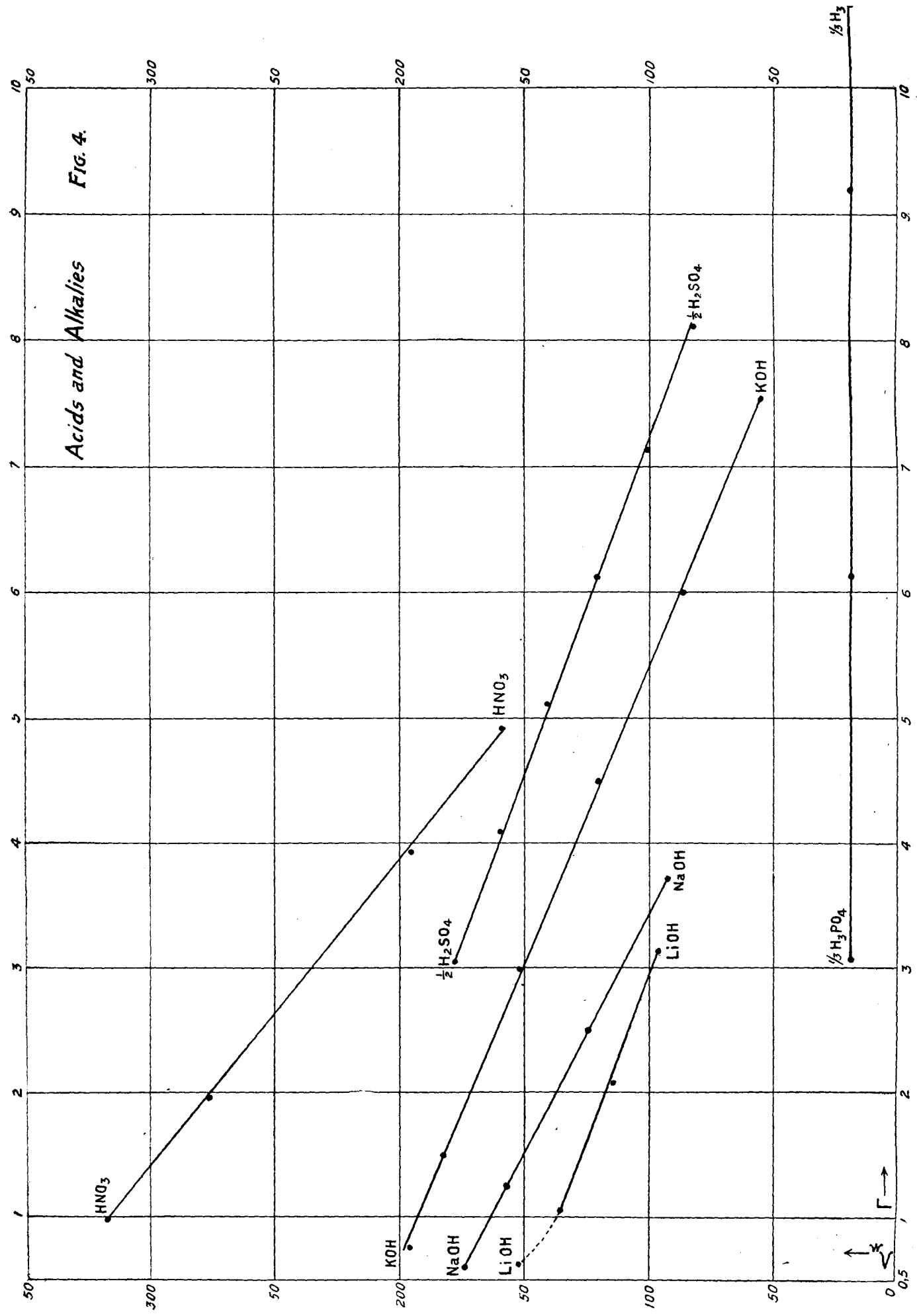
The exact experimental determination of the concentration corresponding to maximum specific conductivity is difficult, owing to the very slight variation of the conductivity with concentration near the maximum.

Now it is important to note that Table A shows clearly that in all cases where such

* κ = specific conductivity.

Fig. 4.

Acids and Alkalies



maxima are known to occur the corresponding concentration is included in the range within which equation (1) is applicable.

I am indebted to Mr G. E. GIBSON for pointing out that this in turn implies that in such cases the position of maximum conductivity may be calculated.

Thus equation (1) may be written

$$k = \alpha\Gamma + b\Gamma^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

for a maximum $\frac{dk}{d\Gamma} = 0$. Hence by equation (3) the condition for maximum specific conductivity is

$$a + 2b\Gamma = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Hence the concentration at which the maximum occurs is $-\frac{a}{2b}$ gramme equivalents per

kilogramme. Also by equation (3) the value of k at the maximum is $-\frac{\alpha^2}{4b}$.

KOHLRAUSCH and HOLBORN (page 99) state that for sulphuric acid a maximum is reached "bei 30%," and for this percentage give $10^4k=7388$ (page 156). The calculated values are 30.9 per cent. and $10^4k=7414$.

The significance and importance of maximum electrolytic conductivity will be discussed in a subsequent communication. This paper is intended as a review of the data published hitherto.

In conclusion I desire to thank Professor MACGREGOR for kind and helpful criticism, and Mr ANDREW KING for valuable assistance in the calculations for Table A.

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