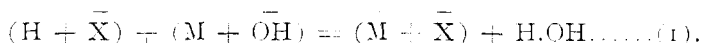


AN ELECTRONIC THEORY¹

BY PHILIP BLACKMAN

SEC. I. The formation of a salt MX from the acid HX and the base M.OH may be represented 'electrolytically' by the equation²



The initial and final electrical states differ by the expression



hence we should expect in the formation of the salt the disappearance of 'electrical conductivity' equivalent to that required by equation (2). This quantity of 'electrical conductivity' will be dependent on (1) the temperature, (2) the molecular concentration (or dilution), and (3) the nature of the acid HX. Suppose these three conditions be fixed, there ought to be a constant quantity for the electrical conductivity corresponding to equation (2).

Let

$$\mu v_{HX}, \mu v_{M_1.OH}, \mu v_{M_2.OH}, \mu v_{M_1X}, \mu v_{M_2X},$$

represent respectively the molecular conductivities (all measured at the same molecular concentration v , and at the same temperature) of the acid HX, the bases $M_1.OH$ and $M_2.OH$, and the salts M_1X , and M_2X . Then according to the argument just advanced,

$$\mu v_{HX} + \mu v_{M_1.OH} = \mu v_{M_1X} + K \dots (3).$$

$$\mu v_{HX} + \mu v_{M_2.OH} = \mu v_{M_2X} + K \dots (4),$$

¹ Being a complete summary, revised, and very considerably enlarged tabularly, of a series of papers by the author published in the *Philosophical Magazine*, London Chemical Society's *Proceedings*, *Chemical News*, and *Journal of Physical Chemistry*. The tables on molecular conductivities of salts are quite original, and a great number of the ionic conductivities in the tables are also original.

² Compare Phil. Mag. [6], **11**, 416 (1906).

where K is a constant. Therefore

$$\begin{aligned} \mu v_{HX} + \mu v_{M_1,OH} - \mu v_{M_1X} \\ = \mu v + \mu v_{M_2,OH} - \mu v_{M_2X} \dots \dots \dots (5). \end{aligned}$$

Table I is an illustration of the above; the data (as in all the other tables, unless otherwise mentioned) are taken from the "Physikalisch-Chemische Tabellen", von Landolt und Börnstein; numbers in brackets are from an early edition of that work, the others from the 1905 edition.

SEC. 2. Equation (5) on simplification becomes

$$\mu v_{M_1,OH} - \mu v_{M_2,OH} = \mu v_{M_1X} - \mu v_{M_2X} \dots \dots \dots (6),$$

which it will be at once evident furnishes a means for calculating the molecular conductivities of salts and bases, whether soluble or insoluble, or stable or unstable, in aqueous solution, whose molecular conductivities cannot be determined by direct measurement.¹ Such results will be found under Table II and Table III. Similarly it can be shown that

$$\begin{aligned} \mu v_{M_1,OH} - \mu v_{M_2,OH} &= \mu v_{M_1X_1} - \mu v_{M_2X_1} \\ &= \mu v_{M_1X_2} - \mu v_{M_2X_2} \\ &= \dots \dots - \dots \dots \\ &\dots \dots \dots (7). \end{aligned}$$

Hence,

$$\begin{aligned} \mu v_{M_1X} - \mu v_{M_2X} &= \mu v_{M_1X_1} - \mu v_{M_2X_1} \\ &= \mu v_{M_1X_2} - \mu v_{M_2X_2} \\ &= \mu v_{M_1X_3} - \mu v_{M_2X_3} \\ &= \dots \dots \dots \\ &= \text{constant} \dots \dots \dots (8). \end{aligned}$$

Equation (8) it will be seen is identical with the hitherto unexplained fact discovered by Kohlrausch and further extended by Ostwald, see "Lehrbuch der allgemeinen Chemie," II, i, 672.

¹ Cf. Jour. Phys. Chem., 13, 144 (1909).

TABLE I (TO SEC. I)

v (at 18°) =	32	10000	2000	1024	1000	500	200	100	50	33.3	20	10	2	1
$\mu v_{\frac{1}{2}}H_2SO_4 + \mu v_{KOH} - \mu v_{\frac{1}{2}}K_2SO_4$	(418)	(470)	—	(468)	(422)	461	442	(387)	409	388	377	(317)	(320)	(287)
$\mu v_{\frac{1}{2}}H_2SO_4 + \mu v_{NaOH} - \mu v_{\frac{1}{2}}Na_2SO_4$	(420)	(461)	385	(481)	(413)	433	433	426 (381)	395	365	368	350 (305)	323 (297)	310 (284)
$\mu v_{\frac{1}{2}}H_2SO_4 + \mu v_{LiOH} - \mu v_{\frac{1}{2}}Li_2SO_4$	(419)	—	—	(482)	459	—	—	415 (390)	—	—	—	342 (314)	328 (392)	304 (268)
$\mu v_{HNO_3} + \mu v_{KOH} - \mu v_{KNO_3}$	(492)	(490)	—	(485)	(439)	484	480	441 (478)	474	—	466	(423)	432	(374)
$\mu v_{HNO_3} + \mu v_{NaOH} - \mu v_{NaNO_3}$	(491)	(480)	—	(494)	(429)	477	475	428 (428)	469	—	465	(411)	434	(364)
$\mu v_{HNO_3} + \mu v_{\frac{1}{2}}BaO_2H_2 - \mu v_{\frac{1}{2}}Ba(NO_3)_2$	(473)	—	—	(481)	477	—	—	473	—	—	—	458	—	401
$\mu v_{HCl} + \mu v_{KOH} - \mu v_{KCl}$	(490)	485	—	(489)	(437)	473	470	(439)	472	—	463	(418)	422	(358)
$\mu v_{HCl} + \mu v_{NaOH} - \mu v_{NaCl}$	(492)	479	—	(490)	(425)	475	473	466 (433)	469	—	463	452 (408)	420	(358)
$\mu v_{HCl} + \mu v_{\frac{1}{2}}Ba(OH)_2 - \mu v_{\frac{1}{2}}BaCl_2$	(470)	—	—	(490)	—	—	—	471	—	—	—	454	—	384
$\mu v_{HCl} + \mu v_{LiOH} - \mu v_{LiCl}$	(493)	—	—	(491)	—	—	—	(442)	—	—	—	444	400	(344)
$\mu v_{HI} + \mu v_{KOH} - \mu v_{KI}$	—	—	—	—	—	—	—	—	—	—	—	(426)	—	—
$\mu v_{HI} + \mu v_{NaOH} - \mu v_{NaI}$	—	—	—	—	—	—	—	—	—	—	—	(427)	—	—
$\mu v_{HI} + \mu v_{LiOH} - \mu v_{LiI}$	—	—	—	—	—	—	—	—	—	—	—	(411)	—	—
$\mu v_{HIO_3} + \mu v_{KOH} - \mu v_{KIO_3}$	—	—	—	(482)	—	—	—	—	—	(442)	—	—	—	—
$\mu v_{HIO_3} + \mu v_{NaOH} - \mu v_{NaIO_3}$	—	—	—	(481)	—	—	—	—	—	(441)	—	—	—	—
$\mu v_{CH_3CO_2H} + \mu v_{KOH} - \mu v_{CH_3CO_2K}$	—	—	—	—	—	177	165	148	144	140	138	134	127	122
$\mu v_{CH_3CO_2H} + \mu v_{NaOH} - \mu v_{CH_3CO_2Na}$	—	—	—	—	—	171	160	152	144	143	141	139	127	117
$\mu v_{H_2C_2O_4} + \mu v_{KOH} - \mu v_{\frac{1}{2}}K_2C_2O_4$	—	—	—	—	292	284	276	273	260	—	250	235	—	170

TABLE II (TO SEC. 2)
Molecular conductivities at 18°

κ	$\frac{1}{2}\text{Ca}(\text{H}_2\text{PO}_4)_2$	$\frac{1}{2}\text{Ca}(\text{HPO}_4)_2$	$\frac{1}{2}\text{CaSiO}_3$	$\frac{1}{2}\text{Li}_2\text{C}_2\text{O}_4$	$\frac{1}{2}\text{MgSiO}_3$	NH_4ClO_3	NH_4IO_3
10000	—	—	—	93	—	119	97
5000	—	—	—	93	—	118	97
2000	—	—	—	92	—	117	96
1000	17	65	152	91	151	116	95
500	17	63	150	90	149	115	94
200	16	61	146	86	145	114	93
100	14	59	141	82	140	111	91
50	—	55	136	78	135	109	90
33.33	11	50	132	—	132	—	89
20	10	53	127	70	127	100	—
10	9	48	120	68	119	96	84
5	—	—	108	59	107	93	79
3.33	—	—	100	—	99	—	73
2	8	36	90	—	88	84	—
1	7	30	73	44	70	—	—

SEC. 3. The foregoing arguments and conclusions may now be most usefully applied to the question¹ of the "relative strengths of acids." Arrhenius showed that if acids be arranged in the order of their relative strengths they were also arranged in the order of their molecular conductivities. The comparison in all cases is so remarkably close that the electrical conductivity method has been accepted as a means for determining the relative strengths of acids. A satisfactory explanation (on the hypothesis of the "degrees of dissociation of acids") has been advanced to establish the connection between the molecular conductivities of acids and their relative strengths, and in this section will be found developed a novel theory as an attempt to supply a proof.

According to Section 1 and Equations (3) and (4) it is evident that had there been in the final solution H and OH^-

¹ Cf. Chem. News, **93**, 284 (1906), and Proc. Chem. Soc., **21**, 237 (1905).

TABLE III
Molecular conductivities at 25°

$v =$	32	64	128	256	512	1024
$\frac{1}{2}\text{Pb}(\text{ClO}_3)_2$	94	101	116	120	125	129
$\frac{1}{2}\text{Pb}(\text{ClO}_4)_2$	103	109	125	129	136	139
$\frac{1}{2}\text{PbBr}_2$	108	114	130	134	140	144
$\frac{1}{2}\text{Pb}(\text{BrO}_3)_2$	85	81	106	109	115	119
$\frac{1}{2}\text{PbI}_2$	108	114	128	133	139	143
$\frac{1}{2}\text{Pb}(\text{IO}_3)_2$	71	77	92	96	101	106
$\frac{1}{2}\text{PbF}_2$	84	91	106	109	115	119
$\frac{1}{2}\text{PbMnO}_4$	93	98	113	116	122	126
$\frac{1}{2}\text{Pb}(\text{NO}_2)_2$	119	124	140	144	152	160
$\frac{1}{2}\text{PbSO}_4$	96	104	122	128	136	142
$\frac{1}{2}\text{PbCrO}_4$	101	109	126	131	138	143
$\frac{1}{2}\text{PbCr}_2\text{O}_7$	93	97	111	112	117	123
$\frac{1}{2}\text{PbSO}_3$	90	98	116	122	129	136
$\frac{1}{2}\text{PbS}_2\text{O}_8$	98	108	128	132	140	146
$\frac{1}{3}\text{Pb}_3(\text{PO}_4)_2$	104	115	123	127	130	132
$\frac{1}{4}\text{CuCl}_2$	123	125	126	128	130	130
$\frac{1}{4}\text{Cu}(\text{ClO}_3)_2$	111	114	115	116	118	118
$\frac{1}{2}\text{Cu}(\text{ClO}_4)_2$	120	123	126	128	128	130
$\frac{1}{4}\text{CuBr}_2$	126	128	131	133	133	134
$\frac{1}{4}\text{Cu}(\text{BrO}_3)_2$	102	104	106	108	109	109
$\frac{1}{2}\text{CuI}_2$	125	127	129	130	131	131
$\frac{1}{2}\text{Cu}(\text{IO}_3)_2$	88	90	92	93	97	98
$\frac{1}{2}\text{CuF}_2$	101	103	105	107	108	108
$\frac{1}{2}\text{Cu}(\text{NO}_2)_2$	134	136	138	139	140	145
$\frac{1}{2}\text{CuSO}_4$	110	114	116	118	120	122
$\frac{1}{2}\text{CuCrO}_4$	115	119	120	122	123	124
$\frac{1}{2}\text{CuCr}_2\text{O}_7$	106	107	109	110	111	112
$\frac{1}{2}\text{CuSO}_3$	107	110	115	117	120	122
$\frac{1}{2}\text{BaCl}_2$	105	113	118	123	128	131
$\frac{1}{2}\text{Ba}(\text{ClO}_3)_2$	95	101	106	111	115	117
$\frac{1}{2}\text{Ba}(\text{ClO}_4)_2$	104	109	116	121	125	128
$\frac{1}{2}\text{BaBr}_2$	109	114	121	126	130	132
$\frac{1}{2}\text{Ba}(\text{BrO}_3)_2$	86	94	99	101	105	108
$\frac{1}{2}\text{BaI}_2$	109	114	120	127	130	136
$\frac{1}{2}\text{Ba}(\text{IO}_3)_2$	72	78	83	87	91	94
$\frac{1}{2}\text{BaF}_2$	87	92	97	101	102	108
$\frac{1}{2}\text{BaMnO}_4$	99	100	104	108	111	114
$\frac{1}{2}\text{Ba}(\text{NO}_3)_2$	100	106	112	117	120	122
$\frac{1}{2}\text{Ba}(\text{NO}_2)_2$	120	125	131	137	142	149
$\frac{1}{2}\text{BaSO}_4$	98	105	113	120	126	131
$\frac{1}{2}\text{BaCrO}_4$	101	110	117	124	129	132
$\frac{1}{2}\text{BaCr}_2\text{O}_7$	94	99	101	104	107	111

TABLE III—(Continued)

$v =$	32	64	128	256	512	1024
$\frac{1}{2}\text{BaSO}_3$	91	100	107	112	119	125
$\frac{1}{2}\text{BaS}_2\text{O}_8$	99	109	118	124	130	135
$\frac{1}{2}\text{SrCl}_2$	—	120	125	130	132	135
$\frac{1}{2}\text{Sr}(\text{ClO}_3)_2$	—	108	113	118	119	121
$\frac{1}{2}\text{Sr}(\text{ClO}_4)_2$	—	116	123	128	129	132
$\frac{1}{2}\text{SrBr}_2$	—	121	128	133	134	136
$\frac{1}{2}\text{Sr}(\text{BrO}_3)_2$	—	101	106	108	109	112
$\frac{1}{2}\text{SrI}_2$	—	121	127	134	134	140
$\frac{1}{2}\text{Sr}(\text{IO}_3)_2$	—	85	90	94	96	98
$\frac{1}{2}\text{SrF}_2$	—	99	104	108	109	112
$\frac{1}{2}\text{BrMnO}_4$	—	107	111	115	116	118
$\frac{1}{2}\text{Sr}(\text{NO}_3)_2$	—	113	119	124	125	126
$\frac{1}{2}\text{Sr}(\text{NO}_2)_2$	—	132	138	144	147	153
$\frac{1}{2}\text{SrSO}_4$	—	112	120	127	131	135
$\frac{1}{2}\text{SrCrO}_4$	—	117	124	131	134	136
$\frac{1}{2}\text{SrCr}_2\text{O}_7$	—	106	108	111	112	115
$\frac{1}{2}\text{SrSO}_3$	—	107	114	119	124	129
$\frac{1}{2}\text{SrS}_2\text{O}_8$	—	116	125	131	135	139
$\frac{1}{2}\text{CaCl}_2$	—	117	121	127	131	136
$\frac{1}{2}\text{Ca}(\text{ClO}_3)_2$	—	105	109	115	118	122
$\frac{1}{2}\text{Ca}(\text{ClO}_4)_2$	—	113	119	125	128	133
$\frac{1}{2}\text{CaBr}_2$	—	118	124	130	133	137
$\frac{1}{2}\text{Ca}(\text{BrO}_3)_2$	—	98	103	104	108	113
$\frac{1}{2}\text{CaI}_2$	—	118	123	131	133	141
$\frac{1}{2}\text{Ca}(\text{IO}_3)_2$	—	82	86	91	94	99
$\frac{1}{2}\text{CaF}_2$	—	96	100	104	105	112
$\frac{1}{2}\text{CaMnO}_4$	—	104	107	112	114	119
$\frac{1}{2}\text{Ca}(\text{NO}_3)_2$	—	109	115	121	123	127
$\frac{1}{2}\text{Ca}(\text{NO}_2)_2$	—	129	134	141	145	154
$\frac{1}{2}\text{CaSO}_4$	—	109	116	124	129	136
$\frac{1}{2}\text{CaCrO}_4$	—	114	120	128	132	137
$\frac{1}{2}\text{CaCr}_2\text{O}_7$	—	103	104	108	110	116
$\frac{1}{2}\text{CaSO}_3$	—	104	110	116	122	130
$\frac{1}{2}\text{BaS}_2\text{O}_8$	—	113	121	128	133	140

ions (*i. e.*, $\text{H}^+ + \text{OH}^- = \text{not H.OH but } \text{H}^+ + \text{OH}^-$), the value of K would have been equal to zero; that is, K would represent the molecular conductivity of water at the stated concentration v and temperature.

It has already been shown that K is a constant for each series only, as it varies with the nature of the acid. This can

only be explained on the hypothesis that the variability is due to the fact that the stronger the acid is the greater does the value of the quantity K become, the maximum relative value (at any one concentration and temperature) being reached in the case of the strongest acid. Assuming for the moment that all acids were of equal strength it would be a necessary consequence that

$$\begin{aligned}\mu v_{\text{HX}} + \mu v_{\text{M}_1\text{OH}} - \mu v_{\text{M}_1\text{X}} &= K_{(\text{HX})} \\ &= \mu v_{\text{HX}_1} + \mu v_{\text{M}_1\text{OH}} - \mu v_{\text{M}_1\text{X}_1} = K_{(\text{HX}_1)} \\ &= \mu v_{\text{HX}_2} + \mu v_{\text{M}_1\text{OH}} - \mu v_{\text{M}_1\text{X}_2} = K_{(\text{HX}_2)} \\ &= \dots\dots\dots = \dots\dots\dots \\ &= \mu v_{\text{HX}_n} + \mu v_{\text{M}_1\text{OH}} - \mu v_{\text{M}_1\text{X}_n} = K_{(\text{HX}_n)} \\ &= \text{constant} \dots\dots\dots (9),\end{aligned}$$

(supposing that the terms be so arranged that

$$\mu v_{\text{HX}} > \mu v_{\text{HX}_1} > \mu v_{\text{HX}_2} > \dots\dots > \mu v_{\text{HX}_n}).$$

In practice, however, this constancy is not observed, as acids are not all of equal strength. The equations may nevertheless be rendered mathematically equal in several ways, the most useful of which, for our purpose, being that which will give quantitative, comparative results. By introducing the factors

$$x_1, x_2, \dots\dots, \text{ and } y_1, y_2, \dots\dots,$$

respectively, such that

$$\mu v_{\text{HX}} = x_1 \cdot \mu v_{\text{HX}_1} = x_2 \cdot \mu v_{\text{HX}_2} = \dots\dots\dots,$$

and

$$\mu v_{\text{M}_1\text{X}} = y_1 \cdot \mu v_{\text{M}_1\text{X}_1} = y_2 \cdot \mu v_{\text{M}_1\text{X}_2} = \dots\dots\dots,$$

the above equations become mathematically equal. Bearing in mind that the greater the equalizing quantities $x_1, x_2, \dots\dots$, are, the smaller must be the respective strengths of the acids, it is at once evident that the relative strengths of the acids $\text{HX}, \text{HX}_1, \text{HX}_2$, etc., are respectively

$$\frac{1}{1}, \frac{1}{x_1}, \frac{1}{x_2}, \dots\dots\dots;$$

or, expressed as percentages,

$$100, \frac{100}{x_1}, \frac{100}{x_2}, \dots\dots\dots$$

But $x_1 = \frac{\mu v_{\text{HX}}}{\mu v_{\text{HX}_1}}, x_2 = \frac{\mu v_{\text{HX}}}{\mu v_{\text{HX}_2}}, \dots$

therefore, the relative percentage strengths of the acids HX, HX₁, HX₂, etc., are respectively

$$100, 100\mu v_{\text{HX}_1} / \mu v_{\text{HX}}, 100\mu v_{\text{HX}_2} / \mu v_{\text{HX}},$$

etc. Table IV, of the relative strengths of some acids at 18°, is especially interesting as it was largely employed in the calculations as explained in the next section.

TABLE IV (TO SEC. 3)
Relative strengths of acids at 18°

<i>v</i>	HCl	HNO ₃	$\frac{1}{2}\text{H}_2\text{SO}_4$	$\frac{1}{2}\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid)	$\frac{1}{3}\text{H}_3\text{PO}_4$	$\frac{1}{3}\text{C}_6\text{H}_8\text{O}_7$ (citric acid)	$\text{C}_2\text{H}_3\text{O}_2$ (acetic acid)
1000	100	99.4	95.9	48.0	28.1	20.7	10.9
500	100	99.4	93.4	46.0	27.4	19.7	8.0
200	100	99.5	86.5	43.9	24.6	—	5.4
100	100	99.5	80.5	42.7	22.9	11.4	3.9
50	100	99.2	77.9	38.9	20.1	—	2.8
33.33	100	99.2	74.7	39.2	18.4	7.6	—
20	100	99.2	70.3	36.9	—	6.1	1.8
10	100	99.7	64.1	33.3	—	4.5	1.3
5	100	99.4	62.5	32.3	—	—	0.9
3.33	100	99.4	62.5	—	—	—	0.8
2	100	99.0	62.4	23.2	—	0.2	0.6
1	100	100.0	62.6	19.8	7.0	0.18	0.4

SEC. 4. The foregoing results show unmistakably that molecular conductivities are additive properties, the molecular conductivity of any substance in aqueous solution being equal to the sum of the atomic or ionic conductivities of its constituent ions. No such regularity apparently exists between the molecular conductivities of the acids, but if the assumption be made that the ionic conductivity of the H ion is a function of the relative strengths of acids, then it is possible to calculate its value, and consequently those of other ions.¹ According to the equations (3) and (4) with the

¹ Cf. Phil. Mag. [6], 12, 150 (1906).

argument thereon, together with the remarks just set forth, the ionic conductivity μv of the $\overset{+}{\text{H}}$ ion may be determined from the equations

$$\begin{aligned} Rv_{\text{HX}} \cdot \mu v_{\text{H}} + \mu v_{\text{OH}'} &= K, \\ Rv_{\text{HX}_1} \cdot \mu v_{\text{H}} + \mu v_{\text{OH}'} &= K_1, \\ Rv_{\text{HX}_2} \cdot \mu v_{\text{H}} + \mu v_{\text{OH}'} &= K_2, \\ &\dots\dots\dots = \dots\dots\dots, \\ Rv_{\text{HX}_n} \cdot \mu v_{\text{H}} + \mu v_{\text{OH}'} &= K_n \dots\dots\dots (10), \end{aligned}$$

(wherein Rv_{HX} , Rv_{HX_1} , Rv_{HX_2} , $\dots\dots\dots Rv_{\text{HX}_n}$ represent respectively the relative strengths of the acids HX , HX_1 , HX_2 , $\dots\dots\dots \text{HX}_n$, all measured at the same concentration v and at the same temperature. For brevity the sign $\cdot = +$ and $' = -$). The calculations effected by means of these equations (10) are so consistent that the assumptions made above may very reasonably be taken as correct.

As an example the ionic conductivities of the ions $\overset{+}{\text{H}}$, OH' , $\overset{+}{\text{K}}$, and Cl' at 18° , and at concentration $v = 500$ are here worked out fairly fully. R_{HCl} , R_{HNO_3} , $R_{\frac{1}{2}\text{H}_2\text{SO}_4}$, $R_{\frac{1}{2}\text{H}_2\text{C}_2\text{O}_4}$ and $R_{\text{CH}_3\text{CO}_2\text{H}}$ are respectively 1.0, 0.9946, 0.94, 0.46, and 0.08; and K_{HCl} , K_{HNO_3} , $K_{\frac{1}{2}\text{H}_2\text{SO}_4}$, $K_{\frac{1}{2}\text{H}_2\text{C}_2\text{O}_4}$, and $K_{\text{C}_2\text{H}_4\text{O}_2}$ are respectively 474, 472, 456, 285, and 163; hence $1.0 \mu_{\text{H}} + \mu_{\text{OH}'} = 474$, $0.9946 \mu_{\text{H}} + \mu_{\text{OH}'} = 472$, $0.94 \mu_{\text{H}} + \mu_{\text{OH}'} = 456$, $0.46 \mu_{\text{H}} + \mu_{\text{OH}'} = 285$, and $0.08 \mu_{\text{H}} + \mu_{\text{OH}'} = 163$, from which, by all possible solutions, it is found that the mean values for μ_{H} is 336. Then $\mu_{\text{OH}'} = \mu_{\text{H.OH}} - \mu_{\text{H}} \times R_{\text{HCl}} = 474 - 337 = 137$; $\mu_{\text{Cl}'} = \mu_{\text{HCl}} - \mu_{\text{H}} \times R_{\text{HCl}} = 376 - (337 \times 1.0) = 39$; $\mu_{\text{K}} = \mu_{\text{KCl}} - \mu_{\text{Cl}'} = 126 - 39 = 87 = \mu_{\text{K.OH}} - \mu_{\text{OH}'} = 233 - 140 = 93$, etc.

In the tables the values given are the means (averages) of values obtained in each case by several calculations.

The letter μ , strictly speaking denoting "molecular conductivity," has been here retained for the sake of avoiding confusion by the introduction of a new distinctive term letter, to represent also "atomic (or ionic) conductivity." The term 'atomic' conductivity is here used in contrast to 'molec-

ular' conductivity, though it may be as well to point out that the term 'atomic' conductivity is rather inappropriate and might be better replaced by the term 'ionic' conductivity. To calculate the molecular conductivity of any salt, acid, or base, respectively, from the ionic conductivities, the equation $\mu v_M + \mu v_X$, $\mu v_M + \mu v_{OH'}$, or $Rv_{HX} \times \mu v_H + \mu v_X$, should be employed.

TABLE V (TO SEC. 4)
Ionic conductivities at 18°

$v =$	1000	500	200	100	50	20	10	2	1
H·	337	336	333	330	329	323	313	291	270
Rb·	90	89	87	85	85	81	77	—	71
Cs·	91	89	87	85	—	—	76	—	—
K·	89	89	88	86	83	80	78	67	63
NH ₄ ·	85	84	82	80	78	75	72	64	63
Tl·	85	85	82	77	76	76	76	—	—
$\frac{1}{2}$ Ba·	75	75	69	66	65	57	52	40	36
$\frac{1}{2}$ Pb·	76	73	69	63	59	49	41	19	14
$\frac{1}{2}$ Sr·	74	70	67	62	61	55	54	36	30
Ag·	73	72	70	67	—	62	58	43	40
$\frac{1}{2}$ Ca·	69	66	64	60	60	54	44	34	29
Na·	66	65	64	61	60	59	58	41	38
$\frac{1}{2}$ Mg·	64	60	56	52	47	42	34	32	28
$\frac{1}{2}$ Zn·	64	60	56	50	45	40	35	29	19
$\frac{1}{2}$ Cd·	—	—	55	46	38	32	26	22	15
$\frac{1}{2}$ Cu·	62	55	48	40	33	27	22	—	13
Li·	56	54	53	52	51	48	45	40	34
OH'	143	140	140	139	138	135	127	122	109
$\frac{1}{2}$ CO ₃ '	45	41	36	32	27	21	15	12	7
Cl'	40	40	40	40	38	37	37	36	31
NO ₃ '	40	40	40	40	38	37	36	34	28
Br'	40	39	38	38	38	37	36	36	—
I'	39	38	37	37	37	37	36	36	36
$\frac{1}{2}$ SO ₄ '	37	37	33	32	29	24	22	21	13
SCN'	30	29	28	28	28	28	26	25	24
ClO ₃ '	28	27	26	26	26	24	21	18	—
F'	21	20	20	20	20	18	16	16	16
$\frac{1}{2}$ SiO ₃ '	12	12	11	19	10	6	—	6	—
$\frac{1}{2}$ C ₂ O ₄ '	12	12	11	11	9	8	7	6	5
$\frac{1}{3}$ PO ₄ '	11	11	11	9	7	6	5	3	2
$\frac{1}{3}$ C ₆ H ₅ O ₇ ' (citrate)	13	12	—	7	—	3	2	1	0.8
IO ₃ '	8	8	7	7	7	5	2	—	—
CH ₃ .CO ₂ '	7	6	6	6	5	4	2	1	0.8

TABLE VI (TO SEC. 4)
Ionic conductivities at 25°

$\nu =$	32	64	128	256	512	1024
H·	350	355	360	360	362	363
Rb·	88	90	94	96	97	97
Cs·	87	90	94	96	97	97
K·	85	86	89	93	95	97
NH ₄ ·	84	87	90	91	93	95
Tl·	80	85	90	93	93	93
$\frac{1}{2}$ Pb·	56	64	72	76	84	87
Ag·	—	72	74	76	76	76
$\frac{1}{2}$ Cu·	61	63	68	71	71	71
$\frac{1}{2}$ Ba·	59	65	68	70	74	77
$\frac{1}{2}$ Sr·	59	64	67	70	71	72
Na·	60	64	67	69	69	69
$\frac{1}{2}$ Mg·	58	61	65	69	71	72
$\frac{1}{2}$ Ca·	53	63	66	69	70	71
$\frac{1}{2}$ Ni·	56	60	64	69	72	74
$\frac{1}{2}$ Co·	56	58	58	66	69	71
Li·	52	53	56	56	59	62
$\frac{1}{3}$ Cr·	27	36	47	58	69	75
$\frac{1}{3}$ Al·	11	19	27	36	45	54
OH'	150	153	154	155	155	155
$\frac{1}{3}$ Cr(CN) ₆ '	54	63	67	69	72	75
$\frac{1}{2}$ S ₂ O ₈ '	52	54	59	66	72	74
$\frac{1}{2}$ SiF ₆ '	32	48	57	75	—	—
NO ₂ '	56	57	57	58	60	61
$\frac{1}{3}$ Fe(CN) ₆ '	45	52	58	61	64	66
$\frac{1}{2}$ Pt(CN) ₄ '	51	52	54	56	59	65
Br'	52	53	55	56	57	58
$\frac{1}{3}$ Fe(CN) ₆ '	35	43	50	52	65	66
$\frac{1}{3}$ AsO ₄ '	41	49	55	58	58	58
$\frac{1}{2}$ S ₂ O ₃	36	44	49	53	58	60
Cl'	51	52	52	52	53	54
$\frac{1}{2}$ S ₂ O ₈	42	49	53	54	55	56
I'	48	49	50	50	51	51
ClO ₄ '	47	48	49	49	50	51
NO ₃ '	44	48	48	48	49	50
$\frac{1}{2}$ SO ₄ '	40	42	44	47	50	53
$\frac{1}{2}$ MoO ₄ '	40	42	44	46	49	52
$\frac{1}{2}$ CrO ₄ '	40	41	43	46	48	50
$\frac{1}{2}$ SeO ₄ '	36	39	41	44	47	49
MnO ₄ '	40	41	42	42	43	44
ClO ₃ '	38	41	42	42	43	44
$\frac{1}{2}$ SO ₃ '	34	38	41	42	43	44
$\frac{1}{2}$ WO ₄ '	36	38	40	41	44	46

TABLE VI—(Continued)

$\nu =$	32	64	128	256	512	1024
$\frac{1}{3}\text{PO}_4'$	—	—	34	39	42	44
$\frac{1}{2}\text{Cr}_2\text{O}_7'$	34	35	37	37	39	41
$\frac{1}{2}\text{PtCl}_6'$	32	36	38	38	39	41
F'	31	32	33	33	34	36
$\frac{1}{4}\text{P}_2\text{O}_7'$	20	26	33	40	46	49
BrO_3'	29	30	31	32	33	34
HSO_3'	24	27	29	29	31	33
$\frac{1}{2}\text{CO}_3'$	14	22	29	37	44	48
AsO_3'	18	18	20	21	24	28
IO_3'	16	17	18	18	20	25
$\frac{1}{2}\text{B}_4\text{O}_7'$	13	13	13	13	16	19
$\frac{1}{4}\text{B}_2\text{O}_4$	13	14	14	15	18	20
$\frac{1}{2}\text{S}_2\text{O}_5$	12	12	12	12	12	12
$\frac{1}{2}\text{SeO}_3$	3	10	16	22	31	34

SEC. 5. On comparing the values in Tables V and VI with those given by Kohlrausch in his "Leitvermögen der Elektrolyte" it is found that the conductivities of the H^+ and OH^- ions are greater, and the NH_4^+ and Cl^- ions are smaller than Kohlrausch's values. But on comparing the conductivities of the positive and negative ions among themselves in both the author's and Kohlrausch's tables, the ratios thus obtained are in very close agreement in the respective tables, as is illustrated in Table VII.

In the tables $\mu\nu_{\text{K}} = 1.0$, and $\mu\nu_{\text{Cl}} = 1.0$, respectively, have been chosen for the purpose of calculating the values.

SEC. 6. Another interesting application of the author's theory is that to the subject of the "existence of ammonium hydrate."¹ In the case of ammonium hydrate, NH_4OH , and of ammonium salts, NH_4X , NH_4X_1 , etc., the equations (7) and (8) are true for the salts only, the quantity $\mu\nu_{\text{NH}_4\text{OH}} - \mu\nu_{\text{M}_2\text{OH}}$ not being equal to this constant, as is very fully illustrated in Table VIII.² It is most peculiar that, whereas

¹ Cf. Chem. News, 95, 133 (1907).

² All quantities indicated by an asterisk (*) were taken from Jour. Phys. Chem., 13, 145 (1909).

TABLE VII (TO SEC. 5)
 "Ionic conductivities" ratios

ν (at 180°) =	1000	500	200	100	50	20	10	
K·	1.0	1.0	1.0	1.0	1.0	1.0	1.0	From the Author's Tables
NH ₄ ·	0.95	0.94	0.93	0.93	0.94	0.93	0.92	
$\frac{1}{2}$ Ba·	0.84	0.84	0.78	0.76	0.78	0.71	0.67	
$\frac{1}{2}$ Sr·	0.83	0.79	0.75	0.72	0.70	0.69	0.69	
Ag·	0.82	0.81	0.79	0.77	—	0.77	0.74	
$\frac{1}{2}$ Ca·	0.77	0.74	0.72	0.69	0.72	0.67	0.56	
Na·	0.74	0.73	0.73	0.71	0.72	0.73	0.74	
$\frac{1}{2}$ Mg·	0.72	0.67	0.64	0.60	0.56	0.52	0.43	
$\frac{1}{2}$ Zn·	0.72	0.67	0.64	0.58	0.54	0.50	0.45	
$\frac{1}{2}$ Cd·	—	—	0.62	0.53	0.45	0.40	0.33	
$\frac{1}{2}$ Cu·	0.70	0.62	0.55	0.46	0.40	0.34	0.28	
Li·	0.62	0.60	0.60	0.60	0.61	0.60	0.61	
$\frac{1}{2}$ CO ₃ '	1.1	1.0	0.90	0.80	0.71	0.57	0.40	
Cl'	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
NO ₃ '	1.0	1.0	1.0	1.0	1.0	1.0	0.97	
I'	0.97	0.95	0.92	0.92	0.97	1.0	0.97	
$\frac{1}{2}$ SO ₄ '	0.92	0.92	0.82	0.80	0.70	0.65	0.61	
K·	1.0	1.0	1.0	1.0	1.0	1.0	1.0	From Kohlrausch's Tables
NH ₄ ·	0.98	0.99	0.98	0.98	0.98	0.98	0.98	
$\frac{1}{2}$ Ba·	0.81	0.81	0.77	0.75	0.70	0.65	0.61	
$\frac{1}{2}$ Sr·	0.76	0.74	0.72	0.69	0.65	0.59	0.55	
Ag·	0.85	0.85	0.85	0.85	0.82	0.81	0.76	
$\frac{1}{2}$ Ca·	0.75	0.73	0.71	0.69	0.63	0.57	0.52	
Na·	0.67	0.68	0.66	0.65	0.65	0.64	0.62	
$\frac{1}{2}$ Mg·	0.67	0.68	0.64	0.60	0.56	0.50	0.44	
$\frac{1}{2}$ Zn·	0.65	0.65	0.61	0.59	0.53	0.48	0.42	
$\frac{1}{2}$ Cd·	0.58	0.55	0.48	0.42	0.35	0.27	0.23	
$\frac{1}{2}$ Cu·	0.64	0.58	0.50	0.44	0.36	0.29	0.26	
Li·	0.53	0.52	0.53	0.52	0.50	0.48	0.46	
$\frac{1}{2}$ CO ₃ '	1.1	1.0	0.95	0.88	0.82	0.73	0.68	
Cl'	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
NO ₃ '	0.92	0.92	0.92	0.92	0.91	0.90	0.91	
I'	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
$\frac{1}{2}$ SO ₄ '	1.0	0.97	0.92	0.90	0.85	0.78	0.75	

equations (7) and (8) are true for all other bases and salts, ammonium hydrate, as just shown, should form an exception, but an explanation is here advanced to explain this anomaly.

TABLE VIII.—(Continued)

The molecular conductivities of the potassium salts are almost the same as those of the corresponding ammonium salts, and the expression $\mu v_{\text{KX}_n} - \mu v_{\text{NH}_4\text{X}_n}$ is consequently near zero in value as is illustrated in Table VIII. It would be very reasonable to expect that the molecular conductivities of potassium hydrate and ammonium hydrate would also have been almost identical in value (when measured under the same conditions of temperature and concentration).

By means of the equation

$$\mu v_{\text{NH}_4\text{OH}} = \mu v_{\text{M}_2\text{OH}} + \mu v_{\text{NH}_4\text{X}_n} - \mu v_{\text{M}_2\text{X}_n}$$

(a particular form of the general equation (6)), it is possible to calculate the "theoretical" molecular conductivities of ammonium hydrate (see Tables IX and X).

From an examination of the above facts the following is a most reasonable conclusion:

"If the ammonia in aqueous solution were entirely converted into ammonium hydrate, the experimental values for the molecular conductivities would be near the calculated theoretical values. But as the experimental values are far below the theoretical ones, the conclusion is that the ammonia in aqueous solution is only partially converted into ammonium hydroxide. Accordingly, the percentage of ammonia existing as ammonium hydrate in aqueous solution is given by the formula

$$100 \frac{\text{experimental } \mu v_{\text{NH}_4\text{OH}}}{\text{theoretical } \mu v_{\text{NH}_4\text{OH}}}$$

(see Tables IX and X for the calculated percentages of ammonium hydrate)."

The accompanying Tables IX and X would seem to indicate that the percentage of ammonia in aqueous solution existing as hydrate of ammonia increases with increased dilution, in other words the more concentrated the solution the less favorable are the conditions for the formation and existence of ammonium hydroxide. With the present limited data of molecular conductivities at varying temperatures at one's disposal, it is impossible to determine definitely by the

TABLE IX (TO SEC. 6)

ν (at 18°) =	1000	500	200	100	50	20	10	2	1
$\mu\nu_{\text{KOH}} + \mu\nu_{\text{NH}_4\text{Cl}} - \mu\nu_{\text{KCl}}$	234.0	232.9	229.8	227.7	224.7	218.5	211.7	196.0	183.7
$\mu\nu_{\text{KOH}} + \mu\nu_{\text{NH}_4\text{NO}_3} - \mu\nu_{\text{KNO}_3}$	234.9	234.8	229.1	227.8	222.8	219.2	214.8	202.1	192.4
$\mu\nu_{\text{NaOH}} + \mu\nu_{\text{NH}_4\text{Cl}} - \mu\nu_{\text{NaCl}}$	225.8	225.2	224.2	223.6	222.1	219.5	214.1	179.8	162.0
$\mu\nu_{\text{NaOH}} + \mu\nu_{\text{NH}_4\text{NO}_3} - \mu\nu_{\text{NaNO}_3}$	226.7	225.6	223.7	223.2	218.5	217.6	214.8	194.5	179.9
$\mu\nu_{\text{NaOH}} + \mu\nu_{\text{NH}_4\text{I}} - \mu\nu_{\text{NaI}}$	—	—	—	—	—	—	—	196.3	181.4
$\mu\nu_{\text{KOH}} + \mu\nu_{\text{NH}_4\text{I}} - \mu\nu_{\text{KI}}$	—	—	—	—	—	—	—	193.2	175.3
$\mu\nu_{\text{KOH}} + \mu\nu_{\frac{1}{2}(\text{NH}_4)_2\text{SO}_4} - \mu\nu_{\frac{1}{2}\text{K}_2\text{SO}_4}$	—	—	—	—	—	—	—	187.7	187.0
$\mu\nu_{\text{NaOH}} + \mu\nu_{\frac{1}{2}(\text{NH}_4)_2\text{SO}_4} - \mu\nu_{\frac{1}{2}\text{Na}_2\text{SO}_4}$	—	—	—	—	—	—	—	188.4	173.8
Average theoretical $\mu\nu_{\text{NH}_4\text{OH}}$	230.1	229.3	226.7	225.6	221.8	218.7	213.8	192.2	179.3
Experimental $\mu\nu_{\text{NH}_4\text{OH}}$	28.0	20.6	13.2	9.6	7.1	4.6	3.3	1.35	0.9
Percentage of NH_4OH in solution	12.2	9.0	5.8	4.3	3.2	2.1	1.5	0.7	0.5

TABLE X (TO SEC. 6)

v (at 25°) =	512	256	128
$\mu v_{\text{Ti.OH}} + \mu v_{\text{NH}_4\text{Cl}} - \mu v_{\text{TiCl}}$ = theoretical $\mu v_{\text{NH}_4\text{OH}}$	248.9	249.3	246.5
Experimental $\mu v_{\text{NH}_4\text{OH}}$	27.5	19.0	13.4
Percentage of NH_4OH in solution	11.0	7.62	5.4

preceding method as to what influence rise in temperature may have in increasing or diminishing the percentage amount of ammonium hydrate in solution.

Thus, though ammonium hydrate is theoretically as strong a base (on the electrical conductivity theory) as potassium hydrate, yet, because of the small quantity of ammonia being converted into the hydrate in aqueous solution, it is in practice one of the weakest bases. But this view renders it rather difficult to explain the great solubility of this gas in water.

If 1 gram-molecule of ammonia¹ be dissolved in water to give v liters of the solution, and the proportion of it converted into ammonium hydrate be denoted by q , the concentrations of the combined ammonia, uncombined ammonia, combined water, and uncombined water are respectively

$$\frac{q}{v}, \frac{1-q}{v}, \frac{q}{v}, \text{ and } 1 - \frac{q}{v}.$$

(The letter 'C' denotes 'concentration' and 'Q' a 'constant'; Q_h = hydrolytic constant; Q_e = electrolytic constant.) According to the 'electrolytic dissociation' theory,

$$Q\text{C}_{\text{NH}_4\text{OH}} = \text{C}_{\text{NH}_3} \times \text{C}_{\text{H}_2\text{O}};$$

¹ The author is indebted to Prof. Dr. R. Luther, of Leipzig, Germany, for the following, from "If one grm.-molecule....." to "..... = K Blackman." Subsequently to this communication Prof. Dr. R. Luther pointed out to the author the analogous work of Prof. Dr. F. Walker, Jour. Chem. Soc., 83, 182 (1903). His work, however, is quite independent of Dr. Walker's research.—P. B.

since C_{H_2O} is constant, we have

$$Q_h C_{NH_4.OH} = C_{NH_3} \dots \dots \dots (i),$$

$$Q_e C_{NH_4.OH} = C_{NH_4^*} \times C_{OH'} \dots \dots \dots (ii),$$

$$C_{NH_4^*} = C_{OH'} = \frac{\mu v}{v_{\infty}^{\mu}} = \frac{a}{v_{Ostwald}} \dots \dots \dots (iii),$$

$$\begin{aligned} C_{NH_4^*} &= \text{approximately } \frac{\text{experimental } \mu v}{v, \text{ theoretical } \mu v} \\ &= \frac{q}{v_{Blackman}} \dots \dots \dots (iv). \end{aligned}$$

$$\begin{aligned} C_{NH_4.OH} + C_{NH_3} &= C_{\text{non-conducting ammonia}} \\ &= \frac{1-a}{v_{Ostwald}} = \text{nearly } \frac{1-q}{v_{Blackman}} \dots \dots \dots (v). \end{aligned}$$

$$\begin{aligned} C_{NH_4.OH} + C_{NH_3} &= C_{\text{non-conducting ammonia}} \\ &= (1 + Q_h) C_{NH_4.OH} \text{ [from (i)]} \\ &= \frac{1-a}{v_{Ostwald}} = \frac{1-q}{v_{Blackman}} \text{ approximately (vi).} \end{aligned}$$

$$C_{NH_4.OH} = \frac{1-a}{v} \cdot \frac{1}{1 + Q_h \frac{1}{v_{Ostwald}}} \dots \dots \dots (vii).$$

From (ii), (iii), and (iv) we obtain

$$\frac{Q_e}{1 + Q_h} = \frac{a^2}{(1-a)v_{Ostwald}} = Q_{Ostwald} \dots \dots \dots (viii),$$

$$= \frac{q^2}{(1-q)v_{Blackman}} = Q_{Blackman} \dots \dots \dots (ix).$$

Tables XI and XII illustrate the similarity between these two constants.

According to the "law of mass action" we have

$$\begin{aligned} C_{\text{uncombined ammonia}} \times C_{\text{uncombined water}} \\ = K \times C_{\text{combined ammonia}}, \end{aligned}$$

(where K denotes a constant) or,

$$\begin{aligned} \frac{1}{K} &= Q = \text{constant} \\ &= \frac{q}{v} \left(\frac{v}{1-q} \right) \left(\frac{v}{v-q} \right) \\ &= \frac{vq}{(1-q)(v-q)} \dots \dots \dots (x). \end{aligned}$$

On performing the calculations the values thus obtained for Q are not the same for different concentrations (see lower parts of Tables XI and XII).

TABLE XI (TO SEC. 6)

v (at 18°) =	1000	500	200	100	50	20	10	2	1	Mean
$Q_{\text{Blackman}} \times 10^5$	1.69	1.79	1.79	1.93	2.11	2.25	2.23	2.47	2.51	2.09
$Q_{\text{Ostwald}} \times 10^5$	1.60	1.86	1.66	1.75	2.34	2.08	1.99	1.69	1.61	1.84
$Q_{\text{(Equation x)}} \times 10^2$	13.89	9.89	6.15	4.49	2.39	2.14	1.49	0.7	0.5	—

TABLE XII (TO SEC. 6)

v (at 25°) =	512	256	128	Mean
$Q_{\text{Blackman}} \times 10^5$	2.66	2.46	2.41	2.51
$Q_{\text{Ostwald}} \times 10^5$	2.65	2.44	2.37	2.49
$Q_{\text{(Equation x)}} \times 10^2$	12.35	8.25	5.72	—

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