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Chemistry. — "*Velocity of ions at 0° C.*" By DEVENDRA NATH BHATTACHARYYA and NILRATAN DHAR. (Communicated by Prof. ERNST COHEN).

From time to time attempts have been made to determine accurately the mobilities of ions at 0°. But there is no systematic work in this line; only isolated cases have been investigated. Even the velocity of hydrion at 0° is uncertain. An exact idea of our very much incomplete knowledge would be obtained from the following summary of the work previously done.

WOOD¹⁾ was the first investigator in this line. He determined the molecular conductivities of sodium chloride, potassium chloride, dichloroacetic acid, and trichloroacetic acid at 0°, and at various dilutions. But his measurements are inaccurate as will be shown subsequently. ARCHIBALD²⁾, BARNES³⁾ and KOHLRAUSCH⁴⁾ also studied some electrolytes. WHETHAM⁵⁾ accurately determined the conductivities of some electrolytes at 0°; but he did not attempt in deducing the velocities of individual ions at 0° from his measurements. KAHLBERG⁶⁾, and JONES and his pupils⁷⁾ also studied some cases, but their measurements are not accurate. The measurements of NOYES and COOLIDGE⁸⁾ agreed with those of WHETHAM. Evidently no systematic work is done in this line.

The ionic mobilities of various ions are fairly accurately known at 18° or at 25° (NOYES and FALK — J. Amer. Chem. Soc. **33** (1911), 1436). But the value for hydrion (H⁺) is not exactly certain even at 18° or 25°. OSTWALD⁹⁾ first used the value 342 at 25°, and then raised it to 347 in *Lehrbuch der Chemie* 1893, **2**, 675. KOHLRAUSCH's¹⁰⁾ provisional value was 318 at 18° or 352 at 25°. Until recently, these values were accepted. NOYES¹¹⁾, and then NOYES and SAMMET¹²⁾ obtained the unexpectedly high value of 365 at 25°. ROTH-

1) Phil. Mag. 1896 (5) XLI, 117.

2) Trans. Nov. Sco. Inst. Sci X, 33, 1898.

3) *ibid* X, 139, 1899.

4) Ann. Phys. Chem. 1898, **66**, 785—825

5) Phil. Trans. 1900.

Proc. Roy. Soc. **71**, 334 (1903).

6) Journal. Phys. Chem. **5**, 339 (1901).

7) Amer. Chem. Journ. **25**, 349 (1901); **26**, 428 (1901); **34**, 557 (1905).

8) Carnegie Institution Publications **63**, 47 (1907).

9) Zeit. Phys. Chem. 1888, **2**, 842.

10) Leitvermögen der Elektrolyte pp. 107—110, 200.

11) Zeit. Phys. Chem. 1901, **36**, 63—83.

12) Zeit. Phys. Chem. 1903, **43**, 49.

MUND and DRUCKER¹⁾ suggested the value 338 at 25°; and then DRUCKER²⁾ used the value 312 at 18° and 345 at 25°. Again, DRUCKER³⁾, GOODWIN and HASKELL⁴⁾, and WHETHAM⁵⁾, by combining their molecular conductivity measurements with the transference ratios obtained by JAHN and his pupils, and TOWER deduced the mean value for hydrion equal to 313 at 18° or 346 at 25°. KOHLRAUSCH⁶⁾ again, and JAHN and his pupils⁷⁾, declared the most probable value of hydrion to be 315 at 18° or 348 at 25°. GORKE⁸⁾ obtained the value 353 at 25° from measurements of picric acid. NOYES and KATO⁹⁾ came to the value 315 at 18° or 348 at 25° from migration ratios of nitric and hydrochloric acids. DRUCKER and KISNJAIR¹⁰⁾ again gave the value 313 at 18° or 346 at 25°. It would be quite evident from these that the value for hydrion is far from being correctly known.

Now, by applying KOHLRAUSCH's formula for the temperature coefficient of mobility we can get the values of ions at 0° from the values given at 18 or 25°. But this empirical formula holds good with rigidity in the neighbourhood of 18°; so results deduced at 0 are rather uncertain. Moreover KOHLRAUSCH himself has changed these values of temperature coefficients many times. For comparison, are added below the tables (see p. 416) of temperature coefficients (α) as published by KOHLRAUSCH¹¹⁾ in 1901, and 1908.

Thus extrapolation to 0° is rather uncertain. With a view to determine exactly the ionic velocities at 0°, this investigation was undertaken. NOYES and FALK¹²⁾ have given very accurate tables collected from the work of numerous investigators for the transference numbers of various substances at almost infinite dilution and at 0°. From the molecular conductivity determination at 0°, the sum of the ionic velocities at 0° is obtained (since $\mu_{\infty} = u + v$), and $\frac{u}{v}$ is taken from NOYES and FALK's tables; thus u and v are obtained.

¹⁾ Zeit. Phys. Chem. 1903, **46**, 827.

²⁾ Zeit. Phys. Chem. 1904, **49**, 563.

³⁾ Zeit. Elektrochem. 1907, **13**, 81.

⁴⁾ Proc. Amer. Acad. 1904, **40**, 399.

⁵⁾ Zeit. Phys. Chem. 1906, **55**, 200.

⁶⁾ Zeit. Elektrochem. 1907, **13**, 333.

⁷⁾ Zeit. Phys. Chem. 1907, **58**, 641.

⁸⁾ Zeit. Phys. Chem. 1908, **61**, 495.

⁹⁾ Zeit. Phys. Chem. 1908, **62**, 420.

¹⁰⁾ Zeit. Phys. Chem. 1908, **62**, 731.

¹¹⁾ Sitzungsber. d. Berl. Akad. 1901, 1026; 1902, 572; Proc. Roy. Soc. **71**, 338 (1903). Zeit. Elektrochem. **14** (1908), 129.

¹²⁾ loc. cit.

Ions	1901 % ₁₈	1908 % ₁₈
Li ^o	+ 0.0261	+ 0.0265
Na ^o	+ 0.0245	+ 0.0244
K ^o	+ 0.0220	+ 0.0217
Rb ^o	+ 0.0217	+ 0.0214
Ag ^o	+ 0.0231	+ 0.0229
H ^o	+ 0.0154	+ 0.0154
Cl'	+ 0.0215	+ 0.0216
F'	+ 0.0232	+ 0.0238
I'	+ 0.0206	+ 0.0213

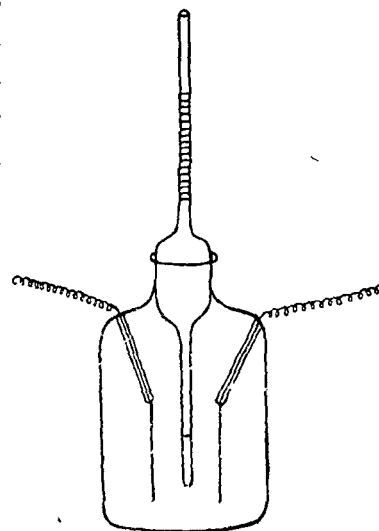
The water used in these experiments was carefully purified by JONES and MACKAY'S ¹⁾ method, and collected in wellsteamed resistance glass vessels. Freshly purified water was used in all experiments. The conductivity of the water used varied from 4×10^{-6} to 5×10^{-6} at 0°.

The measurements were carried out by the alternating current-telephone method in a closed well platinised cell, with a thermometer tightly fitting its mouth. In our hot and moist climate, moisture condenses in the interior of vessels surrounded with ice; so there is the danger of dilution of the solutions in open mouth cells; but this difficulty is removed by having closed vessel for putting in solution. The bath was of pure melting ice.

The temperature as indicated by the thermometer was kept constant for nearly half an hour, and then readings were taken. The cell was now taken out of the bath and made to attain the ordinary laboratory temperature, and diluted with calibrated standard pipettes.

MERCK'S chemically pure substances were purified by repeated crystallisation and dried according to the nature of the substance in question.

Hydrochloric acid was prepared by dissolving in conductivity



¹⁾ Zeit. Phys. Chem. 22, 237, (1897).

water hydrochloric acid gas evolved out of the ordinary pure concentrated hydrochloric acid.

Concentrations of solutions were obtained in most cases by volumetric method, and the results were mostly checked by the concentrations obtained from the weights of the salts dissolved.

The following tables give the values of the molecular conductivities obtained:

I. *Hydrochloric acid.*

Dilution	Molecular conductivity μ_v
31.963	237.0
63.926	259.8
127.852	231.5
255.704	262.9
511.408	263.8
1022.816	264.2
2045.632	264.3
4091.264	264.4

Thus μ_∞ obtained = 264.4.
The value of μ_∞ calculated with KOHLRAUSCH's ionic velocities and temperature coefficients = 265.8.

III. *Lithium Chloride.*

Dilution	μ_v
7.437	47.0
14.874	53.2
29.748	55.6
59.496	57.5
118.992	59.2
237.984	59.7
475.968	59.9
951.936	60.1
1903.872	60.1

μ_∞ obtained = 60.1
 μ_∞ calculated from KOHLRAUSCH's data = 60.5.

II. *Ammonium Chloride.*

Dilution	μ_v
9.984	66.5
19.968	73.8
39.936	75.3
79.872	76.0
159.744	78.4
319.488	79.2
638.976	79.7
1277.952	79.9
2555.904	80.0

Thus μ_∞ obtained = 80.0
 μ_∞ calculated from KOHLRAUSCH's data = 81.7.

IV. *Strontium Chloride.*

Equivalent dilution	Equivalent μ_v
19.576	53.2
39.152	61.3
78.304	64.0
156.608	66.0
313.216	66.7
626.432	68.8
1252.864	70.7
2505.728	71.9
5011.456	72.3

μ_∞ is taken to be 72.5
 μ_∞ calculated from KOHLRAUSCH's data = 73.1.

V. *Magnesium Chloride.*

Equivalent dilution	Equivalent μ_v
30.396	58.8
60.792	59.5
121.584	60.5
243.168	62.3
486.336	64.0
972.672	65.3
1945.344	66.1
3890.688	66.4

μ_∞ is taken to be 66.6
 μ_∞ calculated from KOHLRAUSCH's
 data = 68.3

VI. *Ammonium Nitrate.*

Dilution	μ_v
30.231	77.7
60.462	78.6
120.924	79.2
241.848	79.7
483.696	80.0
967.392	80.2
1934.784	80.2
3869.568	80.3

μ_∞ obtained = 80.3
 μ_∞ calculated from KOHLRAUSCH's
 data = 80.3

VII. *Sodium Nitrate.*

Dilution	μ_v
22.277	62.6
44.554	63.7
89.108	65.1
178.216	65.8
356.432	66.0
712.864	66.5
1425.728	66.8
2851.456	66.9

μ_∞ obtained = 66.9
 μ_∞ calculated from KOHLRAUSCH's
 data = 66.1

VIII. *Potassium Nitrate.*

Dilution	μ_v
39.068	78.4
78.136	80.3
156.272	81.3
312.544	82.5
625.088	83.0
1250.176	83.2
2500.352	83.3
5000.704	83.4

μ_∞ obtained = 83.4
 μ_∞ calculated from KOHLRAUSCH's
 data = 81.1

IX. *Ammonium Sulphate.*

Equivalent dilution	Equivalent μ_v
53.633	73.5
107.267	76.7
214.534	79.2
429.068	80.6
858.136	81.3
1716.272	81.6
3432.544	81.7

μ_∞ taken to be 81.8
 μ_∞ calculated from KOHLRAUSCH'S data = 82.4.

X. *Potassium Sulphate.*

Equivalent dilution	Equivalent μ_v
33.156	72.9
66.312	75.7
132.624	79.0
265.248	81.9
530.496	83.5
1060.992	84.0
2121.984	84.2

μ_∞ taken to be 84.4
 μ_∞ calculated from KOHLRAUSCH'S data = 83.2.

XI. *Sodium Sulphate.*

Equivalent dilution	Equivalent conductivity
17.325	55.9
34.651	58.2
69.302	61.6
138.604	63.8
277.208	65.9
554.416	67.1
1108.832	67.9
2217.664	68.1
4435.328	68.2

μ_∞ obtained = 68.2
 μ_∞ calculated from KOHLRAUSCH'S data = 68.3.

XII. *Calcium Sulphate.*

Equivalent dilution	Equivalent μ_v
467.913	63.3
935.826	67.7
1871.652	71.0
3743.304	71.7

μ_∞ is taken to be 72.

XIII. Magnesium Bromide.

Equivalent dilution	Equivalent μ_v
44.182	59.3
88.365	61.8
176.730	63.7
353.460	65.1
706.920	66.1
1413.840	66.9
2827.680	67.3

μ_∞ is taken to be 67.5

μ_∞ calculated from KOHLRAUSCH'S data = 69.3

XIV. Calcium Bromide.

Equivalent dilution	Equivalent μ_v
21.333	62.7
42.667	65.0
85.334	66.8
170.668	68.4
341.336	69.5
682.672	70.4
1365.344	71.0
2730.688	71.2

μ_∞ obtained = 71.2

Now, NOYES and FALK¹⁾ give the cation transference numbers for HCl and NH₄Cl at 0° at almost infinite dilution as 0.847 and 0.490 respectively. By using these values, the ionic velocities are calculated from μ_∞ determinations for HCl and NH₄Cl. Thus,

Substance		Cation transport number	Ionic velocities
HCl	264.4	0.847	H' 223.9 Cl' 40.5
NH ₄ Cl	80.0	0.490	NH ₄ ' 39.2 Cl' 40.8

Now, the ionic velocity of Cl' is taken as 40.8 as the more accurate figure, and from it the following ionic velocities are deduced by applying KOHLRAUSCH'S law $\mu_\infty = u + v$

Substance	Equivalent μ_∞	Ionic velocities
LiCl	60.5	Li' = 19.3
SrCl ₂	72.5	$\frac{1}{2}$ Sr'' = 31.7
MgCl ₂	66.6	$\frac{1}{3}$ Mg'' = 25.8

Again, by using these values, other ionic velocities are calculated as is shown in the following table:

¹⁾ Loc. cit.

Substance	Equivalent " ∞ "	Known ionic velocities	Required ionic velocities by dif- ference from " ∞ "	Remarks
$(\text{NH}_4)_2\text{SO}_4$	81.8	$\text{NH}_4' = 39.2$	$\frac{1}{2} \text{SO}_4'' = 42.6$	
Na_2SO_4	68.2	$\frac{1}{2} \text{SO}_4'' = 42.6$	$\text{Na}' = 25.6$	
K_2SO_4	84.4	$\frac{1}{2} \text{SO}_4'' = 42.6$	$\text{K}' = 41.8$	
CaSO_4	72.0	$\frac{1}{2} \text{SO}_4'' = 42.6$	$\frac{1}{2} \text{Ca}'' = 29.4$	
NH_4NO_3	80.3	$\text{NH}_4' = 39.2$	$\text{NO}_3' = 41.1$	
NaNO_3	66.9	$\text{Na}' = 25.6$	$\text{NO}_3' = 41.3$	$\text{NO}_3' = 41.1$ from NH_4NO_3
KNO_3	83.4	$\text{NO}_3' = 41.3$	$\text{K}' = 42.1$	$\text{K}' = 41.8$ from K_2SO_4
MgBr_2	67.5	$\frac{1}{2} \text{Mg}'' = 25.8$	$\text{Br}' = 41.7$	
CaBr_2	71.2	$\text{Br}' = 41.7$	$\frac{1}{2} \text{Ca}'' = 29.5$	$\frac{1}{2} \text{Ca}'' = 29.4$ from CaSO_4
BaBr_2	-	-	-	

It would be noticed from the column headed "Remarks" that in no case have ionic velocities differed by more than 0.3, as obtained from different sources.

Below, is added a comparative table of the ionic velocities as obtained by this direct method, and as obtained from KOHLRAUSCH'S table¹⁾ by calculating with his temperature coefficients:

Ions	Velocities at 0° C as obtained directly	Velocities as calculated with temp. coefficients.
H'	223.9	224.3
NH_4'	39.2	40.2
Li'	19.3	19.0
Na'	25.6	26.0
K'	42.1	40.9
$\frac{1}{2} \text{Ca}''$	29.5	X
$\frac{1}{2} \text{Sr}''$	31.7	31.6
$\frac{1}{2} \text{Mg}''$	25.8	26.8
Cl'	40.8	41.5
NO_3'	41.3	40.1
Br'	41.7	42.5
$\frac{1}{2} \text{SO}_4''$	42.6	42.2

¹⁾ Loc. cit.

Evidently then, the temperature coefficients of KOHLRAUSCH can not be relied on to obtain accurate values at 0° C.

WOOD¹⁾ has given the following values for μ_{∞} at 0°: for KCl = 77.8, for NaCl = 65.0, for dichloroacetic acid = 227.0, for trichloroacetic acid = 224.7. Thus from the values obtained by me it is seen that his values for KCl and NaCl are a little too low, whilst his values for the acids are very much too low, since the most probable value of H° is 223.9.

JOHNSTON'S²⁾ rough estimation of the value of H° at 0° = 240 is also far from being correct.

NOYES and STEWART³⁾ have deduced values for H° in an indirect way which can hardly be relied on. Whilst from data for HCl they obtained the velocity for H° at 0° = 224, they, at the same time obtained, by considering H₂SO₄ in the same way the value 235 at 0°.

NOYES and COOLIDGE⁴⁾ give 81.4 as the value of μ_{∞} for KCl at 0°; but it is a little too low.

JONES and WEST⁵⁾ have given μ_{∞} at 0° for NH₄Cl = 74.84; evidently it is too low.

JONES and CALDWELL⁶⁾ give the value for ammonium nitrate = 78.0, which is a value a little too low.

KAHLENBERG⁷⁾ obtains for strontium nitrate the value 66.1. Evidently it is too low, since the correct value would be about 31.7 + 41.3 = 73 (loc. cit).

HILL and SIRCAR⁸⁾ take a very high value for H° at 0°. They write: For μ_{∞} in the case of hydrogen fluoride, we have taken the number 364 at 18° and 325 at 0°. The first number is derived from the ionic conductivities at 18° which are 318 for the hydrogen ion and 46.6 for the fluorine ion. The second number is derived from the following data:

“OSTWALD gives 325 as the ionic conductivity of the hydrogen ion at 25°; at 18° the value is 318 (KOHLRAUSCH and v. STEINWEHR, Sitz.-ber. Berlin. Akad. 1902), being a fall of one unit per degree. Hence at 0° the value would be approximately 300. Correcting the ionic conductivity of fluorine for temperature, the temperature coefficient being 0.0238, we get the value at 0° = 26.6. The sum

¹⁾ Loc. cit.

²⁾ J. Amer. Chem. Soc. **31**, 1015 (1909).

³⁾ J. Amer. Chem. Soc. **32**, (1910), 1140—1141.

⁴⁾ Carnegie Institution Publications 63, 47 (1907).

⁵⁾ Amer. Chem. Jour. **34**, 557 (1905).

⁶⁾ Amer. Chem. Jour. **25**, 349 (1901).

⁷⁾ Jour. Phys. Chem. **5**, 339 (1901).

⁸⁾ Proc. Roy. Soc. Vol. **83 A**, p. 130.

of these ionic conductivities is 326. This number may be derived in another way. H. E. JONES gives 380 as the limiting value for HF at 25°. The value as calculated above for 18° is 364. The difference per degree is 2.3 units, hence the value at 0° is 324. The approximate correctness of the number 325 is shown by the fact that if we assume the amount of dissociation to be little affected by temperature, at any rate in the more concentrated solutions, we get $\alpha = \frac{\mu_v^{0^\circ}}{\mu_\infty^{0^\circ}} = \frac{\mu_v^{18^\circ}}{\mu_\infty^{18^\circ}}$. Substituting 0.0576 for α and 18.30 for μ_v which is the value for the acid of 29.83 %, we get $\mu_\infty = 318$ (at 0°).

“The temperature coefficient for H at 18° is about 0.0153. If this is used to calculate the limiting value for the hydrogen ion at 0°, the number for $\mu_\infty^{0^\circ}$ becomes very much lower than any of these 3 numbers given above, and as a coefficient is only correct in the neighbourhood of 18° we discard this method of calculating.”

It is evident that HILL and SIRCAR have calculated μ_∞ at 0° for HF assuming a very high value for H°. Their value for H° at 0° is about 100 units higher than the value obtained in this investigation in the direct way. Consequently all their calculations for the degree of dissociation of HF with this value for H° are not reliable.

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Chemistry. — “*Properties of elements and the periodic system*”. By NILRATAN DHAR. (Communicated by Prof. ERNST COHEN).

In a former paper (DHAR Zeit. Elektro-Chem. (1913) it has been shown that the heats of ionisation of elements and the temperature coefficient of mobility of ions are periodic functions of their atomic weights. In this paper it will be shown that some other properties are also periodic functions of their atomic weights.

Surface tension, capillary rise etc.

The surface tension of liquids being an important property has been investigated by various workers. There are several methods of determining the value of the surface tension of liquids, the most important ones are (1) the rise in a capillary tube, (2) measurements