261. *The Conductivity of Methoxides and Ethoxides.*

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The investigation of the electrical conductivity of acids in hydroxylic solvents has yielded important results, and their value is very largely due to the fact that the ionisation of the solvent itself gives rise to hydrogen ions. An investigation of the conductivity of bases thus becomes doubly interesting : on the one hand, they provide another class of strong electrolyte, and on the other hand, they give rise to the ion of the solvent other than the hydrogen ion. The hydroxyl ion has been studied by Raikes, Yorke, and Ewart (J., 1926, 630) and by Jeffery and Vogel (*Phil. Mag.*, 1933, **15**, 395), but the methoxide and the ethoxide ion have not been so fully investigated.

Bases react with any acid impurity in the solvent, giving products the conductivities of which can be measured independently. The data for bases have to be corrected for this reaction, and in the process, considerable information is obtained as to the types and amounts of impurities present in conductivity solvents.

Wynne-Jones (*J. Physical Chem.*, 1927, **31**, 1647) measured the conductivity of sodium methoxide in methyl alcohol, and obtained 98·3 for the value at infinite dilution. Robertson and Acree (*ibid.*, 1915, **19**, 381) measured the conductivities of lithium, sodium, and potassium ethoxides in ethyl alcohol, obtaining values for the conductivity at infinite dilution of 31·1, 33·2, and 37·2 respectively. They do not state how the values were corrected for the conductivity of the solvent. Barak (*Z. physikal. Chem.*, 1933, **165**, 272) measured the conductivity of sodium ethoxide, but applied no correction to his results.

The present work is an investigation of the bases of lithium, sodium, and potassium in methyl and ethyl alcohols, and also of the effects of the solvent impurities on the conductivity of these bases.

Preparation of Materials.—Solvents. Methyl alcohol was prepared by the method of Hartley and Raikes (J., 1925, **127**, 524), and ethyl alcohol by that of Copley, Murray-Rust, and Hartley (J., 1930, 2492). Nitrogen was obtained from a cylinder and purified by passage over heated copper, through a tower containing concentrated sulphuric acid, over solid caustic soda, and finally over phosphoric oxide to remove the last traces of moisture. Carbon dioxide was prepared from marble and dilute hydrochloric acid, and dried first with sulphuric acid and then with phosphoric oxide. Ammonia was generated by dropping concentrated solution (*d* 0·88) on solid caustic potash, and dried with solid caustic potash and lime. Mercury was purified as described by Desha (*Amer. Chem. J.*, 1909, **41**, 152). Amalgams were prepared by the method of Wolfenden, Wright, Ross Kane, and Buckley (*Trans. Faraday Soc.*, 1927, **23**, 491). The sodium and potassium amalgams were prepared from the carbonate, and the lithium amalgam from a solution of the acetate. The amalgam was dried by filtering through long capillaries, and was stored in a tap-funnel under dry nitrogen.

Basic solutions. 200 C.c. of alcohol were placed in a round-bottomed Jena flask fitted with an over-ground stopper and an inlet tube which reached nearly to the bottom of the flask. Nitrogen was blown through for about 6 hours, to remove any dissolved oxygen or carbon dioxide. A suitable amount of amalgam was run in, and stirred by passage of nitrogen for about 12 hours. When the solution had reached a concentration of about 0·1*N* it was decanted into a Jena solution flask, and its concentration determined by titration. Such solutions were quite stable.

Alkali methyl and ethyl carbonate solutions. Attempts were made to prepare these carbonates in the solid state, but it was difficult to dry them to constant weight. It was more satisfactory to prepare solutions by dilution of solutions of the bases with slight excess of carbon dioxide solutions. The conductivity of any excess carbon dioxide was almost entirely suppressed by the presence of alkyl carbonate ions. The concentration of these solutions was deduced from that of the alkali solutions.

Hydrochloric acid. Constant-boiling acid, prepared by the method of Foulk and Hollingsworth (*J. Amer. Chem. Soc.*, 1923, **45**, 1220), was used as the ultimate acidimetric standard. This acid was diluted by weight and used to standardise the baryta.

Barium hydroxide. A saturated solution of baryta was boiled to coagulate any barium carbonate, decanted off, and cooled. It was diluted with distilled water which had been boiled to remove carbon dioxide : any water used for the dilution of the standard reagents was treated in this way.

Determination of the Concentration of the Solutions.—The diluted hydrochloric acid and the baryta were about 0·1*N*; for the titration of the base solutions it was convenient to have an acid solution of about 0·04*N*, so the original acid was diluted further, and standardised against the baryta. Bromothymol-blue was the indicator employed. It was very sensitive to carbon dioxide, so the titration flasks were protected from the air. Since the presence of alcohol produced a considerable change in the end-point of the titrations, the magnitude of the effect was measured, and it was found that there was a linear relation between the amount of alcohol present and the effect produced. If C_{true} is the concentration of the base, and $C_{\text{obs.}}$ is its apparent concentration in the presence of $a\%$ of alcohol

$$C_{\text{true}} = C_{\text{obs.}}\,(1 + 0{\cdot}00014a) \text{ for MeOH}$$

and

$$C_{\text{true}} = C_{\text{obs.}}\,(1 + 0{\cdot}00032a) \text{ for EtOH.}$$

Observed concentrations of base solutions were corrected for the amount of alcohol present. Poethke (*Z. anal. Chem.*, 1931, **86**, 399) investigated the effect of alcohol on certain indicators, and checked his measurements by making conductivity titrations; he found that the effect was proportional to the amount of alcohol present, and independent of small quantities of salt in the solution. It was necessary to standardise the base in concentrations of 0·08—0·1*N* and then dilute the solution to about 0·02*N* for the conductivity measurements. If the base solution was too dilute, very variable values for the concentration were obtained.

Ammonia was titrated directly with the standard acid, but it was difficult to obtain reproducible results because the presence of alcohol had a very marked effect on the titrations. It was impracticable to determine the concentration of the carbon dioxide solutions by a volumetric method, and it was therefore estimated gravimetrically as barium carbonate.

Experimental Procedure.—All concentrations are expressed in g.-mols. per litre of solution.

Measurements of conductivity were made by the method of Murray-Rust and Hartley (*Proc. Roy. Soc.*, **1929**, *A*, **126**, 84), and were carried out in a thermostat at 25·00° ± 0·01°. The cell usually employed had a constant of 0·03879, but at various times three other cells were used of constants 0·03408, 0·1833, and 0·1735. These constants are based on Frazer and Hartley's values for potassium chloride in methyl alcohol (*ibid.*, 1925, *A*, **109**, 351). In the diagrams, values of the equivalent conductivity are plotted against the square root of the concentration.

Results for Carbon Dioxide and Ammonia.—The results for carbon dioxide and ammonia are given first, because it is necessary to know their dissociation constants before discussing the correction of the data for the bases. The results are set out in tabular form : at the head of each table is given Λ_0, the equivalent conductivity at infinite dilution, calculated from the mobilities of the individual ions; col. 1 gives values of κ, the specific conductivity (in gemmhos) of the solvent employed; col. 2 the values of $c \times 10^4$, where c is the concentration; col. 3 the values of Λ_c, the equivalent conductivity at concentration c; col. 4 gives values of K, the dissociation constant, which is of the form : $K = [H^{\bullet}][MeCO_3{}'] / [CO_2]$. No solvent correction has been applied.

Methyl alcohol as solvent.

Carbon dioxide; $\Lambda_0 = 190$.

	$c \times 10^4$.	Λ_c.	$K \times 10^{10}$
$\kappa = 0{\cdot}170$	50·8	0·0471	3·1
	92·2	0·0290	2·1
	138	0·0206	1·7
	177	0·0170	1·5
$\kappa = 0{\cdot}091$	11·8	0·111	4·2
	21·7	0·0749	3·5
	33·6	0·0561	3·0

Value accepted = 2×10^{-10}.

Ammonia; $\Lambda_0 = 110$.

	$c \times 10^4$.	Λ_c.	$K \times 10^6$.
$\kappa = 0{\cdot}060$	70·4	1·88	2·1
	125	1·35	1·9
	206	1·04	1·8
$\kappa = 0{\cdot}060$	58·1	2·07	2·1
	111	1·39	1·8
	157	1·14	1·7
	235	0·91	1·6

Value accepted = 2×10^{-6}.

Ethyl alcohol as solvent.

Carbon dioxide; $\Lambda_0 = 80$.

	$c \times 10^4$.	Λ_c.	$K \times 10^{12}$.
$\kappa = 0{\cdot}010$	33·1	0·0039	8
	60·9	0·0025	6
	91·3	0·0019	6
	117	0·0016	5
$\kappa = 0{\cdot}010$	18·5	0·0063	12
	37·8	0·0034	7
	55·4	0·0026	6
	72·8	0·0022	6

Value accepted = 6×10^{-12}.

Ammonia; $\Lambda_0 = 44$.

	$c \times 10^4$.	Λ_c.	$K \times 10^7$.
$\kappa = 0{\cdot}014$	95	0·232	2·8
	240	0·116	1·5
	522	0·070	1·3
$\kappa = 0{\cdot}012$	162	0·153	2·0
	308	0·097	1·5
	479	0·074	1·4

Value accepted = $1{\cdot}5 \times 10^{-7}$

The values of the dissociation constants do not agree well amongst themselves, but approximate values are quite sufficient for the present purpose.

Ammonia shows a very pronounced drift in the conductivity, the value increasing with time, particularly in the dilute range. Some slow reaction is taking place, and this takes time to reach equilibrium. On dilution of the stock solution in the cell, time elapses before the new equilibrium is reached, and the conductivity changes throughout this period. The time required to reach equilibrium is much greater for ethyl than for methyl alcohol. When a *N*-solution is diluted 100-fold, the conductivity takes at least an hour to reach its equilibrium value in ethyl alcohol, but only about 10 mins. in methyl alcohol. No such drift can be detected in the case of carbon dioxide, and it would, in fact, be difficult to detect. The whole question is under investigation in this laboratory.

Solvent Correction.—The conductivity measured is that of the solution, and in general a correction has to be applied before that of the dissolved substance can be obtained. The solvent itself has a certain small conductivity, but this is almost entirely suppressed even by those small quantities of impurity left in the purified solvent. The correction is specific, depending upon the nature of the solvent, the impurities it contains, and the dissolved substance. As Wynne-Jones (*loc. cit.*) has insisted, the most important point about any correction is that it should be reduced as far as possible, because there are certain assumptions underlying any method of solvent correction. The nature and amount of the impurities should then be determined, and a suitable correction applied to the experimentally determined conductivity of the solution.

Water. The conditions in water have been treated in detail by Kolthoff (*Rec. trav. chim.*, **1929**, **48**, 664). The impurities present in conductivity water may be divided into two classes :

acid (such as carbon dioxide) and alkaline (such as ammonia, or any basic substance dissolved from the glass of the apparatus). In practice, it has been found possible to treat the conductivity of such water as being entirely due to dissolved carbon dioxide, and solvent corrections have been successfully applied on that assumption (cf. Kendall, *J. Amer. Chem. Soc.*, 1916, **38**, 1490; 1917, **39**, 7). It has become common practice to use " equilibrium water," *i.e.*, water in equilibrium with the carbon dioxide of the atmosphere, so that the concentration of carbon dioxide can be known with some certainty. Davies (" The Conductivity of Solutions," London, 1929), however, has pointed out that the presence of such a concentration of carbon dioxide in the solution produces a definite increase in the interionic forces and makes an accurate correction difficult. It is hence advisable to reduce the carbon dioxide concentration as far as possible. A small correction is better, in principle, than a more certain, but larger, correction.

Alcohols. The general principles involved in the application of the solvent correction in the alcohols have been discussed by Wynne-Jones (*loc. cit.*). The problem is complicated by the presence of water as an impurity. Even in conductivity alcohol, it cannot be guaranteed that the amount of water present is less than $2 \times 10^{-3}N$. Additions of water (see p. 1205) to carbon dioxide and ammonia solutions in the alcohols show that, even although water has a considerable effect upon the conductivities of these substances, yet the presence of this amount of water will not have an appreciable effect. It has also been shown (Hughes and Hartley, *Phil. Mag.*, 1933, **15**, 610) that this amount of water would not make any appreciable change in the conductivity of a strong electrolyte in either of the alcohols. It appears that the effect of water as an impurity may be neglected.

Alcohols are liable to contain aldehydes as impurities, but it has been shown (Clark, Gatty, Hughes, and Hartley, J., 1933, 658) that, with acetaldehyde in ethyl alcohol, the amount present has only a negligible effect upon the conductivity of electrolytes.

The impurities which may have a chemical effect upon the dissolved electrolytes are: (1) Basic impurities, such as ammonia, and alkali dissolved from the glass of the apparatus; the latter causes of error may be eliminated by using only apparatus which has been soaked for a long time in conductivity water (see p. 1206), and it has been found that ammonia is present in quantities of the order $2 \times 10^{-7}N$. (2) Acidic impurities, such as carbon dioxide, which is usually about $1 \times 10^{-4}N$.

The effects of these impurities have been discussed by Wynne-Jones, but it should be repeated that the solvent corrections to be applied are: (*a*) Salts. The conductivity of the solvent is subtracted from that of the solution. (*b*) Acids. The conductivity of the carbon dioxide is completely suppressed, and any ammonia is converted into the ammonium salt of the acid. (*c*) Bases. The conductivity of the ammonia is suppressed, and any carbon dioxide present is converted into alkali alkyl carbonate. Here the situation is simpler than in water because there is only one type of carbonate formed.

Conductivity of Methyl Alcohol.—Wynne-Jones has corrected conductivity data for sodium methoxide in methyl alcohol on the assumption that the carbon dioxide concentration can be calculated from the conductivity of the solvent. However, it is found that the ammonia plays a very large part in contributing to the conductivity of the solvent. The ammonia is converted into ammonium methyl carbonate, which is the salt of a weak acid and a weak base. This will be partly alcoholysed in solution: $NH_4MeCO_3 + MeOH \rightleftharpoons NH_4{\cdot}OMe + HMeCO_3$, and if z is the fraction of ammonium methyl carbonate alcoholysed, then $z^2/(1 - z)^2 = K_{MeOH}/K_{CO_2} \times K_{NH_3}$, where K_{MeOH} is the ionic product of methyl alcohol, and the other K's are the dissociation constants of the substance denoted by the subscript. Therefore

$$\frac{z^2}{(1-z)^2} = \frac{2 \times 10^{-17}}{2 \times 10^{-10} \times 2 \times 10^{-6}} = 5 \times 10^{-2}, \text{ and } z = 0{\cdot}2.$$

This value of z is that for a pure solution of ammonium methyl carbonate. If the concentration of ammonia is of the order $2 \times 10^{-7}N$, and that of the carbon dioxide $1 \times 10^{-4}N$, the alcoholysis of the ammonium methyl carbonate will be almost completely suppressed by the presence of such large excess of carbon dioxide. Hence $[NH_4^{\bullet}] = 2 \times 10^{-7}$, because the ammonium methyl carbonate will be completely dissociated at such extreme dilution; further,

$$[MeCO_3'] = 2 \times 10^{-7} + [H^{\bullet}]$$

and since

$$[H^{\bullet}][MeCO_3']/[CO_2] = 2 \times 10^{-10}$$

hence,

$$[H^{\bullet}]\{2 \times 10^{-7} + [H^{\bullet}]\}/1 \times 10^{-4} = 2 \times 10^{-10},$$

therefore

$$[H^{\bullet}] = 0{\cdot}8 \times 10^{-7}.$$

The concentrations are therefore $[\mathrm{H}^{\cdot}] = 0{\cdot}8 \times 10^{-7}$, $[\mathrm{NH}_4^{\cdot}] = 2 \times 10^{-7}$, $[\mathrm{MeCO}_3'] = 2{\cdot}8 \times 10^{-7}$. In that the proportion of ammonia to carbon dioxide varies, it is impossible to deduce from the conductivity of the solvent the amounts of either present.

Conductivity of Ethyl Alcohol.—Consider as before alcohol containing carbon dioxide and ammonia at concentrations $1 \times 10^{-4}N$ and $2 \times 10^{-7}N$ respectively. The ammonia will be converted into ammonium ethyl carbonate. For a pure solution of this substance, with $K_{\mathrm{EtOH}} = 2 \times 10^{-19}$, $K_{\mathrm{CO}_2} = 6 \times 10^{-12}$, and $K_{\mathrm{NH}_3} = 1{\cdot}5 \times 10^{-7}$, we find $z = 0{\cdot}2$. In the presence of excess of carbon dioxide, the degree of alcoholysis will be very small. The ammonia can be regarded as being present entirely as ammonium ethyl carbonate. A calculation similar to that made above leads to the following concentrations for the ions in the solution: $[\mathrm{H}^{\cdot}] = 3 \times 10^{-9}$, $[\mathrm{NH}_4^{\cdot}] = 2 \times 10^{-7}$, $[\mathrm{EtCO}_3'] = 2 \times 10^{-7}$. Even although the hydrogen ion has a very large mobility, the conductivity of the solvent will be effectively that of the ammonium ethyl carbonate. Let the concentration of this substance be c, then, since the sum of the mobilities of the ammonium and the ethyl carbonate ion gives a Λ_0 value of 40, one can write $40c/1000$ = specific conductivity of the solvent. For a specimen of ethyl alcohol of $\kappa = 0{\cdot}010 \times 10^{-6}$, the value of c is $2{\cdot}5 \times 10^{-7}N$, and this is the concentration of ammonia in the solvent.

FIG. 1.

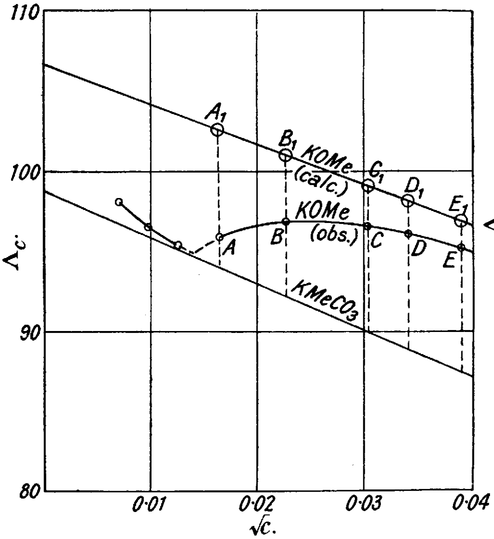
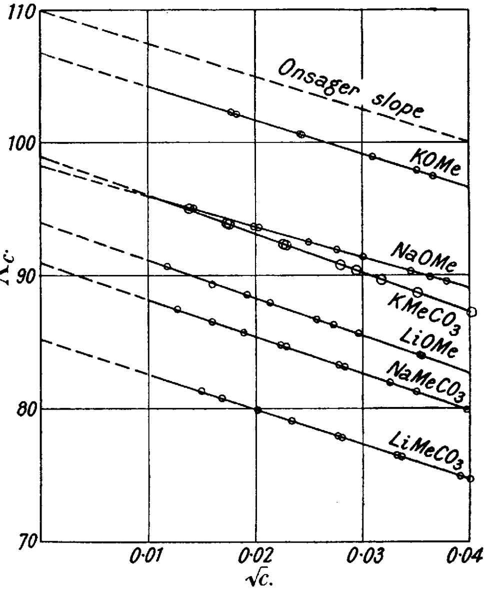


FIG. 2.



It thus becomes possible to apply a rigid correction to conductivity determinations for acids in ethyl alcohol: this correction is very small. It is not possible to calculate the concentration of carbon dioxide present in the solvent.

Correction of Data for Bases.—Because the concentration of carbon dioxide cannot be directly calculated, it is impossible to apply a rigid correction to the data for bases. The method of correction employed is the same for methyl and ethyl alcohol. It rests on the following assumptions: (1) The bases give a straight-line Λ_c–$\sqrt{c}$ relation. (2) The conductivity of the ammonia present can be neglected. (3) The deviations of the observed points from the straight line are due to the presence of carbon dioxide, which partially converts the base into the alkyl carbonate. (4) There is no alcoholysis of the resulting alkyl carbonate; in methyl alcohol, potassium methyl carbonate, which is the salt of a weak acid and a strong base, has an alcoholysis constant: $K_{\mathrm{Alc.}} = K_{\mathrm{MeOH}}/K_{\mathrm{CO}_2} = 2 \times 10^{-17}/2 \times 10^{-10} = 10^{-7}$; similarly in ethyl alcohol, for potassium ethyl carbonate: $K_{\mathrm{Alc.}} = K_{\mathrm{EtOH}}/K_{\mathrm{CO}_2} = 2 \times 10^{-19}/6 \times 10^{-12} = 3 \times 10^{-8}$. In the presence of excess of base, alcoholysis can be neglected.

The observed results for potassium methoxide and potassium methyl carbonate are plotted in Fig. 1. To avoid confusion, the individual points for the latter are not plotted. As the solution of the base becomes more dilute, the concentration of carbon dioxide in the solvent at first is less than, then equals, and finally exceeds the concentration of the base. On the more concentrated side of the sharp break in the curve, the solution is a mixture of the methoxide and the methyl carbonate, and on the more dilute side it is a mixture of the methyl carbonate and excess carbon dioxide. In this very dilute range, alcoholysis becomes appreciable, and the values of the conductivity lie above the methyl carbonate line; when corrected for this alcoholysis, they lie on this line.

Let the concentrations of methoxide originally added to the solution be c_1, c_2, c_3, c_4, and c_5, corresponding to the points A, B, C, D, and E. Let y be the fraction of base converted into the alkali methyl carbonate at the first point A. If Λ_{KMeCO_3} is the equivalent conductivity of the methyl carbonate at this concentration, and if Λ_{KOMe} is the true conductivity of the base at this concentration, then

$$\Lambda_{\text{obs.}} = y\Lambda_{\text{KMeCO}_3} + (1 - y)\Lambda_{\text{KOMe}}$$

A point A_1 is selected arbitrarily as the true value of Λ_{KOMe} at concentration c_1. By substituting this value in the above equation, the value of y is calculated. The concentration of carbon dioxide in the solution is therefore given by yc_1. For the next point the data are as follows :

Total ionic concentration $= c_2$
Fraction present as methyl carbonate $= yc_1/c_2$
Fraction present as methoxide $= (c_2 - yc_1)/c_2$

so that the equation now becomes

$$\Lambda_{\text{obs.}} = \frac{yc_1}{c_2}\Lambda_{\text{KMeCO}_3} + \frac{c_2 - yc_1}{c_2}\Lambda_{\text{KOMe}}$$

where the values of the Λ's are those corresponding to the ionic concentration c_2. In this way the points B_1, C_1, D_1, and E_1 are obtained. If the first arbitrary selection of the point A_1 does not give a straight line for A_1, B_1, C_1, D_1, E_1, a small alteration is made in its value until the best straight line is obtained. The equation for this line is taken as representing the true conductivity of the base. This straightness is the only criterion of correctness, because there is no other method for determining the amount of carbon dioxide in the solvent. It is significant that it is only possible to obtain one straight line by the above process of correction : the choice of the unique straight line in preference to any of the possible curved lines is justified by the nearness of the slope of this straight line to the Onsager slope.

Correction of Data for Alkali Alkyl Carbonates.—In water, it has been shown that all the conductivity of the solvent can be attributed to dissolved carbon dioxide. No correction need be applied to the conductivities of bicarbonate solutions because the bicarbonate ion will be present in large quantities, and will suppress the ionisation of the carbonic acid. Ethyl alcohol provides the other extreme case, because the conductivity can be attributed almost entirely to the presence of ammonium ethyl carbonate, and the conductivity of this substance will not be greatly affected by the presence of other ethyl carbonates (strictly a correction should be made for the change in the total ionic concentration). The conductivity of the solvent must therefore be subtracted from that of the solution. Of methyl alcohol it is at present impossible to speak with certainty : some intermediate correction should be applied, because the presence of a methyl carbonate will not affect the ammonium methyl carbonate, but will suppress the ionisation of the free methyl hydrogen carbonate. A fair compromise is to subtract half the conductivity of the solvent.

Results for Bases.—The results are set out in tabular form. At the head of each table are given Λ_0, the conductivity at infinite dilution, and x, the slope of the conductivity curve. Col. 1 gives κ, the specific conductivity of the solvent; col. 2, $c \times 10^4$, where c is the concentration; col. 3, $\Lambda_{c,\text{obs.}}$; col. 4, $\Lambda_{c,\text{corr.}}$; and col. 5 the differences between $\Lambda_{c,\text{corr.}}$ and values of Λ_c calculated from the equation $\Lambda_c = \Lambda_0 - x\sqrt{c}$.

For the alkali alkyl carbonates there is only one Λ_c column, and that gives the corrected values.

Methyl alcohol as solvent.

Lithium methoxide; $\Lambda_0 = 94{\cdot}0$; $x = 284$.

	$c \times 10^4$.	$\Lambda_{c,\text{obs.}}$.	$\Lambda_{c,\text{corr.}}$.	Diff.
$\kappa =$	3·692	87·20	88·5	±0·0
0·085	7·337	85·61	86·3	±0·0
	12·585	83·51	83·9	±0·0
	18·217	81·88	82·2	+0·3

Sodium methoxide; $\Lambda_0 = 98{\cdot}4$; $x = 236$.

	$c \times 10^4$.	$\Lambda_{c,\text{obs.}}$.	$\Lambda_{c,\text{corr.}}$.	Diff.
$\kappa =$	4·121	91·91	93·4	−0·1
0·039	7·671	90·80	91·6	−0·1
	12·672	89·15	89·7	−0·2
	19·120	87·55	87·9	−0·1

Lithium methoxide; $\Lambda_0 = 94·0$; $x = 284$.

	$c \times 10^4$.	$\Lambda_{c,\text{obs.}}$.	$\Lambda_{c,\text{corr.}}$.	Diff.
$\kappa =$ 0·094	1·434	86·13	90·6	±0·0
	2·871	86·76	88·9	−0·2
	4·524	86·40	87·8	−0·2
	6·495	85·79	86·7	±0·0
	8·666	85·00	85·7	+0·1
	12·477	83·44	83·9	±0·0

Sodium methoxide; $\Lambda_0 = 98·4$; $x = 236$.

	$c \times 10^4$.	$\Lambda_{c,\text{obs.}}$.	$\Lambda_{c,\text{corr.}}$.	Diff.
$\kappa =$ 0·024	1·864	93·47	95·2	±0·0
	3·940	92·92	93·8	±0·0
	6·266	92·07	92·6	+0·1
	9·075	91·05	91·4	+0·1
	11·579	90·08	90·4	−0·1
	14·343	89·31	89·6	±0·0
	17·553	88·51	88·7	+0·1

Potassium methoxide; $\Lambda_0 = 106·8$; $x = 255$.

$\kappa =$ 0·033	3·428	99·86	102·0	−0·1
	5·851	99·39	100·7	±0·0
	9·486	98·09	98·9	−0·2
	13·840	96·66	97·3	−0·2
	17·560	95·68	96·2	−0·1
$\kappa =$ 0·059	3·139	99·64	102·4	+0·2
	5·757	99·16	100·7	+0·1
	11·858	97·21	98·0	+0·1
	20·681	95·13	95·6	+0·5
$\kappa =$ 0·098	0·4928	98·08		
	0·9583	96·62		
	1·602	95·55		

Calcium methoxide.

$\kappa =$ 0·081	1·212	75·3
	2·309	75·7
	3·385	74·2
	5·115	71·4
	6·465	69·3
	9·339	65·5
$\kappa =$ 0·040	0·835	73·4
	1·885	76·4
	3·245	75·5
	4·299	73·8
	5·629	71·7

Lithium methyl carbonate; $\Lambda_0 = 85·3$; $x = 265$.

	$c \times 10^4$.	Λ_c.	Diff.
$\kappa =$ 0·096	2·160	81·62	+0·20
	4·126	79·95	±0·00
	7·531	78·07	−0·01
	10·976	76·62	+0·03
	16·472	74·63	−0·01
$\kappa =$ 0·142	2·872	80·89	+0·03
	5·267	79·26	+0·01
	7·949	77·86	+0·01
	11·690	76·15	−0·09
	15·087	74·98	−0·01

Sodium methyl carbonate; $\Lambda_0 = 91·0$; $x = 277$.

	$c \times 10^4$.	Λ_c.	Diff.
$\kappa =$ 0·082	2·541	86·38	−0·06
	4·941	84·62	−0·06
	8·214	82·84	−0·04
	12·103	80·99	−0·16
	15·696	79·76	−0·05
$\kappa =$ 0·038	1·713	87·68	+0·13
	3·637	85·96	+0·05
	5·402	84·78	+0·02
	7·671	83·58	+0·05
	10·446	82·32	+0·06

Potassium methyl carbonate; $\Lambda_0 = 98·9$. $x = 292$.

$\kappa =$ 0·063	1·802	95·11	+0·11
	3·236	93·71	+0·05
	5·194	92·32	+0·07
	7·675	90·86	+0·05
	10·002	89·43	−0·22
$\kappa =$ 0·050	3·037	93·76	−0·07
	5·532	92·05	−0·01
	8·644	90·36	+0·02
	12·217	88·57	−0·16
	16·522	87·05	−0·02

Ethyl alcohol as solvent.

Lithium ethoxide; $\Lambda_0 = 39·61$; $x = 230$.

	$c \times 10^4$.	$\Lambda_{c,\text{obs.}}$.	$\Lambda_{c,\text{corr.}}$.	Diff.
$\kappa =$ 0·015	1·957	34·60	36·40	+0·01
	4·154	34·11	34·95	+0·03
	6·358	33·26	33·81	±0·00
	9·474	32·14	32·50	−0·03
	12·151	31·27	31·58	−0·01
$\kappa =$ 0·008	2·721	35·51	35·81	±0·00
	6·163	33·80	33·93	+0·03
	9·854	32·29	32·37	−0·02
	14·584	30·77	30·83	±0·00
	18·904	29·63	29·67	+0·06

Sodium ethoxide; $\Lambda_0 = 43·00$; $x = 195$.

	$c \times 10^4$.	$\Lambda_{c,\text{obs.}}$.	$\Lambda_{c,\text{corr.}}$.	Diff.
$\kappa =$ 0·009	1·857	39·00	40·30	−0·05
	3·803	38·54	39·26	+0·04
	7·180	37·38	37·79	−0·02
	10·366	36·40	36·72	−0·05
	15·050	35·20	35·44	−0·05
	19·616	34·19	34·39	−0·04
$\kappa =$ 0·009	1·198	38·43	40·90	+0·05
	2·650	38·71	39·82	+0·02
	4·694	38·08	38·77	+0·06
	7·236	37·23	37·71	+0·02
	10·887	36·18	36·54	+0·05
	13·891	35·39	35·68	+0·04

Potassium ethoxide; $\Lambda_0 = 46·56$; $x = 205$.

$\kappa =$ 0·021	2·759	42·43	43·10	−0·01
	5·705	41·25	41·64	+0·02
	9·676	39·84	40·11	−0·03
	14·117	38·58	38·79	−0·03
	19·603	37·29	37·45	+0·01
	26·530	35·88	35·99	+0·03
$\kappa =$ 0·015	0·1091	43·76		
	0·2908	41·90		
	0·5872	39·50		
	0·7249	39·60		
	0·9002	40·13		
	1·116	40·66		
	2·426	41·62	43·30	−0·12
	3·915	41·37	42·56	±0·00
	5·841	40·79	41·69	+0·02
	9·025	39·82	40·47	±0·00
	12·124	38·97	39·50	±0·00
	16·616	37·85	38·29	+0·01

Lithium ethyl carbonate; $\Lambda_0 = 35{\cdot}70$; $x = 254$.

	$c \times 10^4$.	Λ_c.	Diff.
$\kappa = 0{\cdot}011$	2·503	31·73	+0·05
	4·777	30·15	±0·00
	8·430	28·29	−0·04
	12·236	26·80	−0·02
	15·925	25·61	+0·05

Sodium ethyl carbonate; $\Lambda_0 = 38{\cdot}66$; $x = 318$.

	$c \times 10^4$.	Λ_c.	Diff.
$\kappa = 0{\cdot}010$	1·558	34·71	+0·02
	3·104	33·08	+0·02
	5·422	31·22	−0·03
	7·986	29·63	−0·04
	10·422	28·41	+0·02

Potassium ethyl carbonate; $\Lambda_0 = 43{\cdot}37$; $x = 360$.

	$c \times 10^4$.	Λ_c.	Diff.		$c \times 10^4$.	Λ_c.	Diff.
$\kappa = 0{\cdot}026$	1·522	38·85	−0·03	$\kappa = 0{\cdot}016$	2·370	37·89	+0·03
	3·459	36·68	+0·06		5·023	35·32	−0·03
	5·782	34·64	−0·02		9·610	32·23	±0·00
	8·343	32·90	−0·02		12·995	30·58	+0·17
	11·367	31·28	+0·11		18·034	28·64	+0·43
	16·412	29·15	+0·63				

DISCUSSION OF RESULTS.

Methyl Alcohol.—The results are set out in Fig. 2, and summarised in the following table.

Base.	Λ_0.	$l_{0,\mathrm{OMe}'}$.	Methyl carbonate.	Λ_0.	$l_{0,\mathrm{MeCO}_3'}$.
LiOMe	94·0	54·3	$LiMeCO_3$	85·3	45·6
NaOMe	98·4	52·7	$NaMeCO_3$	91·0	45·3
KOMe	106·8	53·1	$KMeCO_3$	98·9	45·2
		Mean 53·3			Mean 45·4

The agreement between the values for the mobility of the methoxide ion is fair, considering the difficulties of the determinations. The methyl carbonate mobility values agree very well amongst themselves.

Deviations from the Onsager equation.

$$\Delta = 100(x_{\mathrm{obs.}} - x_{\mathrm{calc.}})/x_{\mathrm{calc.}}$$

Base.	Λ_0.	Δ.	Methyl carbonate.	Λ_0.	Δ.
LiOMe	94·0	21	$LiMeCO_3$	85·3	16
NaOMe	98·3	0	$NaMeCO_3$	91·0	20
KOMe	106·8	4	$KMeCO_3$	98·9	23

The deviations of the slopes of the conductivity curves from the Onsager slope, *i.e.*, from perfect behaviour, are tabulated. These deviations are a measure of the degree of ion association in the various solutions. They increase with increasing Λ_0 values for the methyl carbonates, as is usual with salts. For the methoxides, however, the order is different, and lithium methoxide shows a greater deviation from theory than the sodium or the potassium compound. This is anomalous.

Calcium Methoxide.—Measurements were made with this compound to test the behaviour of a diacid base. As expected, it is a weak electrolyte. At the present stage it is impossible to make a solvent correction, because the criterion of correctness applied to strong bases, *i.e.*, a straight-line Λ_c–$\sqrt{c}$ relation, cannot be applied in this case. In order to demonstrate its weakness, the results are plotted in Fig. 3, and uncorrected results for lithium methoxide are put in for comparison. The curves are of different forms, and the form of that for calcium methoxide indicates that it is a weak electrolyte.

Ethyl Alcohol.—The results are set out in Fig. 4, and below :

Base.	Λ_0.	$l_{0,\mathrm{OEt}'}$.	Ethyl carbonate.	Λ_0.	$l_{0,\mathrm{EtCO}_3'}$.
LiOEt	39·6	24·7	$LiEtCO_3$	35·7	20·8
NaOEt	43·0	24·3	$NaEtCO_3$	38·7	20·0
KOEt	46·6	24·6	$KEtCO_3$	43·4	21·4
		Mean 24·5			Mean 20·7

The agreement between the mobility values for the ethoxide ion is good, but that between the values for the ethyl carbonate ion is not so good. When BARAK's results for sodium ethoxide are solvent-corrected, a value of 43·1 is obtained for Λ_0. The position with respect to deviations from Onsager's equation is exactly the same as in methyl alcohol; the lithium base is anomalous.

Deviations from Onsager's equation.

Base.	Λ_0.	Δ.	Ethyl carbonate.	Λ_0.	Δ.
LiOEt	39·6	64	$LiEtCO_3$	35·7	88
NaOEt	43·0	36	$NaEtCO_3$	38·7	130
KOEt	46·6	38	$KEtCO_3$	43·4	149

Water Additions.—Ulich (*Z. angew. Chem.*, 1928, **41**, 1141) pointed out that the addition of a small quantity of water to an alcoholic solution should give valuable information as to the state of an electrolyte in solution. The only relevant physical property which is greatly affected by such an addition is the viscosity, and it might be expected that, for a completely dissociated electrolyte, the fall in conductivity would be equal to the rise in viscosity. It has been shown by Hughes and Hartley (*loc. cit.*), however, that the depression is always less than that required by the increase in viscosity, because the ions become smaller, being partially solvated with water molecules. The results are set out in Table I. The change produced in the conductivity is proportional to the amount of water added, so all results have been adjusted to 1% of water. The percentage change in the equivalent conductivity produced by 1% of water is given for each substance. In both alcohols 1% of water produces a 4% increase in the viscosity.

FIG. 3.

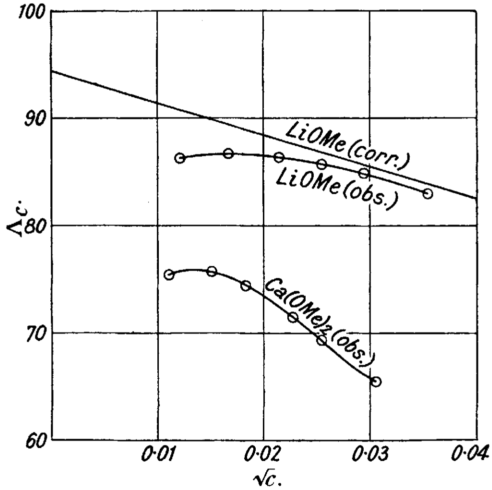


FIG. 4.

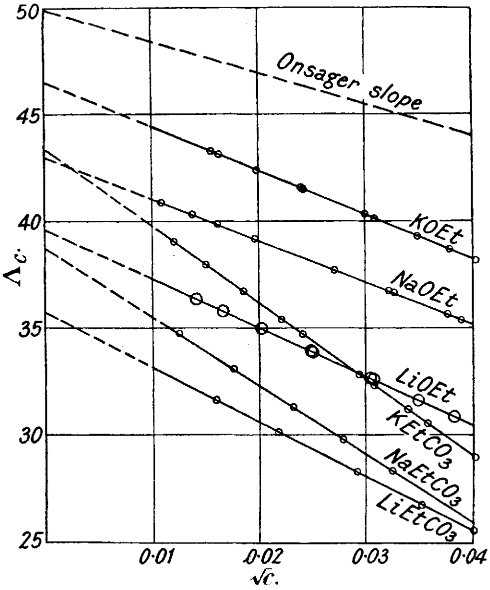


TABLE I.

Methyl alcohol.				*Ethyl alcohol.*			
Substance.	Change in Λ_c, %.	Substance.	Change in Λ_c, %.	Substance.	Change in Λ_c, %.	Substance.	Change in Λ_c, %.
LiOMe	−2·1	$LiMeCO_3$	−2·6	LiOEt	+1·4	$LiEtCO_3$	Ppt. formed
NaOMe	−1·3	$NaMeCO_3$	−2·0	NaOEt	+1·7	$NaEtCO_3$	+2·3
KOMe	−2·0	$KMeCO_3$	−1·8	KOEt	+1·4	$KEtCO_3$	+2·3
CO_2	+6	NH_3	+1	CO_2	+40	NH_3	+26
$Ca(OMe)_2$	+2						

The results in methyl alcohol are straightforward. For the strong electrolytes the depression is less than the 4% demanded by the viscosity increase, but this may be accounted for in terms of the decrease of ionic size in the presence of water. Carbon dioxide, ammonia, and calcium methoxide are weak electrolytes, and the presence of water produces a considerable increase in their conductivities.

In ethyl alcohol, even the strong electrolytes give a small increase in the conductivity.

The change in the ionic size in the presence of water must be greater in ethyl than in methyl alcohol. When these water additions are made, the conductivity values change with time, taking in some cases several hours to come to equilibrium. This suggests that reactions of the type $OEt' + H_2O \rightleftharpoons OH' + EtOH$ are slow. Such drifts with time are also observed in methyl alcohol, but they are more rapid and the changes are much smaller. The drifts are in every case in the direction of lower conductivity. This probably means that the hydroxyl ion has a smaller mobility than the alkoxide ion in the corresponding alcohol.

Glass Surfaces and the Methoxide and Ethoxide Ions.—In the opening stages of this work it was found impossible to obtain reproducible results with bases, but after some months the results settled down to steady values. Afterwards, reproducible results could always be obtained in that particular cell, and for a given solution the older results were always 2—4% higher than these reproducible values. The cell constant did not vary at all, and reproducible results were obtained throughout for the alkyl carbonates. It follows that the discrepancy can be attributed to the behaviour of the alkoxide ions.

In tracing the discrepancy to its source, three other cells were employed besides the usual cell. One of these had plain platinum plates, and the others had plates coated as usual with platinum grey. A series of tests was made with the various cells, and the results given in Table II are for sodium methoxide, the same solution being used in every case. Two of the cells were coated inside with a specially purified paraffin wax–vaselin mixture. Kolthoff (*loc. cit.*) states that it is advisable to coat cells with paraffin wax for use with bases in water.

TABLE II.

Cell.	Constant.		Equation.
Usual cell (Pt grey : aged)	0·03879		$\Lambda_c = 98{\cdot}4 - 234\sqrt{c}$*
Similar cell (Pt grey : not aged)	0·03408		$\Lambda_c = 102{\cdot}0 - 255\sqrt{c}$
Small cell (Pt grey : not aged)	0·1735	Unwaxed	$\Lambda_c = 101{\cdot}0 - 250\sqrt{c}$
		Waxed	$\Lambda_c = 98{\cdot}6 - 230\sqrt{c}$
Small cell (Pt plain : not aged)	0·1833	Unwaxed	$\Lambda_c = 101{\cdot}6 - 255\sqrt{c}$
		Waxed	$\Lambda_c = 98{\cdot}4 - 232\sqrt{c}$

* This result agrees well with those obtained for other sodium methoxide solutions.

It will be seen from Table II that the platinising of the electrodes does not influence the results, but that the discrepancies can be attributed to some effect produced by the glass of the cell. This effect evidently passes away slowly with time, and can also be eliminated by coating the glass with wax. The values of the conductivity obtained in unwaxed or unaged cells are always higher than the reproducible values, and are themselves not reproducible. This suggests that bases may have the specific power of dissolving impurities from the glass. If this type of effect were responsible, a drift with time of the conductivity values would be expected, but no such drift is observed. It is also unlikely that the percentage change in conductivity would be the same over the whole range of concentrations. It is significant that pure solvent can stand for hours without change in conductivity in the same cells which give high values for bases, even though minute amounts of impurity would produce a measurable change in the conductivity.

SUMMARY.

1. The electrical conductivity at 25° has been measured for the following solutions: In methyl alcohol, the methoxides and methyl carbonates of lithium, sodium, and potassium, and in ethyl alcohol, the corresponding derivatives of the same three metals; further, carbon dioxide and ammonia were investigated in both alcohols, and calcium methoxide in methyl alcohol.

2. The following mobility values have been determined: OMe', 53·3; OEt', 24·5; $MeCO_3'$, 45·4; $EtCO_3'$, 20·7.

3. The following dissociation constants have been determined:

In methyl alcohol: CO_2, 2×10^{-10}; NH_3, 2×10^{-6}.
In ethyl alcohol: CO_2, 6×10^{-12}; NH_3, $1{\cdot}5 \times 10^{-7}$.

4. The nature and amounts of impurities present in the solvent have been discussed, and a method worked out for the solvent correction of conductivity data for bases.

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