CCXLI.—*The Electrochemistry of Solutions in Acetone.*
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WHILST a considerable amount of attention has been directed to the electrochemical behaviour of methyl and ethyl alcohols, relatively few measurements are recorded in the case of solutions in acetone. The present paper contains the results of an investigation undertaken to supply to a certain extent this deficiency. The solutes employed were lithium nitrate and silver nitrate, the latter being examined in greater detail. Before giving our own measurements, it is necessary to indicate briefly some of the results obtained by other observers which bear directly on the results obtained by us.*

As regards the electrolysis of saturated silver nitrate solutions in acetone, Kahlenberg (*J. physical Chem.*, 1900, **4**, 349) found that the metal was precipitated in a coherent form, but "the solution conducts so poorly" that it was impossible to verify Faraday's law. In the same paper Kahlenberg gives some results of electromotive force measurements of $\text{Ag}|\text{AgNO}_3$ concentration cells in pyridine and acetonitrile respectively, with regard to which he concludes that the Nernst expressions are inapplicable. Kahlenberg assumes that the liquid/liquid potential difference is negligible, which, in the case of acetone at least, we shall show later is not the case.

The specific conductivity of acetone itself has been measured by Dutoit and Levier (*J. Chim. phys.*, 1905, **3**, 435), the value obtained being $(2-0.48) \times 10^{-7}$ mho at the ordinary temperature (using unplatinised platinum electrodes). H. C. Jones and C. A. Rouiller (*Amer. Chem. J.*, 1906, **36**, 427) obtained the value 1.0×10^{-6} at 0° , our own result being 6×10^{-7} at 18° (using unplatinised electrodes †).

As regards the molecular conductivity of solutes at infinite dilution (λ_∞) in acetone, considerable vagueness exists. Carrara (*loc. cit.*) states that λ_∞ for triethylsulphine iodide is 167 (as determined by direct experiment). Walden (*Zeitsch. physikal. Chem.*, 1906, **54**, 222) found for tetraethylammonium iodide at 25°

* For a general account of the electrochemistry of non-aqueous solutions, compare Carrara: "Elektrochemie der nichtwässrigen Lösungen," Ahrens' *Sammlung*, **12**; also Neustadt, *Diss.*, Breslau, 1909.

† These are preferable to platinised ones, as they eliminate the possibility of catalytic reactions when the solvent is an organic substance.

$\lambda_{\infty} = 225$. Dutoit and Levier (*loc. cit.*) give the following values for some simple salts at 18° :

	Li.	Na.	K.	NH ₄ .
Br	155	158	155.5	157.5
I	157	155	157.5	157.5
CNS	—	169	170.0	171.0
NO ₃ *	132	—	—	—

* Benz, *Diss.*, Lausanne, 1905.

From these results Dutoit and Levier conclude that Kohlrausch's law of the independent migration of the ions is valid for solutions in acetone. The same authors have applied Ostwald's dilution law to some of the above salts, but find that the "constant" falls with increasing dilution.

In connexion with the question of transport numbers, Carrara (*loc. cit.*) draws the conclusion that in general there is a tendency on the part of each ion to reach a limiting value independent of the nature of the solvent. This scarcely seems to be borne out in the case of acetone, however. In the particular instance of silver nitrate, Jones and Rouiller (*loc. cit.*) state that the solubility of the salt in acetone is too slight to make a direct determination of the transport number, but that a value may be obtained by extrapolation from results obtained in acetone-water mixtures, the acetone concentration rising from zero to 75 per cent. Naturally, the extrapolation is a rather large one, and Jones and Rouiller have only felt justified in giving the result as an inequality, namely, the transport number of NO₃' at 25° in acetone >0.62 .

Experiments with methyl alcohol-acetone mixtures also lead on extrapolation to a value for the transport number greater than 0.6.

EXPERIMENTAL.

Kahlbaum's acetone was twice distilled over metallic calcium, the middle fraction being kept in a glass bottle, from which moisture was carefully excluded by calcium chloride tubes.

The most concentrated solution of silver nitrate conveniently prepared was 0.02*N*. The solvent and solutions were kept, and the measurements carried out in weak artificial light, as it was noticed that on exposure to sunlight a brown precipitate forms in the solutions. Under the conditions specified the solutions remain permanently homogeneous.

I.—Conductivity Measurements.

The usual Wheatstone bridge and telephone method was employed. The cell, from which moisture was excluded, contained

two large unplatinised platinum plates close together, the cell constant being small, namely, 0.09213.

The measurements were made at 18°, an oil-bath being employed as the resistances were in all cases fairly large. The following table contains the specific and molecular conductivities of silver nitrate.

TABLE I.

Concentration in gram-mols./litre.	Specific conductivity (mhos) $\times 10^5$.	λ_{∞} . Molecular conductivity.
0.02	14.37	7.19
0.01	10.17	10.17
0.007	7.42	10.60
0.005	5.50	11.00
0.0035	3.97	11.34
0.002	2.51	12.54
0.001	1.46	14.62
0.0005	0.98	19.68

Our values at 18° are slightly lower than those of Laszczynski, and slightly higher than those of Jones and Rouiller (at 25°).

The value of λ_{∞} for silver nitrate cannot be obtained directly. The empirical expression $\lambda_{\infty} \eta = \text{constant}$ (compare Walden, *Zeitsch. physikal. Chem.*, 1906, **55**, 207) independent of the solvent, η being the viscosity of the solvent, does not appear to hold for acetone; thus, on comparing the viscosities of water and acetone, one finds that λ_{∞} for silver nitrate in acetone = 371, a value which is certainly too great. Again, Kohlrausch's expression, $\lambda_v = \lambda_{\infty} - a \sqrt[3]{c}$, where a is a constant and c the concentration, has found application in those cases in which λ_v is a linear function of $\sqrt[3]{c}$; although this condition is approximately fulfilled in the present instance, the values for λ_{∞} given by the formula vary from 45 to 78.

A moderate approximation may, however, be obtained in the following way: According to Laszczynski, λ_{∞} for simple salts in acetone is 1.3 times that in water. For silver nitrate at 18°, $\lambda_{\infty} = 116$, and hence in acetone $\lambda_{\infty} = 151$. This is not very different from the directly determined values for alkali bromides and iodides in acetone ($\lambda_{\infty} = 155$ —160, Dutoit and Levier), and since in water the λ_{∞} for silver nitrate does not differ much from that of these salts, we have assumed that the same holds for acetone solution and have taken λ_{∞} for silver nitrate = 150. The conclusions which we draw from the results in which λ_{∞} is employed are not invalidated, even if a large percentage error (up to 30 per cent.) were involved in this quantity; further, the majority of the electromotive force measurements given later are independent of λ_{∞} .

The following table contains the degrees of dissociation of silver nitrate in acetone, the Ostwald dilution law $\alpha^2/(1-\alpha)v$, and the

empirical expressions $\alpha^3/(1-\alpha)^2v$ and $\alpha^2/(1-\alpha)\sqrt{v}$ of van't Hoff and Rudolphi respectively.

TABLE II.

Molar concentration.	$\alpha = \lambda_v/\lambda_\infty$.	Ostwald K.	van't Hoff K.	Rudolphi K.
0.02	0.048	0.0448	0.0244	0.0342
0.01	0.068	50	362	496
0.007	0.070	37	277	442
0.005	0.073	29	226	407
0.0035	0.075	21	173	360
0.002	0.084	15	141	345
0.001	0.097	14	102	329
0.0005	0.131	09	149	441

The Ostwald constant falls steadily as the dilution increases. The van't Hoff constant is also not very satisfactory, the most consistent values being given by Rudolphi's formula. It is thus apparent that silver nitrate in acetone behaves like a strong electrolyte in not obeying Ostwald's law, but at the same time the extent of the dissociation is that of a weak electrolyte (in water). This opens the question as to what is the criterion to be employed to decide whether an electrolyte is "weak" or "strong."

The conductivity of lithium nitrate in acetone (which is required in connexion with the *E.M.F.* measurements) was also determined, with the following result.

TABLE III.

Lithium Nitrate in Acetone at 18°.

Molar concentration.	Specific conc. $\times 10^3$.	λ_v .	$\alpha = \lambda_v/\lambda_\infty$.	Ostwald K.	Rudolphi K.
0.343*	2.4	7.0	0.053	0.022101	0.02176
0.1715	1.39	8.1	0.061	0.67	160
0.0858	0.82	9.54	0.072	0.48	—
0.0429	0.50	11.6	0.088	0.36	—
0.0214	0.31	14.5	0.110	0.29	0.02200
0.0107	0.20	19.0	0.144	0.26	—
0.0053	0.13	24.5	0.186	0.22	—
0.0026	0.087	33.4	0.253	0.22	0.02430
0.0013	0.057	44.0	0.333	0.22	—
0.00065	0.037	57.0	0.432	0.21	0.02840
0.00032	0.024	75.0	0.568	0.23	0.0120

* Saturated.

The value of λ_∞ for lithium nitrate as determined by Benz (Dutoit and Levier, *loc. cit.*) is 132, and this has been employed in the calculation of the three last columns in the above table.* It will be observed that for dilutions $v > 100$ the Ostwald expression is constant, whilst the Rudolphi formula does not hold—and this

* Kohlrausch's formula is also inapplicable here, because λ is not a linear function of $\sqrt{c}$.

in spite of the fact that the dissociation is much greater than in the case of silver nitrate. Dissociation of itself is therefore not necessarily the source of the inapplicability of the Ostwald law. From the data given above it is found that the concentration of NO_3' in the saturated solution of lithium nitrate is 0.0182 gram-ions per litre at 18° . This quantity is required later.

II.—*Electromotive Force Measurements.*

A calibrated slide-wire potentiometer (Land- und Seekabelwerke) accurate to 0.1 millivolt was employed. The Weston cell was taken as standard ($E.M.F. = 1.0183$ volts). Since it was anticipated that the quantity of current which could be obtained from the silver nitrate concentration cells would be very small, a galvanometer was not employed. Instead, an evacuated capillary electrometer was used. This type of instrument suffers as a rule from the defect that its capacity is too great. The vacuum type, however, is much more sensitive than the ordinary form, probably due to the fact that since air is excluded the quantity of Hg^{++} ions in solution is less than in the ordinary instrument, and hence the capacity of the Helmholtz double-layers is less.* Employing the Weston cell as a source of $E.M.F.$, it was observed that with the electrometer readings could be made to 0.1 millivolt. With the silver nitrate-acetone cells the reading is only accurate to 2 millivolts. The sensitivity is therefore not sufficient for very accurate work.

Electromotive Forces which include Liquid/Liquid Potential Difference.

For the ordinary type of cell,

the expression for the electromotive force at 18° is:

$$E = \frac{2v}{u+v} \frac{RT}{nF} \log \frac{a_1 c_1}{a_2 c_2} \quad \text{or} \quad \frac{2v}{u+v} 0.0577 \log \frac{\lambda_1 c_1}{\lambda_2 c_2}.$$

where λ_1, λ_2 are the molecular conductivities at the AgNO_3 concentrations c_1 and c_2 ; $v/u+v$ = transport number of $\text{NO}_3' = 0.62$.

It was our object to investigate if the Nernst formula held good for acetone solutions. Table IV contains the results obtained, the headings of the columns being self-explanatory.

It will be observed that the differences between observed and calculated values are about as frequently positive as negative. The results obtained therefore support the view that Nernst's formula is applicable. Incidentally, also, the agreement obtained goes to show

* Experiments are being undertaken in this laboratory with a view further to improve, if possible, the sensitivity of the capillary electrometer.

TABLE IV.

Temperature.	Molar concentration of AgNO ₃ .		<i>E.M.F.</i> observed			<i>E.M.F.</i> calculated.
	<i>c</i> ₁ .	<i>c</i> ₂ .	1st determination.	2nd.	3rd.	
19°	0·02	: 0·01	0·014	0·013	{ 0·015 0·013	0·011
19·5	0·02	: 0·007		0·020	0·020	0·028
19	0·02	: 0·005	[0·029]	0·034	0·035	0·033
20	0·02	: 0·0035		0·045	0·045	0·040
19	0·02	: 0·002	0·054	0·052	0·052	0·054
19	0·02	: 0·001	0·056	0·057	0·058	0·070
19	0·02	: 0·0005	{ 0·085 0·086	0·084	0·085	0·087
20	0·02	: 0·00005		0·121	0·121	—
19	0·01	: 0·007		0·012	0·011	0·009
19	0·01	: 0·005		0·025	0·024	0·019
20	0·01	: 0·0035		0·029	{ 0·028 0·027	0·026
19	0·01	: 0·002		0·037	0·038	0·043
19	0·01	: 0·001		0·045	0·045	0·060
19	0·01	: 0·0005		0·074	0·073	0·073
19	0·01	: 0·00005	0·119	0·120	0·118	—
20	0·007	: 0·005		0·013	0·015	0·009
20	0·007	: 0·0035		0·015	{ 0·017 * 0·016	0·019
20	0·007	: 0·002		0·032	0·032	0·033
20	0·007	: 0·001		0·042	0·042	0·050
20	0·007	: 0·0005		{ 0·055 0·056		0·062

* Neustadt measured this combination, his value being 0·016—0·017*v*, which is in good agreement with our result. Neustadt did not attempt to calculate the *E.M.F.*

that the value 0·62 for the transport number of NO₃' in acetone must be fairly correct. Employing this, we can calculate the magnitude of the liquid/liquid potential differences (included in the above measurements) by means of the expression:

$$E_1 = \frac{u-v}{u+v} 0\cdot0577 \log \frac{\lambda_1 c_1}{\lambda_2 c_2}$$

TABLE V.

Liquid/Liquid Potential Difference in Volts (at 18°).

Molar concentration of AgNO ₃ .	P.D. calculated.
0·02 : 0·01	0·002
0·02 : 0·001	0·013
0·01 : 0·007	0·001
0·01 : 0·005	0·004
0·01 : 0·002	0·008
0·01 : 0·001	0·012
0·01 : 0·0005	0·014

The liquid/liquid potential difference is therefore not negligible when the concentration-ratio of the salt exceeds 5.

Attempts to Eliminate the Liquid/Liquid Potential Difference.

As ammonium nitrate has been frequently employed in aqueous solution to eliminate the liquid potential difference, we had hoped to employ it in the present case, but its solubility in acetone is very slight, as is also the solubility of sodium nitrate. Ammonium acetate dissolves to a certain extent, but it is unsuitable for the purpose, since the solution (in presence of air) darkens, and on pouring it into water a green fluorescence is observed, indicating the formation of a compound. The solubility of potassium nitrate in acetone at 18° was found to be 0.001 gram-molecule per litre. A saturated solution of dry lithium nitrate was under the same conditions found to be 0.343*N*. Owing to its greater solubility, lithium nitrate was therefore employed, although the great inequality in the mobility of its ions in water is not a recommendation.* Two sets of experiments were carried out, (*a*) with lithium nitrate (or potassium nitrate) interposed between the silver nitrate solutions, and (*b*) with lithium nitrate present throughout the cell.

(a) Potassium and Lithium Nitrates Interposed.

The following table contains the *E.M.F.* values obtained with potassium nitrate as the middle liquid:

TABLE VI.

Temperature.	Molar concentration of AgNO_3 .		<i>E.M.F.</i> observed.	<i>E.M.F.</i> observed without KNO_3 interposed.
	c_1 .	c_2 .		
19°	0.01 :	0.007	0.011	0.011
19	0.01 :	0.005	0.024	0.024
20	0.01 :	0.0035	0.028	0.028
19	0.01 :	0.002	0.048	0.037
19	0.02 :	0.007	0.020	0.020
19	0.02 :	0.005	0.031	0.035
20	0.02 :	0.0035	0.045	0.045
19	0.02 :	0.002	0.053	0.052
19	0.02 :	0.001	0.058	0.058

The interposition of potassium nitrate has no reasonable effect, as was to be expected from its slight solubility. The measurements in this case were the most difficult to obtain.

The following table contains the results obtained on interposing saturated lithium nitrate solution (0.343*N*) as the middle liquid:

* This is probably of little significance, however, since the Li ion has been shown to be greatly hydrated in aqueous solution, while it may be "normal" in acetone.

TABLE VII.

Temperature.	Molar concentration of AgNO_3 .		<i>E.M.F.</i> observed.	<i>Increase in E.M.F.</i> in volts due to inter- position of LiNO_3 .
	c_1	c_2		
19°	0·02	: 0·01	0·019, 0·020	0·005
19	0·02	: 0·007	0·028	8
19	0·02	: 0·005	0·041	7
19	0·02	: 0·0035	0·052	7
19	0·02	: 0·002	0·068	16
19	0·02	: 0·001	0·065	7
19	0·02	: 0·0005	0·134 (?)	47 (?)
19	0·01	: 0·007	0·017, 0·019	6
19	0·01	: 0·005	0·034	9
19	0·01	: 0·0035	0·035	8
20	0·01	: 0·002	0·064	7
19	0·01	: 0·001	0·053	8
20	0·01	: 0·0005	0·075	2
20	0·007	: 0·005	0·022	8
20	0·007	: 0·0035	0·023	7
20	0·007	: 0·002	0·033, 0·039	6
20	0·007	: 0·001	0·048	6
20	0·007	: 0·0005	0·063	7

The important fact brought out by the above results is that a saturated solution of lithium nitrate *raises* the *E.M.F.* of the cell instead of lowering it, as one would expect in accordance with the following:

$c_1 > c_2$. Liquid/liquid P.D. = E_1 .
Transport number of anion $> 0\cdot5$.
Net *E.M.F.* of cell = E .

$E_1 = 0$.
Net E should be less
than in previous case.

The lithium nitrate solution, instead of eliminating E_1 , sets up a potential difference of its own in the same sense as the E_1 in the original case.

(b) *Lithium Nitrate Solution Throughout the Cell.*

In view of the abnormal behaviour of lithium nitrate when interposed, it is of interest to examine its effect when distributed throughout the cell, in which case, on theoretical grounds, any convenient electrolyte sufficiently soluble should eliminate the liquid/liquid potential difference. First, it is necessary to tabulate the

values for the silver ion concentration in the various solutions when allowance is made for the presence of the saturated lithium nitrate solution. As we have already seen, this solution gives rise to a NO_3^- concentration 0.0182 gram-ions per litre, which may be regarded as remaining practically constant in all cases, thereby throwing back the dissociation of the silver nitrate to a different extent in each solution. The problem would be easy if silver nitrate in acetone obeyed the dilution law, but this is not the case. As an approximation, however, the silver ion concentration in presence of the lithium salt has been calculated, first, by employing the various values found for the Ostwald "constant" at the corresponding molar concentrations of the silver salt, the results being given in the following table, column 2; and, secondly, by employing the mean of the values of the Ostwald constant, the results in this case being given in the third column.

TABLE VIII.

Molar concentration of AgNO_3 .	$[\text{Ag}^+]$ calculated from the corresponding "K."	$[\text{Ag}^+]$ calculated from the mean $K=0.0428$.
0.02	0.0527	0.0307
0.01	0.0275	0.0154
0.007	0.0142	0.0107
0.005	0.0079	0.0077
0.002	0.0016	0.0038
0.001	0.00077	0.0015
0.0005	0.00025	0.00077

The values of the silver ion concentration thus obtained are used to calculate the *E.M.F.* of the cell (containing lithium nitrate throughout), the formula when there is no liquid/liquid potential difference being:

$$E = 0.0577 \log \frac{[\text{Ag}^+]_{\text{I}}}{[\text{Ag}^+]_{\text{II}}},$$

in which the square brackets denote concentration terms. In the following table are given the observed *E.M.F.*'s, the *E.M.F.* calculated from the data in column 2, table VIII, and the *E.M.F.*'s calculated from column 3, table VIII, respectively.

TABLE IX.

Temperature 19°.

Molar concentrations of AgNO_3 .	<i>E.M.F.</i> in volts observed.	<i>E.M.F.</i> calculated from col. 2, table VIII.	<i>E.M.F.</i> calculated from col. 3, table VIII.
0.02 : 0.01	0.013	0.0163	0.0173
0.01 : 0.007	0.0122	0.0166	0.009
0.01 : 0.005	0.0245, 0.0249	0.0313	0.0173
0.01 : 0.002	0.060	0.0715	0.035
0.01 : 0.001	0.069	0.0895	0.0583
0.01 : 0.0005	0.086	0.118	0.0750

It may be noted that with lithium nitrate throughout the cell measurements could be made much more easily than in the previous cases. The error does not exceed 0.5 millivolt.

We may also obtain a series of values by calculation, without taking the silver ion concentration values into account, if we assume that the dissociation of silver nitrate approximately obeys the dilution law, and that the dissociation is small compared to that of lithium nitrate. In such a case we have:

$$\frac{[\text{Ag}^+]_{\text{I}}}{[\text{Ag}^+]_{\text{II}}} = \frac{\text{Molar concentration AgNO}_{3\text{I}}}{\text{Molar concentration AgNO}_{3\text{II}}}$$

The values worked out by this method were practically identical with those given in column 4, table IX.

It will be observed that the found values lie between the two series of calculated values. It is therefore impossible to state with certainty whether there is agreement or not, the indefiniteness arising from the fact that silver nitrate does not obey Ostwald's dilution law accurately.

Summary.

(1) Silver nitrate in acetone is only slightly dissociated. It does not, however, obey Ostwald's dilution law, but gives a good constant in Rudolphi's expression.

(2) Lithium nitrate in acetone is much more dissociated than silver nitrate. For dilutions $v > 100$ Ostwald's law holds well. Rudolphi's expression does not hold.

(3) It has been shown that the electromotive force of the silver nitrate concentration cell in acetone at 19°, arranged so as to contain a liquid/liquid potential difference as well as electrode potential differences, is in quantitative agreement with Nernst's formula, the value of the transport number of NO_3^- being taken as 0.62.

(4) The interposition of a saturated solution of lithium nitrate between the two silver nitrate solutions, instead of eliminating the liquid/liquid potential difference, increases the latter by several millivolts. The introduction of lithium nitrate throughout the cell has the desired effect so far as it has been possible to decide in view of the approximate nature of our knowledge of the silver ion concentration.

In conclusion, we wish to thank Dr. N. T. M. Wilsmore for the interest which he has taken in these experiments.

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