CLXVI.—*The Solubility of Beryllium Oxide in Solutions of its Salts.*

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AQUEOUS solutions of beryllium salts are known to be able to dissolve considerable quantities of the oxide, a property also possessed, but in a much smaller degree, by salts of iron, aluminium, and some other metals. A concentrated solution of the beryllium salt of a strong acid continues to dissolve the basic carbonate with brisk effervescence even after the addition of more than one mole of base to each mole of salt present.

With the sulphate, Parsons (*J. Amer. Chem. Soc.*, 1904, **26**, 1433) found that the solubility of the oxide increased with the concentration of the salt, and in strong solution exceeded two moles to one mole of salt. No definite basic salts could be isolated : on dilution the more highly basic solutions gave flocculent precipitates ; on evaporation all left glassy residues with varying ratios of Be : SO_4. The basic sulphates described by Berzelius and others were shown not to be definite compounds. Similar results were obtained with the oxalate (Parsons and Robinson, *ibid.*, 1906, **28**, 555). Parsons, Robinson, and Fuller (*J. Physical Chem.*, 1907, **11**, 651) showed that the f. p. of beryllium sulphate solution is slightly raised by the addition of the oxide, and its conductivity slightly diminished; they concluded that the basic solutions are not colloidal, since they cannot be separated by dialysis, and are not coagulated by electrolytes. The only suggestion they make to explain the results is that the salt solution acts as a mixed solvent, the oxide dissolving in the salt as camphor dissolves in acetic acid even when it is diluted with water.

Recently Britton (J., 1925, **127**, 2121) has examined electrometrically the effect of adding sodium hydroxide to beryllium sulphate solution. He finds that no precipitation occurs until 1·04 moles of sodium hydroxide have been added for each mole of beryllium sulphate. He concludes that the solution is mainly colloidal, although he admits that it is not coagulated by electrolytes and that it " betrays no sign of colloidality."

We have examined the question by measurements of (1) the solubilities and (2) the viscosities and conductivities of these basic solutions. Parsons's investigation of the system BeO,SO_3,H_2O did not extend beyond solutions containing 5% $BeSO_4$, and his results were vitiated, as he admits, by the absence of any definite solid phase. The only such phase appears to be the normal sulphate $BeSO_4,4H_2O$, and we have therefore determined the effect of addition of the oxide on the solubility of this salt : similar measurements were also made with the selenate and the oxalate. As the existence of an acid oxalate has been asserted and denied, the system $BeC_2O_4,H_2C_2O_4,H_2O$ also was examined.

In addition, the conductivities of neutral and basic chloride and oxalate solutions and the viscosities of neutral and basic chloride, oxalate, sulphate, and selenate solutions were measured.

EXPERIMENTAL.

Solubility of Beryllium Sulphate.—The sulphate was purified by recrystallisation from water. The hydroxide, precipitated with ammonia, was dissolved in ammonium carbonate, precipitated as the basic carbonate by passing in a current of steam, washed, and heated for several hours in water through which a current of air was drawn.

Suitable complexes were made by dissolving this basic carbonate in concentrated solutions of the sulphate, boiling to expel carbon dioxide, and filtering. They were rotated in the thermostat at 25·00° ± 0·05° in rubber-stoppered tubes for periods varying from 20 hours for the more dilute to 200 hours for the most concentrated and viscous solutions, from which the salt crystallised rather slowly. For each analysis two samples were withdrawn through cotton-wool filters into calibrated pipettes, and weighed, giving approximate values of the density. One of these was evaporated to dryness with excess of sulphuric acid and weighed as $BeSO_4$ (which is stable up to 500° : Kraus and Gerlach, *Z. anorg. Chem.*, 1924, **140**, 69) or heated in a muffle and weighed as BeO. In the other, the SO_4 was determined with barium chloride. The moist solids obtained by filtration were analysed in the same way. The increasing viscosity made it impossible to measure the complete isotherm. The solid phase was shown by the residue method to be in all cases $BeSO_4,4H_2O$. As the amount of dissolved beryllium oxide is obtained by difference, and also on account of its very low equivalent weight, the experimental error is necessarily large.

The results are in Table I.

TABLE I.

Solubility of $BeSO_4,4H_2O$ in presence of BeO.

	Per cent.			Molecular ratio.	
$d^{25°}_{4°}$.	$BeSO_4$.	BeO.	Extra $BeSO_4$.	BeO : $BeSO_4$.	BeO : extra $BeSO_4$.
1·278	29·74	—	—	—	—
1·318	31·73	2·16	1·99	0·286	4·55
1·327	32·12	2·62	2·38	0·343	4·62
—	33·86	4·03	4·12	0·500	4·11
1·347	34·55	4·26	4·81	0·517	3·75
—	34·87	5·02	5·13	0·605	4·11
—	36·46	6·10	6·72	0·703	3·81
1·416	37·48	7·73	7·74	0·867	4·19
				Mean	4·14

The solubility of the pure sulphate at 25° was found to be 29·74%, which agrees fairly well with the value, 29·94%, obtained by Britton and Allmand (J., 1921, **119**, 1463).

In the last column is given the molecular ratio of the oxide present to the increase of solubility of the sulphate. It thus appears that 1 molecule of salt dissolves for every 4 molecules of oxide added.

In the analogous case of increasing solubility of lead acetate in the presence of lead oxide (Jackson, *J. Amer. Chem. Soc.*, 1914, **36**, 2346) the results calculated in this way show a much more rapid increase of solubility (about 3 moles of acetate to one of oxide).

To see whether the effect is general, other beryllium salts should be examined. Most of the salts, however, are excessively soluble, and many (*e.g.*, the chloride) crystallise with difficulty, especially in presence of the base. The perchlorate, $Be(ClO_4)_2,4H_2O$, was prepared, but its solubility at 25° was found to be 59·5% (anhydrous salt). The *benzenesulphonate* and the p-*toluenesulphonate*, which have not been previously described, were prepared by crystallisation from a solution of the basic carbonate in slightly more than its equivalent of the acid. These salts gave off their water of crystallisation at 100°; decomposition also commenced at that temperature. The salts were recrystallised from water. The *benzenesulphonate* formed small, elongated tablets [Found : BeO, 6·3. $Be(C_6H_5{\cdot}SO_3)_2,4H_2O$ requires BeO, 6·33%. Solubility at 25° = 53·8% (of anhydrous salt)]. The p-*toluenesulphonate* formed a mass of minute crystals which were only slightly denser than their saturated solution [Found : BeO, 5·9. $Be(C_7H_7{\cdot}SO_3)_2,4H_2O$ requires BeO, 5·91%. Solubility at 25° = 39·2% (of anhydrous salt)].

The great solubility of these three salts, and the difficulty of estimating the anions accurately, make them unsuitable : the only suitable salts seem to be the selenate and oxalate.

Solubility of Beryllium Selenate.—The salt was prepared by dissolving the basic carbonate in a slight excess of selenic acid, made by the oxidation of selenious acid with chloric acid (Meyer and Moldenhauer, *Z. anorg. Chem.*, 1921, **116**, 193), and was twice recrystallised from water. It was free from selenite, and had the composition $BeSeO_4,4H_2O$ (Found : BeO, 11·3; Se, 35·4; H_2O, 32·7. Calc.: BeO, 11·15; Se, 35·3; H_2O, 32·1%). The selenate was determined by reduction to selenium (Jannasch and Müller, *Ber.*, 1898, **31**, 2388). The salt loses rather more than half its water at 100—105°, and the rest at 300°, at which temperature the anhydrous salt is quite stable.

The solubilities were measured as before. The results at 25° are in Table II, each being the mean of two determinations.

The molecular ratio is the same as with the sulphate, within the limits of experimental error.

TABLE II.

Solubility of $BeSeO_4,4H_2O$ in presence of BeO.

Per cent.			Molecular ratio.	
$BeSeO_4$.	BeO.	Extra $BeSeO_4$.	BeO : $BeSeO_4$.	BeO : extra $BeSeO_4$.
36·22	0·046	—	0·008	—
37·05	0·60	0·83	0·098	4·0
38·84	1·98	2·62	0·311	4·5
40·23	2·98	4·01	0·451	4·4
42·11	3·71	5·89	0·536	3·8
				Mean 4·2

Solubility of Beryllium Oxalate.—The salt was prepared from the basic carbonate and slightly more than its equivalent of oxalic acid and the measurements were carried out in the same way as before. Parsons and Robinson (*loc. cit.*) state that the slightest excess of base entirely prevents the crystallisation of the oxalate. This was not confirmed, although the crystallisation from the more basic solutions is rather slow, lasting about a day.

The results at 25° are in Table III.

TABLE III.

Solubility of $BeC_2O_4,3H_2O$ in presence of BeO.

	Per cent.			Molecular ratio.	
$d^{25°}_{4°}$.	BeC_2O_4.	BeO.	Extra BeC_2O_4.	BeO : BeC_2O_4.	BeO : extra BeC_2O_4.
1·179	28·20	0·08	—	0·011	—
1·224	31·73	1·31	3·53	0·160	1·35
1·259	35·01	2·35	6·81	0·260	1·29
1·282	37·17	3·23	8·97	0·337	1·36
—	41·69	4·02	13·49	0·373	(1·13)
1·290	38·20	3·52	10·00	0·367	1·33
					Mean 1·33

The analysis of the moist solids from experiments 2, 3, and 4 showed the solid phase to be in each case the normal oxalate $BeC_2O_4,3H_2O$. In calculating the results in the last column, the small quantity of oxide present in the first experiment was subtracted. The calculated solubility of the pure oxalate at 25° is 27·97%.

The oxalate thus resembles the sulphate and selenate in that its solubility is increased by the addition of the oxide, but the rate of increase is three times as great: 3 molecules of salt for every 4 molecules of oxide added.

In view of the possible formation of complex oxalates, the system was examined on the acid side ($BeC_2O_4,H_2C_2O_4,H_2O$). Rosenheim and Woge (*Z. anorg. Chem.*, 1897, **15**, 283) obtained from a solution containing excess of oxalic acid crystals of the composition

$2BeC_2O_4,H_2C_2O_4,5H_2O$. Parsons and Robinson (*loc. cit.*) could not obtain this, but only mixtures of crystals which were recognised under the microscope as those of the normal oxalate and of oxalic acid; they observed that the last traces of oxalic acid were very difficult to remove from the salt by recrystallisation. Wirth (*Z. anorg. Chem.*, 1914, **87**, 7) found the solubility of $BeC_2O_4,3H_2O$ in water at 25° to be 24·85% (of anhydrous salt), and in *N*/10-oxalic acid 27·75%, from which he concludes that complex acid salts are formed. The former value does not agree with our results, but the latter does, our values for the corresponding solubilities being 27·8% and 27·5%, respectively.

The system $BeC_2O_4,H_2C_2O_4,H_2O$ was measured at 25° by the methods already described. The complexes were heated until homogeneous, and rotated 18—36 hours in the thermostat to crystallise. The results are in Table IV. Compositions are in weights %.

TABLE IV.

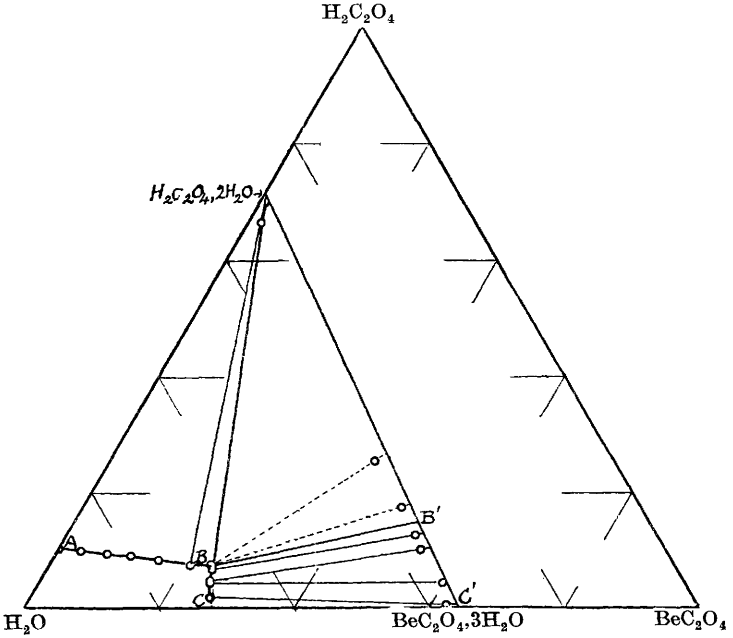
System BeC_2O_4–$H_2C_2O_4$–H_2O at 25°.

		Percentage composition.			
		Solution.		Moist solid.	
No.	$d^{25°}_{4°}$.	BeC_2O_4.	$H_2C_2O_4$.	BeC_2O_4.	$H_2C_2O_4$.
1	1·178	26·55	1·81	62·18	0·45
2	1·187	25·33	4·42	59·85	4·40
3	1·188	25·23	4·79	53·57	10·11
4	1·197	24·49	6·88	51·53	12·68
5	1·184	23·90	7·51	47·15	17·60
6	1·197	24·01	7·46	39·11	25·38
7	1·168	20·78	7·63	1·90	66·76
8	1·139	15·79	8·46	—	—
9	1·112	11·24	9·07	—	—
10	1·087	7·60	9·52	—	—
11	1·064	3·45	10·03	—	—
12	1·043	0·00	10·23	—	—

The results are plotted in Fig. 1. The curve AB gives solutions in equilibrium with $H_2C_2O_4,2H_2O$; curve BC those in equilibrium with solids ranging from B′ to C′ which are obviously mixed crystals of $BeC_2O_4,3H_2O$ and $H_2C_2O_4,2H_2O$. It will thus be seen that there is no evidence for the existence of an acid salt such as that described by Rosenheim and Woge. This mixed crystal formation also explains the difficulty of Parsons and Robinson in removing the last of the oxalic acid impurity from beryllium oxalate by recrystallisation. It is very unusual for a salt to form mixed crystals with its own acid.

Measurement of Viscosities.—Concentrated solutions of the sulphate and the selenate were made up from the crystalline salts; those of the chloride and oxalate by dissolving the basic carbonate in the necessary amount of acid, and determining the composition by analysis. The basic solutions, likewise analysed, were made up in the same way. They were all carefully filtered, and the dilute solutions made up from them by weight. The densities were measured in a pyknometer, and the viscosities in an Ostwald viscometer of period 84·6 seconds with water at 25°. Every value is the mean of two or more concordant results. The values given in Tables V and VI are of the equivalent normality of the salt, and of the relative viscosity (water at 25° = 1).

FIG. 1.



System $BeC_2O_4,H_2C_2O_4,H_2O$ *at* 25°.

It will be seen that the increase of viscosity caused by the base in dilute solutions is relatively small, and is little affected by the nature or concentration of the salt. The viscosity of the solution did not change on standing, or on heating to 100° and cooling again, which indicates that the phenomenon is not colloidal.

Conductivities.—These were measured in the usual way for neutral and basic chloride and oxalate solutions made up and analysed as above described, the results being given in Tables VII—X. The conductivity of the water ($1{\cdot}3$ to $1{\cdot}9 \times 10^{-6}$) was subtracted. The concentrations are equivalent normalities of salt present; the

TABLE V.

Viscosities of neutral and basic solutions of beryllium chloride.

Equivalent normality.	$d^{25°}_{25°}$.	Relative viscosity (water at 25° = 1).	Composition of solution.
0·338	(1·0089)	1·076	Neutral (equivalents Be : Cl = 0·997 : 1·000).
0·683	(1·0178)	1·170	
1·014	1·0265	1·245	
1·936	1·0494	1·524	
2·770	1·0700	1·816	
3·810	1·0948	2·255	
5·308	1·1295	3·065	
7·671	1·1852	5·184	
0·569	1·0182	1·153	Basic (0·476 mole BeO per mole $BeCl_2$).
1·209	1·0394	1·355	
2·255	1·0721	1·761	
3·274	1·1009	2·299	
4·757	1·1437	3·485	
5·990	1·1780	4·943	
7·539	1·2242	8·005	
0·590	(1·0223)	1·192	Basic (0·987 mole BeO per mole $BeCl_2$).
0·899	(1·0339)	1·295	
1·741	(1·065)	1·653	
2·460	1·0902	2·056	
3·602	1·1311	2·970	
4·633	1·1662	4·299	
4·955	1·1762	4·836	
6·028	1·2110	7·322	
7·350	1·2550	13·36	
0·0472	1·0022	1·016	Basic (1·760 moles BeO per mole $BeCl_2$).
0·1080	1·0050	1·036	
0·340	1·0160	1·114	
0·641	1·0301	1·238	
1·055	1·0489	1·441	
1·738	1·0792	1·893	
4·190	1·1855	6·968	

conductivities are also equivalent. The fourth column gives the product of the conductivity and the viscosity. Temperature 25° ± 0·02°. The values for the chloride solutions are in Tables VII and VIII (b = moles of BeO per mole of salt).

In Fig. 2, the product of equivalent conductivity and viscosity is plotted against the cube root of the concentration, the crosses representing the values of Fricke and Schützdeller (*Z. anorg. Chem.*, 1924, **131**, 130) for solutions obtained by double decomposition from beryllium sulphate and barium chloride. It will be seen that the conductivity is less in the basic solutions, but only by about 5%.

The hydrogen-ion concentration in beryllium chloride solutions at 25° has been measured colorimetrically by Mr. W. J. Worboys in this laboratory (results not yet published). He finds this to vary from 1·24% of the salt concentration in *N*/8-solution to 3·68% in *N*/512. If we assume that the hydrolysis takes place thus : $BeCl_2 + H_2O = (BeOH)Cl + HCl$, the practical result will be to

TABLE VI.

Viscosities of neutral and basic solutions of beryllium salts.

Equivalent normality.	$d^{25°}_{25°}$.	Relative viscosity (water at 25° = 1).	Solution.
0·425	(1·019)	1·147	Beryllium sulphate (neutral).
0·644	1·0290	1·221	
1·109	1·0503	1·420	
1·737	1·0782	1·730	
2·638	1·1163	2·312	
3·874	1·1663	3·644	
5·878	1·2454	7·199	
0·455	1·0254	1·189	Beryllium sulphate basic (0·965 mole BeO per mole $BeSO_4$).
0·666	1·0367	1·292	
1·078	1·0593	1·516	
1·654	1·0900	1·926	
2·382	1·1274	2·644	
3·319	1·1747	4·069	
4·022	1·2104	5·843	
5·045	1·2601	10·20	
6·432	1·3240	22·80	
7·702	1·3783	51·1	
8·933	(1·426)	140·6	
0·457	1·0297	1·167	Beryllium selenate (neutral).
0·981	1·0634	1·386	
2·027	1·1288	1·985	
3·111	1·1950	2·903	
4·771	1·2940	5·864	
0·483	1·0373	1·215	Beryllium selenate basic (0·979 mole BeO per mole $BeSeO_4$).
0·983	1·0761	1·508	
2·130	1·1624	2·569	
3·336	1·2464	4·599	
4·737	1·3429	11·00	
0·565	1·0160	1·098	Beryllium oxalate neutral (equivalents Be : C_2O_4 = 0·996 : 1·000).
1·138	1·0325	1·207	
2·324	1·0663	1·493	
3·671	1·1047	1·950	
4·971	1·1419	2·564	
0·556	1·0230	1·156	Beryllium oxalate (0·974 mole BeO per mole BeC_2O_4).
1·085	1·0439	1·329	
2·267	1·0896	1·909	
3·569	1·1426	3·058	
5·011	1·1980	5·757	

TABLE VII.

Conductivities of beryllium chloride (neutral) solutions.

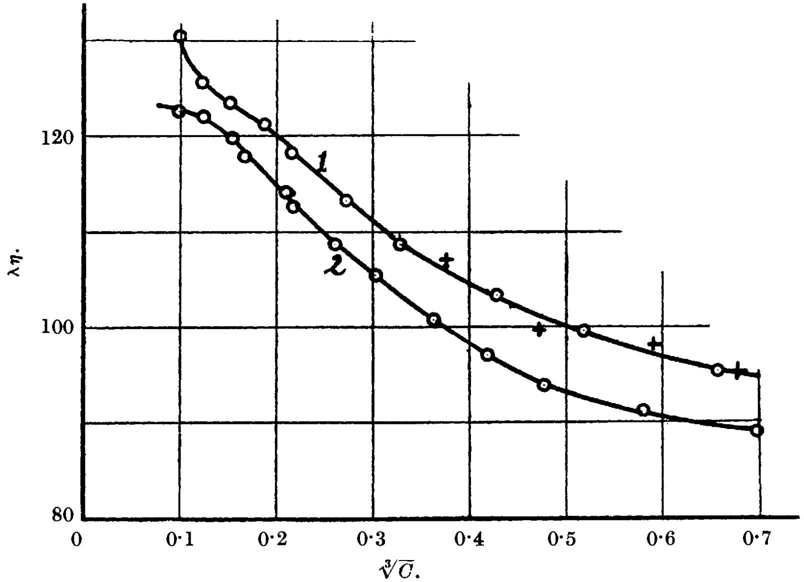
Normality.	Relative viscosity (η).	Equivalent conductivity (λ).	$\lambda\eta$.	$\lambda\eta$ (corr.).
0·001001	—	130·6	130·6	115·8
0·001832	—	125·8	125·8	114·1
0·003467	(1·001)	123·4	123·5	113·7
0·006491	(1·002)	121·1	121·3	113·3
0·009964	(1·002)	118·2	118·4	111·3
0·02014	(1·005)	112·8	113·3	107·5
0·03392	(1·008)	108·1	108·9	103·9
0·07863	(1·019)	101·3	103·3	98·8
0·1387	(1·034)	96·5	99·8	95·7
0·2840	(1·069)	89·4	95·6	—
0·5548	(1·136)	81·1	92·1	—
1·0140	1·245	72·1	89·8	—

TABLE VIII.

Conductivities of beryllium chloride (basic, b = 1·760) solutions.

Normality.	η.	λ.	λη.
0·000967	—	122·9	122·9
0·000972	—	122·8	122·8
0·001850	—	122·2	122·2
0·003568	(1·001)	119·9	120·0
0·004637	(1·002)	117·8	118·0
0·009196	(1·003)	113·7	114·0
0·01015	(1·003)	112·3	112·6
0·01763	(1·006)	107·9	108·6
0·02725	(1·009)	104·4	105·3
0·04724	1·016	99·3	100·9
0·07257	(1·025)	94·9	97·2
0·1164	(1·039)	90·5	94·0
0·1968	(1·066)	85·6	91·3
0·3400	1·114	80·0	89·1
0·6415	1·238	71·4	88·4
1·0546	1·441	63·1	91·0
1·738	1·893	52·7	99·9
4·190	6·968	26·93	187·7

FIG. 2.



Equivalent conductivities of beryllium chloride solutions. Curve 1, *neutral solution. Curve* 2, *basic* (b = 1·760) *solution.*

+ *denotes observations by Fricke & Schützdeller* (*loc. cit.*).

increase the conductivity by an amount corresponding to the hydrogen ion present. By subtracting this amount we find the conductivity of the non-hydrolysed solutions (last column in Table VII). As will be seen, this correction brings the values of the neutral very near to those of the basic solutions, except at high dilutions, where even the latter may still be perceptibly hydrolysed.

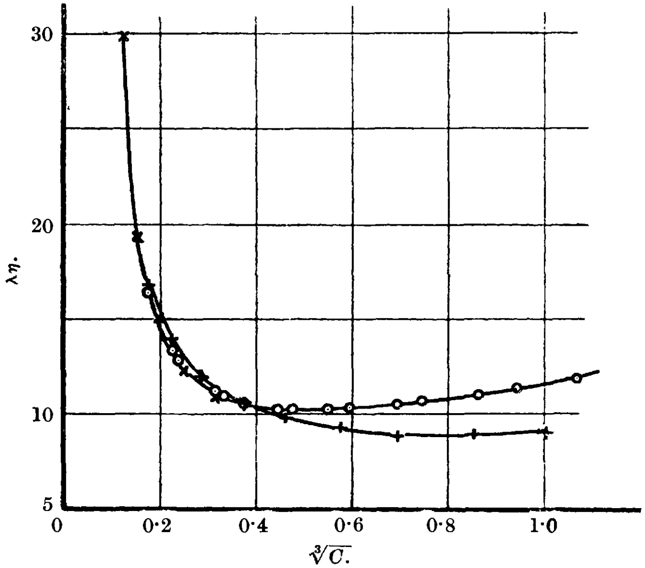
The corrected conductivities of the solutions of the neutral chloride extrapolate to a value for the mobility at 25° of $\frac{1}{2}BeCl_2$ = 118·5, corresponding to 43 for $\frac{1}{2}$Be. Fricke and Schützdeller (*loc.*

cit.) give a value of 30 for the mobility of $\frac{1}{2}$Be. This is based on their values for the conductivities of solutions from 0·05*N* to 0·5*N*; but their correction for hydrolysis is rather uncertain, being founded on a measurement by Wood (J., 1910, **97**, 878) of its value (2·2%) at 0·35*N*, from which they calculated the values at greater dilutions.

The values for the oxalate solutions are in Tables IX and X.

The results are plotted in Fig. 3, the crosses representing those of Rosenheim and Woge (*loc. cit.*).

FIG. 3.



Equivalent conductivities of beryllium oxalate solutions.

⊙ *Neutral solutions.* × *Neutral solutions* (*Rosenheim and Woge*). + *Basic* ($b = 0{\cdot}974$) *solutions.*

TABLE IX.

Conductivities of beryllium oxalate (neutral) solutions.

Normality.	η.	λ.	λη.	Normality.	η.	λ.	λη.
0·00550	1·001	16·38	16·39	0·1657	1·028	9·95	10·22
0·01407	1·002	12·81	12·83	0·2136	1·036	9·97	10·32
0·01180	1·002	13·32	13·35	0·3351	1·057	9·95	10·51
0·03202	1·005	11·08	11·13	0·4164	1·072	9·99	10·71
0 03732	1·006	10·87	10·93	0·6478	1·115	9·87	11·00
0·05323	1·009	10·49	10·58	0·8372	1·149	9·94	11·42
0·08931	1·015	10·12	10·27	1·1403	1·209	9·67	11·69
0·1084	1·019	10·09	10·28				

TABLE X.

Conductivities of beryllium oxalate (basic, b = 0·974) solutions.

Normality.	η.	λ.	$\lambda\eta$.	Normality.	η.	λ.	$\lambda\eta$.
0·00574	1·001	16·79	16·81	0·1897	1·052	8·85	9·31
0·01144	1·003	13·93	13·98	0·3397	1·094	8·02	8·78
0·02359	1·007	11·88	11·96	0·6236	1·178	7·60	8·95
0·05392	1·015	10·35	10·51	1·0245	1·307	6·90	9·02
0·1012	1·028	9·53	9·80				

The conductivities of the oxalate are very small, as may be seen by comparing them with those of the sulphate (Ley, *Z. physikal. Chem.*, 1899, **30**, 245) at the same dilutions.

Dilution (litres per equiv.)	32	128	512
Equiv. cond. of sulphate	66·4	88·7	112·6
,, ,, of oxalate	10·8	15·1	29·8

Further, the equivalent conductivity of the oxalate solution increases at concentrations above about 0·15*N*, which behaviour is probably unprecedented.

Freezing Points of Oxalate Solutions.—The depression of freezing point of aqueous solutions of the oxalate was measured in a Beckmann apparatus. The results are

Mole of salt per 1000 g. of water.	Δ.	Molecular depression.	*i*.
0·0224	0·048°	2·14°	1·15
0·0532	0·119	2·24	1·20
0·1049	0·220	2·10	1·13
0·1771	0·363	2·05	1·10
0·3665	0·720	1·96	1·05

The values of the van 't Hoff factor *i* are, in the stronger solutions, of the same order as those observed by Parsons, Robinson, and Fuller (*loc. cit.*), but at greater dilutions they are considerably lower.

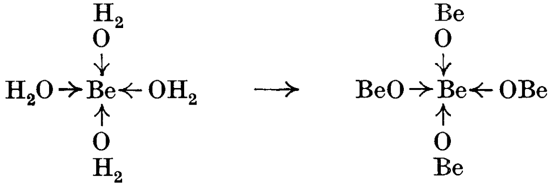
Discussion of Results.

(1) *Sulphate, Selenate, and Chloride.*—The solubility of beryllium oxide in solutions of its salts may be due to three causes. (1) The salt may make the oxide form a colloidal solution; (2) the oxide may form a basic salt, for example of the univalent ion $[BeOH]^+$, or (3) it may attach itself to one of the ions of the normal salt, in which case, since the property is common to beryllium salts in general, it must combine with the beryllium ion. The first hypothesis, that of colloid formation, has not been entirely disproved. The most basic solutions are somewhat turbid, and although they cannot be separated by dialysis, they may contain some colloidal material. But the whole of the dissolved oxide cannot be in this form. Some of the solutions described above contain more than 2, and they can be prepared with as many as 5 moles of oxide per·

litre, a concentration enormously greater than is reached by the colloidal solutions of other metallic hydroxides. Further, the stability of these solutions to the action of heat and of electrolytes is against the view that they are highly concentrated colloids, a view which also fails to explain why the salt is more soluble in presence of the oxide. The bulk of the oxide must be present in some other form. (2) The formation of basic salts of an ion $[BeOH]^+$ would not allow of the solution of more than one mole of oxide for every mole of salt, whereas more basic solutions can be prepared. It would also involve an increase of one ion for every molecule of oxide dissolved—$[Be]A + Be(OH)_2 = [BeOH]_2A$—and hence the addition of oxide should lower the freezing point and probably increase the conductivity, whereas it actually has the opposite effect.

We are therefore left with the third hypothesis, that the oxide combines with the beryllium ion to form a complex kation $[Be,xBeO]^{++}$. This would account for the small change in conductivity (3—7%, mainly due to the disappearance of hydrolysis), since the number of ions would not alter, but the " beryllated " ion might have a slightly different mobility and degree of ionisation. It is also supported by the slight decrease (about 10%) in the freezing point depression of the sulphate observed by Parsons, Robinson, and Fuller (*loc. cit.*). It explains the increase in the solubility of the salt in presence of the oxide as due to the formation of a new complex salt. If we could assume the solubility of the normal salt to be the same in presence of the complex salt as in water, the molecular ratio of the added oxide to the increased solubility of the salt (4·14 with the sulphate and 4·2 with the selenate) would indicate that the complex ion was $[Be,4BeO]^{++}$. The accompanying increase of the anion in the basic solution must, however, somewhat diminish the solubility of the normal salt, although we cannot at such high concentrations calculate the magnitude of this effect. Hence the observed ratio of 4·14 or 4·2 must be greater than the average number of BeO molecules attached to a " beryllated " Be ion.

Now there is good evidence that while the covalency of beryllium cannot exceed 4, it has a strong tendency, particularly in the ionised state, to reach this value. Its soluble salts never have more than 4 molecules of water, but seldom fail to attain this number (the case of the oxalate is discussed below). The same tendency of the atom to pass from the ionised to the covalent state is shown by the low conductivity of the fused chloride and the stability of many of its covalent organic compounds (*e.g.*, the non-ionised basic acetate). Its oxide may thus be expected readily to assume the covalent form $Be{=}O$, which could replace the water of crystallisation of the ion :



$$\begin{array}{c} H_2 \\ O \\ \downarrow \\ H_2O \rightarrow Be \leftarrow OH_2 \\ \uparrow \\ O \\ H_2 \end{array} \longrightarrow \begin{array}{c} Be \\ O \\ \downarrow \\ BeO \rightarrow Be \leftarrow OBe \\ \uparrow \\ O \\ Be \end{array}$$

This replacement will no doubt be incomplete, a series of mixed ions being formed, with the water only partly replaced by BeO, so that on the average there will be less than 4 BeO groups attached to each " beryllated " ion, as we find to be the case.

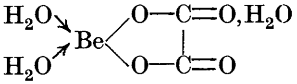
(2) *Beryllium Oxalate.*—The above hypothesis accounts for the behaviour of basic solutions of the sulphate, selenate, and chloride, and should be applicable to any solution containing beryllium ion : but the behaviour of the oxalate, which increases in solubility by about 3 molecules for every 4 of the oxide added, needs further explanation. This salt is peculiar in many ways. It is unique among the oxalates of bivalent metals in being very soluble in water (nearly 30% at 25°) : the oxalates of Mg, Ca, Sr, Ba, Zn, Cd, Hg″, Sn″, Cr″, Mn″, Fe″, Co″, and Ni are all very slightly if at all soluble. It is also almost unique among beryllium salts in not forming a tetrahydrate but only a trihydrate. These facts clearly indicate that it is not a normal oxalate. Further peculiarities which we have found are (1) the conductivity, which even at $V = 512$ is barely a quarter of that of the sulphate, and at greater concentrations falls to about a sixth, showing that (assuming the ionic mobilities to be about the same) the number of ions formed is only about a quarter of that produced by a normal bi-bivalent salt. (2) The increase of solubility of the salt on addition of oxide is three times as great as with the sulphate or selenate (1 : 1·3 instead of 1 : 4·1). (3) Finally the f. p. experiments show that the number of molecules (including ions) in the solution is not much less than it would be with a normal salt.

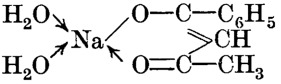
The last fact proves that the compound formed cannot have a high molecular weight, and suggests that the ions have combined to form a non-polar molecule :

$$Be[C_2O_4] \dashrightarrow [BeC_2O_4]$$

which is not improbable in view of the strong tendency (already mentioned) of the beryllium ion to pass into the covalent state, and that of the oxalate ion to form a covalent oxalato-ring, as in Werner's optically active $K_3[Cr(C_2O_4)_3]$. On this simple assumption we should conclude, since the conductivity is reduced to about a quarter, that the solution contains about 3 molecules of oxalato-compound to 1 molecule of salt. The value of i found by the f. p. method would be $1 + \frac{1}{4}\alpha$, if α is the true degree of dissociation of the salt: the observed values of i are from 1·2 at 0·05 molar normal to 1·1 at 0·37. This assumption is further supported by the fact that the compound crystallises with 3 molecules of water. The oxalate group is usually monohydrated, both as an ion and in oxalato-compounds: for example, we have $K_2C_2O_4,H_2O$; $(NH_4)_2C_2O_4,H_2O$; $(NH_4)_2[Hg(C_2O_4)_2],2H_2O$; K_3 and $(NH_4)_3[Cr(C_2O_4)_3],3H_2O$, all salts of kations which are rarely if ever hydrated. Thus one of the H_2O molecules can be attached to the oxalate group. The other two must be joined to the beryllium atom (formula I) if it is to have the stable covalency of 4 which beryllium always attains if possible, and the attainment of which always promotes the formation of covalent links, as in the sodium compound of benzoylacetone (Sidgwick and Brewer, J., 1925, **127**, 2383); this when anhydrous is a salt, but it readily takes up two molecules of water and becomes covalent (formula II), as is shown by its then being soluble in hydrocarbons.

(I.)





(II.)

A non-polar structure of this kind also makes the formation of solid solutions with oxalic acid less inexplicable.

One peculiarity of the oxalate is unexplained: the large increase (1 : 1·3 instead of 1 : 4·1) of solubility on addition of the oxide. If the latter combines only with the beryllium ion, as it does in the solutions of the strong acid salts, the ratio should be the same in both cases; for on the removal of part of the ions in the "berylated" form, the equilibrium between the polar and non-polar modifications will be restored. The only explanation would seem to be that the oxide mainly combines with the non-polar form in the ratio 1 : 1 (presumably replacing a molecule of water), but partly also with the ion, as in the sulphate and selenate, thus lowering the ratio of increased solubility to added oxide from 1 : 1 to 1 : 1·3.

The peculiar form of the conductivity curve, which scarcely falls (and if corrected for viscosity, rises) from $N/5$- to N-solution, seems to be without parallel. Since with increasing concentration the molecular conductivity of the true salt must diminish (as it does with all other salts), and likewise presumably the proportion of true salt to non-polar compound, some other reaction must intervene; but it is difficult to see what this is.

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