P and Q requires. This procedure involves rather large errors and assumes that the rate at which the composition of the solution changes along the line PQ is uniform as to sodium carbonate and the total number of moles present.

Having fixed the position of O it can be predicted that all solutions represented by points above AOZ except those on the periphery must finally attain the composition P when evaporated. Further owing to the fact that certain crystallization paths pass into the glaserite field from the potassium sulfate field there will be a small triangular area limited by the point C, the intersection of OZ and QJ and the line OZ representing solutions which have the same crystallization end-point. In a like manner it can be predicted that that portion of the diagram limited by the two areas already defined and the line YUC represents solutions for which the crystallization end-point is S, and those portions below the last named line represent solutions for which T is the crystallization end-point.

Summary

1. Certain optical and crystallographic properties of the hydrates of sodium carbonate and of the hydrate of the double sodium-potassium carbonate have been ascertained, which can be used in identifying these compounds by means of the microscope.

2. The solubility data necessary for the preparation of complete phase-rule diagrams for the systems H_2O-Na_2CO_3-KCl and H_2O-Na_2CO_3-K_2SO_4 at $25°$ have been determined.

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STUDIES RELATING TO METALLO-ORGANIC COMPOUNDS. IV. THE CONDUCTANCE OF TRIMETHYL STANNYL CHLORIDE IN MIXED SOLVENTS

BY CHARLES A. KRAUS AND WILLARD N. GREER

In preceding numbers of this series it has been shown that the alkyl tin halides are non-conductors when dissolved in solvents of the non-basic type and conductors in solvents of the basic type,[1] such as the amines and the alcohols. It has further been shown that the alkyl metal halides exhibit a marked tendency to combine with ammonia and the amines to form compounds having markedly higher melting points than either of the constituents.[2] While in some instances two molecules of ammonia or amine may combine with an alkyl metal halide, in by far the greater number of instances only a single molecule is involved. Where two molecules of am-

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[1] Kraus and Callis, THIS JOURNAL, 45, 2624 (1923).

[2] Kraus and Greer, ibid., 45, 3078 (1923).

monia or amine combine with an alkyl metal halide, one molecule is, as a rule, held rather loosely while the other is held much more firmly. This is well illustrated by the compounds of ammonia with trimethyl tin iodide, in which case one molecule of ammonia is lost readily at ordinary temperatures, while the second molecule cannot be removed by ordinary means, the compound subliming at higher temperatures or in a vacuum at lower temperatures.

It has been suggested that the electrolytic properties of the alkyl metal halides and of other similar compounds are due to the formation of a complex cation of the ammonium type; for instance, trimethyl tin chloride and ammonia combine to form the compound $H_3NSn(CH_3)_3Cl$, in which the trimethyl tin group is attached to pentavalent nitrogen.[1] This accounts for the absence of electrolytic properties in the case of the pure compounds, as well as in that of solutions of these compounds in non-basic solvents of higher dielectric constant. This view as to the constitution of these compounds may be checked up by studying the conductance of the alkyl metal halides in solution in non-basic solvents on the addition of varying quantities of a basic solvent such as an amine or an alcohol. In the present article data relative to a number of systems of this type are given.

Experimental Part

Measurements were carried out in the usual way, according to the Kohlrausch method, with such improvements as are commonly practiced at the present time. The cell employed for the measurements was that previously employed and described by Kraus and Kurtz.[3] All measurements were carried out at $25.00°$ ±0.01.

Conductance of Trimethyl Tin Chloride in Nitrobenzene on Addition of Pyridine.—A 0.1 N solution of trimethyl tin chloride in nitrobenzene was prepared in the cell, by weighing 9.2234 g. of trimethyl tin chloride into

TABLE I

CONDUCTANCE OF 0.1 N SOLUTION OF $(CH_3)_3SnCl$ IN NITROBENZENE IN THE PRESENCE OF VARIOUS AMOUNTS OF PYRIDINE AT $25°$

Moles pyridine per liter	Spec. cond. $\times 10^4$	Moles pyridine per liter	Spec. cond. $\times 10^4$
0.00676	0.125	0.29	0.324
.0149	.149	0.37	.334
.0249	.167	0.44	.345
.033	.179	0.513	.351
.0416	.190	0.59	.356
.0503	.199	0.66	.359
.059	.208	0.76	.363
.0835	.228	0.84	.364
.119	.254	0.93	.367
.209	.295	1.05	.368

[3] Kraus and Kurtz, THIS JOURNAL, **44**, 2463 (1922).

462.96 cc. of nitrobenzene. Pyridine was added to the nitrobenzene so-
lution by means of a weight pipet of the type described by Kraus and
Callis.[1] The cell was placed in the thermostat, pyridine was added in
various amounts and the conductance of the solution measured. The re-
sults are given in Table I, which requires no further explanation.

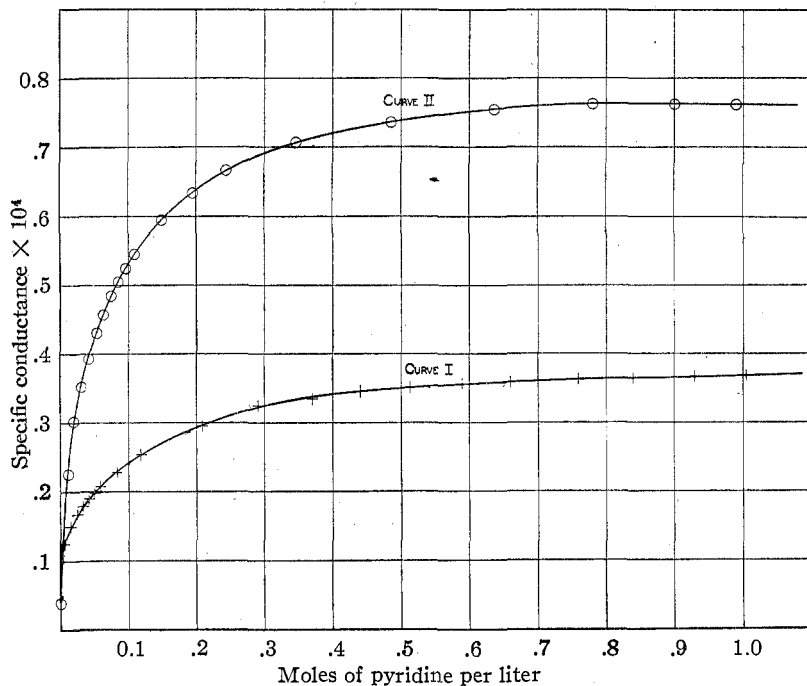The results are shown graphically as Curve I, Fig. 1.

Fig. 1.—The increased conductance of solutions of trimethyl tin chloride in nitro-
benzene (Curve I) and acetone (Curve II) on addition of pyridine

Conductance of Trimethyl Tin Chloride in Acetone in the Presence of Pyridine.

A 0.1 N solution of trimethyl tin chloride in acetone was
prepared in the cell, with 7.7161 g. of trimethyl tin chloride in 387.32 cc.
of acetone. The specific conductance of the acetone was 7.4 × 10^{-7}.
Pyridine was added as before by means of a weight buret. The results are
given in Table II.

The results are shown graphically as Curve II, Fig. 1.

Conductance of Trimethyl Tin Chloride in Mixtures of Acetone and Alcohol.

To a solution of 250 cc. of 0.1 N solution of trimethyl tin
chloride in acetone prepared in the cell was added successively 25 cc. of
0.1 N solution of trimethyl tin chloride in alcohol, the conductance of the
mixture on successive additions being measured. The same procedure

TABLE II

CONDUCTANCE OF 0.1 N SOLUTIONS OF $(CH_3)_3SnCl$ IN ACETONE IN THE PRESENCE OF VARIOUS AMOUNTS OF PYRIDINE

Moles pyridine per liter	Spec. cond. $\times 10^4$	Moles pyridine per liter	Spec. cond. $\times 10^4$
0.0	0.0389	0.109	0.544
.0121	.225	.150	.594
.0198	.302	.195	.633
.0309	.352	.244	.666
.0419	.393	.345	.707
.0536	.430	.485	.738
.0635	.457	.636	.755
.0747	.484	.78	.763
.085	.504	.90	.763
.096	.524	.99	.763

was then repeated, in which 25 cc. of 0.1 N solution of trimethyl tin chloride in acetone was successively added to 250 cc. of 0.1 N solution of trimethyl tin chloride in 95% alcohol.   The results are given in Table III.

TABLE III

CONDUCTANCE OF 0.1 N SOLUTIONS OF $(CH_3)_3SnCl$ IN MIXTURES OF ACETONE AND 95% ALCOHOL

Volume per cent. alcohol	Spec. cond. $\times 10^4$	Volume per cent. alcohol	Spec. cond. $\times 10^4$
0	0.059	55	1.357
5	0.185	60	1.494
10	0.295	65	1.654
15	0.416	70	1.849
20	0.542	75	2.087
25	0.670	80	2.375
30	0.794	85	2.737
35	0.917	90	3.176
40	1.034	95	3.753
45	1.149	100	4.348
50	1.242	...	..

The results are shown graphically as Curve III, Fig. 2.

Conductance of Trimethyl Tin Chloride in Mixtures of Nitrobenzene and Pyridine.—Mixtures of pyridine and nitrobenzene were prepared as in the case of acetone and alcohol and the conductance of these mixtures measured.   The pyridine was purified by treating 600 cc. of a sample which boiled at 116–118° with solid sodium hydroxide.   The mixture was refluxed for 5 hours, the pyridine decanted and distilled.   After three successive distillations a product was obtained which boiled at 115° and gave the value 0.12 $\times$ 10^{-6} for the specific conductance.   The nitrobenzene was purified by redistilling a commercial product several times.   A constant-boiling sample was obtained which gave a value of 0.31 $\times$ 10^{-6} for the specific conductance.   The results are given in Table IV.

TABLE IV

CONDUCTANCE OF 0.1 N SOLUTIONS OF $(CH_3)_3SnCl$ IN MIXTURES OF NITROBENZENE AND PYRIDINE

Volume per cent, alcohol	Spec. cond. $\times 10^4$	Volume per cent, alcohol	Spec. cond. $\times 10^4$
0	0.0019	55	0.421
5	.338	60	.420
10	.383	65	.418
15	.403	70	.412
20	.415	75	.396
25	.423	80	.387
30	.427	85	.373
35	.429	90	.354
40	.430	95	.328
45	.430	100	.295
50	.429	...	...

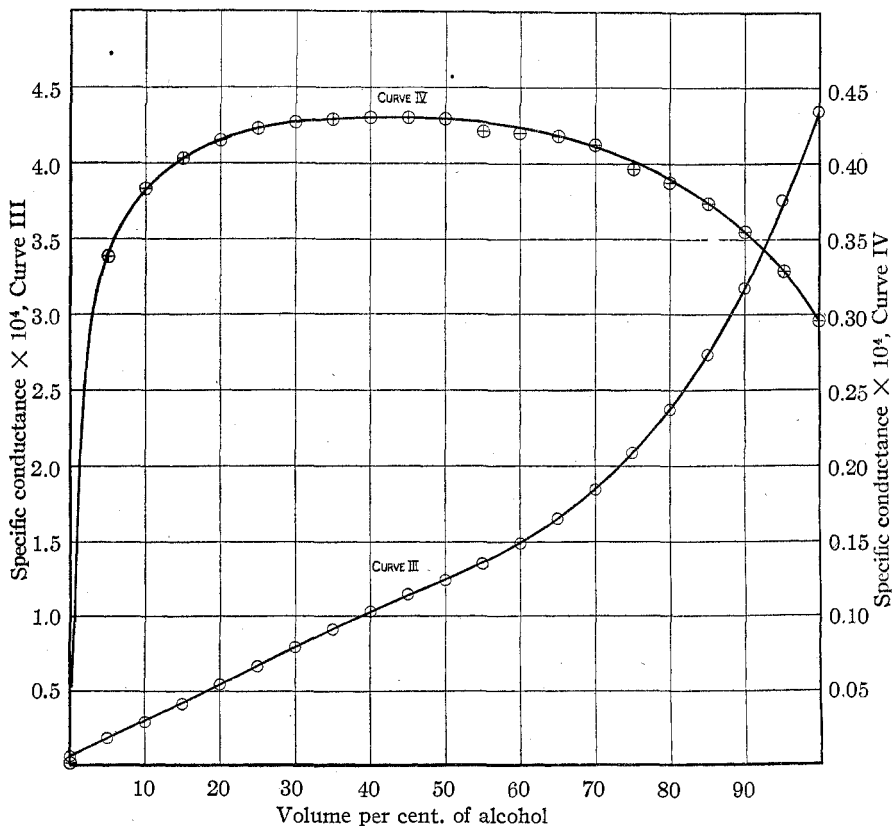The results are shown as Curve IV, Fig. 2.

Fig. 2.—The conductance of solutions of trimethyl tin chloride in mixtures of acetone and alcohol (Curve III) and nitrobenzene and pyridine (Curve IV)

Discussion

In the tables the values of the specific conductance times 10^4 are given. If in Tables I and II the change in volume due to the added pyridine is neglected, then the equivalent conductance will have the same numerical values as given in the column of specific conductances. If the volume change on mixing solutions of pyridine and alcohol and pyridine and nitrobenzene be neglected, then the values of the equivalent conductance are equal to the numerical values given under the columns headed specific conductance.

An examination of the tables and of the figures shows that the properties of solutions of trimethyl tin chloride in acetone and nitrobenzene are chiefly determined by the amount of pyridine which has been added. Considering the results of Tables I and II, shown in Fig. 1, it is seen that the addition of even a small amount of pyridine causes a very large rise in the conductance of the solution. Thus the addition of approximately 0.01 moles of pyridine to 0.1 moles of trimethyl tin chloride in acetone raises the conductance from 0.0389 to 0.225. With further addition of pyridine, further increase of the conductance takes place, so that on the addition of approximately one mole of pyridine the conductance reaches a value of 0.763. As may be seen from the curve, every successive addition of pyridine causes a smaller and smaller rise in the value of the conductance. What holds true of solutions in acetone on addition of pyridine equally holds true for solutions in nitrobenzene on addition of the same compound. This form of the curve is in harmony with the view that the electrolytic properties of these solutions are due to the formation of a salt-like compound between trimethyl tin chloride and pyridine. The values of the ionization in the different solvents can be compared only roughly. The specific conductance of a 0.1 N solution of trimethyl tin chloride in nitrobenzene containing approximately one mole of pyridine is 0.368, while for a corresponding solution in acetone it is 0.763. The fluidity of nitrobenzene at 25° is approximately 54.3, while that of acetone is 304 at 18°. In other words, the fluidity of acetone is about 6 times that of nitrobenzene. In proportion to the fluidity of the solvent medium, therefore, solutions of trimethyl tin chloride in the presence of pyridine are relatively better conductors in nitrobenzene than in acetone, corresponding to the relatively greater dielectric constant of nitrobenzene.

Considering Fig. 2, Curve IV, it is seen that the conductance of 0.1 N solutions of trimethyl tin chloride in mixtures of nitrobenzene and pyridine exhibits a maximum in the neighborhood of 42 volume per cent. of pyridine. The fluidity of pyridine is markedly higher than that of nitrobenzene. It follows, therefore, that the ionization of trimethyl tin chloride in the mixtures lies still nearer the axis of nitrobenzene.

The initial additions of pyridine to nitrobenzene cause a very marked

increase in the conductance due to the formation of the complex ammonium salt, $C_6H_5NSn(CH_3)_3Cl$. The addition of nitrobenzene to the pyridine solution causes an increased conductance as a result of increased ionization due to the greater dielectric constant of nitrobenzene.

The form of the curve for mixtures of acetone and alcohol, as shown in Fig. 2, differs markedly from that for mixtures of nitrobenzene and pyridine. The initial additions of alcohol to acetone cause a marked increase of conductance very nearly as a linear function of the volume composition of the solution. In view of the fact that the fluidity of acetone is much higher than that of alcohol, this indicates a marked increase in the ionization of the electrolyte. The effect, however, is much less marked than it is in the case of mixtures of pyridine and nitrobenzene or pyridine and acetone. Probably acetone itself forms a complex oxonium compound in solution to some extent; and, while alcohol, without doubt, forms a complex oxonium compound with trimethyl tin chloride, it is, in all likelihood, much less stable than the corresponding pyridine compound, which is in agreement with the fact that trimethyl tin chloride is obtained in the pure state on evaporation of the alcohol, whereas in the case of pyridine a compound remains behind. The initial additions of acetone to the alcohol solution cause a marked decrease in the conductance due, without doubt, to a markedly decreased ionization. This is probably in part due to a decrease in the dielectric constant, but probably even on addition of small amounts of acetone the equilibrium of the complex may be measurably affected. In this connection it should be noted that the conductances of solutions containing larger amounts of alcohol are, without doubt, measurably affected by the presence of water. The conductance of a 95% alcohol solution, without addition of acetone, is much higher than would correspond to the conductance of a solution in absolute alcohol, according to measurements recorded by Kraus and Callis,[1] thus indicating a marked influence of water on the conductance of trimethyl tin chloride in alcohol.

Similar changes in the conductance of solutions on addition of suitable substances have previously been recorded in a few instances. In the first place, solutions of salts, which show a marked tendency to take up water of crystallization, exhibit a low degree of ionization in non-aqueous solvents and their ionization is greatly increased on addition of water or an alcohol. This is particularly noticeable in the case of calcium nitrate on addition of water and the alcohols to solutions in acetone. Lithium salts exhibit a similar, although less marked, behavior.[4]

These cases, however, are not strictly analogous to those which form the subject of the present investigation. The behavior of the acids in various non-aqueous solvents on addition of water forms perhaps a much closer

⁴ Jones, Bingham and McMaster, Z. physik. Chem., 57, 193, 257 (1906).

analogy with that of the alkyl metal halides.   It has been shown that the ionization of the acids in the alcohols is greatly increased on addition of water.   This effect has been ascribed to the formation of a compound of the oxonium type, which is more highly ionized than the pure acid[5] or, perhaps better, the alcoholated acid.

Trimethyl tin chloride, as has previously been pointed out, exhibits properties which resemble those of the halogen acids very closely.[1]   They are non-conductors in the pure liquid condition,[6] as well as in solvents of the non-basic type, they are conductors in solvents of the basic type, or in solvents of the non-basic type to which small quantities of solvents of the basic type have been added, they are relatively weakly ionized in solvents of the mean dielectric constant, and they conform to the law of mass action in solvents of relatively high dielectric constant.   What is true of trimethyl tin chloride is, without doubt, also true of other metallo-organic compounds of the type $M^n R_{n-1} X$.   The properties of these compounds may be accounted for on the assumption that the group $(CH_3)_3 Sn$ occupies an intermediate position in the potential series, which brings it into the same class with hydrogen.   Indeed, the group in its compounds resembles hydrogen much more closely than do the elements which occupy a corresponding position in the potential series, owing to the fact that the groups are univalent, while the corresponding elements have a relatively high valence. However, as was pointed out by one of the present authors,[7] these elements likewise exhibit the property of acting amphoterically, that is, either positively or negatively, which is also a property of hydrogen and of groups of the type of the trimethyl tin group and other similar groups, as will be shown in a subsequent article.

[5] Goldschmidt, *Z. physik. Chem.*, **89**, 132 (1915).   Kailan, *ibid.*, **89**, 678 (1915). Braune, *ibid.*, **85**, 170 (1913).

[6] Substances which are not marked conductors of the electric current in the pure liquid condition are not to be classed as true electrolytes, even though solutions of such substances in certain solvents may exhibit electrolytic properties.   Present evidence indicates that the electrolytic properties of such substances in solution are due to the formation of new compounds which are true electrolytes.   No term has thus far been suggested to distinguish substances of this type from true electrolytes; that is, substances which are ionized in the liquid condition as well as in solution.   It is suggested that the term pseudo-electrolyte might be employed to distinguish the class of substances here under discussion from the true electrolytes.*   This prefix is now commonly used to distinguish between the true acids and certain organic substances which exhibit acidic properties in solution due to a rearrangement.   The extension of the use of this prefix to compounds other than the acids should lead to no confusion, while at the same time it would serve to characterize a class of substances which is widely represented.   A pseudo-electrolyte would thus be a compound which itself does not exhibit electrolytic properties but which reacts with certain solvents to form a new compound which is a true electrolyte.

[7] Kraus, *Rec. trav. chim.*, **42**, 588 (1923).

Summary

The conductance of solutions of trimethyl tin chloride in nitrobenzene and acetone on addition of small amounts of pyridine has been measured. A marked increase takes place in conductance on addition of pyridine, and this effect is the greater, the smaller the amount of pyridine already present.

The conductance of solutions of trimethyl tin chloride in mixtures of 0–100% of acetone and alcohol and nitrobenzene and pyridine has been measured. The initial conductance in nitrobenzene is extremely low, indicating that trimethyl tin chloride is practically un-ionized in this solvent. The initial conductance in acetone is markedly higher than in nitrobenzene. While the conductance in acetone on addition of alcohol is increased, this increase is much less marked than it is on addition of pyridine.

The results are in agreement with the view that trimethyl tin chloride itself is not a true electrolyte and that its electrolytic properties in solution are due to the formation of compounds of the oxonium and ammonium type, the trimethyl tin group transferring from chlorine to tetravalent oxygen or pentavalent nitrogen, respectively.

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THE ATOMIC WEIGHT OF LEAD FROM THE BELGIAN CONGO

BY THEODORE W. RICHARDS AND PAUL PUTZEYS[1]

The fundamental relation of the isotopes of lead to the process of radioactive disintegration gives an especial interest to the atomic weights of these isotopes. The difference in the geological histories of uranium deposits in different parts of the world makes it especially desirable that the quantitative relations of the lead in deposits from as many widely separated localities as possible should be examined. Within the past few years, as is well known, a new source of uranium and radium material has been found in the Belgian Congo. Accordingly, we have investigated the atomic weight of lead derived from this source.

The metal employed was obtained from a mixture of several minerals existing in the center of Africa. These all doubtless originated in a common primary deposit of uraninite, of which an analysis has been published.[2a] Among the decomposition products of this primary mineral, Schoep[2b] has discovered several secondary minerals containing lead, namely, curite $(2PbO.5UO_3.4H_2O)$, kasolite $(3PbO.3UO_3.3SiO_2.4H_2O)$, dewindtite $(4PbO.8UO_3.3P_2O_5.12H_2O)$ and stasite $(4PbO.8UO_3.3P_2O_5.12H_2O)$. In all these

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[1] Fellow for the Commission for Relief in Belgium Educational Foundation.

[2a] Steinkuhler, *Bull. soc. chim. Belg.*, **32**, 233 (1923).

[2b] Schoep, *Compt. rend.*, **173**, 1186, 1476 (1921); **174**, 623, 875 (1922).