general way it may be stated that the results were consistent with values calculated from k_1 and the equilibrium constant.

Adsorption of Carbon Dioxide and Hydrogen.—When oxide-covered silver surfaces were treated with carbon dioxide at pressures less than the dissociation pressure of the carbonate, a slow activated adsorption occurred. Thus with oxide equivalent to 19 cc. of oxygen, equilibrium was very closely approached when 1.8 cc. of carbon dioxide had been adsorbed at 132° and a pressure of 9 mm. With 161 cc. of oxygen present, 1.26 cc. of carbon dioxide was adsorbed at 139° and 11 mm., but equilibrium had not quite been reached.

When hydrogen was admitted to oxide-covered silver at −78.5° and 390 mm., 0.1 cc. disappeared from the free space in nine hours and 0.3 cc. in twenty-two hours. In a similar experiment at 0° with 8.8 cc. of oxygen present, 3.0 cc. of hydrogen were taken up in four hours and 7.3 cc. in thirty hours. Although the disappearance of hydrogen seemed to be approaching the quantity of oxygen present, instead of twice this value as would be expected if water were formed, evacuation at 0° removed the calculated amount of gas in the free space and no more. Consequently if there is any adsorption of hydrogen at 0° it must be practically irreversible.

Summary

The adsorption of carbon dioxide and hydrogen has been studied on the same two silver samples previously used in measuring the rates and equilibrium of oxygen adsorption and oxide formation. On bare silver carbon dioxide showed only an instantaneous physical adsorption, with a heat of 5 kcal. Complete covering of the surfaces apparently required very nearly the same volume of carbon dioxide as of oxygen. The physical adsorption of hydrogen was very small even at −183°, but above 200° an activated adsorption occurred which could readily be removed by evacuation at 300°.

On silver surfaces occupied by adsorbed oxygen there was from 0–200° a slow activated adsorption of carbon dioxide, with physical adsorption also occurring at 0°. The energy of activation of the former process was about 4–5 kcal. Evidence of a small activated adsorption of hydrogen at 0° was obtained.

Silver surfaces occupied by silver oxide reacted with carbon dioxide to form carbonate as low as 56°. The equilibrium pressures agreed well with accepted values—a fact which indicates that the oxide was the same as "ordinary" silver oxide thermodynamically. The calculated heat of formation was 17.3 kcal. The rate of formation was proportional to the pressure, was apparently uninfluenced by the amount of oxide present, but decreased markedly as carbonation proceeded. The energy of activation was 13 kcal. Below the equilibrium pressure of the carbonate an activated adsorption of carbon dioxide occurred.

UNIVERSITY, VA.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. X. The Freezing Point of Solutions of an Electrolyte in a Non-Polar Solvent

BY CHARLES A. KRAUS AND RAYMOND A. VINGEE[1]

I. Introduction

Solutions of electrolytes in non-polar solvents have been under investigation in this Laboratory for several years. The electrical conductance of such solutions has been studied and reported in preceding papers of the present series.[2] At the same time, the thermodynamic and the dielectric properties of the same solutions have been studied. In the present paper, results of an investigation of the thermodynamic behavior of solutions of tetraisoamylammonium nitrate in dioxane are reported.

If the results of a study of the thermodynamic properties of electrolytic solutions are to be interpreted, it is necessary that the measurements be carried out at very low concentrations and with a relatively high degree of precision. The freezing point of aqueous solutions of electrolytes has been measured successfully down to concentrations as low as 10^{-3} *N*. Although the freezing

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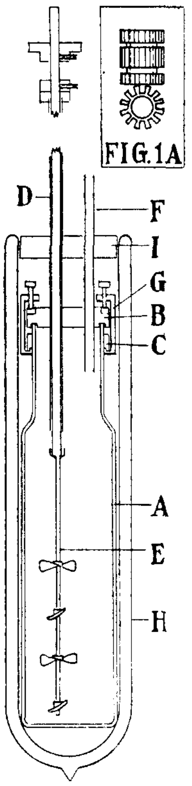
(1) Du Pont Fellow in Chemistry at Brown University.

(2) Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933); Fuoss and Kraus, *ibid.*, **55**, 2387 (1933).

point of solutions in non-aqueous solvents has been one of the most common methods for the determination of molecular weights of non-volatile compounds, this method has never been developed as a precision method in the case of any non-aqueous solvent. Peterson and Rodebush[3] obtained fairly satisfactory results in benzene at concentrations as low as 0.01 *N*. For our present purpose, it was desirable that freezing point measurements be carried to concentrations as low as 10^{-3} *N*, or lower.

Below is described the apparatus developed for determining the freezing point of solutions. This is followed by results of freezing point determinations of solutions of a normal solute in benzene and dioxane, which disclose the reliability of the method and give accurate values of the cryoscopic constants for these solvents. Finally, the freezing points are given for solutions of tetraisoamylammonium nitrate in benzene for a concentration range of 0.001 to 0.011 *N*.



Figs. 1 and 1a.—Showing cell design and method of mounting junctions.

II. Apparatus, Procedure and Materials

The apparatus consists essentially of two cells—one containing the solution, the other, pure solvent—the temperature difference between which is measured by means of a multiple thermocouple. Equilibrium is established by means of suitable stirrers and the whole apparatus is immersed in a liquid whose temperature is thermostatically controlled.

Assembly.—Two cells of as nearly identical dimensions as possible, having a volume of 300 cc., are used to contain the pure solvent and the solution, the temperature difference between which is to be measured. One of these cells A with accessories is shown in Fig. 1. The cells are placed in two silvered and highly evacuated Dewar tubes H. Each cell is provided with a hard rubber top B held tightly in position by means of clamps G engaging the top and the metal band C, which is waxed to the neck of the bottle. Through the top passes a tube D (carrying the stirrer E) and a tube F through which the thermoelement is introduced. The top is also provided with a third tube, not shown in the figure, through which solute is introduced and through which a platinum thermometer may be introduced, if desired, in calibrating the thermocouple. A small tube (not shown in the figure) also connects the interior of the cell with the atmosphere. This tube is connected with a source of dry nitrogen at atmospheric pressure.

The tubes pass through a second hard rubber disk I which fits closely into the top of the Dewar tube and which is waxed in position. In the course of a series of measurements, both tubes are placed in a thermostat and their tops are covered with water to a depth of about 3 cm.

The stirrers were driven at a constant speed of 750 r. p. m. by a synchronous motor. It was found that at lower speeds a satisfactory equilibrium could not be obtained. The tubes passing through the stoppers were constructed of German silver and had a thickness of 0.01 or 0.02 mm. The purpose of the thin alloy tubes was to minimize the heat transfer between the interior and exterior of the cells.

Multiple Thermocouple.—A multiple thermocouple of twelve pairs of copper–constantan junctions was constructed (in two halves), using No. 36 enameled copper wire and No. 32 double silk covered constantan wire. The junctions were soldered by dipping them into a molten cadmium–tin alloy (eutectic mixture) which was covered with a thin layer of rosin. After soldering, the junctions were mounted on a small hard rubber spacer of the type shown in Fig. 1a. The spacer had a diameter of 3.5 mm., a length of 4 mm., and weighed approximately 50 mg. It was provided with a circular groove near each end and twelve longitudinal grooves into which the junctions were fitted. They were tied in place with silk thread at the circular grooves. The cylinders with their junctions were introduced into seamless German silver tubes, 0.2 mm. thick and 35 cm. long, which were provided at one end with platinum tips, 7 cm. long and 0.02 mm. thick. The greater thermal conductivity of platinum over German silver was noticeable. It is highly advantageous to have the junctions bare and as near the surface of the containing tube as possible. The multiple thermocouple was calibrated against a platinum resistance thermometer and gave a reading of 0.002353° per microvolt.

Thermostat.—The freezing point tubes were completely immersed in water in an electrically controlled thermostat whose temperature was adjusted just sufficiently below the freezing point of benzene to compensate for the heat introduced by the stirrers. If compensation is not provided, solvent will either freeze out or melt in the course of a series of measurements and the concentration of the solutions measured becomes uncertain.

Potentiometer and Accessories.—The e. m. f. of the multiple thermocouple was measured by means of a White double potentiometer, of 10,000 microvolt capacity, in conjunction with a Leeds and Northrup high sensitivity galvanometer.

In calibrating the thermoelement, a platinum resistance thermometer was used with a Mueller type of thermometer bridge, both of which had been calibrated by the Bureau of Standards.

Procedure.—After carefully drying and assembling the cells with their tops and stirrers, approximately 225 cc. of solvent were introduced into each cell and the cells were placed in a bath of ice water. A layer of solvent was

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(3) Peterson and Rodebush, *J. Phys. Chem.*, **32**, 709 (1932).

frozen out on the walls of the cells and the solid was melted loose from the walls by removing the cells from the ice-bath. The solid was broken up into minute particles by the action of the stirrers. Approximately one-third of the solvent in the cells was frozen out. The cells were then placed in the thermostat as already described and the temperature difference indicated by the multiple thermocouple was observed. In the course of several hours, this difference gradually fell to a value of the order of a microvolt or less.

A weighed sample of solute, usually in the form of a loose pellet, was introduced and the temperature difference was observed at intervals of a few minutes until it reached a constant value which was maintained for at least fifteen minutes. More solute was then added and temperature readings were made as before.

To determine the concentration of the solution, two samples of approximately 20 cc. each were withdrawn, the solvent was evaporated and the weight of solute determined. In case the concentration of solute was too low to permit of accurate determination, a quantity of a second solute was added just before withdrawing the samples from the cell. Determination of the amount of material in the samples made possible the determination of the total quantity of liquid in the cell and, accordingly, of the concentrations of the various solutions measured.

Materials.—Benzene was purified by treating successively with concentrated sulfuric acid, water, sodium hydroxide and again water. After drying over phosphorus pentoxide and distilling, the residual impurities were eliminated by fractional crystallization. The solvent was stored over sodium–lead alloy (NaPb) and distilled just prior to use. The melting point of the benzene ranged from 5.449 to 5.455°.

Commercial 1,4-dioxane was refluxed over sodium hydroxide and after distillation was boiled for an extended period of time over metallic sodium, fresh metal being added from time to time. The melting point of the final product was 11.780° and the boiling point, 101.24° at 761 mm.

Triphenylmethane was twice recrystallized from alcohol (m. p. 91°) and tetraisoamylammonium nitrate was secured from Dr. R. M. Fuoss, who has described its preparation and purification.[4]

III. Freezing Point of Solutions of Triphenylmethane in Benzene and Dioxane

As a test of the method, the freezing point curves for solutions of triphenylmethane in benzene and dioxane were determined. It was anticipated that triphenylmethane would prove to be a normal type of solute, particularly in the concentration range here under investigation. An accurate determination of the freezing point constant of both these solvents was, moreover, necessary in order to permit interpretation of the results of freezing point measurements with other substances.

Benzene.—The results of two independent series of determinations of the freezing point of solutions of triphenylmethane in benzene are given in Table I.

TABLE I

FREEZING POINT DEPRESSIONS OF SOLUTIONS OF TRIPHENYLMETHANE IN BENZENE

Series 1

Total solvent, 220.0 g.; total liquid, 153.8 g.; formula weight, 244.1 g.

Solute, g.	Moles/1000 g. benzene	F. p. depression	Mol. wt.
0.1632	0.004347	0.02204	243.9
.4268	.01137	.05719	245.8
.8338	.02221	.1119	245.4

Series 2

Total solvent, 210.0 g.; total liquid, 142.8 g.

0.1092	0.003132	0.01598	242.3
.3041	.008721	.04461	241.7
.6085	.01745	.08871	243.2
1.1845	.03397	.1719	244.3
1.6480	.04726	.2392	244.2

Dioxane.—The results of two series of measurements with dioxane as solvent and triphenylmethane as solute are given in Table II.

TABLE II

FREEZING POINT DEPRESSIONS OF SOLUTIONS OF TRIPHENYLMETHANE IN DIOXANE

Series 1

Total solvent, 260.0 g.; total liquid, 162.0 g.; formula weight, 244.1 g.

Solute, g.	Moles/1000 g. dioxane	F. p. depression	Mol. wt.
0.0672	0.001699	0.00798	240.5
.1434	.003626	.01690	242.4
.2272	.005745	.02666	243.5
.5476	.01385	.06430	243.3
.8584	.02170	.1008	243.3
1.595	.04034	.1875	243.1
3.062	.07741	.3579	244.4

Series 2

Total solvent, 260.0 g.; total liquid, 162.6 g.

0.1841	0.004637	0.02136	245.3
.3544	.008928	.04064	248.2
.6420	.01617	.07504	243.5
1.3415	.03379	.1560	244.8
2.2119	.05572	.2569	245.0

Discussion.—The freezing point depressions are shown graphically as a function of concentration in Fig. 2. It will be seen that for both dioxane and benzene the points approximate closely to straight lines. The two independent series of measurements in the case of each solvent are in good agreement with each other and show little consistent deviation. Drawing the best straight lines through the two series of points, the freezing

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(4) Kraus and Fuoss, THIS JOURNAL, **55**, 23 (1933).

point constant for benzene is found to be 5.065° and that of dioxane 4.63°. Values of the freezing point constant, as given in the literature for benzene, vary over a considerable range. Peterson and Rodebush[3] suggest 5.07° as a probable value from available data on the heat of fusion of benzene and adopted a value of 5.1° as being in agreement with their measurements. For dioxane, Anschütz and Broeker[5] report a value of 4.98°, while Hertz and Lorentz[6] report 5.01°. These investigators, however, were not working with a pure solvent, since they report a freezing point of 11.0°, against a value of 11.78° which we have found for our solvent.

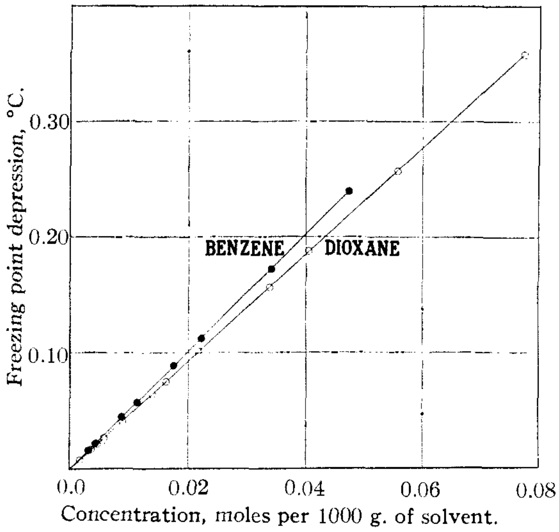

Fig. 2.—Freezing point curves of triphenylmethane in benzene and dioxane.

In the case of the benzene solutions, all the calculated values of molecular weight lie within 1% of the theoretical value and only three points give a deviation above 0.5%. The mean deviation of all the points is 0.5%.

In the case of dioxane, the mean deviation is 0.6% with two points having a deviation greater than 1%, and the remaining points a deviation less than 0.5%.

The consistency of the results would seem to indicate that it is possible to carry out freezing point measurements with a precision of approximately 1% to concentrations as low as about 0.002 N with the apparatus above described.

IV. Freezing Point of Solutions of Tetraisoamylammonium Nitrate in Dioxane

The freezing point of solutions of tetraisoamylammonium nitrate was measured from a concentration of approximately 0.001 N to 0.011 N, which is near the limit of solubility of the salt in dioxane at its freezing point. Since the rate of solution of the salt in dioxane at its freezing point is extremely slow, a concentrated solution of the salt was made and added in weighed amounts to the freezing mixture. (The solubility of the salt increases very rapidly with increasing temperature.) The solution was introduced by means of a special form of pipet with a long delivery tube. It was provided with ground-glass caps to prevent evaporation of the solvent during manipulation. It was necessary to take into account the amount of dioxane added each time with the solution and to calculate the amount of solid dioxane melted in cooling the added solution from room temperature to the temperature of the solution. To compute this latter quantity, the heat of fusion of dioxane was calculated from the freezing point constant. Assuming this constant to be 4.63°, and using R = 1.9864 and T = 284.8, we obtain for the heat of fusion the value 34.80 calories per gram.

In Table III are given the data for a series of measurements of the freezing point depression for solutions of tetraisoamylammonium nitrate in dioxane. The apparent molecular weight given in the last column is calculated on the basis of 4.63° for the cryoscopic constant of dioxane.

Table III

Freezing Point Depressions of Solutions of Tetraisoamylammonium Nitrate in Dioxane

Total solvent, 210.0 g.; total liquid, 158.6 g.; formula weight, 360.4 g.

Solute, g.	Moles/1000 g. dioxane	F. p. depression	Apparent mol. wt.
0.0090	0.00018	0.00078	393.6
.0561	.00111	.00297	637.8
.1058	.00207	.00460	769.1
.1435	.00279	.00554	858.7
.2098	.00402	.00725	945.1
.2510	.00476	.00802	1013
.3032	.00569	.00904	1073
.3503	.00651	.01005	1104
.4349	.00792	.01142	1183
.5049	.00907	.01280	1208
.5670	.01006	.01398	1227
.6363	.01113	.01510	1256

Discussion.—In Fig. 3 the freezing point depressions (Curve A) and the molecular weights (Curve B) are shown as functions of the concentration. The broken line C is the theoretical freezing point curve of dioxane solutions. It is evident that the freezing point curve of these solutions is far less than normal. The apparent

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(5) Anschütz and Broeker, *Ber.*, **59B**, 2844 (1926).

(6) Hertz and Lorentz, *Z. physik. Chem.*, **140**, 406 (1929).

molecular weight reaches a value which is almost four times the formula weight at the highest concentration. At 10^{-3} N the molecular weight is distinctly less than twice the formula weight and at approximately 2×10^{-4} N, the molecular weight is approaching closely to the formula weight, although the freezing point depression here is so small that the error may be considerable. Nevertheless, the error cannot be great enough to bring the molecular weight greatly above the formula weight. The freezing point curve A indicates that it is approaching tangency to the theoretical straight line C as a limit, *i. e.*, the calculated molecular weight is approaching the formula weight.

There are no other data available in the literature on the freezing point of dilute solutions of electrolytes in non-polar solvents. The results here recorded seem to be characteristic of solutions of electrolytes in such solvents generally. Recent determinations with other electrolytes and in other solvents confirm the present result.[7] One might be inclined to account for the abnormal type of freezing point curve by interaction between the ion charges in the sense of the Debye–Hückel theory. A calculation of possible effects of this type shows, however, that the ion concentrations never reach a value sufficiently high so that the interionic effects have a marked influence at the total electrolyte concentrations here under consideration. The conductance of solutions of tetraisoamylammonium nitrate in benzene has been measured in this Laboratory and recorded in a preceding paper of this series.[2] From the viscosity of dioxane, we should expect a Λ_0 value in the neighborhood of 50 for solutions of tetraisoamylammonium nitrate in dioxane. The conductance of solutions of this salt in dioxane at 10^{-3} N and 10^{-2} N, is 1.93×10^{-4} and 5.69×10^{-4}, respectively. This would give ionization values of approximately 3.9×10^{-6} and 1.2×10^{-5} and ion concentrations of 3.9×10^{-9} and 1.2×10^{-7}, respectively. The activity coefficients of the ions in dioxane at these concentrations would be approximately 0.985 and 0.920. These values, obviously, are not of an order of magnitude which could account for the extreme deviation shown by the freezing point curve.

Another explanation that suggests itself and which, indeed, seems to be the only one remaining, is that simple ion-pairs, or electric dipoles, combine to form multipoles, or aggregates, at higher concentrations. Probably a more or less complex equilibrium exists among these aggregates of varying degrees of complexity. Fuoss and Kraus[2] were led to the same conclusion by the results of their investigation of the conductance of solutions of this and other electrolytes in non-polar solvents. They have advanced the view that at very low concentrations, equilibrium exists between free ions and ion-pairs under the action of Coulomb forces. At higher concentrations, owing to forces acting between the ion-pairs and the free ions, so-called ion-triples are formed, which accounts for the minimum universally observed in the conductance curves of solutions in solvents of low dielectric constant. The total concentration of ions in dioxane is too small to influence appreciably the freezing point of solutions in that solvent. On the basis of their conductance studies, Fuoss and Kraus suggest that quadripoles and higher aggregates of ion-pairs are formed at higher concentrations. They point out that, in the case of salts such as tetraisoamylammonium bromide or nitrate in benzene or dioxane, the conductance curve has a marked inflection point at concentrations above the minimum point of conductance. The removal of ions from solution by the formation of quadripoles, a new molecular

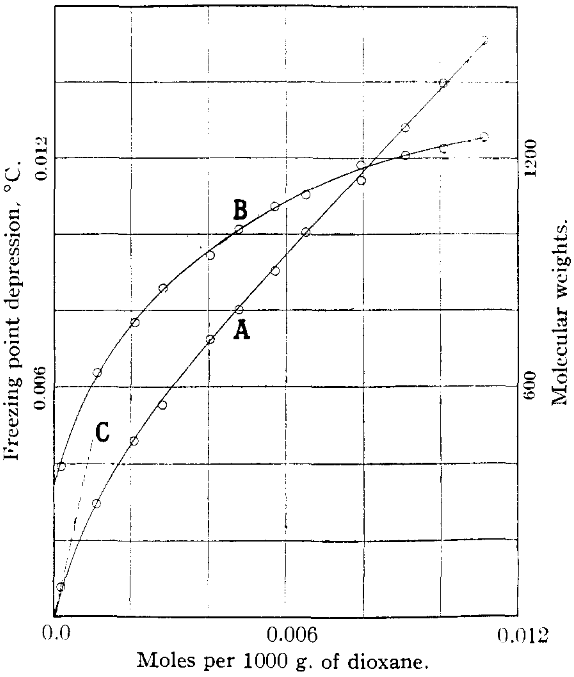

Fig. 3.—Curves showing change of freezing point and apparent molecular weight with concentration.

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(7) Unpublished observations of F. M. Batson in this Laboratory.

species, would necessarily tend to drop the conductance curve. The inflection point in the case of tetraisoamylammonium nitrate in dioxane lies at about 0.0025 N. It is in this region that we have measured the freezing point of these solutions. The freezing point curve indicates that aggregates are being formed very rapidly at concentrations between approximately 2×10^{-4} and 2×10^{-3} N. Over this range of concentration, the apparent molecular weight increases from a value which is very nearly normal, that is, equal to the formula weight, to a value which is approximately twice the formula weight.

Other solutions of electrolytes in non-polar solvents are being studied and the results will be reported in the near future.

V. Summary

A simple apparatus is described for measuring the freezing point depression of solutions in non-polar solvents at temperatures between 0 and 25° with a precision in the neighborhood of 1% down to concentrations as low as 10^{-3} N.

The freezing point curves for solutions of triphenylmethane in benzene and dioxane have been determined. From these curves, the freezing point constants of the two solvents have been found to be 5.065° for benzene and 4.63° for dioxane. With these values for the cryoscopic constants, the calculated values of the molecular weights from the experimentally determined freezing point depressions have a mean deviation of only 0.6% from the theoretical values.

The freezing point depression of solutions of tetraisoamylammonium nitrate in dioxane has been measured from approximately 0.001 to 0.011 N. The freezing point curve deviates greatly from the theoretical straight line, although it approaches this line tangentially at concentrations below 10^{-3} N, the theoretical slope being based on the formula weight. These results are discussed and it is suggested that the deviation from the theoretical slope is due to association of the ion-pairs (in which form the electrolyte is, for the most part, present at concentrations in the neighborhood of 10^{-4} N) to more complex aggregates. According to the observed freezing point depression at the highest concentration, 0.011 N, there are, in the mean, nearly four ion-pairs associated at this concentration.

PROVIDENCE, R. I. RECEIVED AUGUST 5, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Molecular Refractions and Dispersions, in the Ultraviolet, of Salts and of Ions in Water Solution

BY GEORGE S. FORBES AND HERVEY B. ELKINS

Data upon molecular refractions and dispersions of aqueous electrolytes in the ultraviolet are still fragmentary, in spite of investigations by Lubben,[1] Heydweiller[2] and Heydweiller and Grube[3] discussed in part below. We have investigated twenty-four salts over the range $\bar{\nu}$ = 24,000 to 45,000 cm.$^{-1}$ or so far as absorption permitted. We varied both concentration and wave number, obtaining on the average thirty-seven separate values of n for each salt or nearly 900 in all. Using an ultraviolet refractometer made by Hilger for Henri[4,5] we measured n_s, the refractive index, and d, the density of each solution. Substituting in the formula $(n_s^2 - 1)/(n_s^2 + 2)d$ the specific refraction of the solution r_s resulted. From the formula $100r_s = (r_w \times \%$ water$) + (r_{salt} \times \%$ salt$)$, the refraction of the salt, r_{salt} was obtained and multiplied by the formula weight to find R, the molecular refraction in water solution.

An iron spark was used as the light source between 24,000 and 42,900 cm.$^{-1}$ and nickel between 42,900 and 45,000 cm.$^{-1}$. A d. c. arc between electrodes of tungsten steel, consuming 6 amperes, was equally satisfactory. The wave numbers in these spectra were carefully assigned by successive comparisons of these spectrograms with those of cadmium, zinc and copper sparks. All wave numbers used in calibration, when plotted against a millimeter scale, lay on a smooth

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(1) Lubben, *Ann. Physik*, **44**, 977 (1914).

(2) Heydweiller, *ibid.*, **41**, 499 (1913).

(3) Heydweiller and Grube, *ibid.*, **49**, 653 (1916).

(4) Henri, "Étude de Photochemie," Gauthier-Villars et Cie., Paris, 1919, p. 30.

(5) Voellmy, *Z. physik. Chem.*, **127**, 305 (1927).