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 nonpolar 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 $100r_s = (r_w \times \%\ \text{water}) + (r_{\text{salt}} \times \%\ \text{salt})$, 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).

curve. Additional confirmation, in the case of cadmium, was obtained by comparison with a second prism spectrogram on nearly the same scale, with wave lengths marked by Professor G. P. Baxter. Necessary repairs were made on the bearing of the refractometer and a micrometer device added by the Mann Instrument Company of Cambridge. Changes in the setting of the graduated circle could now be read easily with 15″ of arc,

We first measured the refraction of water in the customary manner.[4,5] The triangular cell C, Fig. 1, was filled with a quartz prism P (not shown) having an identical dihedral angle, i = 29°43′48½″, and the plane face of the quartz half-cylinder H was set parallel to the vertical face of the cell, forming, in effect, a rectangular prism of quartz. This unit was mounted in the parallel beam between the two concave mirrors, not in the converging beam as represented in Henri's diagram.[4] Later, Dr. L. J. Heidt of this Laboratory found that if the thin air film between H and C were replaced with water, spectra became sharper and more intense. A narrow polychromatic beam from the spark entered this prism at perpendicular incidence and emerged without deviation into a Féry quartz spectrograph (not shown). This instrument, lent by the Wolcott Gibbs Memorial Laboratory, carried a 2 × 10 in. Agfa portrait or Eastman x-ray film, upon which the normal spectrum of the spark was recorded. After replacing P with water, H was turned through the angle $\phi = (90° - \Theta)$ where Θ was the actual scale reading. A second exposure was then made on top of the first one. After development, the second spectrum was seen to cross the first at that wave number $\bar{\nu}$ where the rotation of H just compensated for the difference between n_w, and n_q the refractive index of quartz. There were two images of each cross spectrum, but we considered only the one with smaller deviation (ordinary ray). Then (1) $n_w = (\sin\phi\cos(i-\phi) + \sin(i-\phi)\sqrt{n_q^2 - \sin^2\phi})/\sin i$.[4] From "International Critical Tables"[6a] n_q for the wave number of the intersection (ordinary ray) was interpolated. Found from Equation (1), n_w did not agree well with n_w interpolated from "I. C. T."[6b] nor was it reproducible. We recalled that Lowry and Allsopp had criticized certain data obtained from an instrument of this type.[7]

At least a part of our difficulties seemed to arise from the cylindrical condensing lens of the spectrograph which produced upon the film images not necessarily identical with those falling upon its slit. After removing the quartz prism and filling the cell with water, the lens had to be shifted to avoid blurring of the cross spectrum, but now the intersection seemed to have moved as well. To avoid this complication, we discontinued the use of the quartz prism and photographed the normal spectrum, but only after removing the cell and turning H out of the light path. In order to avoid certain possible systematic errors such as the effects of possible errors in the graduated circle, we decided to measure ϕ for each salt solution as the difference between (1) the angle to be subsequently calculated, for a given setting of the instrument, from a known value of n_w, and (2) a much smaller angle read directly and precisely from the micrometer screw.

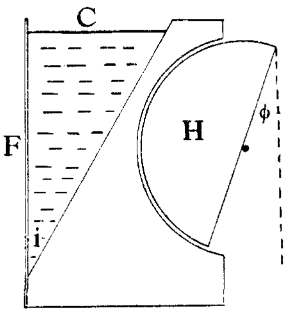

Fig. 1.

A special case will make our procedure clear. After photographing the normal spectrum the cell was replaced and filled with water near 25°. Temperature was recorded so that n could be corrected if necessary. Next H was set at a suitable angle and Θ recorded even though $\phi = (90 - \Theta)$ was to be obtained indirectly. A second exposure was made without any other readjustment of the system. The cell was emptied, dried and filled with a 13.07% solution of mercurous perchlorate. By turning the micrometer screw ϕ was decreased by 26′ and a third exposure made, again without other readjustments. When the film was developed the cross spectrum for water intersected the normal spectrum at $\bar{\nu}$ = 39,650 cm.$^{-1}$, where n_q[6a] (interpolated) is 1.5990, and n_w[6b] is 1.3757. By solving equation (1) we found $\phi = 11°51'$, the angle between F and the half-cylinder face. To save labor we plotted $\sin\phi\cos(i-\phi)$ and $\log\sin(i-\phi)$ against ϕ, also $\log\sqrt{n_q^2 - \sin^2\phi}$ against $\bar{\nu}$ for each of several values of ϕ. That value of ϕ predicting $n_w = 1.3757$ was selected, or interpolated over a range not exceeding one minute. The spectrum corresponding to the solution intersected the normal spectrum

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(6) (a) "I. C. T.," Vol. VI, p. 341; (b) Vol. VII, p. 13.

(7) Lowry and Allsopp, *Proc. Roy. Soc.* (London), **133**, 26 (1931).

where $\bar{\nu} = 27{,}350$ cm.$^{-1}$. By substituting $\phi = 11°51'-26'$ and $n_q = 1.5627$ in (1), n_s comes out 1.3608 referred to air. The specific refraction of the solution, calculated as in the opening paragraph, was 0.0855 and the molecular refraction R was 52.4. As the probable error of R is of the order of 1%, reduction of n and R to vacuum is unnecessary.[8]

The error in any value, n_s, thus determined, should not greatly exceed that of n_w as interpolated from "I. C. T." Systematic errors in the instrument and even in the values assumed for n_q tended to eliminate themselves in our process. coercion—further evidence that our errors were not systematic. The same can be said of our errors in locating intersections, aggravated by faintness and blurring of images when $\bar{\nu}$ was large and by low dispersions when $\bar{\nu}$ was small. Voellmy[5] combated high absorptions by laying a number of thin parallel quartz plates along the hypotenuse surface of the cell C, so that the large liquid prism was reduced to a series of small ones "in parallel." We made trial of this procedure, but in the end decided to rely upon low concentrations, in spite of somewhat increased uncertainty regarding R.

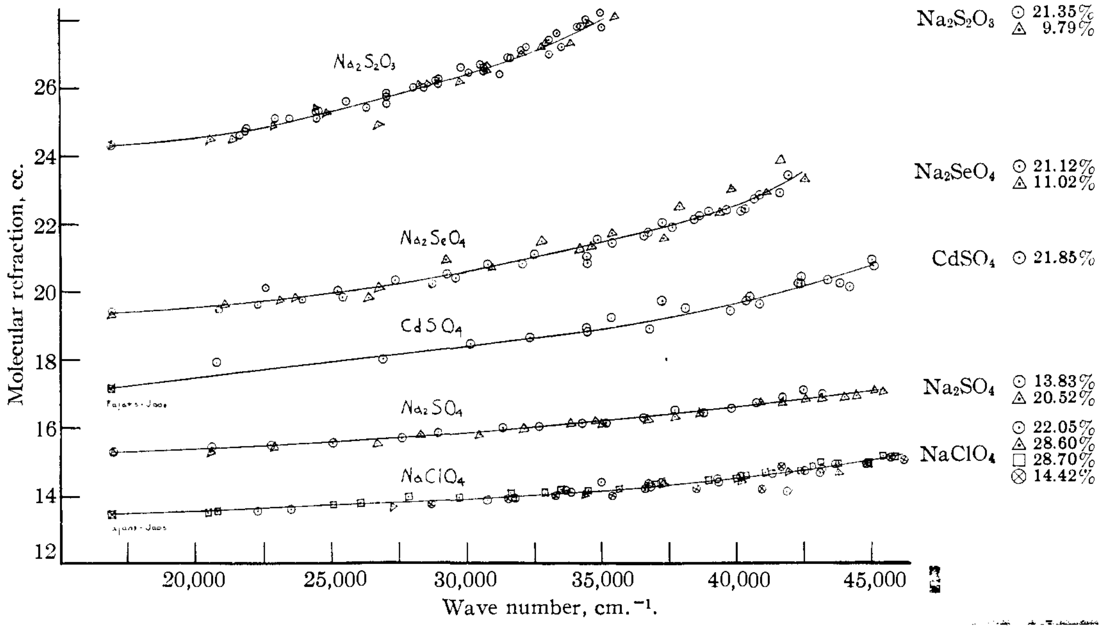

Fig. 2.

If better measurements for water become available our results can be recalculated. As an additional check we calculated $\phi_w - \phi'_w$ corresponding to $\bar{\nu}$ and $\bar{\nu}'$ in each of 79 of the earlier experiments and compared $(\phi_w - \phi'_w)$ with $(\Theta_w - \Theta'_w)$ as read from the graduated circle in each case. These differences irrespective of sign agreed to 0.5'. The algebraic sum divided by 79 was only 0.06' showing that our errors were not systematic. A further confirmation resulted from extrapolation of our plots (Fig. 2) of R against $\bar{\nu}$ to $\bar{\nu}_D$ for the sodium lines and comparing this intersection with R_D given either by Fajans and Joos[9] or others or as determined by us using a Pulfrich refractometer described elsewhere.[8] In all cases our plots passed through R_D without

Materials.—Though our predecessors did not describe the purification and drying of their salts, we infer that their precautions were adequate. They reduced their weights to vacuum. We took many precautions in connection with purification, drying and weighing, density determinations and analyses of solution, which cannot be recorded here. Starting with the best commercial salts available, most of them were dissolved, filtered, recrystallized and sucked dry on sintered glass crucibles or centrifuged. The products were in general ground, dried at 100–120° and when lumpy ground and dried again. Portions were weighed out and dissolved in a weighed amount of water, applying vacuum corrections except to the densest solids. The true densities of these solutions as measured by us were frequently checked against data in "I. C. T."[10] properly interpolated.

Salts such as potassium iodide, sodium thiosulfate or lanthanum chloride, unstable when heated in air, were dissolved and the indeterminate solutions analyzed in duplicate by standard methods. We failed to obtain pure

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(8) Baxter and others, This Journal, **33**, 901 (1911).

(9) Fajans and Joos, *Z. Physik*, **23**, 1 (1924).

(10) "I. C. T." Vol. III.

sodium tellurate from the small sample of pentahydrate available.

Silver and lead carbonates were precipitated, washed and dissolved in perchloric acid to saturation, also mercuric oxide from pure mercury through the nitrate. Lead was determined as sulfate, mercury as sulfide and as iodide, perchloric acid by acidimetry after precipitation of cations as sulfides, filtration and boiling. Half the mercuric solution was shaken (warm) for several days with pure mercury, when the ratio $(Hg^{++})/(Hg_2^{++})$ was found to be 0.003 instead of 0.004.[11] Lithium and thallous chlorides were fumed with perchloric acid. Lithium perchlorate was recrystallized and fused to constant weight in platinum. In the indeterminate thallous solution thallium was determined as iodide.

Professor Grinnell Jones kindly provided a sample of very pure lanthanum chloride. An indeterminate solution was analyzed through silver chloride, and the salt recovered by evaporation of an acidified solution. After adding water, to measure *n* again, the ratio $La_2O_3/6Cl$ checked with that of unhydrolyzed salt.

Sodium sulfite solutions were shaken with solid barium sulfite and analyzed after filtration. The ratio $SO_3^{=}/SO_4^{=}$, was only 7.1, and R was corrected for $SO_4^{=}$ upon this basis. From Chéveneau's data[12] we calculated $R_D = 15.9$, over a unit lower than our extrapolated values. Our work on this salt should be repeated.

As much depended upon R_{NaClO_4}, all operations were carried out with special care. Samples A and B were made through the routine purification. Sample C from twice crystallized carbonate and reagent quality perchloric acid followed by one recrystallization of the product. All samples were dried at 120° for one to two hours. The densities of five solutions of these three samples were several parts in a thousand higher than those interpolated from "I. C. T." for the same concentrations. An additional solution was made by weighing out recrystallized anhydrous carbonate and neutralizing it (methyl orange) with distilled perchloric acid. After expelling carbon dioxide, the solution was evaporated somewhat before weighing the solution and finding the density. The density lay on the same curve as the other five. Evidently Lubben found his densities from the same source as "I. C. T.," for if we correct his densities by our work, and recalculate the composition of his solutions to correspond, his values for R, originally higher than ours, are brought into good agreement with them, and both, upon extrapolation, agree with R_D according to Fajans and Joos.[9]

Figure 2 shows typical plots of R against wave number without regard for the different concentrations involved. Except perhaps in the case of lanthanum chloride we noticed no trend in R with progressive concentration changes. Fajans and Joos[9] found R constant within 0.1 unit (using sodium light) over concentration ranges considerably greater than ours. Assuming the absence of systematic errors, R interpolated from such curves for round values of $\bar{\nu}$ should be reliable within 0.1 to 0.3 unit except for difficultly soluble salts, and for sodium sulfite and lanthanum chloride, with which salts it probably reached 0.5 unit.

Table I gives the molecular refraction for the salts investigated. The corresponding equivalent refractions would result, of course, through division by the valence. Fajans and his collaborators always use R in the latter sense.

Fajans has assigned the values $R_{Na^+} = 0.2$ and $R_{K^+} = 2.2$, both in sodium light. Comparing potassium nitrate with sodium nitrate it appears that $(R_{K^+} - R_{Na^+})$ is very constant at 2.0 in the ultraviolet also, at least as far as $\bar{\nu} = 37{,}500$. So as a first approximation we will assume that the individual values are constant as well. From sodium perchlorate and lithium perchlorate we obtain $R_{Na^+} - R_{Li^+} = 0.6 \pm 1$ (except where $\bar{\nu} = 45{,}000$), whence $R_{Li^+} = -0.4$. Found from the iodates this difference is smaller and less constant. In terms of R_{K^+}, R_{Na^+} and R_{Li^+} the several anionic refractions can be readily calculated.

We referred cationic refractions to $R_{ClO_4^-}$, found in turn by subtracting 0.2 from R_{NaClO_4} discussed at length above. Thereupon we found $R_{ClO_4^-}$ also $R_{NO_3^-}$ and $R_{SO_4^-}$ from the sodium salts (Table I) for the various values of $\bar{\nu}$. Cationic refractions appear in Table II. The additivity principle appears to hold, for thallium, within the limit of error, but hardly so well for lead. The extinction coefficient of both thallium and lead nitrates has been found to increase with increasing concentration,[13] evidence of irregularities in polarizability. Our thallous solutions were less concentrated than the plumbous solutions, which perhaps offers an explanation for the apparent conformity in the case of thallous ion.

Anionic refractions easily result by subtracting R_{Na^+} or R_{K^-} from the data in Table I; separate tabulation is dispensed with.

Relative refractions of two groups of related anions plotted against $\bar{\nu}$ appear in Fig. 3. The end of each experimental curve is reached (irrespective of chemical composition) at a wave number where the extinction coefficient of the salt becomes so large that further progress is impracticable. As expected, the curves are steeper the earlier the appearance of the evidence of strong absorption bands. Among closely related ions

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(11) Ogg, *Z. physik. Chem.*, **27**, 285 (1898).

(12) Chéveneau, *Ann. chim. phys.*, **12**, 217 (1907).

(13) Hartley, *J. Chem. Soc.*, **81**, 556 (1902); **83**, 221 (1903); **101**, 820 (1912).

TABLE I[14]

MOLECULAR REFRACTION

Wave no./cm.	KCl	KBr	KI	KNO_3	$NaNO_3$	Na_2SO_4	Na_2SeO_4	$Na_2S_2O_3$	Na_2SO_3
16,950	11.2*	14.9*	21.5*	13.2*	11.2*	15.3	19.3	24.3	17.1
20,000	11.4	15.1	21.8	13.4	11.4	15.4	19.5	24.5	17.2
22,500	11.6	15.3	22.4	13.5	11.5	15.4	19.7	24.8	17.4
25,000	11.8	15.6	23.1	13.8	11.7	15.6	19.9	25.3	17.7
27,500	12.0	15.9	23.9	14.1	12.0	15.7	20.2	25.8	18.1
30,000	12.3	16.4	25.0	14.5	12.4	15.8	20.6	26.4	18.5
32,500	12.6	17.0	26.4	15.0	12.8	16.0	21.0	27.0	18.9
35,000	12.9	17.7	28.4	15.6	13.6	16.1	21.4	28.0	19.5
36,250	..	..	29.9	16.0	..	..	..	..	..
37,500	13.3	18.5	31.9	16.5	14.5	16.3	21.9	..	20.4
38,750	..	..	35.8	..	15.1	..	..	..	..
40,000	13.7	19.7	..	..	15.9	16.5	22.5	..	..
42,500	14.3	21.8	..	..	..	16.8	23.5	..	..
43,750	14.7	23.3	..	..	..	..	..	..	..
45,000	15.2	..	..	..	..	17.0	..	..	..

Wave no./cm.	$LiClO_4$	$NaClO_4$	$NaClO_3$	$NaBrO_3$	$NaIO_3$	$LiIO_3$	$LaCl_3$
16,950	12.8	13.4*	13.2*	16.2	19.8	19.3	..
20,000	12.9	13.5	13.3	16.3	20.0	19.5	..
22,500	13.0	13.6	13.4	16.4	20.1	19.9	30.8
25,000	13.1	13.7	13.5	16.6	20.4	20.2	31.4
27,500	13.2	13.8	13.6	16.8	20.9	20.6	32.0
30,000	13.4	13.9	13.8	17.2	21.5	21.2	32.8
32,500	13.5	14.0	14.0	17.7	22.2	21.9	33.7
35,000	13.6	14.1	14.2	18.2	23.2	22.8	34.8
37,500	13.7	14.3	14.5	18.9	23.8	..	36.2
40,000	13.9	14.5	14.8	19.9	..	..	37.8
42,500	14.0	14.7	15.2	..	..	..	39.7
45,000	14.2	15.0	..	..	..	..	..

Wave no./cm.	$AgClO_4$	$TlClO_4$	$TlNO_3$	$^1/_2Hg_2(ClO_4)_2$	$Hg(ClO_4)_2$†	$Pb(ClO_4)_2$	$Pb(NO_3)_2$	$CdSO_4$
16,950	18.1*	23.5	21.1	..	31.8**	35.0	31.2	17.1*
20,000	18.3	23.7	21.6	..	32.1	35.4	31.5	17.4
22,500	18.4	24.0	22.1	24.7	32.4	35.8	32.1	17.6
25,000	18.5	24.4	22.7	25.3	32.7	36.2	32.9	17.9
27,500	18.7	24.9	23.4	26.0	33.1	36.8	34.0	18.1
30,000	18.9	25.5	24.3	27.2	33.6	37.5	35.3	18.4
32,500	19.1	26.2	25.5	29.1	34.2	38.4	36.8	18.6
33,750	..	..	..	30.4	..	..	..	..
35,000	19.5	27.1	27.0	32.4	34.8	39.4	38.8	18.8
37,500	20.0	28.3	28.8	..	35.7	40.6	42.2	19.2
38,750	20.3	29.1	29.9	..	36.4	41.3	44.5	..
40,000	20.7	30.0	31.4	..	..	42.2	47.4	19.6
41,250	21.2	..	..	..	..	43.4	..	..
42,500	..	..	..	..	..	..	..	20.1
45,000	..	..	..	..	..	..	..	20.7

† $Hg^{++} + 1.98\ ClO_4^-$. * Fajans and Joos. ** Geffcken.

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(14) After the completion of this research, Mr. F. Twyman of Adam Hilger, Ltd., conferred with us, and later wrote that there were risks of error in combining our refractometer with a Féry spectrograph. Still later, he sent detailed precautions to be observed in handling the optical system, kindly prepared for us by Dr. C. B. Allsopp of the Laboratory of Physical Chemistry, Cambridge University, England. No objection was made to our method of finding ϕ "...provided (1) that the light was incident normally upon the face of the cell in the first place, and (2) that the water was removed, the cell cleaned and dried, and the solution introduced all without any change in the position of the cell."

Under these circumstances it appeared expedient to check typical data, using a Hilger E 3 quartz spectrograph kindly lent by Professor Oldenberg of the Department of Physics of this University. Since Dr. Elkins had left for Europe, Dr. L. J. Heidt of this Laboratory redetermined *R* over the same spectral intervals for KBr, $NaClO_4$ and $NaIO_3$, representing the beginning, middle and end of the main research. Particular care was taken to realize the two conditions laid down by Dr. Allsopp, also to have the principal axis and focus of the front lens of the spectrograph coincide with the principal axis and focus of the back mirror of the refractometer. The new values of *R* agreed with Table I within the limit of error, since n_s was checked within ±0.0011, and no trend of *R* with changing concentration was observed. Returning to the Féry instrument, it was found that correct values for n_s resulted only when its slit was not more than 0.2 mm. high and very narrow, and only when parallel, not converging, light was incident upon the slit. These conditions had been approximated in the main research. If the principal axis of the back mirror of the refractometer was not exactly perpendicular to the slit, all intersections of cross spectra with the normal spectrum were shifted, but the values of n_s obtained by first calculating ϕ_{water} from n_{water} were not perceptibly changed. Reëxamination of the photographs obtained in the main research revealed evidence of small deviations from the perpendicular which could not have vitiated the results.

TABLE II

IONIC REFRACTION

Wave no./cm.	$AgClO_4$ $-ClO_4^-$	$TlClO_4$ $-ClO_4^-$	$TlNO_3$ $-NO_3^-$	$\frac{1}{2}Hg_2(ClO_4)_2$ $-ClO_4^-$	$Hg(ClO_4)_2$ $-2ClO_4^-$	$Pb(ClO_4)_2$ $-2ClO_4^-$	$Pb(NO_3)_2$ $-2NO_3^-$	$CdSO_4$ $-SO_4^-$
16,950	4.75	10.25	10.1	..	5.6	8.55	9.2	2.25
20,000	4.85	10.35	10.4	..	5.7	8.7	9.1	2.4
22,500	5.0	10.6	10.8	11.3	5.8	9.0	9.5	2.6
25,000	5.0	10.9	11.2	11.8	5.9	9.2	9.9	2.7
27,500	5.1	11.3	11.6	12.4	6.1	9.6	10.4	2.8
30,000	5.2	11.8	12.1	13.5	6.4	10.1	11.1	2.95
32,500	5.35	12.4	12.8	15.3	6.8	10.8	11.5	3.0
33,750	..	..	..	16.55	...	..	..	..
35,000	5.6	13.2	13.6	18.5	7.1	11.5	12.0	3.0
37,500	5.9	14.2	14.5	..	7.7	12.5	13.6	3.25
38,750	6.1	14.9	15.0	..	8.2	12.95	14.7	..
40,000	6.4	15.7	15.7	..	..	13.6	15.6	3.45
41,250	6.8	..	..	..	..	14.8	..	..
42,500	..	..	..	..	..	..	..	3.7
45,000	..	..	..	..	..	..	..	4.1

such as the halides both relative refraction and absorption increase more rapidly the greater the ionic mass, except in the case of nitrate and chlorate. Between $\bar{\nu} = 25{,}000$ and $35{,}000$ the steepness of the dispersion curves for cations increases in the order Ag^+, Cd^{++}, Hg^{++}, Tl^+, Pb^{++}, Hg_2^{++}.

We made some preliminary attempts to calculate absorption centers, using the familiar formula[15]

$$R = R_0 + \frac{e^2}{3\pi m}\frac{NP}{\bar{\nu}_i^2 - \bar{\nu}^2} \text{ or } R = \frac{C}{\bar{\nu}_i^2 - \bar{\nu}^2}$$

Instead of solving three simultaneous equations, $\bar{\nu}_i$ was approximated by trial.

Ion	I^-	Br^-	Cl^-	NO_3^-	Ag^+	Tl^+	Pb^{++}	Hg^{++}
λ_i calcd. in Å.	2170	1930	1530	1950	2070	1630	1820	2160
λ_i obs. in Å.[16]	2150	1950	1820					

	Hg_2^{++}	ClO_3^-	BrO_3^-	IO_3^-	$SO_4^=$	$SeO_4^=$	$SO_3^=$	$S_2O_3^=$
λ_i calcd. in Å.	2520	1330	1920	1980	1060	1400	1450	1720

The disagreement for Cl^- suggested a second strong band or bands far down in the Schumann region. After our work was finished, Albert Smith[17] reported, in solid sodium chloride, absorption maxima at 655, 535 and 890 Å.

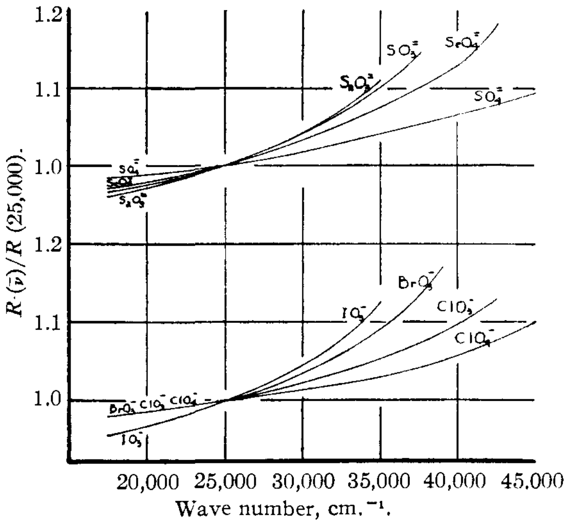

Fig. 3.

We are indebted to the du Pont Fund for financial support in this investigation and to the Wolcott Gibbs Memorial Laboratory for the loan of the Féry quartz spectrograph.

An extension of this investigation is projected.

Summary

An ultraviolet refractometer after Henri was remodeled, and used in conjunction with a Féry quartz spectrograph. Molecular refractions of twenty-four salts were referred to refractive indices of water at the same temperature. Measurements extended from $\bar{\nu} = 24{,}000$ to $45{,}000$ cm.$^{-1}$ or as far as absorption permitted. Ionic refractions and dispersions were calculated with the help of certain assumptions. Centers of absorption were predicted from a simple form of the theoretical dispersion equation, with emphasis upon the limitations of this procedure.

CAMBRIDGE, MASS. RECEIVED AUGUST 16, 1933

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[15] Herzfeld and Wolf, *Ann. Physik*, **78**, 35 (1925).

[16] Scheibe, *Z. Elektrochem.*, **34**, 497 (1928). See also Bonhoeffer and Harteck, "Grundlagen der Photochemie," Verlag Theodor Steinkopff, Dresden, 1933, pp. 159–167.

[17] Smith, *Phys. Rev.*, **44**, 522 (1933), with bibliography.