The activity coefficient values taken from the curve were 0.879 for 1.000 N acid, 1.217 for 2.002 N acid, and 1.816 for 2.987 N acid.

From the values in columns 3 and 4 the following expressions were derived for the cell e. m. f., E_t, at any temperature t from the vicinity of 25 to that of 35°

In 1.000 N hydrobromic acid $E_t =$
$$0.14388 - 0.000078(t - 25)$$
In 2.002 N hydrobromic acid $E_t =$
$$0.09058 - 0.000191(t - 25)$$
In 2.897 N hydrobromic acid $E_t =$
$$0.04845 - 0.000321(t - 25)$$

In these acid solutions as the concentration increases there is a tendency for the mercurous bromide electrode reduction e. m. f. to become increasingly less than the calculated value because of the decrease in activity of the bromide ions due to the formation of bromide complexes. This decrease in reduction e. m. f. is more or less com-

pensated for by an opposing liquid junction potential at the zone of contact of the hydrobromic acid solutions of the two electrodes. Such behavior probably is responsible for the fairly close agreement between the experimental and theoretical values.

Summary

Determinations of the molal reduction e. m. f. of the mercurous bromide electrode at 25° in 0.1002 m hydrobromic acid solutions show that the values obtained in solutions free from air are about 0.5 millivolt higher than those in which air is not completely removed. Both values are accurately reproducible and are -0.1391 volt in air free solutions and -0.1396 volt in solutions containing air, using hydrogen as the reference electrode. Results of e. m. f. measurements made at 25 and 35° in approximately one, two, and three normal hydrobromic acid are also shown.

The Molar Dispersion and Refraction of Free and Bonded Ions[1]

BY NORMAN BAUER[1a] AND KASIMIR FAJANS

Introduction

This paper is a continuation of the series of "Refractometric Investigations,"[2] the main goal of which has been an understanding of the changes occurring in the electronic systems of ions, atoms and molecules when they combine with each other. Since the "valence" electrons are identical with those responsible for the optical behavior in the visible and near ultraviolet, it was justified to expect that optical properties would be especially suited to a study of this problem which is so closely connected with the nature of chemical forces. In fact, for substances having electronic systems of the noble gas type,[3] these refractometric investigations have revealed (see especially I, VII, XXX) the existence of two effects which prove to have great influence on the physical[4] and chemical behavior of substances:

(1) From a doctoral dissertation submitted by N. Bauer at the University of Michigan in June, 1941. The paper was presented in part at the 101st Meeting of the American Chemical Society, April 9, 1941.

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(2) This is paper number LV in the series. The following of the former papers will be referred to by the corresponding Roman numerals. I. K. Fajans and G. Joos, Z. Physik, 23, 1 (1924); VII. K. Fajans, Z. Elektrochem., 34, 502 (1928); IX. H. Kohner, Z. physik. Chem., B1, 427 (1928); X. W. Geffcken and H. Kohner, ibid., B1, 456 (1928); XI. W. Geffcken, ibid., B5, 81 (1929); XII. H. Kohner and M. L. Gressmann, ibid., A146, 137 (1930); XIV. K. Fajans and H. Kohner, ibid., A147, 241 (1930); XX. Z. Shibata and P. Hoelemann, ibid., B13, 347 (1931); XXI. K. Fajans, P. Hoelemann and Z. Shibata, ibid., B13, 353 (1931); XXIII. W. Geffcken, C. Beckmann and A. Kruis, ibid., B20, 398 (1933); XXV. P. Wulff, ibid., B21, 367 (1933); XXVI. A. Kruis and W. Geffcken, ibid., A166, 16 (1933); XXVII. P. Wulff and D. Schaller, Z. Krist., A87, 43 (1934); XXIX. W. Geffcken and A. Kruis, Z. physik. Chem., B23, 175 (1933); XXX. K. Fajans, ibid., B24, 103 (1934); XXXV. P. Hoelemann and H. Goldschmidt, ibid., B24, 199 (1934); XXXVIII. P. Wulff, ibid., B25, 177 (1934); XL. G. Damkoehler, ibid., B27, 130 (1934); XLI. P. Wulff and T. Anderson, Z. Physik, 94, 28 (1935); XLII. R. Luehdemann, Z. physik. Chem., B29, 133 (1935); XLIII. K. Fajans and R. Luehdemann, ibid., B29, 150 (1935); XLVII-LI. A. Kruis and W. Geffcken, ibid., B34, 1-95 (1936).

(3) It has been shown (see, e. g., K. Fajans, "Chemical Forces and Optical Properties of Substances," (Cornell Lectures), McGraw-Hill Book Co., Inc., New York, N. Y., 1931) on the basis of properties such as lattice distances, lattice energies, crystal structure, solubility, formation of complex compounds, color, etc., that deformation phenomena are more pronounced in substances formed from non-rare gas cations (Class II, e. g., AgCl) than in substances derived solely from noble gas ions (Class I, e. g., NaCl). However, the refractometric method has not yet given clear results for the former class of compounds (see XXX, p. 147-151); this seems to have the following reason. For most cases in Class I the refractometric effect caused by anion tightening is very much stronger than the opposite effect. In Class II, because of the deeper mutual interpenetration of the ions, and also because of the larger polarizability of non-rare gas cations, both effects are of the same order of magnitude and partly cancel each other.

(4) See, e. g., K. Fajans, Phys. Rev., 61, 543 (1942).

namely, the tightening of electronic systems by neighboring positive charges and their loosening by negative charges.[5]

The existence of these two effects was first concluded on the basis of the large systematic deviations from additivity which the Lorentz–Lorenz molar refraction R shows. The analysis of these deviations was greatly aided by the derivation (I) of values of the molar refraction of individual gaseous ions, as distinguished from ions in solution or from those in molecules and crystals. Until now such a derivation has been carried out in this series of investigations only for the refraction R_D at a wave length corresponding to the sodium D line. Recent precision measurements of the refraction at various wave lengths in the visible for a number of electrolytes (XLVIII and IL), along with the accumulated data from previous work, now make it possible to obtain a set of provisional values for the molar dispersion of individual gaseous and aqueous ions.

A knowledge of the dispersion furnishes a means of extrapolating R_λ to $\lambda = \infty$. Since

$$R_\infty = \frac{4}{3} \pi N \alpha \qquad (1)$$

one can then arrive at a consistent set of values of the true electronic polarizability (α) of ions.[6] Seldom is R_D more than a few per cent. different from R_∞, and thus R_D has been a sufficiently accurate measure of α for a qualitative investigation of the role of polarizability in the physical and chemical behavior of substances. The R_∞ values should now help in developing the quantitative aspects of this problem.

However, the inclusion of the molar dispersion in this study is of importance in itself because, as this paper will show, it is a property which is even more sensitive to changes in the forces acting on the particles involved than is the molar refraction.

In the present paper we shall limit ourselves to establishing a set of values for the molar dispersion of ions and to showing by a few examples how its large deviations from additivity help in the study of electronic deformation.

1. Extrapolation to Infinite Wave Length on the Basis of Dispersion Theory.—It has been

(5) Concerning a theoretical treatment of the refractometric tightening and loosening effects, see Th. Neugebauer, *Physik. Z.*, **94**, 655 (1935); *ibid.*, **99**, 687 (1936); *Hungarian Acad. Sci.*, **54**, 337 (1936).

(6) For a review of other methods of obtaining α, used by M. Born and W. Heisenberg, L. Pauling, J. E. Mayer and M. G. Mayer, see *e. g.*, J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932, pp. 208–225, and XXX, pp. 128–133 and p. 154.

customary to define the dispersion of a substance as the difference ΔR[7] between molar refractions at two arbitrarily selected wave lengths in the visible (*e. g.*, $\Delta R = R_{H\beta} - R_{H\alpha}$).

For reasons apparent from the Introduction we have chosen the difference between the molar refraction for the sodium D line (R_D) and that for infinite wave length (R_∞) as the measure of the *molar dispersion* **D**. Extrapolations to $\lambda = \infty$ from measurements in the visible were made by the reciprocal plotting method of P. Wulff (XXV), based on the dispersion theory.

According to the dispersion theory,[8] the refraction R may be expressed as a function of the frequency $\nu = c/\lambda$ by an equation of the type

$$R_\lambda = \sum \frac{C_i}{(\nu_0)_i^2 - \nu^2} \qquad (2)$$

The summation includes one term for each of the characteristic frequencies [$(\nu_0)_i$] of the system; the constants C_i are a measure of the probability of transition between the states which define the frequency $(\nu_0)_i$. If a single term is sufficient, then a plot of $1/R_\lambda$ *versus* ν^2 gives a straight line

$$\frac{1}{R_\lambda} = \frac{\nu_0^2}{C} - \frac{1}{C} \nu^2 \qquad (3)$$

The intercept on the $1/R_\lambda$ axis for $\nu^2 = 0$ gives the value of $1/R_\infty$. When more than one term is necessary, then, as Wulff has found, the $1/R_\lambda$ *versus* ν^2 curve is composed of straight lines and hyperbolas, the sum of which approaches a straight line for small values of ν^2.

Experience shows that when the maximum of the first principal electronic absorption band [$(\nu_0)_1$] has a wave length less than about 250 mμ, and when infrared contributions are negligible, the plot becomes linear in the visible part of the spectrum.

In Fig. 1 several typical extrapolations are made from data of different degrees of accuracy for the molar refraction of crystals and the apparent molar refraction of aqueous electrolytes. For the case of solutions measured with the Pulfrich refractometer (see Fig. 1, part B), for which the accuracy is lower than that of the interferometric measurements in part A, the thin dashed lines show the extreme slopes of the possible straight lines which can be put through the experimental points. The errors in **D** (in Tables I, II and III) were estimated by taking half of the

(7) The symbol Δ will be often used to denote the difference between two quantities.

(8) *Cf.* K. F. Herzfeld and K. L. Wolff, "Handbuch der Physik," Verlag Julius Springer, Berlin, 1928, XX, p. 512.
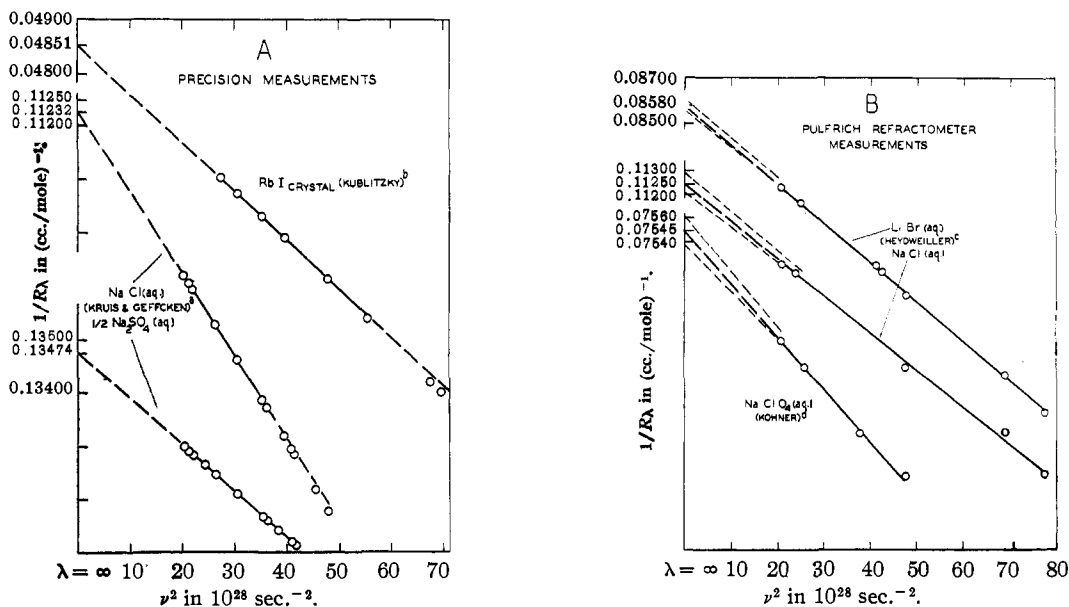
Fig. 1A and 1B.—Typical extrapolations to infinite wave length of the molar refraction of crystals and apparent molar refraction of aqueous electrolytes according to the reciprocal plotting method (P. Wulff, XXV): (a) see Table II; (b) see ref. (29); (c) see ref. (19); (d) see (IX).

difference between the values of $1/R_\infty$ given by the extension of the most probable line (i. e., of the line drawn in full) and that given by the extreme possible line.

The curves in part A of Fig. 1, resulting from very accurate measurements on crystals and solutions, show departure from linearity in the direction of increasing negative slope for increasing values of ν^2. This downward curvature is to be expected on the basis of (2) for substances for which $(\nu_0)_2$ is not very much larger than $(\nu_0)_1$[9]. In general, and especially for the simple inorganic substances treated here, the experimental points fit a straight line the better, the nearer they come to the region over which extrapolation is made; thus the linear extrapolation appears to be well founded.

2. Selection of Data on the Dispersion of Simple Inorganic Substances.—The molar dispersions D given in Tables I, II and III were derived from the results of a large number of in-

vestigators who used various experimental techniques. Therefore, it is necessary to appraise the reliability of the various sets of data.

(a) Gases and Vapors (Table I).—The principal sources of data for gases were Cuthbertson and Cuthbertson,[10,11,13,16] Damkoehler (XL), Larsen,[12] Friberg[15] and Watson and Ramaswamy.[17]

We made the extrapolation to $\lambda = \infty$ for all gases except H_2Se by means of the dispersion formulas given in the original papers, which represented the experimental data (corrected to the ideal gas state) with great accuracy. The estimate of the error in dispersion was made from the relative uncertainty in the indices of refraction.

For H_2Se a plot of $1/R_\lambda$ vs. ν^2 was made in the usual way from the data of Frivold, Hassel and Skjulstad.[14]

(b) Aqueous Solutions of Electrolytes at Infinite Dilution (Table II).—Three principal series of measurements on aqueous electrolytes were used. The most accurate available data, which make the present partition into values of the molar dispersion of individual ions possible, are based on the precision measurements of Geffcken, Kruis and Beckmann (see Table II and XXIII) for five salts at 15 different wave lengths between 6678 and 4358 Å. The refractive indices and the densities of the dilute solutions

(9) An infrared contribution, corresponding to atomic polarization $[(\nu_0)_{i.r.} \ll (\nu_0)_1]$, would show up as a curvature of opposite sign at the red end of the spectrum when the dispersion for shorter wave lengths gives a linear $1/R_\lambda$ vs. ν^2 plot. Among substances included in this paper this was the case only for liquid water and was indicated by the precision measurements on aqueous Na_2SO_4 (see XXVII p. 59 and IL p. 65); the scale of Fig. 1A is too small to reproduce this indication. In such cases the linear part corresponding to the electronic contribution has to be used for the extrapolation. In general the contribution of infrared terms to the refraction in the visible is negligible. See, concerning a wide variety of crystals, e. g., I p. 8, XXXVIII p. 181, and XXVII p. 59; concerning aqueous solutions of electrolytes, e. g., IL p. 61.

(10) C. and M. Cuthbertson, Proc. Roy. Soc. (London), **A135**, 40 (1932).

(11) C. and M. Cuthbertson, ibid., **A84**, 13 (1910).

(12) T. Larsen, Z. Physik, **111**, 394 (1938).

(13) C. and M. Cuthbertson, Trans. Roy. Soc. (London), **A213**, 1 (1913).

(14) O. E. Frivold, O. Hassel and T. Skjulstad, Physik. Z., **37**, 134 (1936).

(15) S. Friberg, Z. Physik, **41**, 378 (1927).

(16) C. and M. Cuthbertson, Proc. Roy. Soc. (London), **A97**, 152 (1920).

(17) H. E. Watson and K. L. Ramaswamy, Proc. Indian Acad. Sci., **A4**, 675 (1936).

TABLE I

MOLAR DISPERSION AND MOLAR REFRACTION OF GASES
CORRECTED TO THE IDEAL GAS STATE IN Cc.

Gas	R_D	D			Reference
He	0.521	0.00351	±	0.04$_3$	(10)
Ne	1.004	.0066	±	.03$_2$	(10)
A	4.203	.064	±	.002	(11), XL
Kr	6.397	.129	±	.003	(11). XL
Xe	10.43$_5$	.298	±	.005	(11), XL
HCl	6.666	.1577	±	.03$_2$	(12)
HBr	9.161	.274$_5$	±	.03$_2$	(12)
HI	13.73	.543	±	.003	(13)
H_2O	3.75$_0$	.085	±	.001	XXXV
H_2S	9.567	.319$_8$	±	.03$_2$	(12)
H_2Se	12.02	.48	±	.03	(14)
H_3N	5.67	.176	±	.003	(13), (15)
H_4C	6.58	.145	±	.001	(15), (16)
H_4Si	11.34	.388	±	.002	(17)

TABLE II

APPARENT EQUIVALENT DISPERSION[a] D OF ELECTROLYTES
IN INFINITELY DILUTE AQUEOUS SOLUTION IN Cc.[b]

1. Interferometric Measurements of Geffcken and Kruis
(XXVI. XXIX. XLVII. XLVIII)

Na^+ + Cl^-	0.329 ± 0.002	NH_4^+ + NO_3^-	0.545 ± 0.003
K^+ + Cl^-	.364 ± .002	Na^+ + $1/2SO_4^-$	.125 ± .003
$1/2Sr^{++}$ + Cl^-	.336 ± .002		

2. Other Results for Noble Gas Cations[c]

		ΔD	Source
Li^+	− Na^+	−0.021 ± 0.008	LiOH. NaOH[18]
Rb^+	− Na^+	.055 ± .05	RbBr[19]
Cs^+	− Na^+	.09 ± .03	CsCl.[19] CsBr[20,21]
NH_4^+	− Na^+	.063 ± .01	NH_4F[19]
$1/2Ba^{++}$	− Na^+	.022 ± .01	$BaClO_4$. $BaCl_2$ (IX)
$1/2Be^{++}$	− Na^+	− .03$_0$ ± .005	$BeCl_2$[20,21]
$1/3Al^{3+}$	− Na^+	− .02$_4$ ± .01	$Al_2(SO_4)_3$ (IX); $Al(ClO_4)_3$ (XI)

3. Non-Rare Gas Cations

		ΔD	Source
Ag^+	− NH_4^+	0.09$_5$ ± 0.01	$AgNO_3$[22]
Tl^+	− Na^+	.55 ± .15	TlF[19]
$1/2Zn^{++}$	− Na^+	.019 ± .01	$ZnSO_4$ (XI)
$1/2Hg^{++}$	− Na^+	.16 ± .02	$Hg(ClO_4)_2$ (XI)
$1/2Pb^{++}$	− NH_4^+	.19$_5$ ± .02	$Pb(NO_3)_2$[20,21]
H^+	− Na^+	− .03 ± .05	H_2SO_4. $HClO_4$ (XII) HNO_3, HI (XLII)

4. Anions

		ΔD	Source
F^-	− Cl^-	−0.289 ± 0.006	KF (XI)
Br^-	− Cl^-	.28 ± .02	NaBr (XX). LiBr. CsBr[19,20,21]
I^-	− Cl^-	1.0 ± .1	KI (XX). NaI[19]
OH^-	− Cl^-	−0.141 ± .004	NaOH[18]
ClO_4^-	− Cl^-	− .117 ± .007	$NaClO_4$ (IX)

[a] In part (1) of Table II the experimental values of $D_{aq.\ salt}$ are given, while in parts (2), (3) and (4) one has values of $\Delta D_{aq.\ salt}$ which represent the differences between $D_{aq.\ ion}$ and that of a reference ion (Na^+, NH_4^+, Cl^-). [b] All measurements were made at 25.0° except those at 18° by Heydweiller and Limann (see ref. 24). [c] The errors given for the differences ΔD were obtained by summing up all the estimated errors in the individual experimental values needed for the calculation of ΔD.

(18) Unpublished measurements of J. H. Faull. Jr., and P. Hoelemann.

(19) A. Heydweiller. *Physik. Z.*, **26**, 526 (1925).

(20) G. Limann. *Z. Physik.* **8**, 13 (1921).

(21) A. Heydweiller, *Z. anorg. Chem.*, **116**, 42 (1921).

(22) N. Bauer. "Dissertation," University of Michigan, 1941.

relative to that of water were determined at 25.0° with an accuracy of 0.0$_7$3 (interferometric method) and 0.0$_6$2 (differential buoyancy method), respectively. Usually about ten measurements were made on each salt between $2M$ and $0.01M$, so that uncertainties in the extrapolation to infinite dilution are very small.[23] Here the error in the apparent molar dispersion D is probably less than 1 per cent., as compared with up to 10 per cent. for measurements with the Pulfrich refractometer.

The values of D for some electrolytes were derived from earlier measurements in the "Refractometric Investigations" made with the Pulfrich refractometer, the use of which had been improved by Kohner and Geffcken (IX. X, XI). In this series, indices of refraction were measured for only three to five spectral lines, thereby making the extrapolation to λ = ∞ less certain.

A large number of salts was measured at 18°[24] by Heydweiller and his co-workers[19,20,21] with the Pulfrich refractometer and with the quartz spectrograph.[25] The number of spectral lines employed in the visible was two to five. For reasons discussed in XIV, the results were not always sufficiently accurate to establish the way in which the apparent molar refraction varied with concentration. thus bringing an uncertainty into the extrapolation to infinite dilution.[26]

The following values of D in cc./mole give examples of the best and poorest agreement between the various sets of measurements on salt solutions

NaCl	0.33 ± 0.03 (Heyd-weiller)	0.329 ± 0.002 (Kruis and Geffcken)
$NaClO_4$	.17 ± .02 (Heyd-weiller)	.212 ± .006 (Kohner)

The values of D for the various strong electrolytes at infinite dilution proved to be additive within the limits of experimental error; therefore it was possible to calculate values for the various ions with respect to reference ions (see footnote a, Table II).

(c) Alkali Halide Crystals (Table III).—The values of index of refraction given by Gyulai,[27] Spangenberg,[28] Kublitzky[29] and Wulff and Anderson (XLI) were used. some of which had already been extrapolated to λ = ∞ by

(23) The maximum which some refraction *vs.* concentration curves show (see LI and XLVIII p. 40) is not found in the corresponding dispersion curves. Therefore the extrapolation to c = 0 appears to be more certain for D than for R.

(24) The temperature coefficient of molar dispersion of aqueous electrolytes can be estimated from XX p. 351 to be less than 0.2 per cent. per degree, compared with about 0.05% per degree for refraction (XXI. p. 358). Therefore the difference between $D_{18°}$ and $D_{25°}$ is smaller than other uncertainties in Heydweiller's measurements. This result makes it also safe to use the values of $D_{cryst.}$ in Table III without a temperature correction because for refraction the values of $(dR/R)/dT$ are even smaller for crystals than for electrolytes (see XXI, p. 361).

(25) The values of $R_∞$ derived here from Heydweiller's data by the reciprocal plotting method differ up to 0.03 cc. from his own values, obtained by plotting $R_λ$ against $ν^2$.

(26) The values of $D_{aq.}$ for rubidium and cesium salts contain an additional uncertainty because of the possible presence of impurities. Therefore even the rather large errors in Tables II and VII for these ions are only a lower limit. Thus it is uncertain whether the difference in the sequence of values shown in Fig. 3 for refraction (K, Cs, Rb) is real.

(27) Z. Gyulai. *Z. Physik*, **46**, 84 (1927).

(28) K. Spangenberg. *Z. Krist.*, **57**, 494 (1923).

(29) A. M. Kublitzky. *Ann. Physik*, **20**, 793 (1934).

Wulff and co-workers (XXXVIII, XXVII). When no measurements of the density were made on the samples used for the refractive index determination. the molar refraction was calculated using the best density values resulting either from direct measurements (see XXVII), or from X-ray determinations given in the "Strukturbericht." Some of the salts were measured above room temperature (up to 66°: see footnote (a), Table III). Concerning the negligible temperature dependence of $D_{cryst.}$ in this interval. see ref. 24.

From Table III it can be seen that the uncertainties in $D_{cryst.}$ vary from 2 to 10%.

TABLE III

MOLAR DISPERSION OF CRYSTALS IN Cc.[a]

(a) Alkali Halides

LiF	0.031	±	0.003	(27)	NaBr	0.42	±	0.01	(27)
NaF	.048	±	.005	(28)	KBr	.52	±	.01	(27)
KF	.080	±	.005	(29)	RbBr	.57	±	.02	(29)
NaCl	.24	±	.01		CsBr	.66	±	.05	(XXVI1)
KCl	.30	±	.01	(XXXVIII)	KI	.95	±	.02	(27)
RbCl	.36	±	.02		RbI	1.06	±	.1	(29)
CsCl	.41	±	.01	(XLI)					

(b) Compounds of Doubly Charged Cations and Anions of Noble Gas Type (Haase[30])

MgO	0.09	±	0.01	SrS	0.95	±	0.09
CaO	.17	±	.02	CaSe	1.11	±	.06
SrO	.39	±	.04	SrSe	1.49	±	.06
BaO	.76	±	.1	BaSe	1.81	±	.08
MgS	.38	±	.02	SrTe	2.13	±	.5
CaS	.71	±	.02	BaTe	3.41	±	.5

[a] The salts measured at other than room temperature are: KF (57°), RbCl (48°), NaBr (66°), KBr (48°), RbBr (35°). RbI (35°) and KI (60°). Concerning the negligible temperature dependence of $D_{cryst.}$ between 25 and 70°, see ref. 24.

(d) Compounds of Doubly Charged Cations and Anions of the Noble Gas Type (Table III).—Measurements of the index of refraction by Haase[30] were used. The number of wave lengths employed varied between 2 and 5. Since, except for BaTe and MgO, the density was not measured by Haase, we have taken densities used by him on the basis of V. M. Goldschmidt's X-ray determinations. The molar dispersion could be evaluated only to within about 10 per cent.

3. Deviations from Additivity for Molar Dispersion and Refraction Based on Direct Experimental Data.

Figure 2 contains experimental data for a selection of gaseous substances isoelectronic with the noble gases. The values of R_D and D are based on n^*, the index of refraction corrected to the ideal gas state. The values of the Lorentz–Lorenz refraction used in Fig. 2 are thus very nearly proportional to $(n^* - 1)/d$, which is a direct measure of the interaction between free particles and the electric field associated with the light waves: $i.$ $e.$, these R_D and D values are practically independent of any alleged imperfections in the Lorentz–Lorenz

(30) M. Haase. Z. Krist., 65. 509 (1927); for MgS see M. Haase, ibid., 68, 82 (1928).

expression possible in the case of condensed systems.[31] The substances in Fig. 2 corresponding to the sets of connected points (e. g., H_2Se, HBr, Kr) have the same number of electrons (e. g., 36) and differ only by the position of the protons, two of which in H_2Se and one in HBr are within the electronic shell, while in Kr all belong to the nucleus. One observes a large change (a decrease, excepting $D_{NH_3} > D_{CH_4}$) in both R_D and D corresponding to the process of successively transferring protons from an electronic shell into the nucleus; e. g., the refraction drops from 11.57 cc. in H_2Se to 9.16 in HBr and finally to 6.40 in Kr, while for dispersion the corresponding values are 0.48, 0.27 and 0.129 cc., respectively.[31a] Thus there can be no doubt that the molar refraction and dispersion are properties which depend on the forces acting on a given electronic system, and indeed are very sensitive to changes in the forces.

Because the interionic forces in crystals and gases are different from those between ions and water molecules in solution, one can understand (cf. I, p. 7; XXX, p. 121) that, as Fig. 3 shows, the apparent molar refraction and dispersion of aqueous alkali and hydrogen halides differ from the corresponding values in the solid and gaseous states. Here it is of especial importance to note that also for electrolytes there is a close analogy between the kind of deviations from additivity exhibited by molar dispersion and by molar refraction (concerning Cs salts, see ref. 26). The magnitude of these deviations for both D and R increases systematically with increase in polari-

(31) See. e. g., N. F. Mott and R. W. Gurney. "Electronic Processes in Ionic Crystals." Oxford University Press. New York, N. Y.. 1940, p. 18. The Lorentz–Lorenz formula is supposed to account only for that part of the internal electric field acting on a given particle which is due to the dipoles induced in surrounding particles by the external electric field of the light waves: the formula does not attempt to include the effect of forces acting between the particles in the absence of the external field. In fact the results of the "Refractometric Investigations" demonstrate that the Lorentz–Lorenz expression fulfills its purpose excellently. The systematic deviations from additivity observed for a wide variety of gaseous. liquid and cubic-solid systems can be understood as a result of known forces acting between particles independently of the light wave. Only the minute deviations from additivity in mixtures of non-ionized liquids cannot yet be explained from this point of view (cf. XXX, p. 108).

(31a) Note added on November 30, 1942. The gradation of molar refraction and dispersion of isoelectronic molecules shown in Fig. 2 proves to be in line with a general principle: The tightness of a given electronic shell decreases (R and D increase) when the positive charges within the shell split or when their distribution becomes less symmetrical. The apparently exceptional gradation $D_{NH_3} > D_{H_4C}$ is due, as is also indicated by the peculiarities of the slopes of the lines leading to H_4Si. to the competition between two factors. In the transition from H_3N to H_4C the splitting of the core N^{5+} into C^{4+} and H^+ causes a loosening. the higher symmetry of H_4C a tightening of the electronic shell. See K. Fajans. J. Chem. Phys., December. 1942.
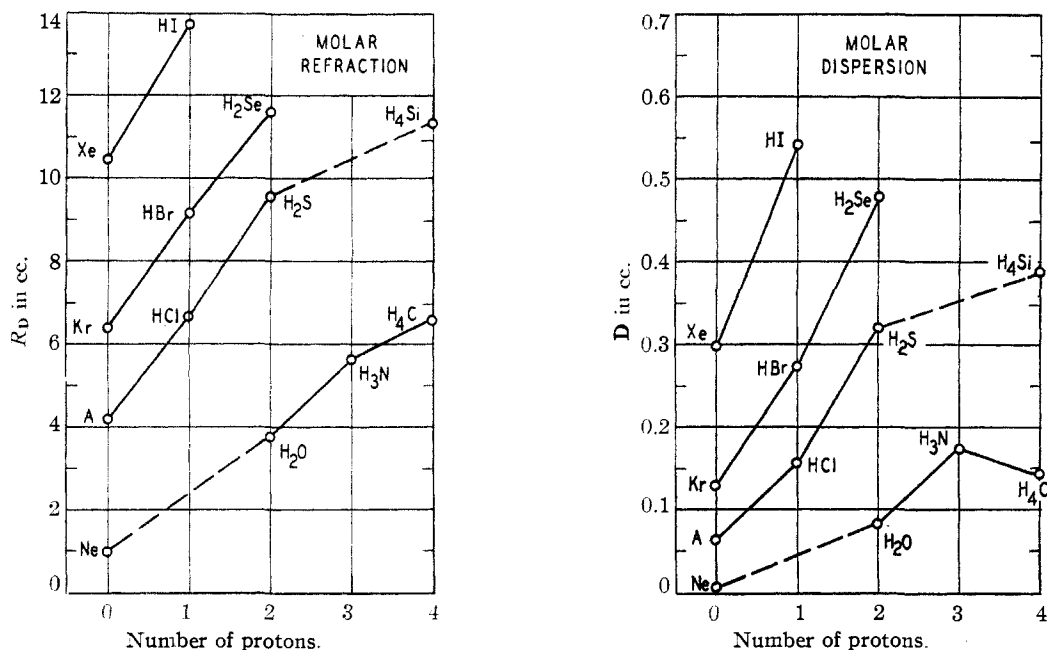
Fig. 2A and 2B.—Analogy between the changes of molar refraction and dispersion of gases due to a successive transfer of protons from the nucleus of the noble gases into the electronic shell.

zability and polarizing power of the particles involved, as has been discussed in former papers for the case of refraction, and as will be shown in Section 8 for dispersion.

4. Square Relation between Molar Refraction and Dispersion.—The similarities between the deviations from additivity of the molar refraction and dispersion noted in Section 3 lead one to expect a simple quantitative relation between these two phenomena. The dispersion theory leads to the following results.

If one assumes that a single term dispersion formula is adequate for representing the experimental data (which is the case, e. g., for noble gases in the visible) one has $R_D = C/(\nu_0^2 - \nu_D^2)$, and $R_\infty = C/\nu_0^2$. From $D = R_D - R_\infty$, $D = (\nu_D^2/C)R_D R_\infty$. Since $R_D \approx R_\infty$ (in general within considerably less than 5%), one has

$$D \approx \frac{\nu_D^2}{C} R_D^2 \qquad (4)$$

Considering the changes occurring in the molar refraction and dispersion of a given particle when it is subjected to an external influence (e. g., when one ion combines with another), and assuming that in this case C remains practically constant,[32] one obtains the following square

relation between R_D and D

$$D \approx \text{constant} \times R_D^2 \qquad (5)$$

therefore

$$\Delta D/D \approx 2\,\Delta R_D/R_D \qquad (6)$$

Thus one expects that a given change in the refraction will correspond to twice as great a relative change in the dispersion. It will be seen in this and following sections that in general, in simple cases, this expectation is fulfilled.[33]

Table IV, based on direct experimental data given in Table I, shows that the square relation applies to the noble gases, the hydrogen halides and H_2O, H_2S, and H_2Se with an accuracy sufficient for our present purpose. The squares of the ratios of the molar refraction for any two of these substances belonging to the same noble gas type agree within about 4% on the average with the corresponding ratios of the molar dispersion, which is surprisingly good in view of the approximations used in arriving at (5).

(32) The dispersion of noble gases and of Li, Na and K halides can be represented with sufficient accuracy in the visible by a single term (equation 2). For those salts of this group for which the cations can be expected to contribute only a few tenths of a per. cent to the total

dispersion (e. g., NaBr), one can compare the values of C and ν_0^2 for a noble gas with those of the corresponding halide ion in the crystal: whereas in such cases the ν_0^2 values differ by a factor of nearly two, the differences between $C_{N.G.}$ and C_{X-} are less than 10%, on the average. Closely connected with this are the results of K. F. Herzfeld and K. L. Wolff, Ann. Physik, 78, 50 (1925), who concluded from multiple term dispersion formulas that the total transition probability (number of electrons in classical theory) for argon was practically the same as that for Cl⁻ in NaCl and KCl.

(33) The ratio of $\Delta R/R$ to $\Delta D/D$ differs considerably from two in relation (12) for the hydration effect of Li⁺, in Fig. 3 for the values for KI and RbI and in Table X. In all these cases, apparent quantities are involved.
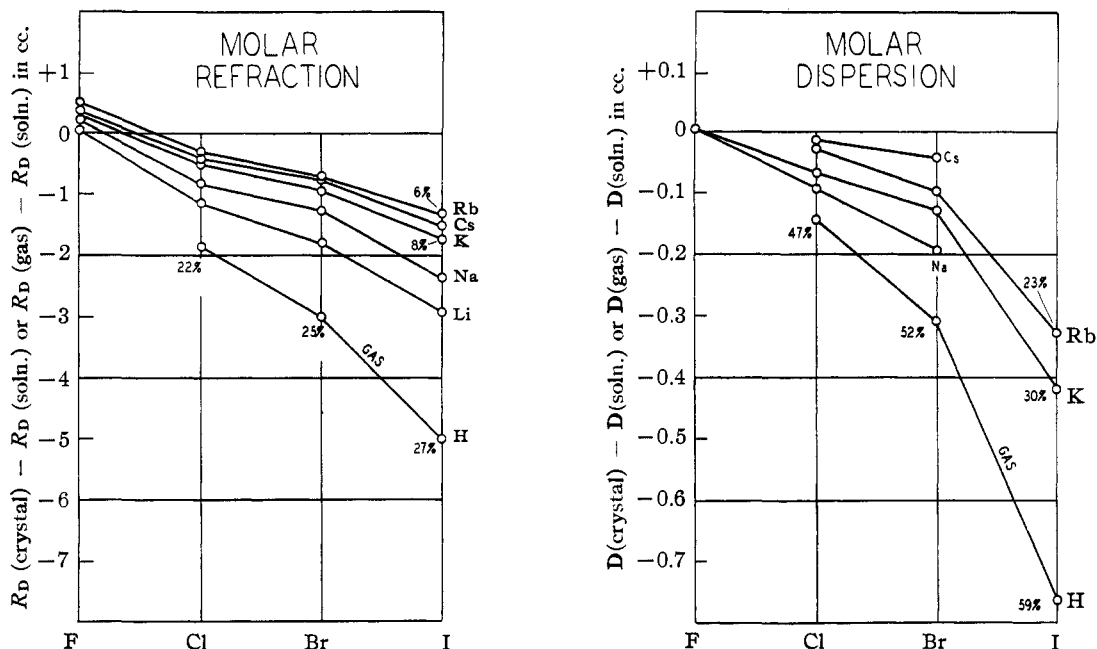
Fig. 3A.—Difference between the molar refraction of solid alkali halides and gaseous hydrogen halides and their apparent molar refraction in aqueous solution. Fig. 3B gives the corresponding differences for the molar dispersion D. The percentage deviations from additivity are given relative to the values of the aqueous electrolytes and are greater for dispersion than for refraction.

In (5) we have neglected the difference between R_D and R_∞, as well as the influence of a second frequency $(\nu_0)_2$. Such neglections will in general be the more justified, the smaller the values of R_D and $1/(\nu_0)_1$ are; therefore it is reasonable to apply the square relation (5) to ions having the same noble gas structure, providing their R_D and $1/(\nu_0)_1$ values are not larger than those of the substances used in verifying the relation (Table IV).[34]

TABLE IV

TEST OF THE SQUARE RELATION (5) BETWEEN MOLAR REFRACTION AND MOLAR DISPERSION

Ratios	For R_D	For R_D^2	For D
HCl/A	1.59	2.52	2.47
HBr/Kr	1.43	2.04	2.13
HI/Xe	1.315	1.73	1.78
H_2O/Ne	3.73	13.9	12.9
H_2S/A	2.28	5.20	5.00
H_2Se/Kr	1.875	3.52	3.69
H_2S/HCl	1.44	2.07	2.02
H_2Se/HBr	1.315	1.73	1.75

5. The Partition of the Molar Dispersion into Values for Individual Ions.—The above results, establishing an analogy between the behavior of the molar refraction and dispersion, justify the attempt to apply to the partition of dispersion

the same principles which have been used in the case of refraction. For the latter, as mentioned in the introduction, it proved to be very helpful to introduce values for the refraction of free gaseous ions.

It is important to emphasize here that the molar refraction and dispersion of free gaseous ions are real physical quantities like those for a noble gas, and are connected by equation (1) with the electronic polarizability α of the free particles. In this respect the molar refraction and dispersion differ from the volume[35] or radii of free ions or atoms, which according to wave mechanics do not have an exact physical meaning.

For any property (X) of analogous ions, the value of which can be assumed to decrease monotonously with increasing forces between the nucleus and the electronic system, one can expect the following regularities to hold. They were in part stated in considering the relative size of noble gas ions,[36] and were extensively used for the derivation of ionic refractions (I and XXX).

(a) For ions possessing the same noble gas (N. G.) structure, the nuclear charge of which

(34) We assume that the agreement in Table IV is not due to an accidental cancelling of effects which might arise from the different symmetry of the particles involved.

(35) However, single ionic values of the apparent molar volume are defined quantities which for the case of infinitely dilute aqueous solutions have been approximately obtained. See, e. g., K. Fajans and O. Johnson, THIS JOURNAL, 64, 668 (1942).

(36) K. Fajans and K. F. Herzfeld. Z. Physik, 2, 309 (1920).

increases in the following series from left to right, one has[37]

$$\cdots > X_{\text{ion}^-} > X_{\text{ion}^-} > X_{\text{N.G.}} > X_{\text{ion}^+} > X_{\text{ion}^{++}} > \cdots \quad (7)$$

(b) For a given noble gas type it should hold that

$$\cdots > \frac{X_{\text{ion}^-}}{X_{\text{ion}^-}} > \frac{X_{\text{ion}^-}}{X_{\text{N.G.}}} > \frac{X_{\text{N.G.}}}{X_{\text{ion}^+}} > \frac{X_{\text{ion}^+}}{X_{\text{ion}^{++}}} > \cdots \quad (8)$$

The inequalities (8) are based on the expectation that a given absolute difference in nuclear charge Z will cause the greater relative change in the property X, the smaller the magnitude of Z.

(c) For particles of a different noble gas type one can expect inequalities (9) to hold for the same reason given for (8); e. g.

$$\frac{X_{\text{F}^-}}{X_{\text{Ne}}} > \frac{X_{\text{Cl}^-}}{X_{\text{A}}} \quad \text{or} \quad \frac{X_{\text{Ne}}}{X_{\text{Na}^+}} > \frac{X_{\text{A}}}{X_{\text{K}^+}} \quad (9)$$

These regularities, in spite of being inequalities, were found (XXX) to provide a basis for the derivation of refraction values for free gaseous ions which is at least as reliable as other methods used for this purpose except for the case of helium type cations. The main difficulty in the derivation is caused by the fact that while the inequalities refer to free gaseous particles, the available experimental data extend only to noble gases and aqueous ions. However, for noble gas ions having strong electric fields it was possible to obtain an estimate of the differences $\Delta_{\text{hydr.}}^R = R_{\text{aq. ion}} - R_{\text{gas ion}}$ between the values of hydrated and gaseous ions (see Table VII, Sec. 6).

In order to obtain a set of values for the molar dispersion of individual ions, we proceeded in two ways which led to results agreeing within the limits of the uncertainties in both methods. One method is analogous to that applied previously (I) to the molar refraction. Besides the uncertainty connected with the hydration effect, the application of this method to the molar dispersion encounters an additional difficulty at present because of the low accuracy of the experimental values of D for the heavier alkali and halide ions.

The other method is based on an application of the square relation (5) between R_D and D. Assuming the values for the molar refraction of free gaseous ions to be known,[38] one can arrive

directly at the values of molar dispersion of gaseous ions, using also the experimental values of R_D and D for the noble gases; comparing the results with the experimental information on aqueous ions one can further try to decide whether or not it is necessary to distinguish here between free gaseous and dissolved ions.

We shall present only the second method, which is based on a new principle and which has proved to be more straightforward than the first one. For reasons given in Section 4, it appears quite safe to use relation (5) in deriving molar dispersions for gaseous alkali and alkaline earth ions; very probably fluoride ion also obeys the square relation.[39] The results of the calculation are given in Table V, along with values for R_D and the ratios which correspond to the regularities expected from relations (8) and (9).

However, it is uncertain whether the application of the square relation to the larger halide ions can give exact enough results because their ν_0 values are considerably smaller than those of the noble gases, and they have large refractions. The results for these ions are therefore given in parentheses (see footnote c, Table V). For the doubly charged negative ions the same reservations apply, in addition to the restriction that here the values of both molar refraction and dispersion represent only extrapolated auxiliary quantities because these ions are not stable in the gaseous state.[40]

6. The Difference between the Molar Dispersion of Ions in the Free Gaseous State and in Aqueous Solution.—From the analogous behavior of refraction and dispersion, one would expect that the tightening of the electronic system of water molecules by cations would produce a negative hydration effect for molar dispersion, i. e., $\Delta_{\text{hydr.}}^D = (D_{\text{aq. cation}} - D_{\text{gas cation}}) < 0$ and that the absolute value of this effect should be greater, the greater the electric field of the cation (see XXX, p. 121). We can test this using the most accurately known values for D_g and $D_{\text{aq. salt}}$: From $(D_{\text{aq.}})_{\text{K}^+} - (D_{\text{aq.}})_{\text{Na}^+} = 0.364 - 0.329 = 0.035 \pm .004$ (Table II, 1) and $(D_g)_{\text{K}^+} - (D_g)_{\text{Na}^+} = 0.0169$ (Table V) it follows that

$$(\Delta_{\text{hydr.}}^D)_{\text{Na}^+} = (\Delta_{\text{hydr.}}^D)_{\text{K}^+} - 0.018 \text{ cc./mole} \quad (10)$$

(37) Relation (7) was first applied to refraction by J. A. Wasastjerna [Oeversikt av. Finska Soc. Foerdhandl., **LXIII A4**, 1 (1920-21); Z. physik. Chem., **101**, 193 (1922)], to ionic radii by A. Landé, Z. Physik, **1**, 191 (1920).

(38) For reasons mentioned in XXX, p. 125 and in ref. (35) under 6c, the refractions given in XXX for gaseous ions can be expected to require some corrections. However, the results of the present paper give additional support to the belief that these refraction values cannot be far from the true ones, and that in any case they represent a consistent set.

(39) Although free fluoride ion can be expected to have an absorption band around 300 mμ (electron affinity $\approx$ 4 volts), which is closer to the visible than that of any of the substances used in verifying (5), the small value of its refraction ($R_{\text{F}^-} = 2.5$ cc. compared with $R_{\text{HI}} = 13.7$) makes it improbable that the second absorption band (ν_0)$_2$ is important in the visible (see Sec. 4).

(40) See, e. g., O. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Company, 1940, p. 101.

TABLE V

MOLAR DISPERSION D^a AND MOLAR REFRACTION $R_D{}^b$ OF GASEOUS IONS IN CC.

	X^-	X^-/X^-	X^-	$X^-/N.G.$	N.G.	$N.G./X^+$	X^+	X^+/X^{++}	X^{++}
					He		Li^+		Be^{++}
D					0.00351		0.0001		0.0000
R_D					.521		(.08)		
	O^-		F^-		Ne		Na^+		Mg^{++}
D	(0.32)	(8.1)	0.039	6.0	0.0066	4.4	0.00149	3.3	0.00045
R_D	6.95	2.84	2.44	2.43	1.004	2.11	.475	1.82	.26
	S^-		Cl^-		A		K^+		Ca^{++}
D	(1.9)	(6.3)	$(0.30)^c$	(4.7)	0.064	3.5	0.0184	2.6	0.0071
R_D	22.7	2.50	9.065	2.16	4.203	1.86	2.255	1.61	1.40
	Se^-		Br^-		Kr		Rb^+		Sr^{++}
D	(2.6)	(5.2)	$(0.50)^c$	(3.9)	0.129	2.9	0.0447	2.2	0.0206
R_D	28.8	2.27	12.66	1.98	6.397	1.69	3.79	1.47	2.58
	Te^-		I^-		Xe		Cs^+		Ba^{++}
D	(4.6)	(4.6)	$(1.01)^c$	(3.4)	0.298	2.5	0.117	1.9	0.061
R_D	40.9	2.13	19.21	1.84	10.435	1.60	6.535	1.38	4.73

^{a} The values of D were derived by using the square relation (5) between R_D and D, the above values of R_D and the experimental values of R_D and D for the noble gases. ^{b} The values of R_D are taken from XXX, Table (3), except for small changes in Xe and Kr, as given by Damkoehler (XL). ^{c} For reasons given in Section 6, we prefer to use (e. g. in Table VIII) the values of $D_{aq.}$ = 0.346, 0.63 and 1.3 cc./mole (Table VI) for Cl^-, Br^- and I^-, respectively, as the provisional estimate of D_g for these ions.

One can see that (10) agrees with the above expectation.

Since there is not sufficient information for evaluating the smaller hydration effect of K^+, we shall neglect it as a first approximation, as was done in the case of refraction[41]; i. e., we put

$$(D_{aq.})_{K^+} = (D_g)_{K^+} = 0.0184 \text{ cc./mole} \qquad (11)$$

The numerical value in (11) comes from Table V. Using the experimental sums and differences given in Table II for aqueous electrolytes, the values of $D_{aq.}$ for all aqueous ions follow at once from relation (11). They are given in Table VI. By subtracting from the $D_{aq.}$ values for

TABLE VI

APPARENT EQUIVALENT DISPERSION OF IONS IN AQUEOUS SOLUTION AT 25° IN CC.^{a}

Li^+	−0.038	$1/2 Be^{++}$	−0.047	F^-	0.057
Na^+	−0.0166	$1/2 Sr^{++}$	− .010	Cl^-	.346
K^+	.0184	$1/2 Ba^{++}$	.005	Br^-	.63
Rb^+	.04	$1/2 Zn^{++}$	.002	I^-	1.3
Cs^+	.07	$1/2 Hg^{++}$	.14	OH^-	0.205
NH_4^+	.046	$1/2 Pb^{++}$	.24	NO_3^-	.50
Ag^+	.141	$1/3 Al^{+++}$	− .041	ClO_4^-	.229
Tl^+	.53	H^+	(− .05)	$1/2 SO_4^-$	.1416

^{a} Based on the experimental values of D for electrolytes at infinite dilution (Table II) and relation (11).

aqueous ions the values of D_g for those corresponding gaseous ions which in Table V are considered to be certain, one obtains the magni-

(41) For the evidence that such solution effects exist also for large ions, see XXI and ref. (35), section 6c.

tude of the hydration effect $\Delta^D_{hydr.}$ The values of $\Delta_{hydr.}$, given in Table VII, allow one to test whether or not the derivation in Section 5 leads to a consistent system.

Assumption (11) leads to the conclusion that for alkali ions larger that K^+, the hydration effect should also be negligible, while for the hydrogen ion,[42] lithium ion and small cations of double or triple charge, the value of $\Delta^D_{hydr.}$ should have a negative sign and its absolute value should be larger than that for Na^+.

Table VII not only agrees with the above conclusion,[43] but in addition it shows that qualitatively the gradation of $\Delta_{hydr.}$ is the same for the molar dispersion as for the molar refraction. In a quantitative respect one can only state that relative to the magnitude of R_D and D of one mole of water, the hydration effect is considerably greater for dispersion than for refraction. For example, one has for Li^+

$$\Delta^D_{hydr.}/D_{liq.H_2O} = -0.038/0.082 = -0.46$$

while

$$\Delta^R_{hydr.}/R_{liq.H_2O} = -0.33/3.72 = -0.09 \qquad (12)$$

It is of especial interest that for F^- a positive value of $\Delta^D_{hydr.}$ is obtained, analogous to the

(42) For the apparent molar dispersion of aqueous hydrogen ion one finds D = −0.05 ± 0.05. The large error is due to uncertainties in extrapolating values of D_{acid} to infinite dilution; therefore it is not warranted to place H^+ in Table VII. However, the plot of hydrogen halides in Fig. 3 is not appreciably affected by such an error.

(43) Concerning Rb^+ and Cs^+, see ref. 26.

TABLE VII

DIFFERENCES $\Delta_{hydr.}$ BETWEEN AQUEOUS AND FREE GASEOUS IONS FOR THE MOLAR REFRACTION R_D AND THE MOLAR DISPERSION D IN CC.

1. Refraction^a $[(R_D)_{liq.H_2O} = 3.72$ cc./mole]

	OH$^-$	F$^-$	Cs$^+$	Rb$^+$	K$^+$	Na$^+$	Li$^+$	Ba^{++}	Sr^{++}	Be^{++}	Al^{3+}
$\Delta_{hydr.}^R$	+0.34	+0.16	0.0	0.0	0.0	−0.27	−0.33	−0.36	−0.69	−2.12	−2.49
Ion/Na$^+$	−1.3	−.6				1	1.2	1.3	2.5	7.85	9.2

2. Dispersion.^{b} $[D_{liq.H_2O} = 0.0825$ cc./mole (XLVIII)]

	OH$^-$	F$^-$	Cs$^+$	Rb$^+$	K$^+$	Na$^+$	Li$^+$	Ba^{++}	Sr^{++}	Be^{++}	Al^{3+}
$\Delta_{hydr.}^D$	+0.056	+0.018	(−0.05 ± 0.03)	(0.0 ± 0.05)	0.0	−0.018	−0.038	−0.05	−0.04	−0.094	−0.12
Ion/Na$^+$	−3.1	−1.0				1	2.0	2.7	2.2	5.2	6.7

^{a} The values of $\Delta_{hydr.}^R$ are taken from XXX, p. 121.

^{b} The values of $\Delta_{hydr.}^D$ are based on Tables V (VIII for HO$^-$) and VI and the assumption (11); concerning Cs$^+$, see ref. (62.)

corresponding refractometric effect. The positive sign indicates a loosening of the electronic shells of the adjacent water molecules by the action of the field of the small fluoride anion (see the similar result for OH$^-$ in Section 7.)
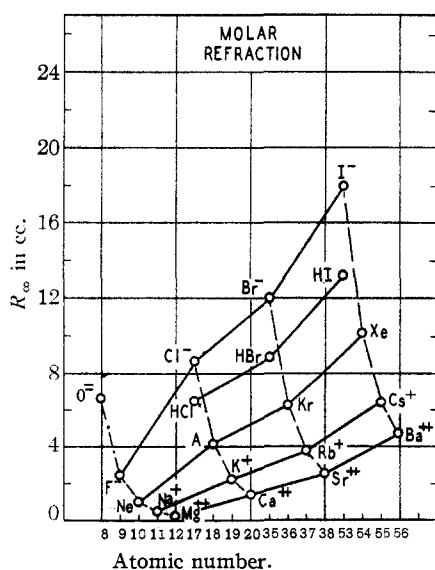
It would be premature to draw definite conclusions concerning the values of $\Delta_{hydr.}^D$ for the heavier halide ions. A comparison of values in Table V with those in Table VI indicates that the D derived from the square relation for gaseous Cl$^-$, Br$^-$ and I$^-$ is smaller than that for the aqueous ions by 0.05, 0.13 and 0.1 cc., respectively. However, because of the uncertainty in D_g. for the large halide ions (see Section 5) and in D_{aq}. for Br$^-$ and I$^-$ (see Table II), the above values of the hydration effect are not reliable.

We shall, as was done for refraction, provisionally use the values of D_{aq}. in Table VI as being equal to those for the free gaseous Cl$^-$, Br$^-$ and I$^-$ ions. These values of D do not lead to contradictions with the regularities expected in the ratios (8) and (9) for gaseous ions; we have, e. g.
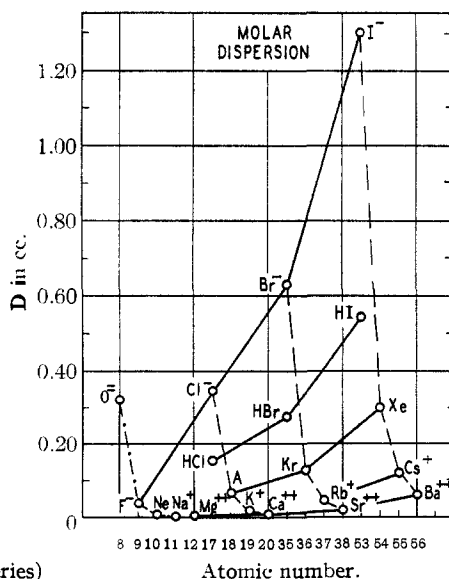
$$Cl^-/A > Br^-/Kr > I^-/Xe$$
$$5.4 \qquad 4.9 \qquad 4.3$$

7. The Change of Molar Dispersion by the Addition of Protons.—In Section 3 it was shown that the molar dispersion generally decreases when protons are transferred from the electronic shell of a hydride into the nucleus. Now, having the values of D for individual ions, we can discuss the effect of protons being brought from outside

8 9 10 11 12 17 18 19 20 35 36 37 38 53 54 55 56
Atomic number.   (interrupted series)   8 9 10 11 12 17 18 19 20 35 36 37 38 53 54 55 56
                                                           Atomic number.

Fig. 4A.—Comparison of the molar refraction for infinite wave length: 1, of ions and atoms of a given noble gas type as a function of the nuclear charge (dashed lines): 2, of analogous ions, atoms, and molecules belonging to different periods (full lines); 3, of hydrogen halide molecules with the corresponding halide ions. Fig. 4B gives the same for the molar dispersion D (D = R_D − R_∞). In all cases the relative changes are larger for dispersion than for refraction.

TABLE VIII

THE CHANGE OF MOLAR DISPERSION BY THE ADDITION OF PROTONS

(I)	I^-	HSe^-	HS^-	Br^-	Cl^-	HO^-
D_I	1.3	(1.14)	(0.75)	0.63	0.346	(0.149)
ΔD	0.76	(0.66)	(.43)	.36	.188	(.064)
D_{II}	.54	.48	.320	.274	.158	.085
(II)	HI	H_2Se	H_2S	HBr	HCl	H_2O
$Q_I^D = (D_I - D_{II})/D_I$	0.58	(0.58)	(0.57)	0.57	0.54	(0.43)
Q_I^D/Q_I^R	2.03	2.04	2.04	2.05	2.04	2.04

the electronic shell into either (1) the nucleus (e. g., the process $Cl^- \rightarrow A$) or (2) into the electronic system (e. g., $Cl^- \rightarrow HCl$).

The data for case (1) are contained in Table V and represented graphically in Fig. 4B which gives a plot of D for ions, atoms and molecules as a function of atomic number, and which is naturally analogous to the corresponding figure for refraction (Fig. 4A). We notice that the absolute change in the molar dispersion caused by the addition of one proton depends on the polarizability of the initial particle; e. g., the decrease is 0.28 cc. (93% of D_{Cl^-}) for the process $Cl^- \rightarrow A$, and 0.046 cc. (72% of D_A) for $A \rightarrow K^+$. The percentage change is, as implied in the square relation, about twice as great for molar dispersion as for refraction.

For case (2) we have a chemical change according to the equation $H^+ + I = II$, in which I is the initial, II the final particle. These changes are simpler than other chemical processes in the respect that the electronic system of only one of the reacting particles is involved. The introduction of positive charge into the electronic system causes the electrons to be more tightly bound, i. e., its polarizability becomes smaller. The observed diminution ΔR of the refraction R_I^D of a charged anion or neutral molecule (I) caused by the addition of protons was found (XXX)[43a] to obey a simple exponential relation

$$Q_I^R = \Delta R/R_I^D = 0.2859 \ (1 - e^{-0.2848R_I^D}) \quad (13)$$

The relative change of refraction Q_I^R increases with R_I^D and reaches the value 0.2847 for I^- ($R_I^D = 19.21$) which is nearly equal to the limiting value 0.2859 for $R_I = \infty$.

Table VIII, for which the unbracketed values are either known experimentally or obtained above (see footnote c, Table V) and for which the bracketed ones are derived below, shows that the change of molar dispersion by protons behaves qualitatively in an analogous way. The relative

(43a) See also K. Fajans and N. Bauer. *J. Chem. Phys.*, **10**, 410 (1942).

change $Q_I^D = (D_I - D_{II})/D_I$ for dispersion increases from 0.54 for Cl^- to 0.57 for Br^- and 0.58 for I^-.[44] For all three halide ions the ratio Q_I^D/Q_I^R equals 2.04, showing again that the molar dispersion is about twice as sensitive as refraction. This relation can be made the basis for a derivation of ionic dispersions for gaseous HO^- HS^- and HSe^- from the known values of H_2O, H_2S and H_2Se. Assuming the ratio $Q_I^D/Q_I^R = 2.04$ to apply to these substances as well, and using the known values of Q_I^R $(XXX, p. 134)$, one obtains Q_I^D given in Table VIII. Since D_{II} is known, we have the bracketed values of D_I in Table VIII at once.

The comparison of $(D_{OH^-})_g. = 0.149$[45] with $(D_{OH^-})_{aq.} = 0.205$ leads to a positive hydration effect $\Delta_{hydr.}^D$ which again fits qualitatively with the idea of a loosening of water molecules due to adjacent anions.

8. Changes in Molar Dispersion of Ions in Crystals and Complex Ions.

The decrease in molar dispersion discussed in Section 7 is caused by the tightening action of protons. This tightening of an electronic system also shows up in cases where the positively charged particle attached to it has an electronic system of its own. Thus for the alkali halides the tightening effect in dispersion is apparent from the regular increase in the absolute values of the negative differences $D_{cryst.} - D_{aq. ions}$ in Fig. 3[46]; i. e., in the order of increasing polarizability of the anion (from Cl^- to I^-) and of increasing field of the cation (from Cs^+ to Li^+).[26]

In general one expects the tightening effect to be more or less compensated by the loosening action of negatively charged particles. This loosening effect shows up in the refraction of

(44) The quantity $Q_{II}^D = \Delta D/D_{II}$ also shows a regular but more rapid gradation: i. e., Q_{II}^D changes from 1.12 (Cl^-) to 1.41 (I^-). If we use the values of D_{X^-} derived from the square relation (5), the value of Q_I^D is approximately 0.46 for all three ions.

(45) Use of the square relation as an alternative method of calculation gives $(D_{OH^-})_g. = 0.148$.

(46) The regularities of Fig. 3 are not affected by comparing $D_{cryst.}$ with $D_g.$ instead of with $D_{aq.}$.

fluorides of the heavier alkali ions (see Fig. 3). Of these salts, data on the dispersion are available only for potassium fluoride; here, as expected, the molar dispersion of the crystal ($D = 0.080$) is larger than that of free gaseous ions ($D_{g.\ ion} = 0.057$).

In the case of compounds of doubly charged noble gas ions (BeO to BaTe), the large deviations from additivity of the molar refraction[30] generally show the expected gradations.[47] An example of similar behavior for the molar dispersion is given by the differences in Table IX, obtained from the most reliable D values in Table III. The reason for the large differences between corresponding Δ values can be expressed in the simplest way by stating that the tightening effect is greatest in MgS, as expected.

TABLE IX

DEVIATIONS FROM ADDITIVITY FOR THE MOLAR DISPERSION OF COMPOUNDS HAVING DOUBLY CHARGED IONS

	D in cc.	Δ		D in cc.
CaS	0.71 ± 0.02	**0.54**	CaO	0.17 ± 0.02
Δ	$.33 \pm .04$		Δ	$.08 \pm .03$
MgS	$.38 \pm .02$	**0.29**	MgO	$.09 \pm .01$

The molar dispersion of oxide ion is the most reliable among the values calculated for doubly charged anions (see Section 5); it is of interest to compare this $D_{O^-} = 0.32$ cc. with the values of the apparent molar dispersion which $O^=$ shows in compounds. One obtains $D_{O^-\ app.}$ given in Table X, by subtracting the value of D_g for the attached positive ion (Table V[48]) from the

TABLE X

THE APPARENT MOLAR DISPERSION OF THE OXYGEN OCTET IN CRYSTALS AND COMPLEX IONS, IN CC.

Attached cation	Ba^{++}	Sr^{++}	None	Ca^{++}	H^+	Mg^{++}	S^{6+}	Cl^{7+}
Apparent D_{O^-}	0.70	0.37	0.32	0.16	0.149	0.09	0.070	0.057
Apparent R_{O^-}	7.91	6.81	6.95	6.03	4.76	4.24	3.68	3.31

corresponding value for the crystal (Table III) or complex ion $SO_4^=$, ClO_4^-, and OH^- (Tables VI and VIII). Concerning the corresponding data for refraction, see refs. (30) and XLIII and Table

(47) K. Fajans. Z. Krist., **66**, 325 (1928).
(48) It is apparent from extrapolating the values in Table V that R and D are negligibly small for S^{6+} and Cl^{7+}.

V. We note from Table X that again the dispersion of a given electronic system subjected to various force fields shows relatively larger changes than the corresponding ones previously found for refraction; e. g., on going from the free ion to the oxygen octet in perchlorate, where $O^=$ is deformed by the field of Cl^{7+}, D_{O^-} changes by a factor of 5.6, R_{O^-} by a factor of 2.1.

Especially significant in Table X is the high value of $D_{O^-\ app.}$ in BaO. It gives support to the former conclusion (VII) that the oxygen ion appreciably loosens the barium ion. This conclusion was based on the fact that also the apparent refraction of $O^=$ in BaO (7.91) is higher than the refraction obtained for free oxide ion (6.95) by extrapolation from the R values for other noble gas ions.

Summary

1. The difference $D = R_D - R_\infty$ between the molar (Lorentz–Lorenz) refraction for the sodium D line and that extrapolated to infinite wave length from measurements in the visible is used as measure of the *molar dispersion.*

2. For isoelectronic substances, the dispersion of which can be represented by a single term formula in the visible, one is led to expect that D is approximately proportional to the square of R_D. It is shown that this *square relation* applies satisfactorily to noble gases (N. G.), hydrogen halides and H_2O, H_2S, H_2Se.

3. The molar dispersion D_g for free gaseous ions of the noble gas type is obtained by applying the square relation to the corresponding values of molar refraction found previously and to the experimental data on $R_{N.\ G.}$ and $D_{N.G.}$ A comparison of the gradations of D_g with the gradations of the experimental molar dispersions for aqueous electrolytes leads to an estimate of the effect of hydration on the apparent ionic dispersion.

4. The molar dispersion proves to be a property which is even more sensitive to changes in the forces acting on the electronic systems of ions and molecules than is the molar refraction; in general the relative changes in D are about twice as great as the corresponding changes in R_D.