Molecular Arrangement and XRay Diffraction in Ionic Solutions

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Solutions containing heavy ions in water were examined with Cu $K\alpha$ radiation, care being taken to avoid effects of general radiation. The diffraction patterns of saturated solutions of $Th(NO_3)_4$ and $UO_2(NO_3)_2$ consist mainly in a *pronounced* ring, *shifting* to smaller angles and getting fainter with increasing dilution. This indicates a more or less regular arrangement of the ions in the liquid, for which the name "superarrangement" will be used to distinguish it from the arrangement with smaller periodicity of the water molecules. Both arrangements are of course of the "liquid-type." The above results show that the "super-arrangement" expands and gets more diffuse with increasing dilution, as might be expected. Another kind of pattern is exhibited by solutions of $AgNO_3$, $Pb(NO_3)_2$, $Ba(NO_3)_2$ and lead acetate. Here the intensity does not show pro-nounced maxima and minima. More especially it does *not decrease markedly* when the diffraction angle tends to zero. An explanation is offered, assuming the existence of a large fraction of undissociated molecules, with a gaseous distribution. A third class is formed by solutions of LiI, RbBr, LiBr and other alkali-halides. These yield a *broad* ring the position of which is *in*dependent of concentration. It is shown that these facts may be accounted for by ascribing this ring mainly to the interference between the scattering from a *heavy ion* and that from the *water molecules* around it. To clear up some of the above points a few experiments are made with solutions of analogous light ions. Finally a general theory on diffraction by solutions is formulated and applied to some of the experimental cases.

§1.

THERE are reasons to expect that the distribution of ions in solution is less at random than in a gas of corresponding density (or in a solution of neutral molecules). I have been occupied for some time in seeing if some information may be gained on this subject by the method of x-ray diffraction.[1, 2, 3]

From a theoretical point of view it would perhaps be preferable to investigate *dilute* solutions. The Debye-Hückel theory may then be expected to be at least a close approximation to the facts. Now this theory gives a more or less definite picture of the arrangement of the ions. The influence of this arrangement on the diffraction pattern may be easily calculated.[1] The experimental verification would, however, require very accurate (preferably absolute) measurements as the relatively strong scattering from the *solvent* is superposed on the effect in question.

For this and other reasons I have paid more attention to *strong* solutions (1–10 normal) of *heavy* ions.[4] Though at first the experimental results appeared rather puzzling, I believe that I have secured a sufficient agreement with theory

to be able to draw some essential conclusions. For different reasons the interpretation is more difficult than with simple liquids: (1) the scattering from the solvent is always more or less present, (2) a large number of *a priori* possibilities exists for the "structure of strong solutions," and (3) only a very restricted number of heavy electrolytes possess a sufficient solubility to make their study possible. Because of these complications it has proved to be practically impossible to work back from the diffraction pattern to the structure in the same way as for simple liquids[5] (see, however, §8).

§2.

To get a first orientation about the problem we shall for the moment suppose that only one kind of the ions in solution scatters appreciably

[1] Prins, Zeits. f. Physik **56**, 617 (1929).
[2] Prins. Zeits f. Physik **71**, 445 (1931).
[3] Prins, Naturwiss. **19**, 435 (1931) (in particular work of Krishnamurti quoted there).
[4] See for light solutions references 1 and 3 and G. W. Stewart, J. Chem. Phys. **2**, 147 (1934).

[5] F. Zernike and J. A. Prins. Zeits. f. Physik **41**, 184, 1927 (see also work of other authors quoted there). The method indicated in this paper and developed more fully in (1) is the same as that applied afterwards by Debye and Menke to the same problems (Phys. Zeits. **31**, 797 (1930) and elsewhere). It should be observed, however, that in a more primitive form analogous ideas occur in older papers of different authors; in the first place Keesom, Debye and Raman (reference 7). I avoid the word "cybotaxis," though it aims at the same conception, because it is often used in a sense, with which I cannot entirely agree. For instance the assumption of cybotactical "groups" with "optimum size" and "expanding anisotropically" (Phys. Rev. **37**, 9 (1931)) appears to me not be to justified by the subject. With this I do not mean to detract from the main idea underlying the word cybotaxis and the many important experimental contributions connected with it.

stronger than the water molecules and that there is no large difference between the size of this ion and that of the water molecules (e.g., CsOH or LiI). In this case it appears profitable to separate the scattering power of the ion into a part equal to that of water, say A, and a "surplus scattering power" B. It is clear that the scattering power A is in this case distributed over the whole volume in much the same way as if it were filled with water alone. The amplitude which the scattering from this distribution causes at a definite point of the diffraction pattern (at a certain moment) will be called $\mathbf{A}$, that from the rest $\mathbf{B}$. The observed intensity is then proportional to the mean value of the square of the amplitude:

$$I = \overline{(\mathbf{A}+\mathbf{B})^2} = \overline{\mathbf{A}^2} + 2\overline{\mathbf{A}\mathbf{B}} + \overline{\mathbf{B}^2}. \qquad (1)$$

The first term in the right-hand sum simply represents the diffraction pattern of water (modified in the sense of Fig. 6). The second term may be considered as due to the interference of the scattering from the heavy ion with that from the surrounding water molecules. This term is easily seen to be of more importance than the last term if B is small. As follows from Table II (§8) and Fig. 7 this is the case with the alkali-halides (§6). On the other hand the last term is more important when B is large. This is the case with the salts of Th, U and Pb. (§§4, 5).

The last term $\overline{\mathbf{B}^2}$, of course, represents the diffraction pattern due to the surplus scattering power alone and it is through this term that the arrangement of the heavy solute particles can be detected, this being the principal object of this investigation. Regarding this arrangement two extreme cases may be considered.

(1) The ions (or molecules) of the solute may be distributed in a random* way (as in a gas).

(2) Under the influence of the mutual forces they may tend to form a more or less regular arrangement. This arrangement will then be superposed on the "liquid-arrangement" of the solvent molecules in much the same way as the "superlattice" in some alloys is superposed on

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* Even in a gas the distribution is not *completely* at random as the molecules cannot interpenetrate. This "geometrical packing effect" is, however, of minor importance throughout this investigation, as the "dilution" is in general at least 1 : 10.
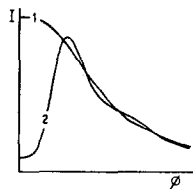

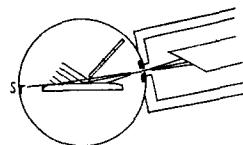FIG. 1 Diffraction pattern of a gaseous distribution (1) and of a "liquid-arrangement" (2).

FIG. 2. Experimental arrangement for x-ray reflection at heavy liquids.

the finer-meshed "lattice" constituted by the packing of all the metal atoms. This suggests the name *"superarrangement"* for the *arrangement of the solute*. It will of course presumably be of the liquid-type.

Now in the first case the diffraction pattern will be of the type represented by curve 1 in Fig. 1, while in the second case it is of type 2. Curve 1 is simply identical with the scattering curve for the isolated molecules (or ions), curve 2 is more complicated. It differs essentially from 1 in possessing a minimum at zero angle and a maximum ("amorphous ring") at some definite larger angle. Both the maximum and the minimum will be the more pronounced the more regular the arrangement is.[3] Moreover the maximum should shift to smaller angles with increasing dilution (proportionally to its cubic or perhaps square root).

It may be added that the first and second term in (1) give rise to curves of type 2, the maximum, however, *not* shifting with concentration. These notions will suffice to guide us in the description of the experiments. A more complete theory is given in §8.

§3. EXPERIMENTAL METHOD

Because of the high absorption coefficients of heavy atoms the application of the usual Debye-Scherrer method, in which the radiation passes through the substance, would require rather thin films of liquid. It is possible to make these by enclosing the liquid between mica windows[3] which are eventually drawn together by its capillary action. Some of the following results have been verified by this method. However as it is cumbersome to get the most favorable thickness (except for light liquids, Fig. 6) the

arrangement[6] shown in Fig. 2 was in general preferred.

The x-rays from a copper target strike the liquid surface under a glancing angle of about 3° and the *reflected* pattern is photographed on a cylindrical film. The slit (1.5 mm long, 0.4 mm wide) is covered by 10μ Cu foil, the film by a homogeneous 12μ Ni foil. These foils serve to monochromatize the radiation. The most important factor in this respect is, however, that the tube is operated at a tension of not more than 15 kv. The exposure time is 3–10 hours. The concentration of the solution is kept roughly constant during this time. Sometimes the solution was stirred continuously so as to make sure that the surface layer was not different in constitution from the bulk of the solution. It should be observed that the radiation penetrates into the liquid over a distance of at least some microns; there are many reasons to assume that so thick a surface layer has the same structure as the liquid in bulk.

In this article the results are shown as photometer curves. The top line* always indicates the galvanometer zero point (100 percent blackening). Two scales are given, one for the "glancing angle" (i.e., half the diffraction angle) φ and one for the variable s, defined by.**

$$s = 4\pi \sin \varphi/\lambda = 2\pi/d, \quad \text{where} \quad 2d \sin \varphi = \lambda. \quad (2)$$

It should be observed that with the experimental arrangement used the blackening at large angles is shifted a little to smaller angles as the radiation from the first half of the liquid cannot reach the film in this case (Fig. 2). This effect has roughly been corrected for in the curves by a corresponding transformation of the scales, but the blackening at, say, $s > 2$ is still considerably distorted. In order to locate a large angle maximum more accurately, in some cases the tube with attached spectrograph was set at the corresponding glancing angle.[6] No correction is then necessary. In general no high precision is claimed for the numerical results in this article.

The absorption in the liquid does not play a

large role in distorting the blackening. The smaller the glancing angle of emergence, the stronger the absorption but also the larger the effective surface (see Fig. 2). Only at very small angles the relative intensity observed may be a *little* too low, not only because of the absorption, but also because the screen (S), which cuts off the direct (and totally reflected) ray, may also cut off part of the diffracted radiation.

§4. RESULTS. CLASS I

We shall first discuss the results for thorium and uranyl nitrates, which for our purpose may be grouped together as class I.

As is apparent from Fig. 3, the principal peak present in the case of the saturated solution moves to smaller angles and gets less pronounced with increasing dilution. This points to the conception that the Th^{++++} ions are arranged in a liquid superarrangement embedded in the liquid arrangement of the water molecules, the interionic distances in the superarrangement increasing and at the same time getting less sharply defined with increasing dilution.

The position of the peaks may also be calculated or at least estimated theoretically from the number of Th ions per cm^3 solution. For this purpose a knowledge of the density of the solutions would, however, be needed and no sufficient data seem to exist. I have made a rough estimation by extrapolating the volume contraction for analogous ions and found a sufficient agreement with the experimental positions. This corroborates the above conception.

It should be pointed out that this conception is quite the opposite of the existence of colloidal or "subcolloidal" crystals of thorium nitrate or hydroxide dispersed in the medium. The above facts are incompatible with this alternative picture of the "structure of solutions" which seems to be held by many. The difference is of course that our superarrangement is *homogeneously* distributed throughout the solution. The same seems to me to be true for solutions in general;* for different cases the superarrangement may of course range from a pronounced "liquid" to a pronounced gaseous distribution.

[6] J. A. Prins, Physica 6, 315 (1926). D. Coster and J. A. Prins, J. de Physique 9, 153 (1928).
    * The lower line has no special meaning.
    ** A factor 10^8 is systematically omitted in the s-values; in other words s is expressed in A^{-1}.

* Exception must be made for the case of a mixture of two liquids at a temperature close to that of complete intermiscibility.
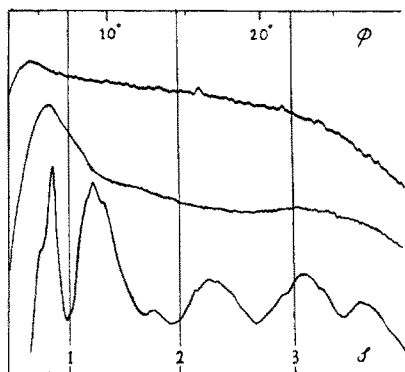
FIG. 3. Photometer curves of class I. Diffraction by thorium-nitrate solutions. Lower curve, Th (No₃)₄ : 6H₂O, solid, taken with broad slit. Middle curve, Th(NO₃)₄ : H₂O = 1 : 15, saturated solution. Upper curve, Th(NO₃)₄ : H₂O = 1 : 40, diluted solution.

These considerations do not exclude the possibility that a *small* fraction of the Th ions may be present as colloidal crystals, e.g., of $Th(OH)_4$ and that these may cause the solution to show the Tyndall phenomenon.

Analogous results as with $Th(NO_3)_4$ were found in a slightly less pronounced way with $UO_2(NO_3)_2$. In this case the saturated solution is not so viscous as in the previous case and the presence of colloidal particles is still less probable.

§5. CLASS II

A more diffuse kind of diffraction pattern is shown by saturated and diluted solutions of $Pb(NO_3)_2$, Pb acetate, $AgNO_3$ and $Ba(NO_2)_2$. In this case *no sharp* maxima are present and *no marked decrease of intensity* is to be seen when zero diffraction angle is approached. These circumstances make it difficult to investigate the influence of concentration on the position of the maxima. At any rate, however, this influence does not appear to be strong. Typical photometer curves are reproduced in Fig. 4. The slight decrease at small angles in these curves *may* be an experimental defect (see §3).

As the diffraction patterns show only weak characteristics, they do not afford a good foothold for a theoretical explanation. As is shown more fully in §9, the difference between this class and the previous one may be explained by assuming
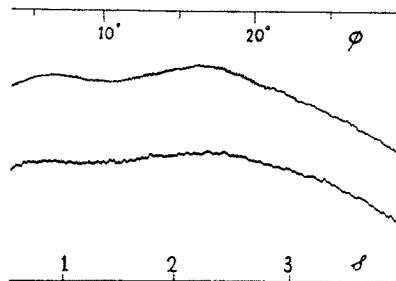

FIG. 4. Diffraction by solutions of class II. Upper curve, $AgNO_3 : H_2O = 1 : 10$. Lower curve, $Pb(NO_3)_2 : H_2O = 1 : 30$.

that at least a large fraction of the heavy constituents are more or less distributed at random in the present case. It is reasonable to suppose these heavy constituents to be *undissociated molecules*.

It seems quite probable *a priori* that undissociated molecules should be distributed in a more "gaseous" way than ions. I feel obliged however, to point out that in reality a phenomenon *may* be present here which is of a more general nature than the difference between charged and neutral particles. I mean a difference which may crudely be designated by distinguishing between "hygroscopic" and "non-hygroscopic" particles. It is at least remarkable that the salts of class I crystallize with water of crystallization, while those of class II crystallize without it. This way of looking at the difference in question is not opposite to the previous one. On the contrary: it appears quite natural that ions should be "hygroscopic," while in general neutral salt molecules should be less so. Viewed in this way, it might be only a matter of terminology. I think it better, however, to insist on the idea of hygroscopy (or hydrophily) because this idea may also be applied to some neutral ·molecules. Let us first formulate the idea in question:

"Hygroscopic" particles in general crystallize with a definite or with an indefinite amount of water, their saturated solutions are very viscous and may easily be undercooled. *These properties are linked up in the present argument with a tendency of the particles to form a superarrangement, where every particle is permanently surrounded by water molecules only.*

As examples of neutral molecules to which this idea might apply I suggest fructose ("hygroscopic") and glucose (not or at least less "hygroscopic"). This seems to me to find confirmation in the x-ray patterns of the solutions.[3] The well-known difference between "emulsoidal" and "suspensoidal" *sols* may be of exactly the same kind.

§6. Class III

The diffraction patterns of the alkali-halides I have investigated differ radically from the two preceding types. They consist in a diffuse ring at a considerable angle *not* shifting appreciably with changing concentration (the contrasts, however, diminishing a little on dilution). The diameter of the ring shows only small variations for different substances, being larger for the bromides than for the iodides (Fig. 5) and slightly larger for RbBr than for NH₄Br and LiBr.

These facts find a natural explanation if we assume the ring to be largely due to the interference of the scattering from a heavy ion (I^-, Br^-, Rb^+) with that from the surrounding water molecules. As has been pointed out in §2, we may expect this effect, due to the "mixed term" in (1), to be relatively more important here than in the previous cases, where the surplus scattering power is larger. For the same reason the absence of an "inner ring" in the present case does not prove that all tendency to a superarrangement is absent, but only that it cannot be very strong.*

The following numerical data corroborate the above explanation. From theoretical considerations we may expect the diffraction angle of the maximum 2φ to be related to the distance a between the center of the heavy ion and that of a water molecule touching it by the relation:

$$\lambda = 2(fa) \sin \varphi.$$

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* It is possible for example that in Fig. 5 the left-hand part of the curve for Li I is partly due to such an inner ring. Because of its diffuseness, however, it would be hardly possible to observe an eventual shift with concentration. On the other hand in class I (and perhaps in class II too) there seems also to be a large angle maximum independent of concentration. With $Th(NO_3)_4$ it is situated at about $s = 3.0$. It is reasonable to explain this maximum as due to the "mixed term" too. In all cases a large fraction of the intensity at $s \geqq 2$ is of course due to the term $\overline{A^2}$ in (1) i.e., to the water alone.
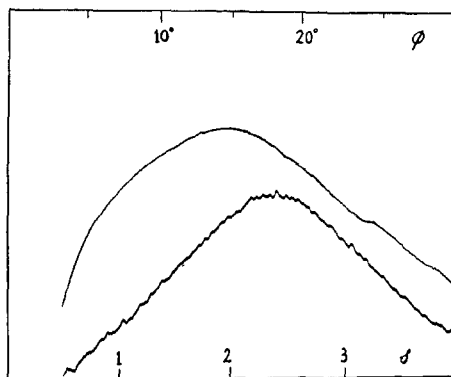

FIG. 5. Diffraction patterns, class II. Solutions of alkali-halides. Upper curve: LiI : H₂O = 1 : 15 molar. Lower curve: RbBr : H₂O = 1 : 9 molar.

Here f is a factor for which by slightly different ways of reasoning any value between 0.8 and 1 may be found.[7] We shall here somewhat arbitrarily put it equal to 0.85. The preceding formula may then be written:

$$a = \lambda/1.7 \sin \varphi$$

or by referring to (2)

$$a = 7.4/s. \tag{3}$$

The values for a calculated by means of this formula from our experimental s-values are given in Table I (third column). They may be com-

TABLE I. *Distances in A between centers of ions and of surrounding water molecules.*

Ion	s observed	a from (3)	a from ionic radii
I^-	2.0	3.7	3.6 = 2.2 + 1.4
Br^-	2.3	3.2	3.4 = 2.0 + 1.4
Rb^+	2.5	3.0	2.9 = 1.5 + 1.4
Th^{++++}	3.0	2.5	2.5 = 1.1 + 1.4

pared with the values calculated from the well-known ionic radii, derived from crystallographic data (water molecule $r = 1.4A$).

The numerical agreement between column 3 and 4 is better than our rough measurements and calculations give a right to expect and might even

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[7] W. H. Keesom and J. de Smedt, Proc. Amst. Acad. **25**, 118 (1922); C. V. Raman and K. R. Ramanathan, Proc. Ind. Ass. for Cultiv. Science **8** (2), 127 (1923). P. Debye, Phys. Zeits. **28**, 135 (1927). See also references 6 and 1.

be slightly fortuitous. But the parallelism between the two columns can hardly be accidental and is a strong support in favor of the interpretation of the results advocated in this paragraph.

The preceding diffraction patterns of class III have in common with those of class I that the intensity decreases markedly when the diffraction angle tends to zero. It cannot be assured experimentally that the intensity tends to zero and indeed it follows from theory (§§8, 9) that only a certain *not very small* limiting value should be approached (Fig. 8). Nevertheless the experimental decrease may be said to be clearly marked.

This feature gets more and more lost when the following series is successively investigated: (class III), $CsNO_3$, $SrBr_2$, $BaCl_2$, $Ba(NO_2)_2$, $Ba(NO_3)_2$, Ba acetate, (class II). This suggests that the salts between classes III and II must be considered as transition cases from class III to class II, in good accord with their position in the periodic system.

§7. LIGHT IONS AND WATER

To make sure that the small angle intensity observed with $Pb(NO_3)_2$ etc. (§5) is not due to the presence of the NO_3^- ion alone I have also photographed the diffraction pattern of a $NaNO_3$ solution with a mole ratio of 1 : 10. No small angle scattering of any importance was observed. The pattern resembled that of an equivalent NaCl solution. This pattern may be interpreted as mainly due to the arrangement which the *water molecules* assume in the electric field of the ions, these being too light to contribute appreciably to the diffraction pattern themselves.

This conception of a *rearrangement of water by ions* is due to Bernal and Fowler[8] who made use of experimental results of Meyer.[9] According to this conception in pure water the H_2O molecules are arranged in a "tetrahedral" and more especially in a "quartz-like" liquid arrangement. This arrangement is due to the peculiar electrical constitution of the H_2O molecules consisting of two positive and two negative poles arranged tetrahedrally in the (almost spherical) surface of the molecule. This constitution causes every
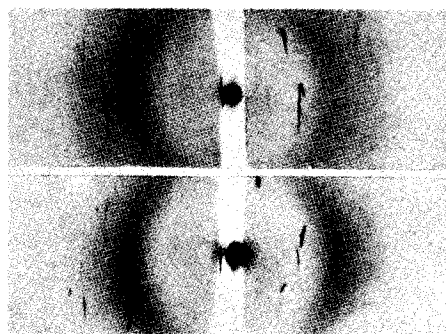
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[8] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).
[9] H. H. Meyer, Ann. d. Physik **5**, 701 (1930).

FIG. 6. Debye-Scherrer photographs taken with Cu $K\alpha$ radiation penetrating a liquid layer 0.5 mm thick between mica windows 3μ thick. Upper figure, pure water. Just outside the main ring a weaker second ring is present. Lower figure, LiOH : $H_2O = 1$: 10 (saturated). The two rings have fused to one of slightly larger diameter than the main ring of pure water.

molecule to be surrounded by only *four* neighboring molecules which join it each with one of their poles (+ to − of course). This tetrahedrical arrangement is, however, wrenched loose by the strong electric field of the ions, if these are introduced. A more or less close packing, where every molecule has more than four neighbors, is the result. This not only accounts for the well-known volume contraction observed on adding an electrolyte to water but also for the changing of the peculiar x-ray diffraction pattern of water to the more universal pattern of a close-packed liquid (see Fig. 6).

Fig. 6 represents some experiments I have made with solutions of NaOH and LiOH to confirm and extend the analogous results of Meyer, who used NaCl and LiCl solutions. To these the objection might be raised that the *scattering* by the Cl⁻ ion contributed appreciably to the modified pattern. This objection may be shown not to be very serious, as has already been observed by Meyer, but I have thought it would be more convincing to show the effect with LiOH. In this case the objection loses all significance as the scattering by the Li⁺ ion is negligible and that of the OH⁻ ion may well be identified with that of a H_2O molecule.

Incidentally it may be mentioned that I have the impression that 5 normal solutions of LiOH and NaOH do not produce *quite* so large a modi-

fication of the pattern as equivalent solutions of LiCl and NaCl.

§8. Theory

Without an exact theoretical treatment any discussion would become too vague. We shall make use of the theory given by Zernike and Prins[5] for ordinary liquids, as it is very well suited for the present case of solutions. In this theory the arrangement of the molecules and ions is expressed by a *distribution law* $g(r)$ for the *distances* between the molecular (or ionic) centra. As was shown by the authors it is then possible to calculate the x-ray pattern from the distribution function and *vice versa.*[5]

For the sake of simplicity we shall begin by supposing the water to contain only one kind of heavy ions, or stated more accurately: We suppose a certain volume to contain N particles of scattering power (see below) A and n particles of scattering power a; the particles of the first kind will be called (water) molecules, those of the second kind ions. The scattering by the volume in question will then at some definite point of the diffraction pattern give rise to an amplitude:

$$A_1+A_2+\cdots+A_N+a_1+a_2+\cdots+a_n,$$

where the separate terms indicate the amplitudes of the elementary waves from the different particles. Now what is wanted is the intensity, in other words the mean square of the above quantity:

$$I=\overline{(A_1+A_2+\cdots A_N+a_1+a_2+\cdots a_n)^2}.$$

This works out to a sum of all possible products, occurring in three types:

$$\sum_{NN}A_kA_l+2\sum_{Nn}A_ka_l+\sum_{nn}a_ka_l.$$

The mean value, e.g., of the first sum may now be found by first taking together all terms having A_k as first factor, then taking the mean of this aggregate keeping A_k constant and finally taking the mean over A_k. This gives

$$\overline{A_k(A_1+A_2+\cdots+A_k+\cdots+A_N)}$$

$$=\overline{A^2}+\overline{A}^2\int_0^\infty dr4\pi r^2g(r)[\sin (sr)/sr].$$

Here A denotes the mean* amplitude of the elementary wave scattered by one molecule. For spherically symmetrical molecules $\overline{A^2}=\overline{A}^2$ and so we may designate both quantities with A^2. This then is the exact definition of the "scattering power" A introduced above. As regards the integral in the right-hand expression it is equivalent to the mean sum over l (excluding $l=k$) figuring in the left-hand expression. The sin $(sr)/sr$ and the distribution function $g(r)$ enter into it in virtue of the phase differences existing between A_k and A_l for all possible distances and diffraction angles. Finally the second summation (over k) now yields a factor N (or n in the third sum) as all indices have disappeared. So finally:

$$I=NA^2\left[1+\int_0^\infty dr4\pi r^2g(r)\frac{\sin (sr)}{sr}\right]$$

$$+2NAa\int_0^\infty dr4\pi r^2g'(r)\frac{\sin (sr)}{sr}$$

$$+na^2\left[1+\int_0^\infty dr4\pi r^2g''(r)\frac{\sin (sr)}{sr}\right] \quad (4)$$

or, designating the three integrals, respectively, by $G(s)$, $G'(s)$, $G''(s)$:

$$I=NA^2[1+G(s)]+2NAaG'(s)$$
$$+na^2[1+G''(s)]. \quad (5)$$

In these formulae primed letters refer to the distribution of ions with respect to a water molecule; doubly primed letters refer to the distribution of ions with respect to one of them.

If the case of a 1 : 10 Li I solution is considered as an example and the presence of the Li⁺ ions is disregarded, then one may put $n=N/10$, $a=5A$ (see Table II). This renders the second term more important than the third, which explains the remarkable features of the diffraction patterns of class II, mentioned in §4. On the other hand with higher values of a the last term gets more important. *If* the distribution function g'' corresponds to a superarrangement this last term may be held responsible for the shifting peak found with class I (§4). *If* on the other hand the distribution expressed by g'' is more or less a gaseous one, the presence of the

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* In (4) A means the maximal amplitude. This causes $\frac{1}{2}NA^2$ to appear where here in (5) NA^2 appears.
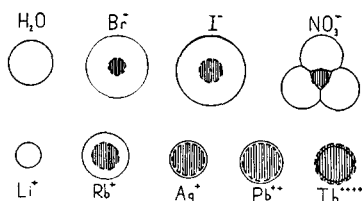
FIG. 7. Dimensions and scattering power of some ions. If the shaded volume is supposed to contain an electron density 10 times that of water it will give the right surplus scattering power.

last term accounts largely for the features of class III, at least in the case of lead salts. In the case of $AgNO_3$ the preponderance of the third term is dubious and a closer examination (§9) is needed to check the agreement between theory and experiment.

In all cases our principal aim is to get a knowledge about g''. This may be derived from an accurate determination of $1+G''$. This object may be facilitated by *comparing* the diffraction pattern for a heavy electrolyte such as CsOH with the one for an analogous light electrolyte such as NaOH. If the two diffraction patterns, reduced to the same value of N, are subtracted, we should expect the first term to disappear, while the second term might perhaps be estimated with sufficient accuracy to find the last term. This method was alluded to in the last part of §1.

In Fig. 7 and in Table II numerical data on the

TABLE II. *Dimensions and scattering power of some ions and of H_2O.*

	H_2O	Br⁻	I⁻	NO_3^-	Rb⁺	Ag⁺	Pb⁺⁺	Th⁺⁺⁺⁺
Radius in A	1.40	1.95	2.20	1.3–2.6	1.49	1.13	1.32	1.10
Effective number of electrons	10	35	53	32	35	45	74	80
Surplus number of electrons	0	7(15)	14(25)	2(11)	23	40	66	75
Radius broken circle Fig. 7	0	0.58	0.73	0.5	0.85	1.03	1.22	1.27

scattering powers and dimensions of the ions, discussed in this article, are exhibited. The scattering power is represented by the "effective number of electrons" which may be found from the total number of electrons by eventually taking into account the anomalous scattering of K and L electrons. For some purposes it is more useful to know the "surplus scattering power," obtained by diminishing the previous quantity by the amount of electrons that would be needed to

fill the volume of the ion with the same electron density as is present in a water molecule.* It is easy to transcribe formulae (4) and (5) under the assumption that a denotes the *surplus* scattering power and N the *total* number of particles. The first term should then almost completely coincide with the *lower* diffraction pattern exhibited in Fig. 6.

§9. ONE-DIMENSIONAL MODELS

We shall assume in this paragraph that no forces exist between any particles in the liquid except of course insofar as they keep it together in a definite volume. It is then possible in principle to calculate the diffraction patterns from (4), as the g-functions are completely defined by this assumption and by the dimensions of the particles and the available free space. In practice it is, however, too difficult to perform this calculation in the three-dimensional case. The analogous calculation is, however, easily made rigorously in the one-dimensional case and the result may be expected to provide a rather good picture of the corresponding three-dimensional case. We shall show in this way that the diffraction patterns of class II and III may be understood without introducing new principles.

Consider a straight line of length L containing a large number αN of "molecules" of length a and scattering power A and a large number $\beta N(\alpha+\beta=1)$ of "ions" of length b and scattering power B. The total free space $L-\alpha Na -\beta Nb$ divided by N will be called the mean free space per particle l. On the assumptions stated above the arrangement is a matter of geometrical probability. By an argument analogous[10] to that used by Zernike and Prins[5] the following expression may be derived for the diffraction pattern of the arrangement (considered as section of a plane "grating" at normal incidence):

$$I/N = \text{real part of } \alpha A^2 + \beta B^2$$
$$+ \frac{2(\alpha A e^{isa/2}+\beta B e^{isb/2})^2}{1-ils-(\alpha e^{isa}+\beta e^{isb})}. \quad (6)$$

* Instead of this density the electron density of close-packed water *in bulk* should be taken if the ion is relatively large. The corresponding figures have been added in parentheses in Table II. The truth lies somewhere between these numbers and those preceding them.
[10] The mathematical treatment may be simplified by introducing generating functions for the intermolecular distances.
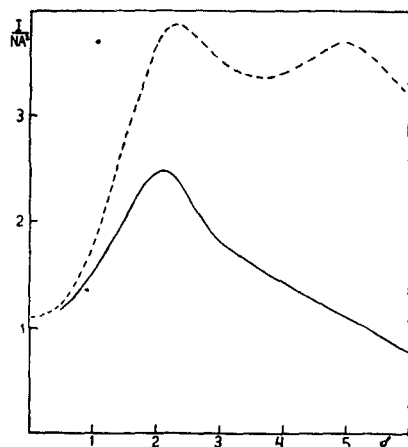
FIG. 8. Theoretical diffraction pattern for one-dimensional I^- solution (1 : 10). Broken curve represents expression (6). Full curve is derived from it by taking into account the "atomic scattering powers" for H_2O and I^- from the Thomas-Fermi model.

In this expression $s = 2\pi \sin \psi/\lambda$ ($\psi =$ diffraction angle), this quantity is the analog of the variable s from (1) in the three-dimensional case.

To get the case of a 1 : 10 I^- solution we put: $\alpha = 0.9$, $\beta = 0.1$, $b = 2a$, $l = a$, $B = 5A$, $a+l = 2.8A$. The result is shown in Fig. 8, which should be compared* with Fig. 5.

To discuss expression (6) we may separate it in four terms: (1) The term $\alpha A^2 + \beta B^2$ which will be called the "gas-term." It is the most important term for large values of s. (2) The first term arising from working out the quadratic numerator contains the factor A^2 and will be called the "water-term." (3) The second term arising in the same way and containing AB will be called the "mixed term." (4) The third term arising in the same way and containing B^2 will be called the "ionic term."

In our case the mixed term is slightly more prominent than the water term and both terms are more prominent than the ionic term. If the mixed term alone were present the position of the maximum would roughly correspond to a

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* For different reasons the s-scales cannot be expected to correspond exactly. A satisfactory agreement may, however, be established in this respect, too, by a more careful elaboration of the correspondence.

"grating constant" $a+l+b+l$ in other words to the mean distance between the centers of an ion and a neighboring water molecule. With increasing dilution the water term gets more predominating and the maximum slowly shifts to the position corresponding to the distance between adjoining water molecules. This shift is, however, so slow that it is no wonder that it has not been noted experimentally (§6) with concentrations varying at most from 1 : 5 to 1 : 20. With the other alkali-halides the difference between the dimensions of the ion and the water molecule is too small to give rise to an appreciable shift.

The same model may more or less serve for the $AgNO_3$ and $Pb(NO_3)_2$ solutions when the salt *molecule* is substituted for the I ion. It has in both cases roughly the same dimensions as the I ion. The principal difference consists in the following two points:

I. The scattering power of the salt molecule is larger than that of the I ion.

II. The "molecular scattering curve" for the salt molecule shows a steeper decrease beginning at a smaller angle than the "ionic scattering curve" of I^-.

Circumstance I renders the gas term 1 (see above) relatively more prominent. This makes the minimum at small angles less marked. Circumstance II has an analogous effect. A rough calculation shows that even with $AgNO_3$ (and *a fortiori* with Pb salts) the practical disappearance of the minimum found experimentally (Fig. 4) may be well explained in this way.

The shifting peak of class I can of course *not* be explained by the model of this paragraph. It is due to special forces (§5) causing a superarrangement. On the other hand we may now be pretty sure that an analogous superarrangement is not present to an appreciable degree with class II (and that with class III it cannot be very strong) as the experimental results appear to be explained without introducing it.

At this stage I believe that only very accurate (and if possible absolute) measurements could provide more precise information. It is certainly disappointing that the elements 85 and 87 are not available for this purpose.