ABSORPTION SPECTRA OF TETRA-ALKYL AMMONIUM SALTS.

(Contributions to the Theory of Co-ordinate Linkage IX.) 1)

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Introduction.

It is well known, that the conventional theory of valency as developed by Lowry, Sidgwick, a. o. 2 assumes that only certain configurations of shared electrons confer stability to a molecule. The stability of the electron octet, emphasised in analogy with the configuration of the heavier rare gases by Langmuir, was the starting point of this theory, and later on also other configurations of 12 and 16 shared electrons have been admitted. Consequently it was assumed, that molecules which do not follow this generalised octet rule, possess different kinds of non-electrovalent linkage. Thus, in the nitro-compound the two bonds in the NO₂ group shall be different and only one of them shall be true covalent bond. These considerations find their brief formulation in Sidgwick’s covalency rule, which postulates the maximum number of true covalent bonds to be 4 for the second short period (Li-F), 6 for the two following short periods and 8 for the heavier atoms. A number of arguments have been put forward against this conception and a theory which ascribes chemical stability to any molecule in which the sharing electrons form completed orbitals and the molecule as such is in a term of 1Σ type is also possible. 3 Whereas the first theory is a development of Lewis’ octet rule, the second emphasises Lewis’ pair-bond conception and follows more the ideas of Grimm and Sommerfeld. 4 In such a theory the maximal number of (covalent or electrovalent) bonds always equals the number of outside electrons of the atom and different types of non-electrovalent bonds are not necessary. Thus nitrogen in nitro-compounds or in N₂O₅ is simply penta-covalent, because it possesses 5 valence electrons. The obvious differences of analogous atoms of the different periods find their explanation in energetical considerations. The non-existence of NCl₅ together with the existence of PCl₅ is then due to the
Fig. 1. \((\text{CH}_3)_4\text{NCl}\).

Fig. 2. \((\text{CH}_3)_4\text{NBr}\).

Fig. 3. \((\text{CH}_3)_4\text{NI}\).

Fig. 4. \((\text{C}_2\text{H}_5)_4\text{NCI}\) in different solvents.

Fig. 5. \((\text{C}_2\text{H}_5)_4\text{NBr}\).

Fig. 6. \((\text{C}_2\text{H}_5)_4\text{NI}\).

Fig. 7. \((\text{C}_3\text{H}_7)_4\text{NCl}\).
higher energy of excitation necessary to split the $s^8$ group of electrons of the nitrogen atom. It should be mentioned in this connection, that during the preparation of various nitrogen fluorides Ruff and his collaborators have found quite definite evidence of the existence of NF$_5$. Sometime ago Ebert and Lange in the course of cryoscopical measurements found certain deviations from the behaviour, expected by the Debye-Hueckel theory in the case of strong solutions of certain tetra-alkyl ammonium halides, which clearly show, that some of these salts do not dissociate completely in water. The effect becomes more marked with the increase in mass of the organic radical and the substitution of halogens possessing lower electronic affinity. These measurements, however, are not qualified to distinguish between the non-dissociated molecules with a true covalent nitrogen-halogen bond, and pairs of ions, i.e., non-dissociated but still electrovalent molecules kept together by electrostatic forces, or the effect of formation of association of the ions themselves or of ions and water molecules. For the theories of valency, however, it would be of great interest indeed, to find out, if in solutions of tetra-alkyl ammonium halides there is really an equilibrium between electrovalent and covalent molecules, because it would contradict

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*Fig. 8. $(C_3H_7)_4$ NBr.*

*Fig. 9. $(C_3H_7)_4$ NI.*
the first and confirm the second of the above theories. Even if the percentage of covalent molecules is small, the existence of molecules in which nitrogen possesses five single covalent links would be of interest. Ebert and Lange emphasise, however, that it will not be possible to interpret their results by the introduction of one kind of interaction only and therefore it could be hoped for, that investigations of the absorption spectra may contribute at the same time to the question of the structure of highly concentrated solutions of electrolytes in water. From these points of view we have undertaken an investigation of the absorption spectra of these salts in solutions of high concentrations \( c = 1.0 \) to \( 0.1 \) \( m \) as well as in those of low concentrations \( c = 0.01 \) to \( 0.00001 \) \( m \).
Absorption Spectra of Tetra-Alkyl Ammonium Salts

Solutions of High Concentration.

For the measurements of the absorption spectra we employed at first a method, used in this laboratory and, besides later minor improvements, originally described elsewhere. As in many other similar methods, twin spectra of the solution and (with reduced illumination) of the solvent are taken with different concentrations and absorbing layers, and the wavelengths of equal intensity observed visually. The introduction of a discharge tube with stagnant gas, giving the continuous hydrogen spectrum, makes certain simplifications possible. The results, obtained with this method, indicated certain deviations from Beer-Lambert law and have been supplemented by precision measurements, in which the intensities of twin spectra of solution and solvent with equal illumination were directly measured by means of a recording microphotometer.

Fig. 12. (C₅H₁₁)₄ NCl (iso) in different solvents.

Fig. 13. (C₅H₁₁)₄ NBr (iso) in different solvents.
FIG. 14. (C₅H₁₁)₄ NI (iso).
FIG. 15. (C₅H₁₁)₄ NCl (Normal).
FIG. 16. (C₅H₁₁)₄ NBr (Normal).
FIG. 17. (C₅H₁₁)₄ NI (Normal).
Absorption Spectra of Tetra-Alkyl Ammonium Salts

The results of the first series are given in the diagrams of figures 1 to 17. Here the absorption coefficient $k$ is defined by the equation $I = I_0 \cdot 10^{-kd}$, $I_0$ and $I$ being the intensities of light, entering the medium and emerging from it, $c$ and $d$ stand for the concentration of the solution and the thickness of the layer. The concentration of these solutions was of the order 1.0 to 0.1 m. The absorption curves are shown in figures 1 to 17.

**Table I. Maxima of Salts $R_4NX$.**

<table>
<thead>
<tr>
<th>$R_4$</th>
<th>Chloride</th>
<th>Bromide</th>
<th>Iodide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda (m\mu) \log K$</td>
<td>$\lambda (m\mu) \log K$</td>
<td>$\lambda (m\mu) \log K$</td>
</tr>
<tr>
<td></td>
<td>Ist Max.</td>
<td>II Max.</td>
<td>Ist Max.</td>
</tr>
<tr>
<td>$\text{CH}_3$</td>
<td>..</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>Max. conc.</td>
<td>1 m</td>
<td>0.1 m</td>
<td>0.2 m</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5$</td>
<td>diffuse</td>
<td>diffuse</td>
<td>..</td>
</tr>
<tr>
<td>Max. conc.</td>
<td>0.2 m</td>
<td>0.2 m</td>
<td>0.2 m</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_7$</td>
<td>270 1.3</td>
<td>320 0.25</td>
<td>270 1.1</td>
</tr>
<tr>
<td>Max. conc.</td>
<td>0.1 m</td>
<td>0.2 m</td>
<td>0.1 m</td>
</tr>
<tr>
<td>$n=\text{C}_4\text{H}_9$</td>
<td>320 0.55</td>
<td>270 1.2</td>
<td></td>
</tr>
<tr>
<td>Max. conc.</td>
<td>0.1 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n=\text{C}<em>5\text{H}</em>{11}$</td>
<td>364 0.55</td>
<td>274 1.4</td>
<td>274 0.6</td>
</tr>
<tr>
<td>Max. conc.</td>
<td>0.1 m</td>
<td>0.1 m</td>
<td>0.005 m</td>
</tr>
<tr>
<td>$t=\text{C}<em>6\text{H}</em>{11}$</td>
<td>~360 0.35</td>
<td>272 1.4</td>
<td>~330 0.15</td>
</tr>
<tr>
<td>Max. conc.</td>
<td>0.1 m</td>
<td>0.1 m</td>
<td>0.005 m</td>
</tr>
</tbody>
</table>

From the comparison of the curves it will be seen that from $R=\text{C}_3\text{H}_7$ onwards selective absorption obtains. Mostly we have one well-defined and sharp maximum at about 270 m$\mu$ and another, more diffuse one preceding it at about 310 m$\mu$. The first one is always sharp. In (C$\text{}_4\text{H}_9$)$_4\text{NI}$ it is apparently only superimposed on the ascent of the band which is exhibited by the iodine ion at 227 m$\mu$. For such diffuse maxima we have taken the turning points of the curves as maxima and have deducted the probable value of the short wave ascent from its $k$ value. The results are
summarised in Table I. It is interesting to note, that in general the selective maxima occur with heavier radicals, but in each series the chloride appears to develop them stronger than the bromide or iodide. In \((C_2H_{14})_4\) NCl, \(i.e.,\) the heaviest of the chlorides, the maximum at 310 \(m\mu\) is just indicated, but a further maximum at about 365 \(m\mu\) is developed, which could not be found in the other curves. This latter one appears quite distinct in the \(n\)-molecule and is still indicated in the iso-compound. In the series with \(R = C_2H_5\), the chloride shows already indications of the maxima, even if only diffuse and at low values of \(\log k\), the bromide and iodide show a continuous end absorption only, like the salts with \(R = CH_3\). In the series with \(R = C_5H_9\) we find a slight decrease of the \(\log k\) values in the same directions, which is more strongly marked in the series with \(R = n - C_5H_{11}\), where the \(\log k\) values of the main maximum at 274 \(m\mu\) decreases from 1.4 in the chloride to 0.6 in the bromide. The corresponding figures for the iso-forms are 1.4 for Cl, and 1.2 for Br.

Since the main maximum possesses about the same wave-length independent of \(X\) being Cl, Br or I, it seems reasonable to assume, that this selective absorption belongs essentially to hydrated \(R_4N^+\) ions. On the other hand, the maxima appear only with heavier radicals, and it contradicts every experience to assume that the selective absorption if it belongs to the \(C - N\) link, should obtain only when longer chains are attached to the C atom.

Furthermore, if this absorption would be due to the \(R_4N^+\) ions alone, the differences in intensity (\(\log k\)) values between chlorides, bromides and iodides and those between the normal and iso forms of \((C_2H_{11})\) NBr and \((C_5H_{11})\) NI could not be explained.

Further corroboration is furnished by the optical behaviour of these salts in the presence of foreign salts. The solution of \((C_2H_5)_4\) NCl, where the maxima are still found indistinct at low values of \(k\), shows, that all curves in the presence of foreign ions are shifted in the same sense against the curve in water; only the absorption coefficient is increased and the curves are slightly shifted towards red. Those in solutions of the three chlorides LiCl, NaCl, and KCl are close together, while those in solutions of KBr and KI show stronger effects. (Cf. Fig. 4.)

We have then measured solutions of \((C_5H_{11})_4\) NCl, where the maximum is more distinct than in the former ones, in the presence of NaCl, KCl, and KBr and of \((C_5H_{11})_4\) NBr in the presence of Na2SO4 and BaCl2. It can be seen (Figs. 12 and 13) that again the curves of the former salt in solutions of NaCl and KCl are close together, whereas the \(\log k\) value reaches appreciably higher values and the curve broadens in the presence of the Br ion. Here the influence of the negative ion is clear. The changes of the
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absorption coefficient to our mind are more important than those of wavelength. Table II gives the wave-lengths in \( \mu \) of the maxima obtained.

**Table II.**

<table>
<thead>
<tr>
<th>Chloride</th>
<th>272</th>
<th>Bromide</th>
<th>277</th>
</tr>
</thead>
<tbody>
<tr>
<td>In water</td>
<td></td>
<td>In water</td>
<td></td>
</tr>
<tr>
<td>In water + NaCl</td>
<td>276</td>
<td>In water + Na(_2)SO(_4)</td>
<td>275</td>
</tr>
<tr>
<td>In water + KCl</td>
<td>275.5</td>
<td>In water + BaCl(_2)</td>
<td>275</td>
</tr>
<tr>
<td>In water + KBr</td>
<td>275</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It does not appear to us to be impossible that the differences of wave-length are below the sensitivity of the experimental method and that these experiments do not allow us to distinguish accurately between the wave length of the maxima in the presence of foreign ions. We cannot be certain whether the differences between 276 and 275 \( \mu \) are real. It can be seen, however, that the maximum of the bromide, compared with that of the chloride, in water without additional salts, is certainly shifted towards red and that, independent of this, the maximum obtains a position at about 275 to 276 \( \mu \) in the presence of foreign salts.

**Some Remarks on Optical Effects in Concentrated Solutions of Strong Electrolytes.**

The interpretation of these effects leads us to the question of the structure of solutions of strong electrolytes at higher concentrations. It is well known, that the theory of Debye-Hueckel still needs further development to explain the behaviour of such highly concentrated solutions, \( c \) being about 1 to 0.01 \( m \). From the point of view of the optical behaviour of strong electrolytes and particularly as regards absorption spectra the problems connected with this question have been discussed by Scheibe\(^8\), von Halban,\(^9\) and Fromherz,\(^10\) and their collaborators. Scheibe and Fromherz interpret the observed changes in the selective absorption of various ions due to the presence of foreign salts, in terms of changes in the deformation of the absorbing ions in the unlike field of the anti-ions, which may form a surrounding atmosphere of opposite charge or may form pairs with the absorbing ions according to the conceptions put forward by Bjerrum\(^11\) to adapt the Debye-Hueckel theory of strong electrolytes to higher concentrations. Von Halban and his collaborators have on the other hand always
maintained that other influences exist too and in the last paper of Kortuem13 not the interaction between oppositely charged ions but the effects of hydration and dehydration, or, in other words, the interaction of the absorbing ion with the dipole molecules of the solvent are held mainly responsible for the observed changes of the absorption curve.

To our mind it is evident, that both effects play a rôle and that the observed changes as for instance those of the absorption of $R_4N^+$ ions above cannot be expressed in terms of one parameter only. A simple reference to the properties (hydration, polarisability, or diameter) of the anti-ions alone is not sufficient and the influence of the ions of like charge is certainly present here as well as in other instances as shown in previous papers of this series. We have mentioned above that also Ebert and Lange8 have come to a similar conclusion from cryoscopical measurements and a number of authors have already emphasised that the structure of solutions of electrolytes at higher concentrations is rather a complex phenomenon. Special mention may be made of the measurements of Darmois13 on the optical activity of tartrates in the presence of neutral salts, which have led him to the assumption, that dehydration and deformation influence the optical activity in the opposite way.

But the conclusion that the interaction effects in higher concentrated solutions of strong electrolytes are of a complicated nature and that various different effects exist side by side, is about the only one which in the present moment can be made with certainty. How difficult it is, to predict the result of any one of the various possible effects, say of hydration or deformation of the absorbing ion, on its selective absorption, will be seen, when the Franck-Condon diagram which has already served as a useful instrument in so many discussions on the absorption and emission of isolated molecules in the vapour state, is made the basis of discussion.

The three-dimensional Franck-Condon diagram of a molecule $A^+(BC)^-$ — we may think of KOH—may be represented schematically in a simplified manner in Fig. 18. The ground level of the ion $(BC)^-$ may be formed by the union of $B+C^-$ and the level of these separated constituents $A^++B+C^-$ will be above that of the neutral atoms $A+B+C$, since generally the electronic affinity of C will be smaller than the ionisation potential of A. In any case we will find, in analogy to diatomic and polyatomic molecules in the vapour states, a number of repulsive curves and an absorption of light, i.e., a transition from the ground level to any one of them, will produce a region of continuous selective absorption which may be correlated to a process of photo-dissociation or to the tearing off of the superfluous electron of the negative ion in solution, the latter spectra may also be due to the
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transition of the electron to a molecule of the solvent under formation of e.g., OH\(^{-}\) ions as shown by Franck and Haber\(^{14}\) but such complication shall not be considered here. It is, however, evident, that the absorption of light is represented by the upper part of the energy diagram, which belongs essentially to the (BC)\(^{-}\) ions, representing its dissociation or formation, in which the A\(^{+}\) ion does not take any part, but is considered to be at infinite distance, in the level of the separated constituents B + C\(^{-}\) as well as in that of the ground level of the ion (BC)\(^{-}\). The formation of A\(^{+}\)(BC)\(^{-}\) originates from the latter one and is represented in the lower part of the diagram. If we consider now those conceptions which assume in higher concentrated solutions the formation of associations of the A\(^{+}\) and the (BC)\(^{-}\) ions, either as atmospheres of oppositely charged ions or particularly as pairs of unlike ions, this will be a process in which A\(^{+}\) ions are not any longer at an infinite distance from the (BC)\(^{-}\) ions and which is therefore connected with this lower part of the energy diagram. Any change due to deformation of the ion (BC)\(^{-}\) in its unexcited level will therefore have quite different effects on the two parts of the diagram, since this level forms the lower state for the representation of the selective absorption and the upper one for the formation of undissociated ions A\(^{+}\)(BC)\(^{-}\). According to Kortuem's measurements the absorption spectrum of dinitrophenol does not undergo any change in concentrations of medium strength (up to 0.01 m) in which activity coefficients, conductivity and similar observations indicate already deviations from the theory of Debye-Hückel. For still higher concentrations he finds changes of the optical properties, but these do not go parallel with those formed by means of thermodynamical and electrochemical measurements. He concludes that the interaction of the absorbing ion with the molecules of the solvent is the essential effect, and not that between the ions of opposite charge. From the above diagram it is evident, that this

\[ \text{Fig. 18. Scheme K of Franck-Condon Diagram of a Triatomic Salt.} \]
is by no means conclusive for the reason, that absorption and approach of unlike ions belong to quite different parts of the energy diagram.

In Fig. 19a the lower part of this diagram has been used to represent the process of hydration of the system A⁺ (BC)⁻. In the process of hydration or solvation a certain amount of energy is liberated, which has to be added for all internuclear distances and brings about a lower position of the U : r curve. If the undissociated molecule is an electrovalent one* the hydration energy of the two ions together represents naturally a much bigger amount than that of the undissociated molecule because the number of water molecules held by the two separate ions and the force by which they are bound to them is much larger than for the neutralised molecule itself. This is evident for those simpler diatomic salts for which all figures, i.e., ionisation potential, electronic affinity and energy of hydration of the two ions and the heat of formation of the gaseous compound are known; Potassium chloride may serve as an example and its Franck-Condon diagram is given in figure 19b. In KCl the level of the separated ions is about half a volt above that of the separated neutral and unexcited atoms. The energy of hydration is known to be 73 k. cal./mol. for K⁺ and 89 k. cal./mol. for Cl⁻ and hence the level of the separated ions in the state of hydration lies about 7 volts below that of the unhydrated ones or about 6.5 volts below that of the separated neutral atoms. The ground level of the undissociated gaseous ionic molecule (K⁺Cl⁻) lies about 103 k. cal. or 4.5 volts below that of the neutral atoms or still about 2 volts above that of the hydrated ions and the energy of hydration for this form will be very small.

* The term electrovalent is used, when the adiabatic excitation of the vibrational levels of the ground state dissociates a molecule into ions, and a molecule is called covalent, when the adiabatic dissociation of its ground state involves neutral atoms.
because the opposite charges cancel each other. The fact, that KCl dissociates in aqueous solutions shows already that the hydration energy of the undissociated molecule is less than this difference of about 40 k. cal./mol. and that the level of the separated hydrated ions has become the lowest one of the system. The great difference of the hydration energy of the two systems K⁺ + Cl⁻ and (K⁺Cl⁻) turns the U : r curve into a repulsive one and as a matter of fact the above is only a description of the process of hydrolytic dissociation by means of the Franck-Condon diagram. Similar repulsive curves have to be expected quite generally for molecules dissociating into ions and even if the electrovalent curve of the non-hydrated molecule is not that of the ground level but near to it, that involving the separated hydrated ions may intersect the potential curve of the ground level and may become the lowest one of the system.¹⁴ as in AgCl.

Two conclusions become evident at once from this description by means of the U : r curves. In Fig. 19a the lowest dotted curve represents the dissociation process due to the difference of hydration energy and is shown here as a repulsive curve. If, however, the concentration is increased and the number of water molecules at the disposal of the individual molecule A⁺(BC)⁻ is appreciably decreased, the energy of hydration decreases too, and the original curve of the gaseous state being the limiting case in which the hydration energy vanishes, higher curves of the hydrated system should be expected, showing a labile minimum in the neighbourhood of the internuclear distance of the gaseous molecule. An attempt to draw such a curve is shown by the upper dotted curve of Fig. 19a, but in any case such curves with a slight minimum must come into existence if the additional energy of hydration is sufficiently decreased. Such a minimum may be taken as the energetical representation of Bjerrum's pairs of ions.

*Fig. 19b.* Franck-Condon Diagram of KCl.
Secondly, this diagram of the position of the electronic terms of the system A+(BC)-, depending on \( r \), does not give any indication as to the change of the selective absorption of the ion (BC)-. In this description \( r \) represents the distance between the cation and the (BC) anion, the latter one is taken as an entity and the change of the relative position of its own electronic terms, on which its optical properties depend, does not appear at all, and has no direct connection with the dissociation process of the cation and the anion. Hence one set of observations like electrical conductivity, concerning the system A++(BC)-, may well indicate the existence of non-dissociated ions in such concentrations, in which absorption measurements show that the relative position of the terms of the (BC)- ion itself has not yet changed.

The change of wave-length as produced by the addition of hydration energy to the system depends again on whether the hydration of the undissociated ion (BC)- or that of the separated system B + C- is the greater. Fig. 20 represents the case in which the separated system B + C- gains more energy than the complex ion (BC)-. The change in wave-length produced in this way is always a small effect and we may therefore assume that the general form of the potential curve remains unchanged and that excited states become less and less affected. If then the energy difference between the unhydrated system (full lines) and the hydrated one (broken lines) is bigger on the right-hand side for the separated constituents than on the left-hand side for the completed ion, the effect of such an increase of energy will be to shift the region of selective absorption slightly towards red, and the dehydrating effect of the presence of ions of like or unlike charge in the solution will shift the maximum towards shorter wave-length. This effect seems to exist in certain of Warner’s complex salts, investigated
earlier,\(^1\) e.g., when the absorption curves of \(\text{Na}_3[\text{Rh Cl}_4]\) does not differ, in the presence of NaCl and KCl but is shifted towards the ultra-violet when the additional salt is replaced by \(\text{Na}_2\text{SO}_4\). Indeed it is very plausible to assume that the hydration energy of such a complex ion is less than the sum of those of its constituent ions and the characteristic influence of the ions of like charge can be explained in this way quite well. When, however, the hydration energy gained by the separated system happens to be smaller than that of the united ion, just the reverse effect has to be expected, and in cases like the \(\text{R}_4\text{N}^+\) ions it is not easy to decide, which hydration energy may be the larger one. It could be argued that the field in the neighbourhood of a completed ion will always be smaller because the charge is the same as in the separated constituents, while the radius is bigger. But this will not be true always; the charge is not evenly distributed but localised in the molecule and new dipole moments may be produced in the \(\text{N} - \text{R}\) bonds. More often, however, the hydration energy of the separated system should be bigger and therefore hydration should produce a shift towards longer, and dehydration by the neutral salts added to an aqueous solution, towards shorter wave-lengths. Such considerations seem to explain also most of the effects observed on the absorption curves of organic molecules in different solvents.

Superimposed on this effect is that of the deformation of the absorbing ion by the field of an added foreign ion. Whereas the first effect may be produced by ions as well of like and of unlike charge, this second effect may be expected to be characteristic for the ion of opposite charge, because such ions will be found in the neighbourhood of the absorbing ion or will pair with it at stronger concentrations. Not very much can be said about the result of such a deformation on the absorption itself. In the Franck-Condon diagram such an effect will produce a change in the internuclear distance of the minimum position and, furthermore, the energy of dissociation and the whole force system and the slope of the curves will be changed. In this connection, however, the rule of Fajans and Joos\(^{16}\) may be mentioned, according to which the electronic configuration of a cation will be loosened while that of the anion consolidated by the mutual deforming influence. This rule has been confirmed by many observations on monoatomic ions. We will assume that it holds also for more complex ions, because at least for the anions there should not be much difference. This is not so certain for cations, because the complex cations possess outside electrons, which the monoatomic ones mostly have lost. We remember again, that the effects in question are only slight, and we assume therefore that the changes on the potential curves are slight too and may be neglected increasingly
for the higher terms. In this case we expect that the absorption maximum of a cation will be shifted towards longer wave-lengths, that of an anion towards shorter wave-lengths as a result of the deforming influence of an ion of opposite charge. In the Franck-Condon diagram, the consolidation of the electronic configuration may be compared to the normal case of band spectroscopy in which the ground level possesses a smaller $r$, larger vibrational frequency and larger energy of dissociation than the excited level and the loosening of the electronic structure to the reverse, normal case. The ground level corresponds to the ground level of the undeformed, the excited to the ground state of the deformed molecule. If the repulsive curve does not suffer more than very slight changes, the energy difference between that and the ground level will be decreased in the former and increased in the latter case. Such a conception appears well qualified to explain many effects observed on the absorption curves of inorganic ions and is more or less identical with certain conceptions, developed by Scheibe and his collaborators.

There is, however, still another effect possible already discussed by Fromherz. These two cases of deformation, essentially a decrease or increase of the polarisability, may effect mainly the absorption coefficient and not the wave-length. According to the theory of dispersion, the polarisability is directly proportional to the absorption coefficient and inversely proportional to the frequency, and anions in the field of deforming cations can then show a decrease in the absorption coefficient, cations in the field of deforming anions an increase.

We have seen, that the selective absorption of the tetra-alkyl ammonium salts appears gradually with increasing weight of the radical and is not identical in $n$ and $i$ forms. This effect appears to be due to the deformation of the ion in the field of the hydrating water molecules, which is different according to the size and arrangement of the radical and therefore we have ascribed the selective absorption to the hydrated ions. The dehydrating effect of Cl$^-$ is bigger than that of Br$^-$ and consequently the larger deformation in (C$_4$H$_{11}$)$_4$ NBr produces a maximum at a slightly longer wave-length than in (C$_4$H$_{11}$)$_4$ NCl. At the same time there is a marked difference of intensity between chlorides, bromides, and iodides, the $k$ values of the chlorides being the greater one. This effect cannot be ascribed to the dehydrating influence of the anion as the Cl$^-$ ion is the more hydrated and hence the more dehydrating one, and this effect has to be interpreted as a true deformation of the cation by the anion. These absorptions concern mainly, but not entirely, the value of the absorption coefficient and come therefore under the last of the above headings. But
it is clear, that both effects, the interaction with the molecules of the solvent and with the oppositely charged ions have to be considered.

This is corroborated by the optical effects, produced by foreign ions. All three curves of \((C_2H_7)_4NCl\), in the presence of NaCl, KCl and KBr lie at longer wave-lengths than that in water only, the KCl and NaCl curve closer together, that in a KBr solution more apart. This indicates the deforming influence of the anion on the cation and the effect of the Br\(^-\) ion is probably slightly the stronger because the radius of the hydrated Br\(^-\) ion is smaller than that of the hydrated Cl\(^-\) ion and it can approach the cation more closely. Again the dehydrating effect of the positive ion can be seen from the curve of the bromide in a solution of BaCl\(_2\), which is much above that in Na\(_2\)SO\(_4\), but only as far as the absorption coefficient is concerned.

The curves of \((C_2H_7)_4NCl\) in the presence of foreign salts show exactly the same behaviour. On account of the deforming influence of the anion on the \(R_4N^+\) ion, all curves are slightly shifted towards the red and have increased \(k\) values. Those due to the Cl\(^-\) ion are all closer together, than the other ones, the effect being more marked in the order Cl\(^-\)< Br\(^-\)< I\(^-\), i.e., in the order in which the radius of the hydrated halogen ions decreases and the minimum distance of approach therefore decreases too.

These few remarks will be sufficient to show, that the effect of both kinds of interaction have to be considered and that the long wave-length maxima are due to the hydrated \(R_4N^+\) ions.

**Measurements on the Absorption Band of the Iodine Ion, at Low Concentrations.**

Further experiments concern such solutions of low concentrations for which Beer's Law has been found to be rigorously valid in many cases and particularly for the bands of the iodine ion. This gives us an opportunity to ascertain whether there exist indications of a true covalent nitrogen-halogen bond. This was done by a precision method, as mentioned above, since the percentage of such covalent molecules is necessarily very small. A sample microphotogram of two solutions of \((C_6H_{11})_4NBr\), taken on the same plate together with that of the source of light through distilled water only is shown in Fig. 21, Plate XXII. In each case the exposure time is exactly equal, the one solution, however, has a strength of \(\frac{M}{10}\) in an absorption cell of 9.99 mm. length, whereas the other solution had a strength of \(\frac{m}{100}\) and the length of the absorption cell was 99.983 mm. It can be seen, that the absorption curves join exactly on the long wave side, showing that the
illumination was indeed identical and no errors due to slight changes in the adjustment have occurred. In the region of the selective absorption itself, however, the curve of the more concentrated solution lies definitely slightly below that of the more diluted one. In spite of the same number of molecules being present the number of absorbing centres has decreased, indicating that the number of association complexes, formed by the R₄N⁺ ion, decreases with increasing concentration.

From the discussion above, it is obvious that different interpretations of these maxima between 300 and 270 mμ are possible, and therefore such deviations from Beer's Law even without shift of wave-length are not conclusive for the existence of a true covalent bond. They may be taken as indicating the existence of still another form of association, but they do not give a definite answer as to the nature of such a second not dissociated form. There is, however, another possibility definitely to test whether this second associated form really is identical with a molecule, which possesses a covalent nitrogen-halogen bond covalent. Scheibe⁸ has found two bands belonging to the iodine ion, with maxima at about 226 and 192 mμ. There is no doubt, that these two bands belong to the negatively charged iodide ion; the energetical difference of 7900 cm⁻¹ of the two bands agrees with the doublet separation of the ⁵P ground level of the iodine atom of 7600 cm⁻¹ and these two regions of absorption have been correlated to photo-dissociation processes I⁻ + hv = e + I (⁵P₁/₂) and I⁻ + hv = e + I (⁵P₃/₂) and it is probable that the electron forms OH ions subsequently. Fig. 22 shows the first of these two bands in a solution of concentration of (CH₃)₄NI. The photometer curve indicates that the absorption of the iodine ion persists in solutions of tetra-alkyl ammonium iodides. Its maximum was measured at 227 mμ.

We have then compared the absorption of different concentrations. In order to increase the accuracy of the photometric measurements the exposure time was arranged in such a way, that all plates were not too dark but the spectra were just slightly grey; accordingly the maxima themselves are not very pronounced on these records. Fig. 23 shows the absorption of two solutions of (C₆H₁₁) NI, firstly with = \( \frac{m}{10,000} \) and \( d = 10 \text{ mm.} \), secondly with = \( \frac{m}{2,000} \) and \( d = 2 \text{ mm.} \). Again the absorption curve of the more concentrated solution lies definitely below that of the more diluted one. In Fig. 24 the first of these two solutions is replaced by an even more diluted one, \( = \frac{M}{100,000} \) and \( d =100 \text{ mm.} \) it can be seen that the difference between the curves is still increased. Again the curves join exactly in the unabsorbed
region, showing that adjustment and illumination did not change. All curves have been taken from the same plate, to avoid possible differences of blackening due to developing. Similar results obtain also with lighter salts, e.g., \((\text{CH}_3)_4\text{NI}\). The effect is certainly small and we do not intend to work it out quantitatively. But there is no doubt, that qualitatively the concentration of the iodine ion decreases with increasing concentration.

Scheibe and Fromherz and their collaborators have shown in a number of investigations, that for the maxima of the iodine ion at such low concentrations as used here, Beer's Law is rigorously valid. Moreover, at low concentrations from 0.001 onwards also other optical measurements of absorption spectra, refractive index, etc., as well as thermo-dynamical and electrochemical measurements have shown, that the properties of the ions are independent of concentrations. Furthermore, whenever with much higher concentrations a change of the \(k\) values of the bands of \(I^-\) has been observed it was accompanied by a change in wave-length, whereas in our measurements the wave-length of the maximum remains constant and the absorption coefficient alone is changed.

The optical constancy of these bands is very well known indeed and since the same amount of iodine was present in these solutions and since this particular band is characteristic for the negative iodine ion there appears to be only one possible interpretation, namely, that a certain percentage of iodine ions has lost its ionic character. This evidently means, that there exists still another form of the tetra-alkyl ammonium iodides, with which the dissociated molecules of the salt are in equilibrium, in which they possess a true covalent \(N-I\) bond, and that nitrogen under favourable conditions can be penta-covalent in agreement with a pair-bond theory of valency.

The solutions of tetra-alkyl ammonium halides are apparently a mixture of three different forms. The bulk of a solution of \(R_4\text{NX}\) in water at low concentration is dissociated in \(R_4\text{N}^+\) and \(X^-\) ions, as long as \(R\) is \(\text{CH}_3\) or \(\text{C}_2\text{H}_5\). When \(R\) becomes heavier, association complexes are formed by the hydrated ions, in which also \(X\) plays a rôle (pairs of ions ?), and the percentage of such complexes appears to be comparatively large at concentrations of 1 to 0.1 \(m\). At the same time at least the iodides are in equilibrium with a small percentage of a third form which is characterised by a covalent bond between nitrogen and iodine.

In previous papers of this series\(^{1,17}\) we have already come to the conclusion, that the term 'complex salt' now-a-days is used for quite different classes of molecules. We have defined as "genuine complex salts" such compounds, in which the complex ion preserves its individual identity as such also in solution and in which physical measurements like absorption
spectra or Raman effect indicate some kind of true chemical, non-electro-
statical linkage between the central ion and those molecules or ions which
surround it. This definition excluded all cases of crystal water, or crystal
alcohol, etc., where a definite co-ordination number is produced not by the
number of co-ordinate bonds but by the geometrical properties of the crystal.
It excludes furthermore cases like the hydrated ions of the transition
elements, in which the absorption spectrum indicates that the water molecules
are held as loose associations on account of electrostatic forces. It is interesting
to note, that Day, Hughes, Ingold and Wilson\textsuperscript{18} on account of quite
different observations have come to the same conclusion in the latter case.

But also in the class of genuine complex salts the co-ordinate bond
appears to be the representation of quite different physical mechanisms
in various cases. The absorption spectra of tetra-alkyl ammonium salts
do not show any phenomenon which could not be attributed to ordinary
covalent bonds between carbon and nitrogen. On the contrary, the
transition to covalency of the nitrogen-halogen bond, which was observed
for a small percentage in low concentrations directly contradicts the con-
ception of the co-ordinate bond as originally developed by Werner. The
most simple and straightforward description of the mechanism of linkage
appears to be to attribute 5 covalent bonds to the N atom on account of its
5 outside electrons $2s^2\ 2p^3$. It is clear that among the five bonds that
between nitrogen and halogen will be much more polarised than the four
nitrogen-carbon bonds, and hence this bond will be the one which becomes
electrovalent under the influence of additional outside energies like that of
hydration or of the crystal lattice. If this is so, the tetra-alkyl ammonium
salts do not belong to the same class as for instance the hexa cyanides of Co,
but have to be considered as simple derivatives of pentavalent nitrogen.
To our mind this conclusion is strongly corroborated by the fact, that,
according to their absorption spectra,\textsuperscript{19} also inorganic nitrates are covalently
bound in the vapour state and exhibit an electrovalent bond only in solu-
tion. The different chemical behaviours of the fifth bond of nitrogen appear
to find its explanation more by considerations of bond energies and polar-
sation than by the assumption of a special quality of this bond.

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Fig. 21. Photom. Record, \((\text{C}_3\text{H}_{11})\) NBr.

Fig. 22. Photom. Record, \((\text{C}_3\text{H}_{11})\) N absorption.

Fig. 23. Photom. Record, \((\text{C}_3\text{H}_{11})_4\) N.

Fig. 24. Photom. Record, \((\text{C}_3\text{H}_{11})_4\) N.
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EXPLANATION OF FIGURES IN THE PLATE.

Fig. 21. Photometer record of \((\text{C}_2\text{H}_4\text{H}_{11})_4\) NBr solution. 0.1 m. and 9.99 mm., 0.01 m. and 99.98 mm.

Fig. 22. Photometer record of \((\text{CH}_3)\_4\) NI solution.

Fig. 23. Photometer record of \((\text{C}_2\text{H}_4\text{H}_{11})_4\) NI solution. 0.005 m. and 2 mm., 0.001 m. and 10 mm.

Fig. 24. Photometer record of \((\text{C}_5\text{H}_{11})_4\) NI solution. 0.005 m. and 2 mm., 0.0001 m. and 100 mm.