SOME OBSERVATIONS ON SELECTIVE REFLECTION FROM SOLUTIONS IN THE INFRA-RED.

By A. K. Ångström.

DRUDE'S[1] theoretical considerations led him to regard the ultra-violet absorption lines as due to the vibration of particles of the size of an electron, while the particles giving rise to the infra-red absorption bands have a mass of the order of magnitude of the molecule.

In accord with the theory the investigations of Pfund,[2] Morse,[3] Langford[4] and others, and specially the comprehensive works by Coblentz[5] indicate that the mechanism giving rise to strong maxima of reflection in the infra-red spectrum, in the case of salts, is localized within the acid radical. Salts of the same acid have characteristic reflection-maxima, whose positions are more or less independent of the positive radical. Further investigations have shown that a change of the positive radical generally gives rise to a slight change in the period of the vibration, in such way that an increase in the molecular weight of the base causes a shift of the absorption (reflection) band to longer wave-lengths. Several relations have been tried in order to express this shift as a function of the molecular weight of the constituents; none of them seems to be of general applicability.

Under conditions, where the absorption coefficient is unusually large, as is the case for most crystals at several points in the infra-red spectrum, and for water in the infra-red, the *reflecting power* gives an important means of detecting the position and slight variations in the absorption bands, a method; first used in the classical investigations of Rubens and Nichols.

In the present note, I will describe some measurements with aid of the spectrometer and the Nichols' radiometer, where the selective reflection properties of water have been used in order to detect slight variations in the free period of vibration, when different compounds are dissolved

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[1] Annalen der Physik, *14*, 677, 1904.

[2] Astrophysical Journal, XXIV., 19, 1906.

[3] Physical Review, *25*, 500, 1907.

[4] Physical Review, *33*, 137, 1911.

[5] Coblentz, Investigations of Infra red Spectra. Publ. by the Carnegie Inst. of Washington. Parts IV. and V.

in the water. These observations are closely connected with the problem of the rôle of the solvent in solutions, a problem that has been extensively studied by H. C. Jones and his collaborators at Johns Hopkins University. The observations of Guy, Shaeffer and Jones[1] indicate that under special conditions there occurs a shift of the spectral bands of the solvent to the long wave-lengths with an increase in the concentration of the dissolved substance. They observed further that the absorption power of the solution was sometimes considerably less than the absorbing power of the water present in the solution. This seems to be the case when this dissolved substance is a strongly hydrated salt, and the view held by the authors is that this shift and this change in the absorption power is due to a chemical reaction taking place in the solution, a part of the water combining with the dissolved substance to form hydrates. Such a hypothesis will evidently account for the observed facts. It has, however, since been pointed out by G. H. Livens,[2] that the results obtained by Guy, Shaeffer and Jones can be derived from the dispersion and absorption theory in the form given by Lorentz without any hypothesis in regard to intramolecular changes taking place in the solution. The point brought forward by Livens seems well worth the attention of the upholders of the solvate theory. From the purely physical point of view, it seems however difficult to account for the fact that the observed shift only occurs in measurable degree in the case when the dissolved substance is a strongly hydrated salt.

Before the results of Jones and the theoretical considerations of Livens were communicated, I had begun a study of the influence of the dissolved substance upon the strongly marked water band at 3 μ, that gives rise to a very sharp and definite reflection maximum at 3.18 μ. The absorption of water in this region is such that a layer of only 3 μ thickness absorbs almost totally, and it is therefore preferable to use the reflection properties as an indicator of the selective conditions.

As the study has brought forward some facts that require to be taken into consideration in forming a view upon the question, some preliminary results are here published.

INSTRUMENTS.

The general arrangement of the apparatus is shown in Fig. 1. A reflection spectrometer with mirrors of 6 cm. aperture and 54 cm. focal length was used. By aid of the Wadsworth mirror prism arrangement, the spectrometer arms could be kept fixed and an adjustment for minimum

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[1] American Chemical Journal, *49*, 265, 1913.

[2] Physikalische Zeitschrift, *14*, 660, 1913.

deviation of one wave-length (*D*-line) held for all. The adjustment for minimum deviation was made in accord with Coblentz' description,[1] and a check on the adjustment was obtained by noting the position of the carbon dioxide band in the bunsen flame and the unchanged position of the selective reflection maximum of water at 3.20 μ during the observations.

Concerning the spectrometer, it may be mentioned, that the angle through which the prism table was rotated was measured with aid of telescope and scale, the tiny mirror being fastened to the top of the prism. The sensibility of the arrangement was such that 1 mm. on the scale corresponded to 1.5 minutes' rotation of the prism table. As one minute's rotation corresponds to about 0.12–0.15 μ in the investigated interval and the readings were made accurately to 0.1 mm., the accuracy in the wave-length determinations is about 0.01–0.02 μ.

The advantage of this way of determining the deviation over a direct reading on the spectrometer circle, lies in the possibility of the observer keeping as far away as possible from the heat-sensitive instrument during the observations. In the beginning and end of every observation series, the readings on the telescope scale were checked with the direct readings on the spectrometer circle. The spectrometer and the heat-measuring instrument, the radiometer, were both enclosed in a way that totally protected against air currents.

The Nichols' radiometer was surrounded by cotton and a blackened metal case, in the manner described by other observers. The mica vanes had a width of 0.80 mm., which corresponded to the same width of the spectrometer slit. The sensitiveness was such that a meter candle gave rise to a deflection of about 750 mm. The vacuum corresponded to maximum sensitiveness. The leak was so small that the sensitiveness remained practically the same during several days. When the writer returned after three months' absence, it was found that the sensitiveness of the radiometer had only diminished by 20 per cent. through increase of the pressure. Slight variations in the sensitiveness arose from temperature changes.

A 110-volt Nernst glower fed by the current from a 120-volt storage battery was used as source of radiation. The glower was well protected against air currents. The radiation was found to be constant within 1.5 per cent.

Method of Observing.

The following observation series were taken: (1) Reflection from a silvered plane mirror, whose reflecting power was assumed to be unity. (2) Reflection from the water surface. (3) Reflection from the solution.

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[1] Coblentz, loc. cit., Part I.

In some cases a second determination of the energy distribution in the spectrum of the Nernst glower was made. This second determination gave, as a rule, results that agreed within 0–2 per cent. with the former determination.

The main purpose being to detect occurring shifts in the position of the reflection maximum, no attempt was made to measure the absolute value of the reflecting power.

RESULTS.

1. *Salts.*

Several solutions of different salts in water were investigated: $NaCl$, Na_2SO_4, KNO_3, $CuSO_4$, $SrCl_2$ and $CaCl_2$. Among these $NaCl$, Na_2SO_4, KNO_3 and $CuSO_4$ produced no shift in the position of the reflection maximum possible to detect. Fig. 1 shows the reflection curve of a saturated solution of Glauber's salt as compared with the same curve for water. The selective characteristics are somewhat weakened but the position of the reflection maximum remains the same as for the pure solvent.

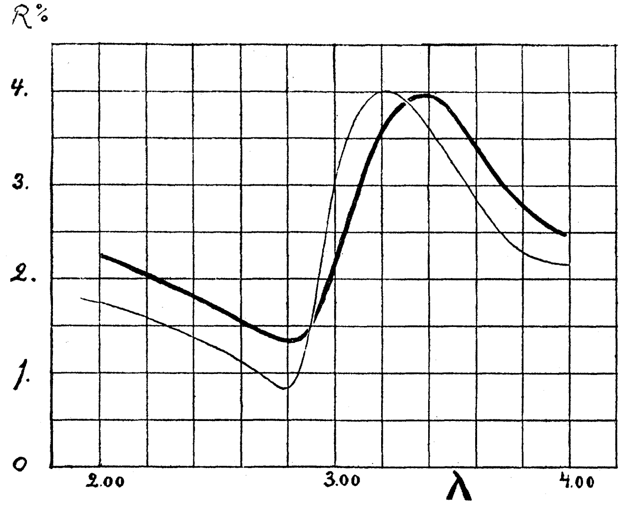

Fig. 1.

Light curve: Reflection from H_2O.

Heavy curve: Reflection from saturated solution of Na_2SO_4.

In the case of the strongly hydrated salts $SrCl_2$ and $CaCl_2$, the conditions are different. As the curves (Fig. 2) show, the selective properties have here been subjected to a considerable shift to the longer wavelengths. As both the maximum and the minimum are shifted by about the same amount, the shift must be a consequence of a real change in the position of the absorption band.

Such a shift evidently corresponds to what is to be expected in the case where a part of the water molecules combine with the dissolved substance to a dissolved hydrate. The hydroxyl-group is now combined with a positive radical of larger atomic weight than before, and analogous with the conditions of sulphates and carbonates, a shift to the longer wave-lengths is to be expected.

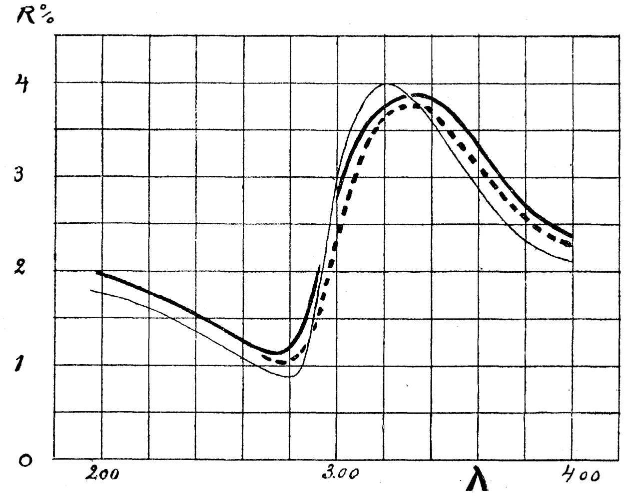

Fig. 2.

Light curve: Reflection from H_2O.
Heavy smooth curve: Reflection from saturated solution of $CaCl_2$.
Heavy dotted curve: Reflection from saturated solution of $SrCl_2$.

2. *Hydrates.*

After this result was obtained, it was found desirable to look for a similar shift in the cases where the dissolved substance is a real hydrate. For, when it has been shown that the same phenomenon occurs when known hydrates are dissolved in the water, the results obtained for the hydrated salts may be said to lead to a certain hypothesis. Consequently NaOH and KOH were investigated.

Figs. 3 and 4 give the results of an examination of concentrated solutions of sodium and potassium hydrate. The selective characteristics are evidently shifted to the longer wave-lengths by a considerable amount. For KOH the maximum occurs at 3.4 μ, for NaOH at 3.35 μ. For water the maximum and the minimum occur at 3.20 and 2.80 μ respectively.

3. $SO_2\begin{matrix}-OH\\-OH\end{matrix}$.

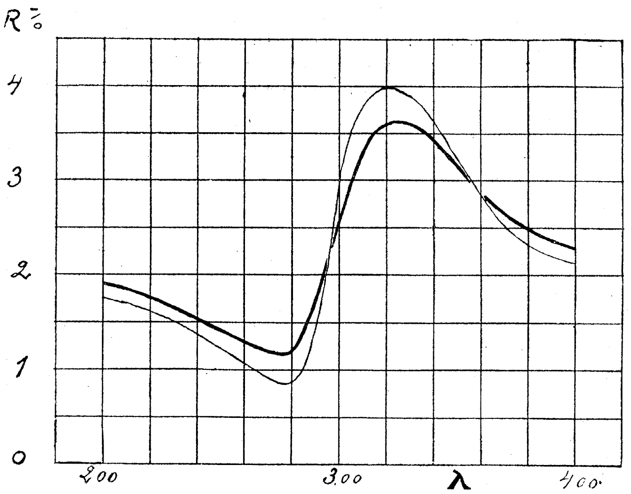

Fig. 3.

Light curve: Reflection from H_2O.
Heavy curve: Reflection from saturated solution of KOH.

Under certain conditions we may also regard sulphuric acid as a hydrate. As will be seen from Fig. 5 some interesting changes in the reflection properties occur when the acid is diluted.

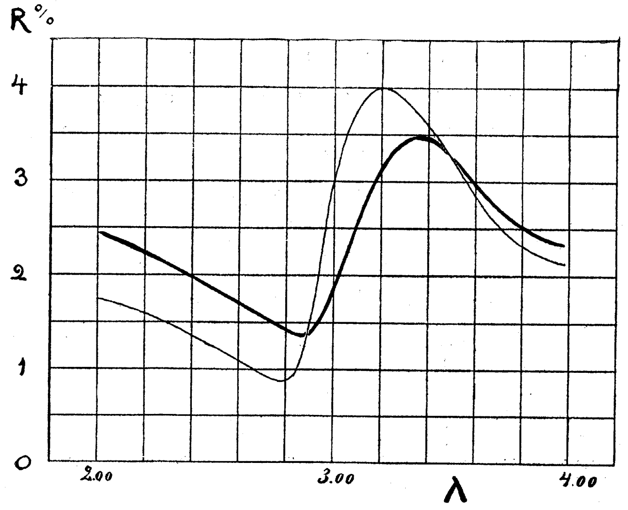

Fig. 4.

Light curve: Reflection from H_2O.
Heavy curve: Reflection from saturated solution of NaOH.

Fig. 5 shows the relation between reflected energy and deviation for various solutions of H_2SO_4 in water.[1] The reflection maximum decreases with an increase in the concentration. At the same time a considerable shift to the longer wave-length is noticed. When a concentration of about 75 per cent. is reached the reflection has a minimum. Between 75 per cent. and 100 per cent. the reflection maximum increases rapidly, showing that the concentrated acid has a marked reflection maximum at 3.55 μ corresponding to a strong absorption band at about 3.20 μ.

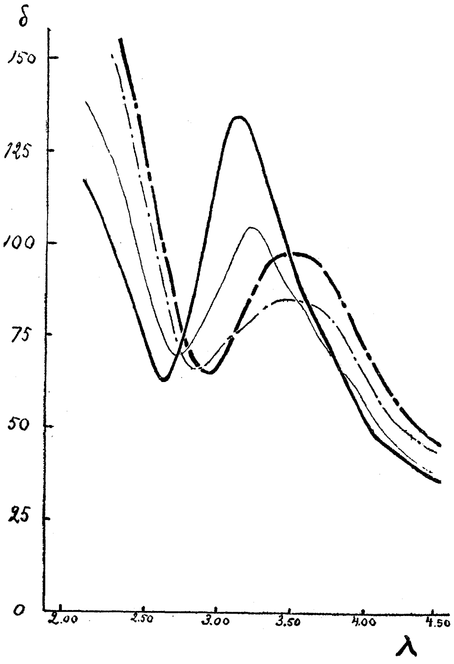

Fig. 5.

Heavy smooth curve: Energy reflected from H_2O.
Light smooth curve: Energy reflected from 32 per cent. $H_2SO_4 + H_2O$.
Light dotted curve: Energy reflected from 75 per cent. $H_2SO_4 + H_2O$.
Heavy dotted curve: Energy reflected from 98 per cent. H_2SO_4.

That sulphuric acid has a strong absorption band at about 3.20 μ, together with the fact that an absorption band at about 3.00 μ is characteristic of all compounds containing the hydroxide groups, seems to indicate that in the *undissociated sulphuric acid molecules* the hydrogen and oxygen are combined in such a way as to have the optical properties

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[1] The form of the curve depends upon the energy distribution in the spectrum of the Nernst lamp.

of the hydroxide group. That the absorption band which in the case of water occurs at 3.0 μ is here somewhat shifted to the longer wave-lengths is only a natural consequence of the greater molecular weight of the acid.

The reflection curves show another interesting feature. It has been shown by Coblentz,[1] that the reflecting power of a compound in solution is practically proportional to the concentration, provided that no changes occur in the part of the molecule in which the mechanism giving rise to the reflection maximum is localized. If no such changes take place in the solution, the reflection power of the solution ought always to lie between the reflecting power of the constituents. From the data obtained from various solutions of sulphuric acid, it is obvious that the reflecting power of a 75 per cent. solution between the wave-lengths 3.2–3.6 μ is considerably less than the reflecting power of the constituents. At 3.28 μ, for instance, the reflecting power is only 85 against 105 for the water and 97 for the concentrated sulphuric acid. This disappearing of the reflection band reminds one strongly of similar conditions found by Pfund[2] for the reflection maxima of sulphuric acid at wave-lengths between 8 and 11 μ.

In our present case, it is interesting to notice this disappearing of the reflection maximum at 3.2 μ in connection with the generally accepted hypothesis that this band is due to the presence of the hydroxide group. In the undissociated H_2SO_4 molecules, the hydrogen and the oxygen are combined in such a way that it seems natural that they should show the optical properties of the hydroxide group. When the acid is dissolved in a dissociating solvent, the molecules are first broken down into $H\ H^{\cdot}SO_4$ ions and finally into $H_2^{\cdot}SO_4$ ions—complete change to the latter taking place at infinite dilution. The connection between the hydrogen and the oxygen forming the hydroxide group is consequently broken through the dissociation of the molecule. The concentration of the OH group—we consider the part furnished by the acid—is not proportional to the concentration of the acid, but decreases more rapidly with increased dilution. Such a dissociation process will evidently account for the observed weakening in the reflection maximum. We must, however, here take into consideration that the conditions probably are complicated through the formation of complexes, the acid molecules combining with the water molecules to dissolve hydrates. In such a process, similar to what we may suspect in the case of $SrCl_2$ and $CaCl_2$, a part of the water used as solvent is probably not present in the solution as water, but enters

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[1] Coblentz, loc. cit., Part IV., p. 106.

[2] Loc. cit.

as a constituting part in a new compound that does not necessarily have the properties of its constituents.

Summary.

It has been shown in this paper:

1. That the selective reflection maximum of water at 3.20 μ is shifted to the longer wave-lengths when the strongly hydrated salts $CaCl_2$ and $SrCl_2$ are dissolved in the water.

2. That no appreciable shift occurs when NaCl, Na_2SO_4, KNO_3 and $CuSO_4$ are dissolved in the water.

3. That the reflection maximum is shifted by a considerable amount toward the longer waves when a real hydrate (NaOH, KOH) is in the solution.

4. That concentrated sulphuric acid shows the reflection maximum characteristic for the OH group.

5. That this maximum tends to vanish when the molecule is broken down through dissociation.

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