

ABSORPTION SPECTRA OF THE SULPHITE AND SULPHATE IONS.

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Received November 12, 1934.

ABSORPTION spectra of molecules formed by tetravalent and hexavalent sulphur have been investigated recently by various authors. The results obtained by them, however, are not completely concordant. Lorenz and Samuel¹ could not confirm certain measurements of Getman² whereas Ley and Arends³ could not find certain bands measured by Lorenz and Samuel and doubted the existence of other ones without new investigations of their own. We have therefore measured and remeasured the absorption spectra of certain sulphur compounds and present the results in this paper.

The experimental technique for liquids and solutions was the same as that normally used in this laboratory and described elsewhere.⁴ In the following diagrams the absorption coefficient K is given depending on wave-length and is defined by the formula $I = I_0 10^{-Kcd}$ in which I_0 and I are the intensity of light before and after the absorption, c and d (in cms.) stand for concentration of the solution and the thickness of the absorbing layer.

We have also measured the absorption curve of certain compounds in the crystalline state. Since we are not interested for the purpose of this paper in the absolute value of the absorption coefficient, which is more easily determined in the solutions of these salts, we adopted an extremely simple method. We covered a quartz plate with micro-crystalline dust of the salt in question and using for the continuous source the H_2 spectrum we took a spectrogram of the salt and on the same plate the spectrum of the source alone. Both spectra were then measured by the recording micro-photometer and the difference of density traced depending on wave-length. Since the layer is not uniform and furthermore direct unabsorbed light reaches the slit of the spectrograph through unavoidable interstices quantitative determination of K is not possible. So long as the layer is kept thin, the

¹ L. Lorenz and R. Samuel, *Zs. Phys. Chem. (B)*, 1931, **14**, 219.

² F. H. Getman, *J. Physic. Chem.*, 1926, **30**, 266. (Here also the older literature. Cf. also J. W. Mellor, *Comprehensive Treatise, etc.*, 1930, **10**, 198 ff.)

³ H. Ley and B. Arends, *Zs. Phys. Chem.*, 1932, **15**, 311.

⁴ R. Samuel, *Zs. Phys.*, 1931, **70**, 43.

maxima come out quite well. If, however, the layer is too thick the curve obtained has to be corrected with respect to the diffuse reflection on the surface and since very little is known about the diffuse reflection in the ultraviolet, and especially very little about the function by which it depends on the wave-length in the case of non-metallic substances, this correction might produce slight errors. The existence, however, of certain regions of selective absorption can be found quite well by this method. Fig. 2 shows such a curve in which the difference of blackness D of the two spectra is traced directly against λ .

The results of both the measurements of solutions (or liquids) and solid crystals are presented in the following curves and tables and we will proceed at once to discuss the results obtained.

Compounds of Tetravalent Sulphur.

The absorption curve of the sulphite ion in Na_2SO_3 , KHSO_3 , etc., is especially interesting since it has a direct bearing on the transition from covalent to electrovalent linkage. In NaHSO_3 Getman found no selective absorption in fresh solutions of a strength of 0.05 and 0.025 mol. Only after some hours there appeared a selective maximum at about 265 $m\mu$ which after some days shifted to 270 $m\mu$. He found further that SO_2 in water possesses a characteristic band just at about 270 $m\mu$ which agrees quite well with the absorption of gaseous sulphur dioxide as measured by Watson and Parker.⁵ Getman believed therefore this band to belong to the SO_2 molecule. Lorenz and Samuel found in fresh solutions of NaHSO_3 of greater strength (1 mol. and 0.1 mol.) a selective absorption band with a main maximum at 255 $m\mu$ and a second subsidiary maximum at 275 $m\mu$. This band, however, does not follow Beer-Lambert's law but the intensity decreases with dilution. The authors ascribe it therefore to the homopolar linkage between hydrogen and oxygen which becomes electrovalent on dilution. On the other hand, they found a sharp selective maximum at 300 $m\mu$ in solutions of Na_2SO_3 at low values of K which therefore belongs to the sulphite ion. This maximum should appear in diluted solutions of the sodium hydro-sulphite in case the equilibrium is shifted towards the electrovalent form. It was, however, not possible to ascertain this point.

We have measured therefore again the absorption curve of KHSO_3 and of K_2SO_3 in solutions and of KHSO_3 and Na_2SO_3 in the crystalline state.

The three curves of KHSO_3 (Fig. 1) are taken with 0.01, 0.1 and 1 mol. solutions respectively. The two latter ones agree with those of Lorenz and

⁵ W. W. Watson and A. E. Parker, *Phys. Rev.*, 1931, **37**, 1484.

Samuel, again the substance is not found to follow Beer-Lambert's law. The

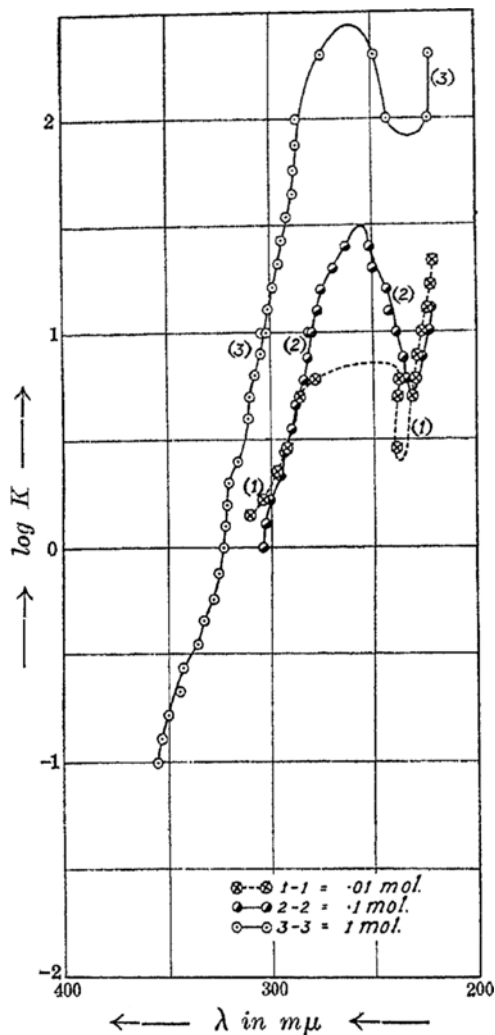


FIG. 1. KHSO_3 in water.

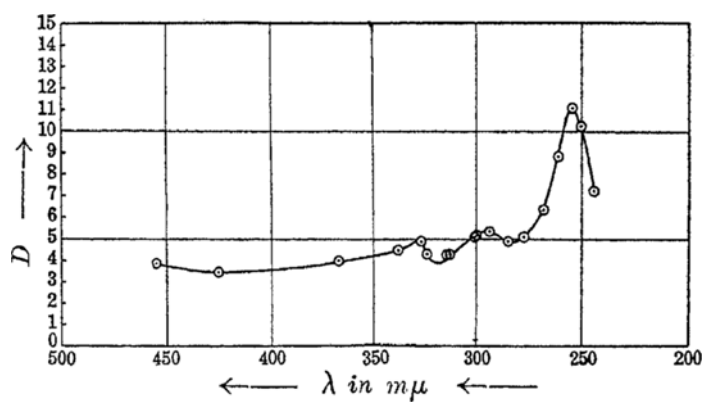


FIG. 2. KHSO_3 .

main maximum lies at about $258 \text{ m}\mu$, the shape of the curve indicates subsidiary maxima at $275 \text{ m}\mu$, $315 \text{ m}\mu$ and $335 \text{ m}\mu$. The first curve, however, taken with the weak solution of 0.01 mol . shows only a broad selective absorption whereas the distinct maximum at $258 \text{ m}\mu$ has disappeared completely. This curve does not show details any longer. Comparing curves 2 and 3, we find some indications of a new very feeble maximum at about $295 \text{ m}\mu$ in curve 2 which is entirely missing in curve 3 and therefore would be clearly brought about in still lower dilutions. Its existence, however, remains doubtful.

The absorption curve of KHSO_3 in the crystalline state (Fig. 2) shows maxima at 327 , 293 and $254 \text{ m}\mu$ of which at least the two latter seem to be doubtless genuine. The last of them is sharp and well defined, but the subsidiary maximum at $275 \text{ m}\mu$ has disappeared. In the crystal of Na_2SO_3 we find maxima at 312 and $257 \text{ m}\mu$, whereas Lorenz and Samuel

found a sharp maximum at 300 and indications of a subsidiary maximum at $245 \text{ m}\mu$ in solution.

Taking all the results together, we obtain Table I. Several authors² have tried to correlate the maximum at $275 \text{ m}\mu$ with the free SO_2 molecule. The change of intensity

on dilution is attributed to a change in equilibrium so that the non-absorbing

TABLE I.

Substance	Authors	Absorption Maxima in $m\mu$	Remarks
NaHSO ₃ diff. solutions.	L. & S.	275 255	
KHSO ₃ sol. 1 mol...	K. & S.	(335)? (315)? 275 258	
KHSO ₃ „ 0.1 „ ..	K. & S.	(295) 275 258	
KHSO ₃ „ 0.01 „ ..	K. & S.	← broad → maxim.	
KHSO ₃ crystal ..	K. & S.	(327)? 293 254	
Na ₂ SO ₃ solution ..	L. & S.	300 (245)	
Na ₂ SO ₃ crystal ..	K. & S.	312 257	

forms H₂SO₃ or HSO₃⁻ with homopolar linkage between O and H prevail more and more and several reactions are suggested to explain this process. It is not quite clear why the equilibrium shall shift just in this direction on dilution. To our mind just the reverse behaviour would have appeared as the more probable one. In any case our results do not seem to agree with this explanation. We have been able to split the maximum in question into two maxima at 275 and 258 $m\mu$ and have found the last one in the crystal itself; thus it certainly does not belong to the SO₂ molecule. If therefore the first maximum would belong to sulphur dioxide and the number of SO₂ molecules would decrease with dilution, this would explain the decrease of the maximum at 275 $m\mu$, but we should expect the maximum at 258 $m\mu$ to increase in the same proportion. This, however, is not the case. On the other hand we know that certain radicals give rise to the same selective absorption in quite different molecules. A well-known example is the carbonyl group and we might mention also the similarity¹ of the curves of $O=S\begin{matrix} \swarrow Cl \\ \searrow Cl \end{matrix}$ and $S=\begin{matrix} \swarrow Cl \\ \searrow Cl \end{matrix}$ in which the maxima, according to the vapour spectrum⁶ of SCl₂, seem to be due to the S-Cl linkage only. Therefore it would not be astonishing at all if molecules like H₂SO₃ or HSO₃⁻ would show bands similar to those of SO₂. From this it is quite clear that the results can best be described in the following way: The first region of absorption of all these substances lies at about 255 $m\mu$. The selective maximum is present in all solutions of different strength of the HSO₃⁻ ion, the SO₃²⁻ ion and in the two respective crystals.

⁶ R. K. Asundi and R. Samuel, *Curr. Sci.*, 1934, 2, 433.

We therefore correlate this maximum with the electrovalent form of these molecules. The second maximum at $275 m\mu$ is present only in solutions containing the HSO_3^- ion. It does not follow Beer-Lambert's law but varies in its K value with dilution, and is missing in the crystal of KHSO_3 and in solution and crystal of Na_2SO_3 . We therefore correlate the maximum at $275 m\mu$ with the undissociated ion HSO_3^- . It exists, as long as this linkage is covalent but disappears gradually the more the electrovalent form prevails and the more the equilibrium favours the existence of the SO_3^{2-} ion. The SO_3^{2-} ion possesses besides this a weaker maximum at about $300 m\mu$ which is missing in strong solution of the HSO_3^- ion.

Compounds of Hexavalent Sulphur.

Whereas solutions containing the sulphate ion do not show any selective absorption down to the limit of transparency of the quartz spectrograph, Lorenz and Samuel found absorption bands in such compounds in which one

TABLE II.

Substance	Authors	Absorption Maxima in $m\mu$	Remarks
Na_2SO_4 solution ..	L. & S.	Nil	
NaHSO_4 solution ..	L. & S.	305 250	
KHSO_4 solution ..	K. & S.	~ 300 (250)	very broad.
KHSO_4 crystal ..	K. & S.	← 330 broad 294 → 262 max.	
NaCH_3SO_4 solution ..	L. & S.	~ 270	very broad.
NaCH_3SO_4 solution ..	K. & S.	~ 270	very broad.
$(\text{CH}_3)_2\text{SO}_4$ substance ..	L. & S.	~ 275	
$(\text{C}_2\text{H}_5)_2\text{SO}_4$ solution (in ether)	K. & S.	270	
$(\text{C}_2\text{H}_5)_2\text{SO}_4$ substance ..	K. & S.	270	
HCISO_3 substance ..	K. & S.	315 270	

or both of the linkages between oxygen and the positive partner might have become covalent, *i.e.*, in sodium bisulphate, sodium methyl sulphate and dimethyl sulphate. These bands appear only at low values of log K, *i.e.*, log K = -1 or less (d in cm.) and Ley and Arends could not find the bands of NaHSO_4 and doubt therefore also the existence of those in the

other substances mentioned above.* We have therefore repeated some of the experiments and added the absorption curves of some other related substances. The maxima obtained in sodium bisulphate in solution are slightly less sharp than those found by Lorenz and Samuel, their positions in the spectrum are, however, not changed (Fig. 3). NaHSO_4 in the crystalline state shows the same maxima, but slightly shifted towards the red. In sodium methyl-sulphate we find a broad region of selective absorption, whose centre of gravity might be at about $270\text{ m}\mu$ (Fig. 4). Diethyl sulphate measured directly in substance, shows a maximum at $270\text{ m}\mu$, in almost perfect agreement with that found earlier in dimethyl sulphate. The position of this maximum remains unchanged in solution of ether; in

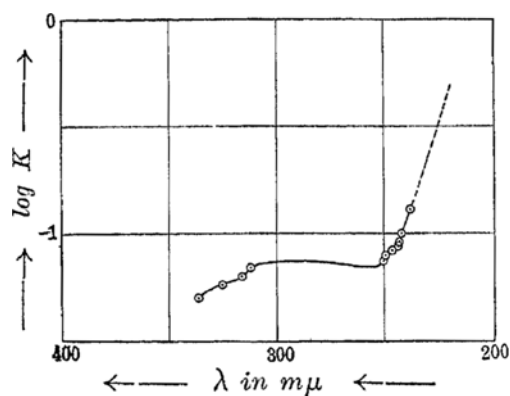


FIG. 3. KHSO_4 in water.

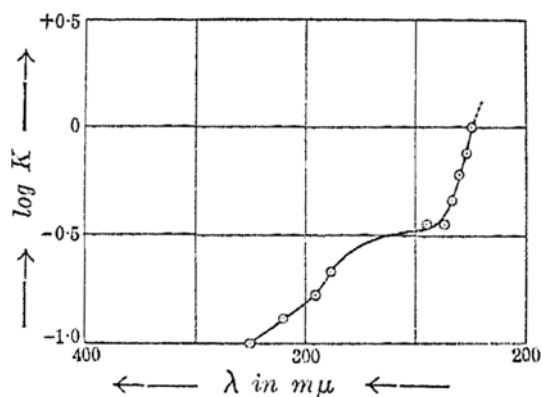


FIG. 4. $\text{Na}\cdot\text{CH}_3\cdot\text{SO}_4$ in water.

alcoholic solutions the maximum splits into two at about 272 and $258\text{ m}\mu$. We attribute this to the hydrolysis produced by a small percentage of water in the alcohol used and mention it, because it seems to be significant that now the bands of $(\text{C}_2\text{H}_5)_2\text{SO}_4$ and that of the RSO_4^- ion exist side by side. In chloro-sulphonic acid† (in substance) in which one of the $-\text{OR}$ groups is replaced by chlorine, whereas one $-\text{OH}$ group remains present, we find a maximum at 315 and again a second one at $270\text{ m}\mu$. The results are summed up in Table II.

To our mind there does not exist any necessity of formulating these substances as genuine complexes in the sense of Werner nor with semi-polar

* They attribute the disagreement to impurities in the substances, used by the earlier authors. This, however, is certainly not the case since the substances used by Lorenz and Samuel were purified specially. Since the results of these authors are confirmed by us under completely changed conditions, we are inclined to attribute the disagreement to the fact, that the continuous H_2 spectrum is better suitable as a source of light.

† The values of log K given in Fig. 6, are arbitrarily chosen.

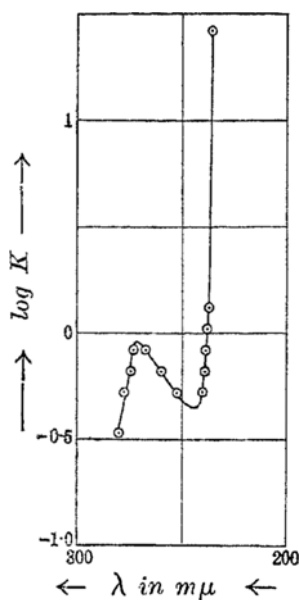


FIG. 5. $(\text{C}_2\text{H}_5)_2\text{SO}_4$
in substance.

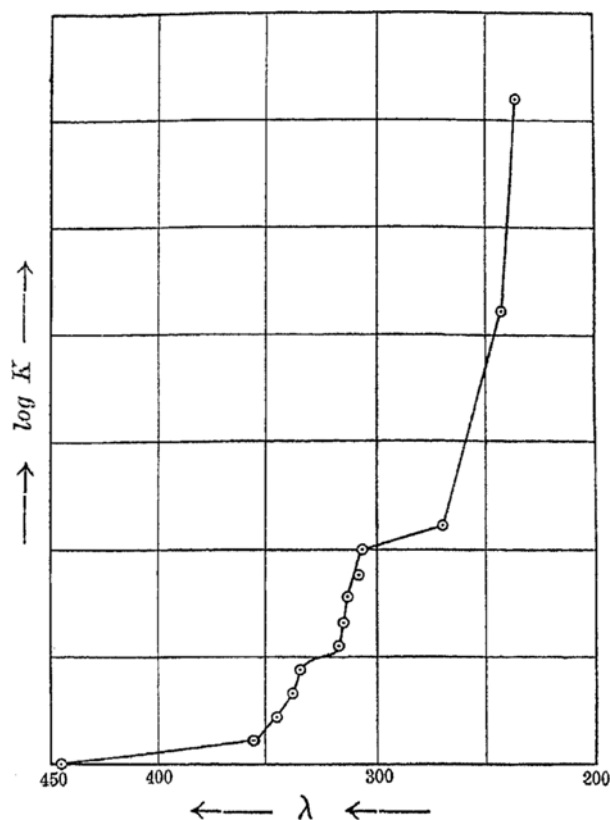
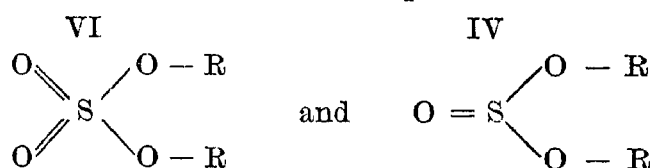


FIG. 6. $\text{H}\cdot\text{Cl}\cdot\text{SO}_3$ in substance.

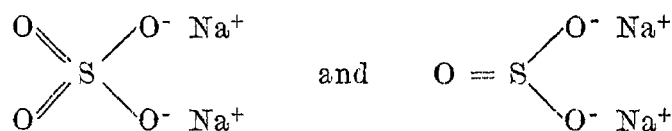
double bonds in the sense of Sidgwick.⁷ Since we do not believe in the existence of different kinds of non-electrostatic linkages (because there does not exist a single experimental proof for this assumption),⁷ we use for the molecules of tetravalent and hexavalent sulphur the old structural formulæ



of chemistry in which each valency represents one electron of either atom in question which have entered the same energetic group of the molecule according to the electron pair bond theory of wave mechanics. In tetravalent sulphur its four outside 3p electrons alone, in hexavalent sulphur all outside electrons including the two 3s electrons are active. Thus the linkage is brought about by the formation of electronic groups in the molecule; this,

⁷ Cf. R. Samuel, Report on "Absorption Spectra and Chemical Linkage," Part IV (*Indian Ac. of Sc.*, in Press). R. F. Hunter and R. Samuel, *J. Chem. Soc.*, 1934, 1180. H. Lessheim, Jul. Meyer and R. Samuel, *Zs. f. Phys.*, 1927, **43**, 199; *Zs. f. Anorg. and Allg. Chem.*, 1927, **165**, 253.

however, does not mean that they revolve in the same "path" as in the older theory. The transition from covalent to electrovalent linkage is therefore described by a second superimposed effect, by the variation so to speak of the topographical position of those two electrons, which form the linkage. If the ionisation potential of the positive partner is small enough and the electronic affinity of the negative partner is big enough, the electron of the first one will still be coupled to that of the second one, but it will be torn off from its own nucleus. To put it in other words: In the Frank-Condon diagram the ionic curve will then form the lowest energy level of the molecule, and this depends to a certain extent on outside forces, molecules may be covalently bound in the vapour state but become electrovalent molecules through additional forces present in the crystal lattice or produced by the dipole moments of the molecules of a solvent. In our case alkali atoms will always be bound electrovalently on account of their low ionisation potential (Na=5.12, K=4.32 volts), hydrogen with an ionisation potential of 13.53 volts will be covalently bound in the isolated molecule but probably electrovalently so in crystals and solutions whereas the transition to electrovalent linkage becomes impossible if an organic radical is the positive partner (mean ionisation potential of tetravalent carbon = 36.2 volts⁸). We shall express the electrovalent form of the compounds by a formula like



indicating that the binding pair is now completely in the field of the negative partner.

We have already mentioned above that this point of view gives us the possibility to describe the results obtained with derivatives of tetravalent sulphur in the most simple manner. Again the absorption spectra of compounds of hexavalent sulphur indicate a similar behaviour. (a) As long as both -O-R linkages are electrovalent no selective absorption exists. (b) If one of the R's is replaced by hydrogen, probably in covalent linkage, there appear two regions of selective absorption, the first at about 300 $m\mu$ and the second at about 250 $m\mu$ in solutions, and 260 $m\mu$ in the crystalline state. (c) If an organic radical replaces one or both alkali atoms in definite covalent linkage, the first region of absorption disappears and the second band shifts slightly towards the red.

⁸ Cf. R. Samuel and L. Lorenz, *Zs. f. Phys.*, 1929, 59, 53.

In compounds of tetravalent and hexavalent sulphur containing the SO_3 and SO_4 group respectively the difference between covalent and electrovalent linkage is distinctly marked in the absorption spectra. Thus the conditions resemble those of nitric acid, its salts and esters, where similar changes are known to take place since a long time. In the case of KHSO_3 (and H_2SO_3 of 2) in which the bands reach such high values of K that observations in solutions of different strength are possible with absorption tubes of reasonable length, the transition from covalent to electrovalent linkage with dilution is directly observed. We consider this as a further example favouring rather the older structural formula of chemistry, interpreted by the electron pair bond theory, in which there is only a difference of degrees but not of quality of the covalent and electrovalent bond in the same molecule under different external conditions.

The figures obtained in both cases are rather similar, irrespective of the presence of SO_3 or SO_4 group. We find the same regions of absorption at about 250, 275 and 300 $m\mu$. This seems to indicate that the $-\text{O}-\text{R}$ linkage is not influenced to any high degree by the conditions in the centre of the molecule.