

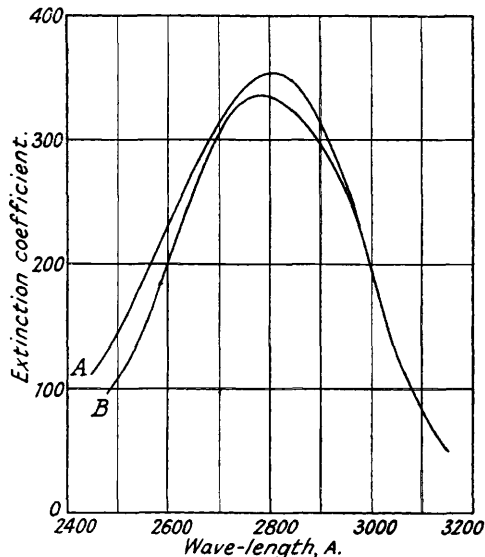
571. *The State of Sulphur Dioxide dissolved in Sulphuric Acid.*

By V. GOLD and F. L. TYE.

The near-ultra-violet absorption spectrum of sulphur dioxide in solution in sulphuric acid (100%) and in oleum (19% free SO_2) has been found to be similar to the spectrum in other solvents and in the gas phase. It is concluded that sulphur dioxide dissolves in sulphuric acid without chemical change.

CONCENTRATED sulphuric acid is a good solvent for a variety of compounds, but only few of these are known to dissolve without accompanying chemical change. In particular, many substances which are not normally considered basic, dissolve in sulphuric acid by virtue of an ability to accept

Ultra-violet absorption of sulphur dioxide in sulphuric acid and oleum.



(A) Sulphuric acid (100%).
(B) Oleum (19% free SO_2).

and dilution of the resulting oleum with more 98% acid. The composition of the 100% acid was checked by its freezing point. The concentration of oleum was determined by volumetric acidimetry. Solutions of sulphur dioxide were prepared by bubbling the dried gas (syphon) through the solvent, followed by dilution of the stock solution as required. Absorption spectra were determined photographically by means of a Hilger medium quartz spectrograph used in conjunction with a Spekker photometer and an iron spark source. Beer's law was tested over the concentration range 0.0005–0.005M. for solutions in sulphuric acid and over the range 0.001–0.005M. for those in oleum (19% of free SO_2), and found to hold within the limits of accuracy of the analyses. The spectra are represented graphically in the figure. Extinction coefficients (ϵ) are defined by the usual relation, $\log_{10} I_0/I = \epsilon cl$ (l = thickness of absorbing layer, in cm.; c = concentration, in moles/litre).

Volumetric Determination of Sulphur Dioxide.—10 ml. of the acid solution were pipetted slowly and with shaking into a stoppered bottle containing water (100 ml.) and a two-fold excess of standard iodine solution. The excess of iodine was titrated against standard sodium thiosulphate solution. Blank titrations were carried out on the "pure" solvent (used in the reference beam of the spectrophotometer) and a correction applied for its content of sulphur dioxide. The method agrees substantially with the procedure used by Miles and Carson (*J.*, 1946, 786).

a proton from the solvent and to pass into solution as the conjugate acid cation (Hammett, *Chem. Reviews*, 1933, 13, 61). Sulphur dioxide is appreciably soluble in sulphuric acid and it was therefore of interest to investigate its molecular state in this system.

A study of this problem by means of ultra-violet absorption measurements was also of practical relevance. It has been found by several workers that certain specimens of sulphuric acid appear opaque to ultra-violet light in the region λ 2800 Å. and are useless as solvents for the measurement of absorption spectra in this region, and that a transparent acid can only be prepared in the absence of reducing impurities. It seems plausible to attribute this opacity to sulphur dioxide, which is known in the gas phase to have a banded absorption region stretching approximately between λ 2400 Å. and λ 3400 Å., with a maximum intensity of absorption near λ 2800 Å. (Watson and Parker, *Physical Rev.*, 1931, 37, 1484), but direct evidence of this point has hitherto been lacking.

EXPERIMENTAL.

The solvent acids were prepared by distillation of sulphur trioxide into AnalaR 98% sulphuric acid

DISCUSSION.

In the Table the extinction coefficients and the wave-lengths of maximum absorption are given for sulphur dioxide in several solvents and for the pure substance in the gaseous and the liquid phase. It is seen that for all solutions the position of the maximum remains virtually unchanged from that for sulphur dioxide gas, and that the value of the extinction coefficient and

State of SO ₂ .	$\lambda_{\max.}$ (A.).	$\epsilon_{\max.}$	Source of data.	State of SO ₂ .	$\lambda_{\max.}$ (A.).	$\epsilon_{\max.}$	Source of data.
Gaseous	2961	402.2 *	Garrett ¹	Solutions :			
"	2840	—	Schaefer ²	In H ₂ O	2750	440 †	Ley and König ³
Liquid	2850	~800	Garrett ¹	"	2760	—	Schaefer ²
Solutions :				" aq. H ₂ SO ₄ (0—10N.) ...	2760	—	Schaefer ²
In hexane	2900	250	Ley and König ³	" H ₂ SO ₄ (100%)	2800	360	This work
" pentane	2900	—	Schaefer ²	" oleum (19% free SO ₃) ...	2780	340	This work
" chloroform ...	2900	—	Schaefer ²				
" EtOH and MeOH	2760	—	Schaefer ²				

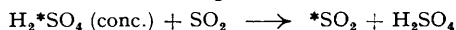
* Results for low resolution, pressure ~500 mm.

† An allowance has been made for equilibrium of reaction between solvent and solute.

¹ *J.*, 1915, **107**, 1324. ² *Z. anorg. Chem.*, 1918, **104**, 212. ³ *Z. physikal. Chem.*, 1938, **B**, **41**, 365

the shape of the absorption curve are changed only by a small amount, in spite of the drastic change of conditions. On the basis of his comparison of the absorption spectra of aqueous solutions of sulphur dioxide and of the gas, Wright (*J.*, 1914, **105**, 2907) had already concluded that sulphur dioxide in water must be largely present in the form of SO₂ molecules, and this opinion was endorsed by later workers. It now seems fairly certain that the same conclusion may be drawn for the solutions in sulphuric acid and dilute oleum, and that the solubility of sulphur dioxide is not due—at least not to any large extent—to specific chemical interaction with the solvent and provides no evidence for the existence of the conjugate acid species HSO₂⁺. If it should be objected that such interaction is extremely unlikely on general intuitive grounds and need not be seriously considered, we would refer to the analogous weak basicity which has recently been postulated for the molecule SO₃, a species which, by a similar criterion, could normally be regarded as even less likely to function as a base (HSO₃⁺ as active species in sulphonation : Stubbs, Williams, and Hinshelwood, *J.*, 1948, 1065; Brand, *J.*, 1950, 1004). Our failure to detect any large conversion of SO₂ into HSO₂⁺ cannot, however, be used as evidence against a minute concentration of the active species HSO₃⁺ in sulphonating media.

Lewis and Bigeleisen (*J. Amer. Chem. Soc.*, 1943, **65**, 1144) have attributed the high acidity of oleum to the ability of the sulphur to transfer sulphur trioxide (an "acid" in the sense of the word used by G. N. Lewis). However, the experiments with solutions in oleum suggest that no definite compound SO₂SO₃—which could be regarded as the anhydride of dithionic acid—is formed under these conditions. This is significant because Miles and Carson (*loc. cit.*) have reported a great increase in solubility as the sulphur trioxide content of oleum increases. The interaction which is responsible for this effect is clearly not one which is profound enough to disturb the optical electrons of sulphur dioxide. We also conclude that the possible reaction SO₂ + H₂SO₄ → H₂S₂O₆ to form dithionic acid (analogous to the formation of disulphuric acid, H₂S₂O₇, from sulphur trioxide) does not proceed readily under our conditions, although it is conceivable that the slow radioactive exchange reaction



(Norris, *J. Amer. Chem. Soc.*, 1950, **72**, 1220) may involve this reaction as an intermediate step.

The increase in solubility observed by Miles and Carson must be due to molecular interaction of some kind which comes into play at the highest acidities. If we wish, we may describe the sulphur dioxide as "solvated" to a different extent in the various media, as long as we do not understand by this term any interaction to produce a molecular species in which the solvating molecules exert a significant effect on the electronic structure of the solute. We may perhaps link the case of sulphur dioxide with the organic oxygen compounds whose solubilities in aqueous sulphuric acid were investigated by Hammett and Chapman (*J. Amer. Chem. Soc.*, 1934, **56**, 1282). These workers found an enormous increase in solubility with increasing acidity of the medium, but in a region of solvent composition where other methods have shown that the solute is not present in solution in the form of the conjugate acid. However, all the compounds for which this increase of solubility with acidity of the medium has been observed in the past are of a potentially basic character, *i.e.*, by increasing the acidity of the solvent even further, conversion into the conjugate acid could eventually be achieved (and it may be that the same would apply

to sulphur dioxide). This suggests that solution is accompanied by a chemical process which is a precursor to proton transfer and therefore only occurs with basic species. Similar considerations concerning the state of solutes in sulphuric acid have recently been advanced by Gillespie and Millen (*Quart. Reviews*, 1948, **2**, 290), who regard this incipient manifestation of basic behaviour which accompanies solution as the formation of a 1 : 1 complex between the solute and sulphuric acid by hydrogen bonding.

In conclusion, it is suggested that the measurement of light absorption in the near ultra-violet could be developed into a more convenient and precise method for the determination of sulphur dioxide in sulphuric acid than the iodimetric procedures usually followed.

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