

Table 2

T_{tr}/T_m	CF_2	CCl_2	(CF_2)
Δ_{Straza}	0.852	0.901	0.881
$\Delta_{Stusion}$	4.64	4.86	4.98
	1.87	2.40	2.60

Finally, we may add that we have also measured the coefficient of expansion and compressibility of ammonium chloride above and below the λ -point (-30.5°). Our results lead to values of c_v of 18.5 cal./mole at -44.55° , and 18.7 cal./mole at -19.31° and 0° . These figures fit in very well with those reported by Lawson¹, and confirm the conclusion he reached about the nature of the transition in this substance.

A full account of this work will be published elsewhere.

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Solid Phase Determinations in the System Aluminium Sulphate/Sulphuric Acid/ Water using Tracer Technique

IN the system aluminium sulphate/sulphuric acid/water, the solid phase in the range 50–60 per cent sulphuric acid has been reported to be either $Al_2(SO_4)_3 \cdot 9H_2O$ ^{1,2} or $Al_2(SO_4)_3 \cdot 10H_2O$ ³ at temperatures between 20° and 60° , the composition of this solid being deduced by the Schreinemakers⁴ method of tie-line convergence. However, in view of (a) the high molecular weight of aluminium sulphate compared with sulphuric acid and water, (b) the relative position in the equilateral triangle of the solubility curve, (c) inaccuracy in the position of the solution and moist solid points owing to the well-known difficulty of determining sulphuric acid in presence of aluminium sulphate, the published tie-lines show equally good convergence at points representing the 8, 9 or 10 hydrates or the 1:1 acid sulphate with eleven to thirteen molecules of water of crystallization.

This and similar cases⁵ of ambiguity may be resolved by adding to the solubility mixture a suitable indicator substance which remains throughout in the liquid phase. Provided this indicator does not significantly alter the phase equilibrium and can be determined accurately in trace quantities, then the composition of the moist solid phase can be corrected for the contaminating liquid phase. Radioactive caesium sulphate has been found to fulfil these severe conditions very well: only 0.05 c.c. of 0.045 per cent aqueous solution of approximately 15 μ C. activity was required in a 50-gm. solubility mixture. This was not added until after the ternary mixture had been brought to equilibrium at 30° to avoid any co-precipitation of the tracer with the solid phase. The saturated solution and moist solid phase after convenient dilution were analysed for aluminium by precipitation with 8-hydroxyquinoline, for sulphuric acid by an accurate titration procedure, while counts were carried out in Type M6 Geiger-Müller liquid counters. Self-absorption errors were negligible because the counted solutions, after dilution with an

equal volume of water, gave exactly half the original count. The solid phase was shown in this way to have the composition 51.4 per cent $Al_2(SO_4)_3$, 15.9 per cent H_2SO_4 , 32.7 per cent H_2O , and must therefore be $Al_2(SO_4)_3 \cdot H_2SO_4 \cdot 12H_2O$. This composition has been confirmed by using trace quantities of manganous sulphate as indicator, the manganese being determined colorimetrically as permanganate. The composition in this case was 51.5/15.1/33.4. It is surprising that this acid sulphate can be isolated in the pure state by simple filtration and thorough washing with 'Analar' acetone under anhydrous conditions, the composition of the dry 50° product being 51.4/15.1/33.5.

Other acid sulphates of composition 1/1/8 (two forms) and 1/1/2 have been encountered in this system, and full details will be published shortly elsewhere in collaboration with Prof. H. Bassett.

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Electrical Conductivity and Magnetic Susceptibility of Ovalene

OVALENE ($C_{32}H_{14}$) has the most compact configuration of rings among the condensed aromatic compounds which have so far been obtained. From this point of view, it is of interest to know the electrical and magnetic properties to be attributed to the π -electrons of this molecule.

Ovalene was synthesized by the method of Clar¹ with modifications, and purified by repeated sublimation *in vacuo*. The measurement of the electrical conductivity as well as the magnetic susceptibility was carried out with a powder specimen. The electrical conductivity σ can be expressed as $\sigma = \sigma_0 \exp(-\Delta\varepsilon/2kT)$, in the same manner as for the other condensed aromatic compounds². The values of σ at 15° C. and $\Delta\varepsilon$ were found to be 4.4×10^{-16} ohm⁻¹.cm⁻¹ and 1.13 eV. respectively. The electrical conductivity of ovalene is less than that of violanthrone or isoviolanthrone which were reported in the previous paper. In a series of measurements on a number of the condensed aromatic compounds, we have found that the electrical conductivity depends mainly on the number of π -electrons alone, and not on the configuration of the rings. On the other hand, the magnetic susceptibility is largely influenced by the shape of the molecule.

Molecular susceptibility was found to be $\chi_M = -(353.8 \pm 2.8) \times 10^{-6}$, by Gouy's method. $\chi_M = \frac{1}{3}(K_1 + K_2 + K_3)$ can be assumed, where K_1 and K_2 are the molecular susceptibilities along two directions in the plane of the rings and K_3 is that perpendicular to the plane. It can also be assumed that $K_1 = K_2 = \Sigma\chi(C=) + \Sigma\chi(H)$, and calculated from Pascal's constants on the basis of spherical symmetry. H. Shiba and G. Hazato³ have shown that it is a good approximation to put $\chi(C=) = \chi(C) + \frac{1}{2}\chi(\text{diethylene})$