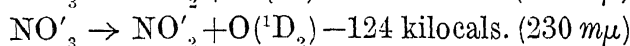
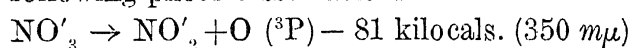


## Letters to the Editor.

The Photo-dissociation of Single Crystals of Potassium and Sodium Nitrates under Polarised Light.

In a previous communication<sup>1</sup> by Mr. Guha and one of us it was suggested that the well-known absorption bands of inorganic nitrates in the ultra-violet, having their long wave-length limits at about 350  $m\mu$  and 230  $m\mu$  respectively, may be attributed to the following photo-dissociations:—



The observation with single crystals of  $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$ , etc., in which the  $\text{NO}'_3$  ions are all oriented parallel to one another, that both the absorption bands are strongly polarised, the ordinary rays being absorbed much more strongly than the extraordinary rays, was interpreted as indicating a corresponding difference between the photo-dissociative activities of the two rays.

We have recently made some experiments on the photo-dissociation of solid inorganic nitrates, particularly with a view to testing the above conclusions. The following are the main results obtained:—

(1) All the nitrates studied, namely those of K, Na,  $\text{NH}_4$ , Sr, Ba, Al, Cd and Pb, showed definite dissociation under the action of light (from a quartz mercury lamp) of wave-lengths shorter than about 250  $m\mu$  (region of the stronger absorption band), as tested by the formation of nitrite. The

<sup>1</sup> *Curr. Sci.*, 1943, 2, 476; *Proc. Ind. Acad. Sc.*, 1934, 1, 242.

actual long wave-length limit of the photo-active region of the spectrum was not determined.

(2) The dissociation appears to be confined to a thin surface layer of the crystal, about 20 $\mu$  thick. The absence of permanent dissociation in the interior is attributable to the recombination of the products of dissociation.

(3) Experimenting under linearly polarised light (obtained by passing the light from the arc through a quartz double-image prism), with single crystals of  $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{NaNO}_3$ , it was found that the dissociation is much greater when the electric vector of the exciting light is in the plane of the  $\text{NO}'_3$  ions (ordinary ray) than when it is along the normal to their planes.

(4)  $\text{KClO}_3$  crystals also show a similar anisotropic photo-dissociation.

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Absorption Spectra of Sulphur-Chlorides and -Oxychlorides in the Vapour State.

IN continuation of previous work already reported,<sup>1</sup> it was found necessary to study the absorption spectra of the series of compounds— $\text{SCl}_2$ ,  $\text{S}_2\text{Cl}_2$ ,  $\text{SOCl}_2$  and  $\text{SO}_2\text{Cl}_2$ . This work is now complete and we present a summary of the results obtained.

<sup>1</sup> *Curr. Sci.*, 1934, 2, 433.

Substance	A		B			C			D		
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
$\text{SCl}_2$	5825	5165 ?	4550	3860	3700	2770	2610	2450	2350	2280	2260
$\text{S}_2\text{Cl}_2$						2770	2580	2390			
$\text{SOCl}_2$						2900	2450	2400			
$\text{SO}_2\text{Cl}_2$									2600—continuous		

*a* gives the beginning, *b*, the maximum and *c*, the end of absorption in wavelengths (A. U. in air).

The data for the last three substances are in reasonable agreement with those obtained in their liquid states.<sup>2</sup> It is seen that all the first three compounds show an absorption band in region C. In every case the band is very strong. The maximum of the band is not constant but shows definite shift from compound to compound. These and other considerations rule out the apparent possibility of the band being due to a common impurity. On the other hand they indicate that this absorption is to be connected with the common link, *viz.*, the *p-p* linkage between S and Cl, which all these molecules possess. The absorption spectrum of  $\text{SCl}_2$  is analogous to that of  $\text{OCl}_2$ .<sup>3</sup> The slight maximum in the region A at 5165 is doubtful and may after all be fortuitous, due to reflection losses in the intensity of the continuous beam. If this is so, region A is just a continuation of the absorption in region B brought about by increase in pressure.

Very often absorption bands due to  $\text{SO}_2$  present themselves in the spectra of all of these molecules but they can be avoided with due precautions. The general appearance of these bands on the plates is not always the same and varies with different pressures of the vapours of the accompanying molecules. Actual measurement, however, proves that these bands are due to  $\text{SO}_2$ . In particular the band system referred to in our previous communication is now definitely traced by us to  $\text{SO}_2$ . Details will be published shortly.

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#### On the Ratio of the Temperature Coefficients of Surface Tension and Density.

"MEASUREMENTS have shown that . . . there is marked parallelism between the temperature coefficient of surface tension . . . and the coefficient of expansion. The greater the latter, the greater also is the decrease in surface tension per degree, and the ratio

$$\frac{\text{temperature coefficient (of surface tension)}}{\text{coefficient of expansion}}$$

is approximately the same—between 2 and 3

<sup>2</sup> *Zeit für Physikalische Chemie* (B), 1931, 14, 219.

<sup>3</sup> *Ibid.*, 1931, 15, 127.

—for a very large number of liquids."<sup>1</sup> No formal proof of this observation appears to have been put forward so far. A simple proof based on Laplace's theory of Capillarity is therefore given below.

Laplace assumes that the range of molecular forces is the same for all bodies and that at equal distances the force is proportional to the density of the substance, thus implying that the function  $\psi(z)$  is the same for all bodies.<sup>2</sup> This hypothesis, though leading to results incompatible with experiments on interfacial tension, can however be assumed to hold for the same liquid at different temperatures. From Laplace's theory we obtain for the surface tension,  $T$ , of a liquid that

$$T = \frac{1}{2} \sigma^2 \int_0^{\infty} z\psi(z) dz \quad \dots \quad (a)$$

where  $\sigma$  is the density of the liquid. Assuming, by our hypothesis, that  $\int_0^{\infty} z\psi(z) dz$  does not vary with temperature,  $\theta$ , we get

$$\frac{dT}{d\theta} = \sigma \frac{d\sigma}{d\theta} \int_0^{\infty} z\psi(z) dz \quad \dots \quad (b)$$

Dividing (b) by (a),

$$\frac{1}{T} \frac{dT}{d\theta} = 2 \frac{1}{\sigma} \frac{d\sigma}{d\theta}$$

which proves that the required ratio is equal to 2, because  $\frac{1}{\sigma} \frac{d\sigma}{d\theta} = -\frac{1}{v} \frac{dv}{d\theta}$ , where  $v$  is the volume of the liquid. This ratio obtained by Laplace's theory is in close agreement with the experimental observation that it lies between 2 and 3.

The fact that the observed value is always greater than 2 is significant and can be accounted for by assuming that,  $\psi(z)$  remaining the same, the range of molecular attraction,  $c$ , varies with temperature. It follows that

$$\frac{dT}{d\theta} = \sigma \frac{d\sigma}{d\theta} \int_0^c z\psi(z) dz + \frac{1}{2} \sigma^2 \int_c^{c+\frac{dc}{d\theta} d\theta} z\psi(z) dz$$

<sup>1</sup> *Surface Tension and Surface Energy* by R. S. Willows and E. Hatschek, 1915, p. 7.

<sup>2</sup> *Vide Properties of Matter* by J. H. Poynting and J. J. Thomson, 1922, p. 179.