

Experiments are in progress to examine further the quenching action of van der Waals forces.

S. SAMBURSKY.  
G. WOLFSOHN.

Department of Physics,  
Hebrew University,  
Jerusalem.  
Sept. 16.

- <sup>1</sup> Weiss, J., *Nature*, **152**, 176 (1943).
- <sup>2</sup> Bowen, E. J., and Williams, A. H., *Trans. Farad. Soc.*, **35**, 765 (1939).
- <sup>3</sup> Franck, J., and Livingston, R., *J. Chem. Phys.*, **9**, 184 (1941).
- <sup>4</sup> Bowen, E. J., and Norton, A., *Trans. Farad. Soc.*, **35**, 44 (1939).
- <sup>5</sup> Sambursky, S., and Wolfsohn, G., *Phys. Rev.*, **62**, 357 (1942).
- <sup>6</sup> Rollefson, G. K., and Dodgen, H. W., *J. Chem. Phys.*, **12**, 107 (1944).
- <sup>7</sup> Sambursky, S., and Wolfsohn, G., *Trans. Farad. Soc.*, **36**, 427 (1940).
- <sup>8</sup> Weil-Malherbe, H., and Weiss, J., *Nature*, **149**, 471 (1942).

### Methyl Iodide Flame Bands

In 1937, Vaidya<sup>1</sup> reported that he had observed in the spectrum of the flame of methyl iodide burning in oxygen, two systems of bands which he described as being degraded to the red, and without any visible fine structure. Thirty-five bands were observed between 4265 Å. and 5720 Å.

In an endeavour to find out if I-O or C-I were the emitter of these bands<sup>2</sup>, we photographed the spectra of electrodeless and normal discharges through the vapours of various organic iodine compounds, and also through mixtures of iodine in oxygen. No new bands were observed. We then repeated Vaidya's experiments on the flame spectra of methyl iodide, under nearly the same conditions as his.

Twenty bands, degraded to the red and having a rotational fine structure, were observed in the wave-length range of Vaidya's bands. There was no marked difference at any point in the rotational structure of these bands, and vibrational analysis showed that they all belonged to the one system, the frequencies (cm.<sup>-1</sup>) of the band heads being given very well by the equation:

$$\bar{\nu} = 21548.5 + [541.8(v' + \frac{1}{2}) - 16(v' + \frac{1}{2})^2] - [686(v'' + \frac{1}{2}) - 6.5(v'' + \frac{1}{2})^2].$$

Allowing for the fact that Vaidya's ground-state frequencies are two units (cm.<sup>-1</sup>) less than ours, this equation is practically the same as his for his "B system". In fact it predicts some of Vaidya's bands which we did not observe; for example, Vaidya gives a band head at 5339.7 Å., our equation predicts one (1-5 band) at 5334 Å. Our values for the wave-lengths of the band heads do not agree very well with Vaidya's; they are in some cases 5 Å. different. Our values are the means of six separate estimations, the order of accuracy being ± 0.2 Å.

Three estimations were made direct from the plate using a comparator (5.76 Å./mm.), and three from microphotometer tracings (0.81 Å./mm.). The instrument used for photographing the bands was a Hilger E 185 concave grating spectrograph.

R. C. BLAKE.  
T. IREDALE.

Physico-chemical Laboratories,  
University of Sydney.  
Sept. 24.

- <sup>1</sup> Vaidya, *Proc. Ind. Acad. Sci.*, A, **6**, 122 (1937).
- <sup>2</sup> Gaydon, "Spectroscopy and Combustion Theory", 162 (1942).

### Entropy and Elasticity in Keratin and Myosin

A GOOD deal of attention has been directed lately<sup>1</sup> to the question of rubber-like elasticity in high polymers, and experiments based on thermodynamic arguments have emphasized, in the case of rubber itself, the importance of the contribution of decreasing entropy to the load at high extensions. That high elasticity is not always due to entropy is, however, shown by my results for keratin (Cotswold wool), which confirm what on other grounds has always appeared certain, that the normal elastic mechanism in keratin involves chiefly the internal energy: extensions up to some 20 per cent are accompanied by an increase in entropy; and although at higher extensions the entropy decreases, it is only at a rate which contributes relatively little to the load. Similar results have been reported by Bull<sup>2</sup> for human hair.

The part played by entropy changes in the elastic behaviour of 'generalized' wool<sup>3</sup> (fibres relaxed at high extensions in dilute caustic soda solution and allowed to revert to their initial lengths before washing) is perhaps of greater interest, for such fibres can be made to contract ('supercontract') by treatment with hot water or steam, a phenomenon recalling the thermal contraction shown by many high polymers. I find that when generalized wool fibres which have not been allowed to supercontract are stretched in cold water, the entropy decreases and thus makes a positive contribution to the load. As the extension increases beyond 1 per cent, however, the internal energy contribution rises rapidly, and so far outstrips the entropy effect that the latter is already only some 10 per cent of the total load at 15 per cent extension. Somewhat similar behaviour is shown by fibres supercontracted by amounts up to 20 per cent of the initial length by treatment with warm water. Results for one fibre are shown in Fig. 1; it was stretched in water to the initial length from a length 15 per cent less, and then released. In the complete cycle of extension and contraction there is little or no hysteresis in the entropy effect, and (except perhaps at the very lowest extensions) the total load is greater than the entropy contribution both for stretching and recovery. It is thus unnecessary to invoke the entropy in order to explain the reversible elasticity over this range.

When larger supercontractions have been induced by the action of steam, the entropy effect becomes of greater importance. In Fig. 2

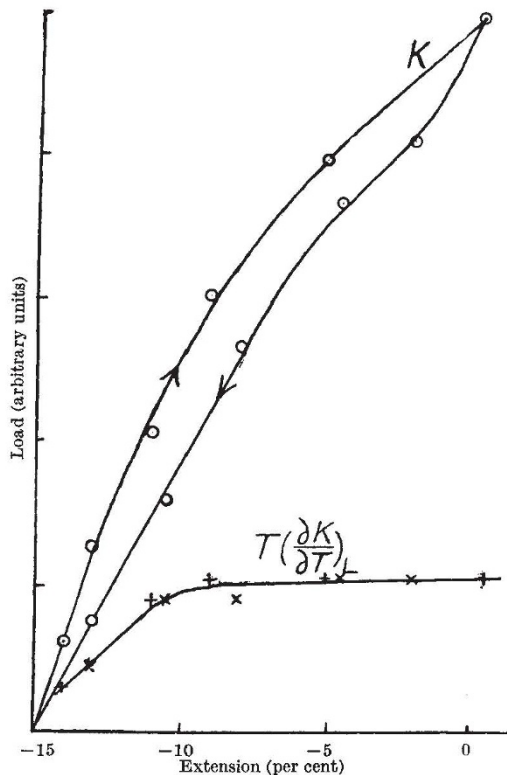


Fig. 1.

are shown the results for a fibre supercontracted by nearly 40 per cent which was taken through a cycle of extension and contraction in water. It will be seen that during the initial stages of the extension the entire load may be attributed to decreasing entropy; and that during the contraction the internal energy may be regarded as responsible down to about 20 per cent below the initial length, beyond which stage the contraction must be entirely due to the entropy.

This sort of behaviour is not unexpected in the light of our knowledge of the molecular changes accompanying high supercontractions, for X-ray photographs of fibres treated similarly to the one considered here show the presence of a considerable amount of partially disoriented β-keratin. For the fibre of Fig. 1, on the contrary, the X-ray

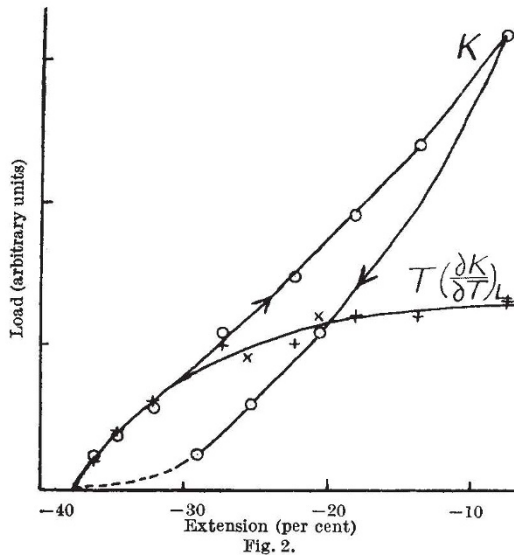


Fig. 2.

FIGS. 1 AND 2. SHOWING THE TOTAL LOAD (K) AND THE ENTROPY CONTRIBUTION (T(∂K/∂T)<sub>L</sub>) FOR SUPERCONTRACTED WOOL FIBRES IN WATER. THE INTERNAL ENERGY LOAD IS THE DIFFERENCE OF THESE, (∂U/∂L)<sub>T</sub> = K - T(∂K/∂T)<sub>L</sub>. THE TEMPERATURE RANGE FOR WHICH (∂K/∂T)<sub>L</sub> WAS OBSERVED WAS 20°-40° C.