Fluorescence Lines in the Spectrum of Light Scattered by Calcite

USING several clear specimens of calcite, the scattered spectrum has been photographed in each case under specially favourable conditions of illumination with a Littrow quartz spectrograph and a cooled mercury arc. Besides the Raman frequencies that may be attributed to one or other of the usual exciting radiations, three new lines at 2838 A., 2883 A. and 2905 A. have been recorded in nearly all the specimens, though there appear to be slight variations in intensity from specimen to specimen. All our attempts to detect these radiations in the source itself have been unsuccessful and they cannot be interpreted as Raman shifts. The first of these is strong and the other two are relatively weak. It is not possible to attribute them to any specific element; but it seems fairly clear that they are to be regarded as a sharp-line fluorescence spectrum, occasionally met with in crystals. As a check on their being attributable to calcite, the scattered spectrum of a large clear specimen of barytes was photographed under similar conditions; but the lines in question were not found.

Similar lines were found by Rasetti¹ in calcite and in fluorite but at about 3100 A. They were attributed to gadolinium by Tomaschek². We have looked for these also, but in the spectrograms obtained by us, this region, which is in the neighbourhood of the pair of strong mercury lines at 3126 A. and 3132 A., contains a number of Raman lines arising therefrom. The conditions of our experiment are therefore not favourable for recording the fluorescence lines already reported by Rasetti.

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^a Nature, 128, 495 (1931).

Melting Point of Adsorbed Liquids

Batchelor and Foster¹ found, by examination of the vapour pressure – temperature curves, that dioxan adsorbed on a ferric oxide gel of pore radius ~ 100 Å. melts sharply about 6° C. below the normal melting point of the bulk liquid. During a recent investigation of the sorption of amines by silica gel, a similar effect has been observed with ethylenediamine.

A sample of silica gel was saturated with excess of ethylenediamine and the vapour pressure measured over a range of temperature just above and below the normal melting point. These pressures were identical with those determined on pure ethylenediamine in the absence of gel, and the plot of log pagainst 1/T (curve a) shows a sharp break at 10° C. The values quoted in the literature for the melting point lie between 8° and 11° C. The amine was then pumped off until the desorption equilibrium pressure fell to 5.41 mm. at 25° C. This represents a relative pressure of 0.403 and corresponds to a pore radius of 25 A. as calculated by application of the Kelvin equation. The equilibrium pressure was then measured over a range of temperature, giving the results shown in curve b. There is again an abrupt change of slope at the melting point, but for the liquid



(a) Pure ethylenediamine (top and right-hand scales).
(b) Ethylenediamine adsorbed on silica gel (bottom and left-hand scales)

held by capillary condensation this discontinuity occurs at $3 \cdot 2^{\circ}$ C. and indicates a lowering of melting point of $6 \cdot 8^{\circ}$ C.

Unfortunately, the physical constants and adsorption data necessary to enable the theoretical lowering to be calculated by the method of Batchelor and Foster are not at present available; but this result confirms their original observation of the existence of a sharp melting point below the normal value for an adsorbed liquid held by capillary condensation.

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¹ Trans. Farad. Soc., 40, 301 (1944).

Correlation between Initial Young's Modulus and Differential Heat of Sorption at Zero Regain for Cellulosic Fibres

DERIVATIONS of the differential heat of sorption of dry textile fibres (ΔH_0) from measurements of heat of wetting have yielded values which are approximately equal for the cellulosic fibres (c. 250-300 cal./gm.). This has been taken to imply that the *type* of reaction, that is, hydroxyl bonding with water, is similar for all cellulosic fibres, and that varying hygroscopicity is dependent on the relative amount of material within the fibre which is available for moisture sorption¹⁻⁴.

A statistical analysis has been carried out on the comprehensive measurements of Rees³ and Guthrie⁴, utilizing an empirical relationship of linearity between the logarithm of heat of wetting and the moisture regain (that is, moisture expressed as a percentage of the dry weight). This analysis has shown that the differential heats of sorption of the various dry