

Both vibration and dissociation rates are sensitive to the presence of impurities. Addition of 2 per cent water vapour reduced the dissociation time to 100 μ sec. for a shock with equilibrium temperature 2,445°K. The vibrational relaxation time was measured as only 23 μ sec. at 2,270°, and was too short to record at the higher temperatures for which results were obtained for pure carbon dioxide.

Carbon dioxide possesses three vibrational modes; the symmetrical mode ν_1 has a frequency of 1,388 cm^{-1} , the transverse mode ν_2 one of 667 cm^{-1} and the asymmetric mode ν_3 one of 2,349 cm^{-1} . Ultra-sonic dispersion is dominated by relaxation of the lowest frequency mode ν_2 and shows a relaxation time which at high temperature would be much too short to observe under our conditions. ν_1 makes a smaller contribution to the specific heat at low temperature and does not show a well-defined dispersion frequency; it is usually assumed that inter-conversion of energy from one mode to another on collision would lead to the two frequencies having the same relaxation time, although there is at least one report⁴ of a shelf on the sound dispersion curve which might be identified with separate relaxation of ν_1 . The asymmetric mode ν_3 has too high a frequency to make an appreciable contribution to the specific heat in the temperature range of ultra-sonic studies. It has seemed uncertain whether a separate relaxation time should exist for this high-frequency mode or whether inter-conversion of energy between the three vibrational forms should lead to a single relaxation time. For sulphur dioxide, there is evidence for two separate relaxation times⁵. The present results appear to indicate that carbon dioxide has a separate relaxation time for the asymmetric mode which is of the same order as the vibrational relaxation times of nitrogen and carbon monoxide, which have comparable vibrational frequencies (2,360 cm^{-1} and 2,170 cm^{-1} respectively). This separate relaxation of ν_3 seems reasonable, since it is difficult to visualize an efficient process of transfer of vibrational energy between the asymmetric and valence modes.

The relatively long time for the dissociation of carbon dioxide and the influence of water on this is of interest for the time to attain equilibrium following combustion. There is much evidence for delayed burning of carbon monoxide and for the action of water vapour as catalyst.

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Phase Transitions in Interlamellar Films

A PREVIOUS communication¹ has described the interlamellar sorption of straight chain amines by graphitic acid. Attention was then directed to a break in the curve of spacing against chain-length, occurring between 9 and 10 C-atoms per molecule.

This we now believe to be due to the change of the sorbed film from the liquid to the solid state. If this

assumption is accepted, it follows that the sorbed films solidify more readily than the pure substances, for which the liquid-solid transition occurs between 11 and 12 C-atoms.

Evidence for the assumption is provided by observation, on the X-ray diagram, of a diffraction in the region of 4.3A. This consists of a broad band on the diagram of the complexes with the lower amines, but it sharpens to a sharp line concurrently with the spacing shift. This band or line is presumably due to the spacing between neighbouring chains.

Further evidence is provided by X-ray diagrams of sorption complexes with mixtures of two amines, that is, hexylamine and decylamine. These give intermediate spacings which, when plotted against the proportion of higher amines in the mixture (Fig. 1) give a straight line. The point for pure

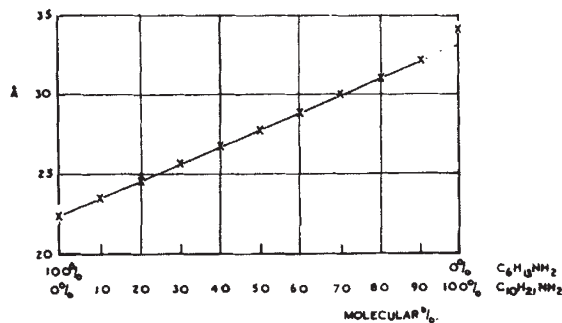


Fig. 1. Interlayer spacings of graphitic acid complexes with mixtures of hexylamine and decylamine, plotted against proportion of higher amine

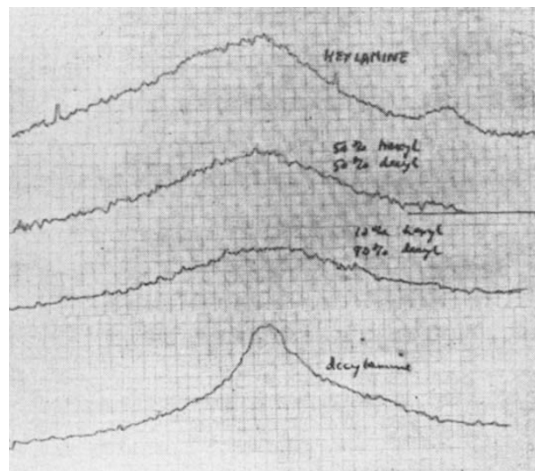


Fig. 2. Microphotometer curves of the diffraction maximum in the region of 4.3A. for certain of the above mixtures in Fig. 1

decylamine, however, lies off the sharper line. Here again, the nature of the diffraction at 4.3A. changes concurrently with the break in the graph (Fig. 2). We have made several similar observations.

Detailed observation suggests that the liquid-solid change in these sorbed films is not sharp, but that the 4.3A. line sharpens over a range of values following the break.

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