

Thus in the thermodynamics of surfaces, the expression  $\partial n/\partial A$ , the rate of change of the molar number,  $n$ , due to the change of surface area,  $A$ , alone is at once interpretable as the surface excess or amount adsorbed per unit area.

(4) The new definition is essential when the variables are dependent, and it is much to be preferred when dealing with variables which are independent with difficulty. Many such cases occur in thermodynamics. For example, the fundamental equation for the reversible energy change,  $dE$ , of a simple one-component system is:

$$dE = T.dS - P.dV + \mu.dn \quad (4)$$

However, if we wish to determine  $\partial E/\partial S$  by the standard definition we must first enclose the system in a rigid enclosure so that the entropy,  $S$ , may be changed by reversible heating without altering the volume,  $V$ , or the molar number,  $n$ . If we wish to determine  $\partial E/\partial V$  by the same method, the rigid enclosure must be a perfect thermal insulator to keep  $S$  constant and it must have a piston frictionless and also thermally insulating to change  $V$  reversibly. With the new definition these details need scarcely trouble us. Further, if we wish to determine  $\partial E/\partial n$  according to the standard definition, an insuperable difficulty arises since we cannot increase  $n$  reversibly without at the same time causing volume and entropy changes. We are forced, therefore, to correct the amount  $dE$  due to the material, the entropy and the volume added unavoidably in one process, by subtracting the energy increments,  $T.dS$  and  $-P.dV$ , due to the entropy and volume changes respectively. This is exactly the process described in more general terms by equation (3). In this case we are forced to use the new definition.

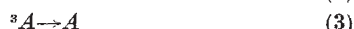
G. A. ELLIOTT

Department of Chemistry,  
University of Western Australia,  
Nedlands.

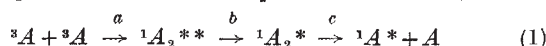
<sup>1</sup> For example, see Kirkwood, J. G., and Oppenheim, I., *Chemical Thermodynamics*, 249 (McGraw-Hill Co., 1961).

### Delayed Fluorescence Spectrum of Pyrene Solutions at Low Temperatures

Parker and Hatchard<sup>1</sup> have convincingly demonstrated that delayed fluorescence exhibited by dissolved aromatic hydrocarbons  $A$  originates in the interaction of two triplet states, and that at low light intensities the overall process 1, followed by 2, is controlled by the first-order process 3 which is almost entirely responsible for triplet state decay under these conditions.



To account for the presence of the dimer band in the delayed fluorescence spectrum of pyrene<sup>2</sup>, these authors<sup>3</sup> suggest that process 1 involves Colpa's doubly-excited state  ${}^1A_2^{**}$  and the excimer  ${}^1A_2^*$  as intermediates, that is:



where the energy-dependent process 1c competes with excimer fluorescence, process (4).



This mechanism accounts for the observation<sup>3</sup> that the ratio of intensities  $I_D/I_M$  of dimer to monomer bands in the delayed spectrum approaches a limiting non-zero value at zero concentration of  $A$  at room temperature; moreover, it requires a negative temperature coefficient of  $I_D/I_M$  which is indeed observed above 0° C as shown in Fig. 1.

At lower temperatures, however, the ratio  $I_D/I_M$  has a positive temperature coefficient and as shown in Fig. 1 this ratio is higher at -72° C than at 71° C for a  $10^{-3}$  M solution in ethanol. Since the singlet-triplet splitting in

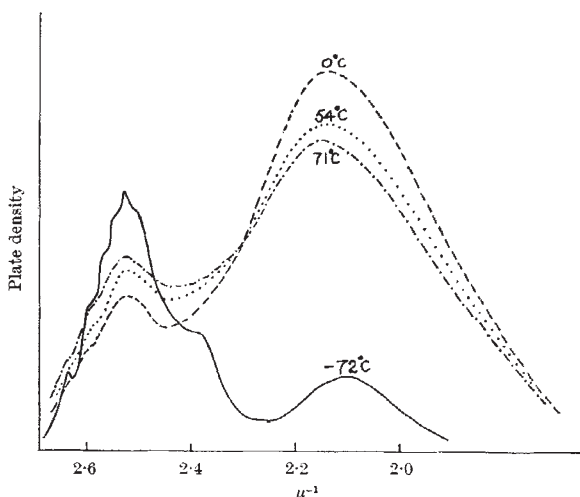


Fig. 1. Microdensitometer traces of plates exposed to delayed fluorescence of pyrene ( $1.44 \times 10^{-3}$  M in ethanol) at temperatures shown

pyrene is some  $10,000 \text{ cm}^{-1}$ , this is unlikely to be due to a thermal repopulation of the fluorescent from the triplet states which in any event would lead to a negative temperature coefficient of  $I_D/I_M$  in this region.

The dominance of the monomer band in the delayed fluorescence spectrum at lower temperatures (and higher viscosities) may be understood if process 1 can occur directly at greater distances than those required for the formation of dimeric intermediates by processes 1a and 1b, and if the latter processes are suppressed under these conditions due to energy requirements. This mechanism would require that the ratio  $I_D/I_M$  approach zero at zero concentration since photoassociation would follow rather than precede the formation of the excited singlet state; this aspect is being currently investigated.

Long-range triplet-triplet state interaction has been suggested by Muel<sup>4</sup> to account for the square-law intensity dependence of delayed fluorescence exhibited by 3,4-benzopyrene in rigid media, while Nieman and Robinson<sup>5</sup> have recently demonstrated the occurrence of long-range energy migration between triplet state traps in  $C_6D_6$ -doped crystals of benzene at very low temperatures.

This work is being supported by the U.S. Department of Army through its European Office.

C. TANAKA  
J. TANAKA  
E. HUTTON  
B. STEVENS

Department of Chemistry,  
University of Sheffield.

<sup>1</sup> Parker, C. A., and Hatchard, C. B., *Proc. Chem. Soc.*, **147**, 386 (1962); *Proc. Roy. Soc., A*, **269**, 574 (1962).

<sup>2</sup> Stevens, B., and Hutton, E., *Nature*, **186**, 1045 (1960).

<sup>3</sup> Parker, C. A., and Hatchard, C. G., *Trans. Farad. Soc.*, **59**, 284 (1963).

<sup>4</sup> Muel, B., doctoral dissertation (Univ. Paris, 1962).

<sup>5</sup> Nieman, G. C., and Robinson, G. W., *J. Chem. Phys.*, **37**, 2150 (1962).

### Annealing of Pyrolytic Graphite under Pressure

PREVIOUS measurements on specimens of pyrolytic graphite have indicated  $p$ -type semiconduction in the  $c$ -axis direction<sup>1</sup> with predominantly  $n$ -type metallic conduction in the  $a$ -axis direction, conferring a net electrical anisotropy ( $\rho_c/\rho_a$ ) of about 5,000. The thermal conductivity is also markedly anisotropic, with  $K_a/K_c$  about 250 at room temperature, with values of  $K_a$  up to five times that of copper, and twice that of diamond<sup>2</sup>. The scientific and technical interest of this anisotropy makes it desirable to obtain large specimens of graphite with near single crystal perfection in order to investigate and exploit these properties.