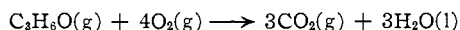


TABLE VII
THE MOLAL THERMODYNAMIC FUNCTIONS OF ACETONE IN THE IDEAL GAS STATE^a

T, °K.	$(F^\circ - H_0^\circ)/T$, cal. deg. ⁻¹	$(H^\circ - H_0^\circ)/T$, cal. deg. ⁻¹	$H^\circ - H_0^\circ$, kcal.	S° , cal. deg. ⁻¹	C_p° , cal. deg. ⁻¹	ΔH_f° , ^b kcal.	ΔF_f° , ^b kcal.	log ₁₀ K _f ^b
0	0	0	0	0	0	-47.74	-47.74	Infinite
273.15	-56.31	12.65	3.454	68.96	16.95	-51.40	-37.53	30.03
298.15	-57.45	13.04	3.889	70.49	17.90	-51.72	-36.30	26.61
300.00	-57.53	13.07	3.922	70.60	17.97	-51.74	-36.20	26.37
400	-61.52	14.79	5.916	76.31	22.00	-52.93	-30.84	16.84
500	-65.03	16.63	8.317	81.66	25.89	-53.94	-25.20	11.02
600	-68.22	18.47	11.084	86.69	29.34	-54.78	-19.36	7.05
700	-71.19	20.25	14.18	91.44	32.34	-55.46	-13.40	4.19
800	-74.00	21.93	17.55	95.93	34.93	-55.98	-7.34	2.00
900	-76.67	23.51	21.16	100.18	37.19	-56.38	-1.25	0.32
1000	-79.22	24.98	24.98	104.20	39.15	-56.61	+ 4.91	-1.08
1100	-81.68	26.34	28.98	108.02	40.85	-56.80	11.06	-2.19
1200	-84.02	27.62	33.14	111.64	42.32	-56.87	17.23	-3.14
1300	-86.28	28.80	37.45	115.08	43.61	-56.88	23.42	-3.94
1400	-88.46	29.90	41.86	118.36	44.74	-56.85	29.57	-4.62
1500	-90.54	30.92	46.38	121.46	45.72	-56.78	35.77	-5.21

^a In order to maintain internal consistency and incremental accuracy, the values in this table are given to more significant figures than are justified by their absolute accuracy. ^b The standard heat, standard free energy, and common logarithm of the equilibrium constant for the formation of acetone by the reaction: $3C(\text{graphite}) + 3H_2(g) + 1/2O_2(g) \rightarrow C_3H_6O(g)$.

and atomic weights¹ the reported value becomes 435.39 kcal. mole⁻¹ for the heat of combustion of acetone in the reaction



taking place at 298.15°K. and a total pressure of approximately one atmosphere. Sufficient experimental details were not provided to make possible a reliable adjustment to the reaction in which all materials are in their standard states. However, the corrections involved would be small and tend to cancel one another so that for present purposes the standard heat of combustion of gaseous acetone is adopted as 435.39 kcal. mole⁻¹. This value, in conjunction with the heats of formation of water and carbon dioxide²⁹ yields, for the heat of forma-

(29) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945). These data were adjusted to an atomic weight of carbon of 12.011 for use in the present calculations.

tion of acetone in the reaction



at 298.15°K. with reactants and products in their appropriate standard states, $\Delta H_f^\circ = -51.72$ kcal. mole⁻¹.

The heat of formation at 298.15°K. of acetone, the thermodynamic functions in Table VII, and the thermodynamic functions of hydrogen, carbon and oxygen²⁹ were used to calculate values of the heat of formation, free energy of formation, and logarithm of the equilibrium constant of formation of acetone at selected temperatures from 0 to 1500°K. These data also are presented in Table VII.

Acknowledgment.—The work reported in this paper was supported by the Office of Ordnance Research through contract DA-23-072-ORD-685.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF ROCHESTER]

Concentration Dependence of the Absorption and Fluorescence Spectra of Mixed Crystals of Anthracene with Phenanthrene at 77°K.¹

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RECEIVED JULY 6, 1956

The absorption and fluorescence spectra of anthracene have been studied at 77°K. in mixed crystals with phenanthrene, using concentrations of anthracene ranging from 0.6 to 100%. The origins of the absorption and fluorescence transitions vary in different ways as a function of the concentration of anthracene in the mixed crystal. The mechanism of energy transfer and fluorescence is interpreted on the basis of trapped excitons. It is postulated that the driving force for formation of the trapped exciton state in the crystal is due to the interaction of an electronically excited anthracene molecule with an unexcited anthracene molecule in an attempt to form a dimer.

Introduction

The absorption and fluorescence spectra of

(1) This research was supported by the Office of Ordnance Research, U. S. Army, under Contract DA-30-115 ORD-728 with the University of Rochester.

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anthracene at low temperatures recently have been studied, both in dilute mixed crystals with naphthalene and phenanthrene³ and in crystalline anthracene.⁴ From the studies of the mixed crystal spectra,³ it was possible to determine the symmetry properties of the lowest excited singlet state and to

(3) J. W. Sidman, *J. Chem. Phys.*, **25**, 115 (1956).

(4) J. W. Sidman, *Phys. Rev.*, **102**, 96 (1956).

measure vibrational frequencies in the ground and in the excited state with an accuracy comparable to the methods of conventional infrared and Raman spectra. The study of the crystal spectra⁴ revealed additional effects of the crystal on the molecular transition. The results of the studies of the crystal spectra were applied to Frenkel's theory of the exciton,^{5,6} and an attempt was made to give a semi-empirical interpretation to several of the terms in Frenkel's theory.

Since the spectra of anthracene have been studied both in dilute mixed crystals and in crystalline anthracene, it appeared desirable to obtain information about the effect of concentration on the spectra of mixed crystals. Although the solubility of anthracene in naphthalene is very small, it is known that anthracene and phenanthrene form a continuous series of solid solutions over the entire concentration range from 0 to 100% anthracene.⁷ In this work, the absorption and fluorescence spectra of anthracene have been measured as a function of concentration in mixed crystals with phenanthrene at 77°K., in order to study further the effects of the environment on the electronic transition.

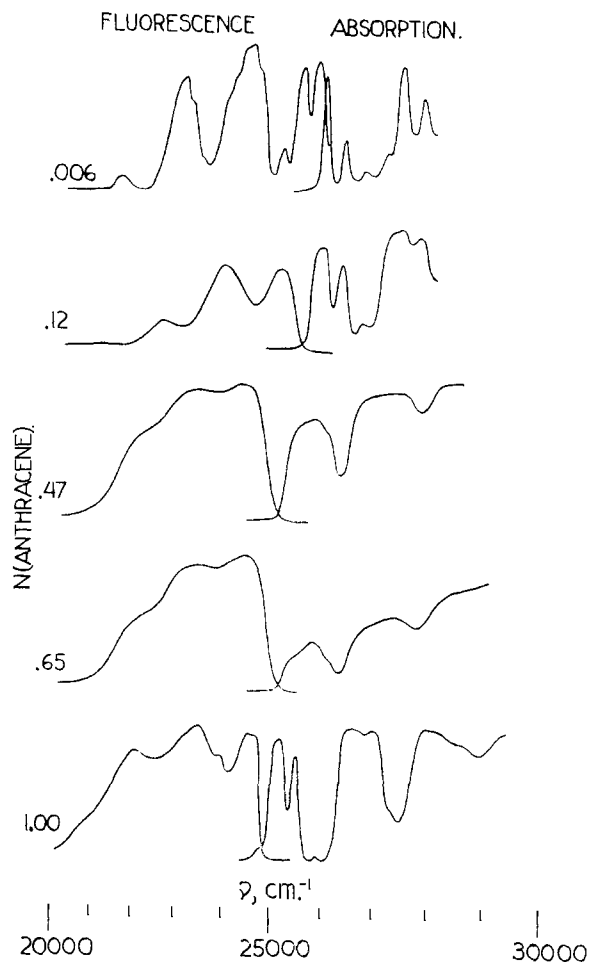


Fig. 1.—Absorption and fluorescence spectra of mixed crystals of anthracene with phenanthrene, 77°K.

- (5) J. Frenkel, *Phys. Rev.*, **37**, 17, 1276 (1931).
 (6) J. Frenkel, *Physik. Z. Sowjetunion*, **9**, 158 (1936).
 (7) G. Bradley and J. K. Marsh, *J. Chem. Soc.*, 650 (1933).

Experimental

The spectrograph, Dewar vessel and other apparatus in this research are similar to those which were used in the earlier work.^{3,4} A Bausch and Lomb quartz prism Littrow spectrograph was employed in conjunction with Kodak I03-F plates. A tungsten filament lamp was used as a light source for absorption spectra, and a medium-pressure Hanovia Mercury arc with a Corning 5860 filter was used to excite the fluorescence of anthracene by illumination with the lines of the $\lambda 3660 \text{ \AA.}$ group in the Hg emission spectrum.

The mixed crystals were prepared by fusing mixtures of anthracene and phenanthrene between quartz disks, followed by repeated mixing and fusing of the mixed crystals to ensure the maximum homogeneity. The samples were immersed directly in liquid nitrogen (77°K.) during the exposure. The mixed crystal was analyzed for anthracene by dissolving it in a 4 to 1 mixture of methanol and ethanol and determining the concentration of anthracene by ultraviolet absorption spectrophotometry.

The rapid cooling of the melt prevented the separation of two phases, even in the case of equimolar mixtures of the two components. In a few cases, the appearance of a second phase was evidenced by the clouding of the mixed crystal, and such samples were not further studied. A small area (approximately 1 mm. \times 2 mm.) was used in recording the spectra and in performing the analyses. By using small samples which had been cooled rapidly from the melt, it was possible to ensure homogeneity of better than 10% of the actual anthracene concentration in the intermediate range, with considerably greater homogeneity in the very low and very high concentration ranges.

Results

Microphotometer tracings of the absorption and fluorescence spectra are shown in Fig. 1. The origins of the absorption and fluorescence spectra in the mixed crystals were estimated by comparing the spectra of the mixed crystals in the intermediate range with the spectra of the dilute mixed crystals (0.6%) and of crystalline anthracene (100%). The spectra of the mixed crystals in the intermediate range are very much broader than the spectra of either the dilute mixed crystal or the crystal, and the estimation of the 0-0 band may be subject to errors of up to 150 cm.^{-1} in the case of the broadest spectra. The estimated origins of the

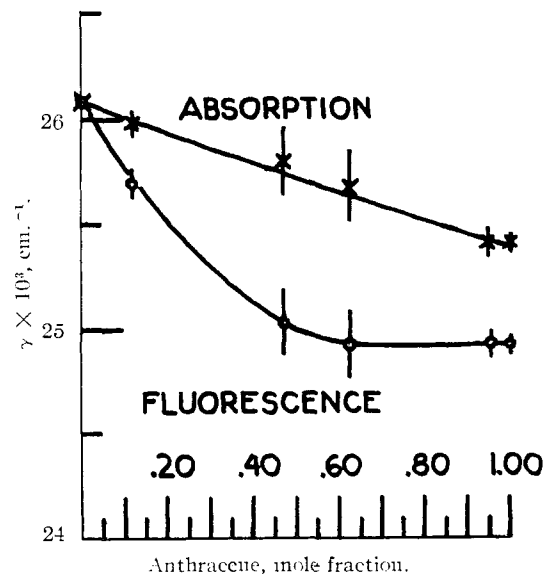


Fig. 2.—Concentration dependence of the origins of the absorption and fluorescence spectra of mixed crystals of anthracene with phenanthrene, 77°K.

absorption and fluorescence spectra of the various mixed crystals are shown in Fig. 2.

One unexpected feature of the fluorescence spectra of some molecular crystals is a gap of several hundred cm^{-1} between the origins of the absorption and fluorescence transitions which have been shown from the spectra of the mixed crystals to correspond to the same electronic transition. This gap appears in crystalline naphthalene,⁸ phenanthrene⁹ and anthracene.⁴ It previously has been suggested⁴ that the gap may be due to formation of a trapped exciton⁶ in the molecular crystal. In the molecular crystal, the exciton will be trapped if a distortion of the lattice in the vicinity of the excited molecule leads to a decrease in the energy of the system.⁶ A gap between the origins of the absorption and fluorescence spectra thus far has not been observed in dilute mixed crystals.

It is seen from Fig. 2 that the gap between the average origins of the absorption and fluorescence transitions occurs in the mixed crystals as soon as the concentration of anthracene exceeds a few per cent. Förster¹⁰ has discussed intermolecular energy transfer and fluorescence in condensed phases, and has shown that the probability of energy transfer between solute molecules increases with increasing concentration of the solute, since the average distance between solute molecules then decreases. In the case of crystalline anthracene,⁴ it is possible that the driving force for formation of the trapped exciton state is due to the attempt of an excited molecule to dimerize by combining with an unexcited molecule of the same chemical species. In this connection, it should be noted that irradiation of anthracene in liquid solution at room temperature in the region of its first electronic absorption band does lead to the formation of dianthracene.¹¹ The gap between the origins of absorption and fluorescence does not occur in the spectra of the dilute mixed crystals, but only in the crystal⁴ or in the more concentrated mixed crystal (Fig. 2).

(8) D. S. McClure and O. Schnepf, *J. Chem. Phys.*, **23**, 1575 (1955).

(9) D. S. McClure, *ibid.*, **25**, in press (1956).

(10) T. Förster, *Ann. Physik*, Ser. 6, **2**, 55 (1948).

(11) C. A. Coulson, L. E. Orgel, W. Taylor and J. Weiss, *J. Chem. Soc.*, 2961 (1955).

This is consistent with the idea that the trapping of the exciton is due to incipient photodimerization between molecules of the same chemical species.

On this basis, it is possible to give a plausible account of the mechanism of energy transfer and fluorescence in the mixed crystals of intermediate anthracene concentration. Since energy transfer between solute molecules can occur in the mixed crystals of intermediate concentration, the energy will migrate until it comes to a site at which it can be trapped. A site at which two anthracene molecules occupy adjacent lattice position is capable of acting as a trap by a mechanism analogous to formation of a trapped exciton state in the crystal, *i.e.*, by a process corresponding to incipient dimerization followed by rapid loss of a few hundred cm^{-1} of electronic energy as heat when the two anthracene molecules adjust to new lattice positions and orientations. Since permanent dimerization is impeded in the lattice of the crystal, fluorescence radiation may then be emitted from this distorted site.

The proposed mechanism is not inconsistent with the curves in Fig. 2. Whereas the absorption curve appears to vary linearly over the entire region, the fluorescence curve decreases sharply at first and then levels off at concentrations above 50% anthracene. Since the curves vary in a different way, it appears necessary to assume that the sites which fluoresce are different from the sites which give rise to the absorption spectrum.

The energy levels of the trapped exciton state, like the energy levels of the individual molecules, should depend on the nature of the environment. The fact that both the absorption and fluorescence spectra of mixed crystals in the intermediate concentration range are broader than the corresponding spectra of either the dilute mixed crystals or the crystal is attributed to lack of a uniform environment in the more concentrated mixed crystals.

Acknowledgments.—It is a pleasure to acknowledge that the initial stimulus to study this problem came from a suggestion by Professor D. S. McClure. The continued interest of Professor A. B. F. Duncan in this research is also gratefully acknowledged.

ROCHESTER, NEW YORK