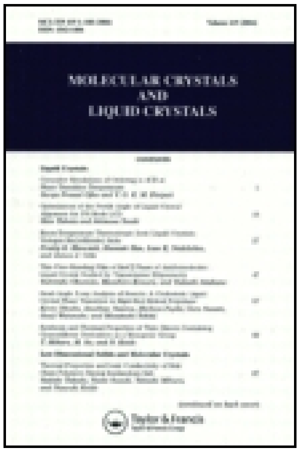

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The Anthracene-Carbazole System

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The Anthracene–Carbazole System

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Abstract—The heat capacities of anthracene and carbazole from 180 °K to their melting points and their enthalpies of fusion have been determined. A peak in the heat capacity–temperature curve of carbazole indicates a transition at 420 °K with an associated enthalpy of transformation of 65.5 cal/mole.

The phase equilibrium diagram of anthracene and carbazole has been determined by calorimetric and X-ray techniques. A eutectic occurs at 4.5 wt pct carbazole and 489.1 °K and a peritectic at 50 wt pct carbazole and 499.1 °K. Five solid phases, α, α', β, γ and γ' occur in the system, the structures of the phases being closely related to one another. The α' phase appears to be an ordered form of the α terminal solid solution and is centred on a composition of 10 pct carbazole. The transformation temperature of the 10 wt pct carbazole alloy from α' to β is 479 °K and the enthalpy of transformation is 308 cal/mole.

1. Introduction

Carbazole is a major impurity in anthracene, even after extensive purification. A knowledge of the phase equilibria between the two compounds is necessary to understand the effect of small amounts carbazole on the purification and the properties of anthracene. Pascal[1] has reported a complete range of solid solutions between the compounds and this has been confirmed by Kravchenko and Eremenko[2] although Kitaigorodskii[3] has pointed out that consideration of the crystal symmetry suggests that this cannot be correct. A later determination of the phase diagram by Brandstatter-Kuhnert and Weil[4] showed a minimum in the solidus and in the liquidus at approximately 5 pct carbazole and a peritectic point at 66 pct carbazole and 497 °K. No determinations of phase boundaries in the solid have been reported.

The difficulty in removing small amounts of carbazole from anthracene by zone-refining[5] suggests that an extensive terminal solid solution is not formed at low carbazole concentrations. This conclusion is supported by the manner in which the mechanical properties of anthracene single crystals vary with small additions of carbazole.[6] The phase diagram between anthracene and carbazole has therefore been determined using calorimetric and X-ray techniques as part of a more general investigation of the properties of anthracene. In addition, some of the thermodynamic properties of both compounds have been studied.

2. Materials

The materials used were Hopkin and Williams " Blue Fluorescent Grade " anthracene and " purified " carbazole. The anthracene was purified to a total impurity level of less than 30 ppm, as determined by mass spectroscopy, by the procedures outlined elsewhere[5] and the carbazole to the same level by recrystallization and sublimation followed by zone-refining.

Alloys between the two compounds were prepared in approximately 200 mg. batches by sealing weighed amounts under nitrogen in $\frac{1}{8}$ in. diameter pyrex capsules and holding for 30 minutes at 550 °K. The alloys were rapidly cooled in air to room temperature, reheated to just below the solidus temperature estimated from the melting points of the two compounds, and held for 4 hours before slowly cooling. Melting point determinations on samples from various parts of the ingot indicated that homogeneous alloys were produced by this procedure, at least for carbazole contents between 10 and 100 pct. The slope of the solidus and liquidus makes such a test insensitive for alloys containing less than 10 pct carbazole but as the partition coefficient of carbazole in anthracene is close to unity,[7] segregation should not occur at these concentrations.

The thermodynamic properties and X-ray diffraction patterns of samples which had been held at room temperature (approximately

0.6 of the absolute melting point) for 6 months were identical with those from freshly prepared samples. This gives some indication that equilibrium conditions were reached during the sample preparation. X-ray diffraction patterns taken at different temperatures, both increasing and decreasing, confirmed that comparatively short times are necessary at temperatures above ambient before equilibrium conditions are reached.

The composition of the anthracene–carbazole alloys is quoted in weight percent carbazole, which, in this case, is close to mole percent.

3. The Thermodynamic Properties of Anthracene and Carbazole

The heat capacities and enthalpies of fusion of anthracene and carbazole were determined using a Perkin–Elmer DSC–1B scanning calorimeter. In this calorimeter, the difference in power needed to heat the sample and a standard at a constant rate is measured as a function of temperature. The temperature calibration over the range 200° to 600°K was carried out using the melting points of high purity mercury, indium, tin and lead.[8] The heat capacity and enthalpy of fusion of 99.999 pct tin[8] were used as standard values in determining these properties of the compounds.

The samples, usually 10 to 20 mg., were sealed in vapour tight aluminium capsules and heated in the calorimeter at rates from 1° to 32°K/minute. The heating rate did not affect the determination of the heat capacities or enthalpies of fusion, providing all calibrations were carried out at the same rate, but at the higher heating rates the apparent melting point was moved to higher temperatures. The melting points of anthracene and carbazole, therefore, are quoted for heating rates of 1°K/minute.

The melting point and enthalpy of fusion of zone-refined anthracene were 490.0° ± 0.3°K and 6,680 ± 26 cal/mole respectively, and those of zone-refined carbazole were 519.3° ± 0.3°K and 6,430 ± 52 cal/mole. The error limits quoted are the standard deviations from the arithmetic means of 10 determinations in the case of melting points and five determinations for the enthalpies of fusion. For comparison, Goursot, Girdhar and Westrum[10] have reported values of 489.7 °K and 7,020 ± 40 cal/mole for the melting point and enthalpy of fusion of pure anthracene. The melting point of carbazole of unspecified purity has been given as 519 °K[9] and 517 °K[4]. Anthracene and carbazole have entropies of fusion of 14.0 and 12.4 cal/ °K mole respectively, the relatively high values indicating that they do not belong to the class of molecular crystals in which molecular rotations take place.[11]

The measured heat capacities of anthracene from 180 °K to its melting point and of carbazole from 180° to 420 °K could be represented (to within ± 2 pct) by the equations

$$C_p = 15.0 + 0.0375T + 0.225T^2 \times 10^{-3} \text{ cal/°K mole}$$

for anthracene

and

$$C_p = 10.0 + 0.048T + 0.216T^2 \times 10^{-3} \text{ cal/°K mole}$$

for carbazole

The similarity between the molecular sizes and crystal structures of the two compounds[12] is reflected by their heat capacities which are within 5 cal/°K mole of one another over the entire temperature range investigated.

After completion of the present work, values for the heat capacity of anthracene between 5° and 520 °K as determined by adiabatic calorimetry became available.[10] There is reasonable agreement between the results obtained by the two methods; the values at 200° and 400 °K, for example, being 31.5 and 66.0 cal/ °K mole respectively by scanning calorimetry and 32.69 and 68.82 cal/ °K mole respectively by adiabatic calorimetry. In view of the different systematic errors inherent in the two methods of determining heat capacitites the latter are probably the better set of values.

The heat capacity–temperature curve for carbazole determined at low scan speeds showed a transition at 420 °K (Fig. 1). This transition occurred isothermally when carbazole was heated

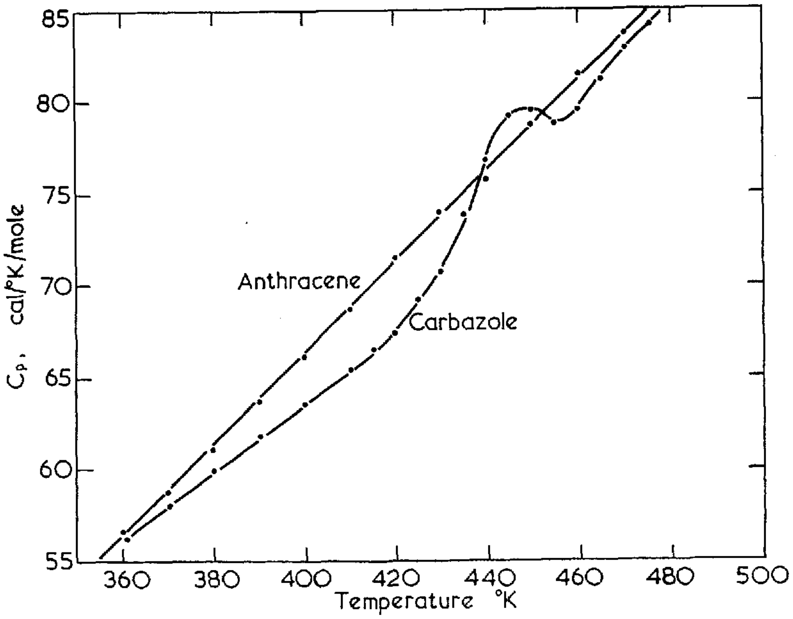

Figure 1. The heat capacities of anthracene and carbazole in the range 360° to 490°K.

rapidly to 420 °K and held at temperature. The enthalpy of transformation was 65.5 ± 9.0 cal/mole. X-ray diffraction powder patterns taken with a 19 cm. high temperature camera showed that the crystal structure of carbazole was orthorhombic both above and below the transition temperature. No change in the width of the resonance line in the N.M.R. spectrum was observed on heating through the transition, indicating that it is not associated with a free rotation of the molecules.

4. Solidus and Liquidus in Anthracene–Carbazole System

The solidus and liquidus from 0 to 100 pct carbazole were determined by calorimetric methods at a heating rate of 1 °K/minute. Typical melting point curves for low and high carbazole alloys are shown in Fig. 2. At low carbazole concentrations the solidus (melting point) was taken as the intersection of the heat capacity

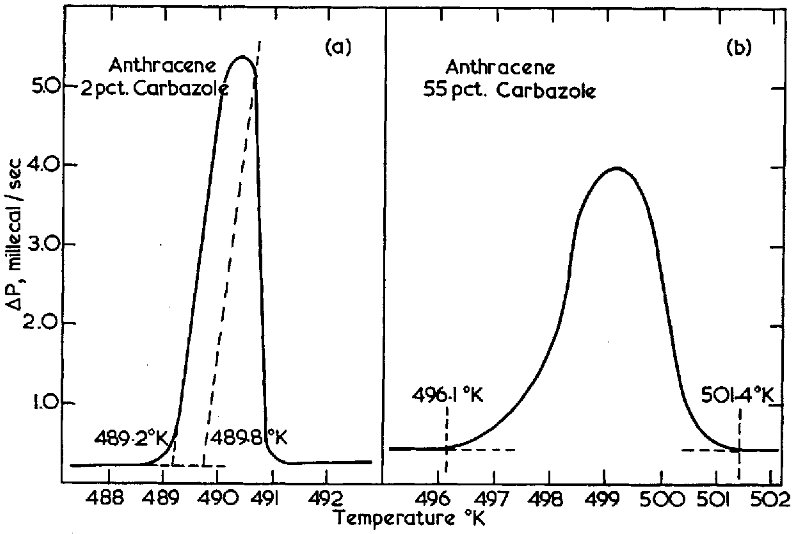

Figure 2. Typical melting point curves for alloys containing low and high concentrations of carbazole showing the methods adopted for determining the position of the solidus and liquidus in each case.

curve of the solid and the leading edge of the melting curve and the liquidus as the intersection of the heat capacity curve with the line parallel to the leading edge drawn through the point at which the melting curve begins to return to the base-line (Fig. 2(a)). Using the present calorimeter, the two points of intersection coincide for pure materials. At carbazole concentrations at which the slope of the leading edge of the melting curves deviated markedly from that for the pure compounds the solidus and liquidus are taken as the points of departure and return respectively to the base heat capacity line (Fig. 2(b)). The standard deviation from the arithmetic mean of determinations of the solidus was 0.2 °K and that of the liquidus 0.3 °K. In Figs. 3, 4 and 5, each experimental point represents the average of at least five determinations.

The calorimetric results indicated that the temperature of the solidus and liquidus varied only slightly as the composition was changed from 0 to 12 pct carbazole (Figs. 3 and 4). A eutectic

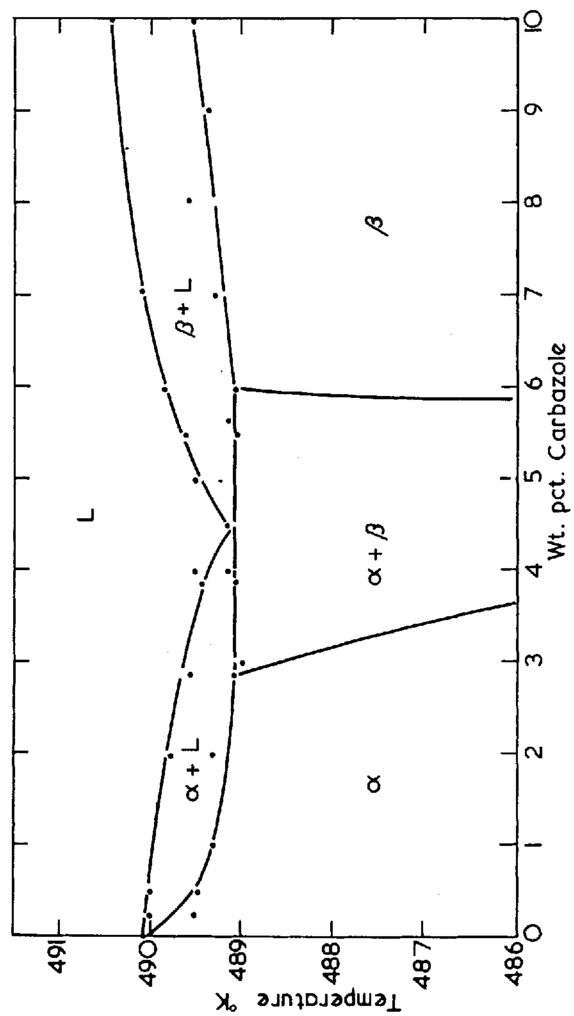

Figure 3. The solidus and liquidus in the anthracene–carbazole system in the region 0 to 12 pct carbazole.

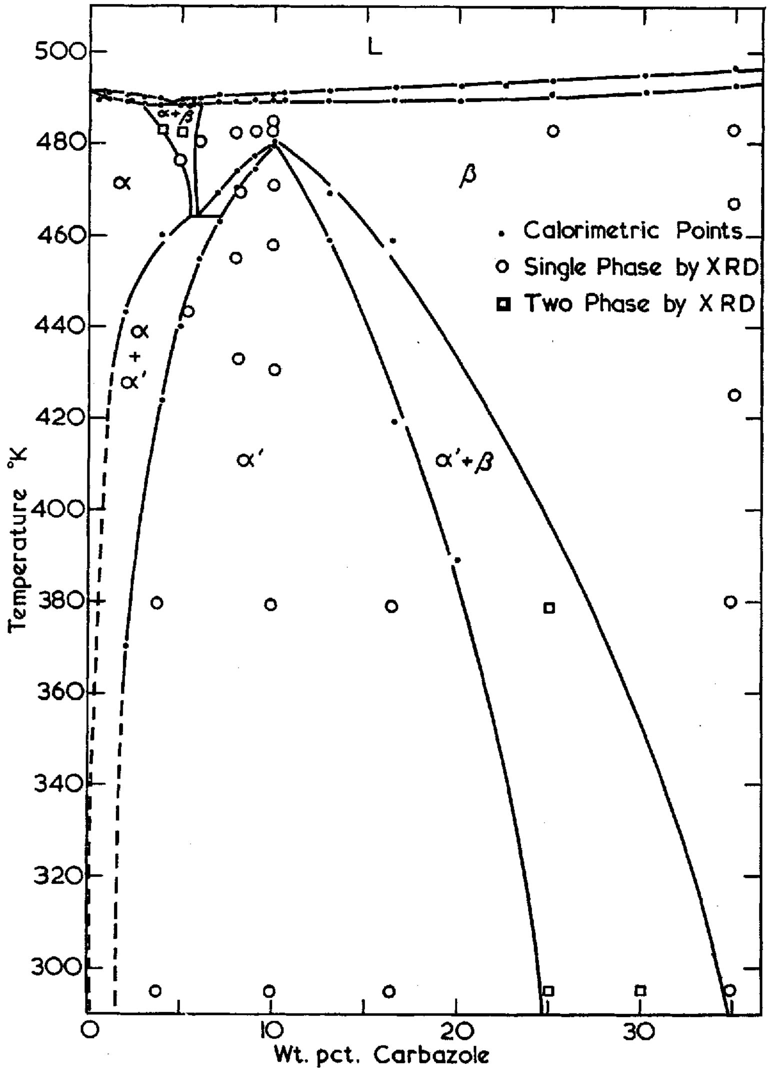

Figure 4. The anthracene-carbazole phase diagram in the region 0 to 30 pct carbazole.

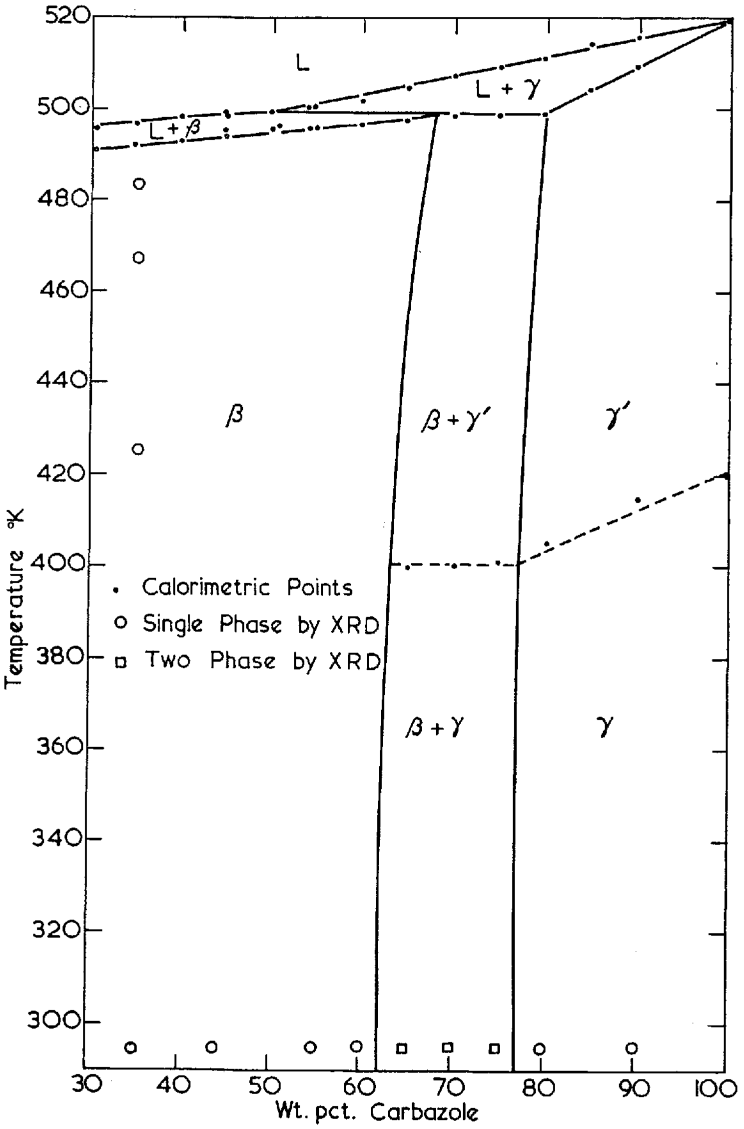

Figure 5. The anthracene–carbazole phase diagram in the region 30 to 100 pct carbazole.

occurred at 4.5 pct carbazole and 489.1 °K, rather than the shallow minimum in the solidus and liquidus observed by Brandstatter-Kuhnert and Weil.[4] A peritectic point occurred at 50 pct carbazole and 499.1 °K, the peritectic horizontal extending to 80 pct carbazole (Fig. 5).

The temperatures of the solidus and liquidus are in general agreement with the results of Brandstatter-Kuhnert and Weil[4] rather than the earlier workers,[1,2] although they differ somewhat in detail. This is not surprising as Brandstatter-Kuhnert and Weil determined the solidus and liquidus by optically observing the start and finish of solidification of samples in small capillaries. It is to be expected that calorimetric methods will yield more accurate results.

5. Phase Boundaries in the Solid

The phase boundaries in the solid were determined by calorimetric and X-ray methods. The accurate determination of phase boundaries by a dynamic method such as scanning calorimetry depends on the heating rate being comparable with, or slower than, the rate at which the solid state reaction takes place. Under these conditions equilibrium can be reached at each temperature. Fortunately, the kinetics of the solid state reactions in the anthracene–carbazole system are sufficiently rapid for the boundaries between two phases to be determined from changes in the slope of the heat capacity curve and, in the case of $\alpha' - \alpha$ and $\alpha' - \beta$ boundaries, by the occurrence of isothermal enthalpy increments providing slow rates of heating are used. A series of heat capacity–temperature curves were determined at different heating rates for each composition, the heating rates being progressively decreased until a constant transformation temperature was obtained. It was usually found that the position of the phase boundary was constant at heating rates of 0.5, 1, 2, 4 or 8 °K/minute, indicating that equilibrium conditions were being reached, but moved to higher temperatures at higher heating rates. At carbazole concentrations between 0 and 3 pct, however, the transformations were sluggish and some difficulty was found in accurately establishing the phase boundaries.

Once the general outline of the phase boundaries in the solid had been established, X-ray diffraction powder photographs were taken with a 19 cm. high temperature camera using CuKα radiation from samples with compositions on either side of the boundaries. In addition, powder patterns from specimens of various compositions were taken at different temperatures, the specimens being allowed to come to equilibrium at each temperature. The result of these experiments confirmed that the kinetics of the solid state reactions in this system are rapid, only short times being necessary at each temperature for equilibrium to be reached. There was close agreement between the phase boundaries determined by the calorimetric and the X-ray methods (Figs. 4 and 5).

5.1. PHASE BOUNDARIES IN THE REGION 0 TO 30 PCT CARBAZOLE

The phase relations in this region of the diagram are complex, with three phases, α, α' and β occurring rather than the single solid solution proposed by earlier workers. The structures of these three phases are closely related, as will be discussed in section 6. A eutectoid decomposition of β into α and α' occurs at 6.1 pct carbazole and 464 °K and a congruent maximum in the boundaries between α' and β occurs at 10 pct carbazole and 479.3 °K (Fig. 4). Isothermal holding of partially transformed specimens during calorimetric runs indicated that, for a given composition, α and α' could co-exist over appreciable temperature ranges, as could α' and β (Fig. 4). The co-existence of α' and β was confirmed by X-ray diffraction studies.

The heat capacity of α' from 300 °K to the temperature of transformation was slightly higher than that of pure anthracene but showed no tendency towards an increasing temperature dependence as the temperature approached that of transformation (Fig. 6). The transformation of α' to α or β was associated with a peak in the heat capacity/temperature curves (Fig. 6). The enthalpy and entropy of transformation both reached maximum values at 10 pct carbazole (Table 1).

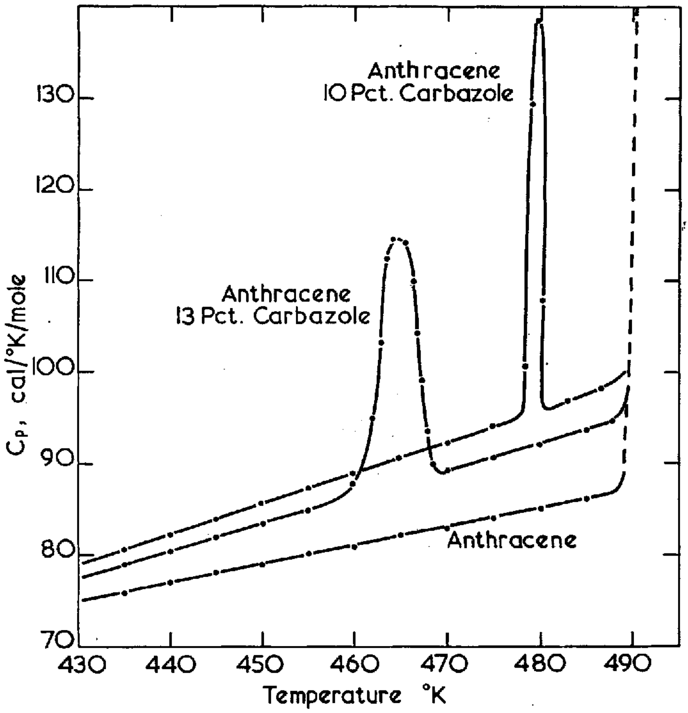

Figure 6. The heat capacity of α′ phase alloys containing 10 to 13 pct carbazole from 300 °K to their melting points compared with that of pure anthracene over the same temperature range.

Table 1 The Enthalpies and Entropies of Transformation of α′ Phase Alloys

Composition pct carbazole	Temp. of transformation °K	ΔH_t (cal/mole)	ΔS_t (cal/°K mole)
2.0	371	52 ± 12	0.14
4.0	422	102 ± 2	0.24
7.0	463	239 ± 11	0.52
8.0	470	234 ± 16	0.50
10.0	479	308 ± 15	0.64
13.0	459	194 ± 16	0.42
16.6	419	66 ± 9	0.16
20.0	387	17 ± 5	0.05

5.2. PHASE BOUNDARIES IN THE PERITECTIC REGION

X-ray diffraction patterns taken at room temperature indicated that the phase boundaries between β and γ must run almost parallel to the temperature axis from the peritectic temperature to room temperature (Fig. 5). Under these circumstances, heat capacity–temperature curves for alloys in this region were of limited use in establishing the position of the boundaries.

Heat capacity measurements from 300 °K to the melting point showed that a transformation occurred in the γ terminal solid solution at temperatures from 400 ° to 420 °K, depending on composition. No change in structure was detected by X-ray diffraction on heating through the γ to γ' transformation temperature. The temperature of transformation and the enthalpy, which decreased with decreasing carbazole concentration, indicate that it is associated with the transformation in pure carbazole (Fig. 5).

The presence of the peak in the heat capacity–temperature curve gives a means of identifying the presence of the γ phase in alloys containing high percentage of carbazole.

6. X-ray Diffraction Data

The different phases occurring in the anthracene–carbazole system were investigated by X-ray diffraction. Powder photographs were taken using a focussing camera with crystal monochromatized Cu radiation, and single crystal rotation and oscillation photographs were taken with filtered Cu radiation. Complete structure analyses were not attempted, but in the case of carbazole the lattice parameters and space group were found, enabling a partial determination of the structure to be made.[12] It appeared from the X-ray data that all the crystal structures in this system were simply related and based on layers of molecules parallel to the (001) plane closely packed in a herringbone array.

The α terminal solid solution has, of course, the structure of anthracene. This is monoclinic with two molecules in the unit cell forming a single closely packed layer. The long axes of the molecules are approximately parallel to the *c*-crystallographic axis.[13]

The α′ phase was not distinguished from α by X-ray methods. Powder photographs showed no change in the lattice parameters, and single crystal photographs showed no trace of any extra reflexions which might have indicated the formation of a superlattice. However, since the carbazole concentration in the α′ phase is relatively low for superlattice formation, and the carbazole and anthracene molecules are very similar in configuration and in X-ray scattering ability, superlattice reflexions will at best be weak, so that failure to observe them does not necessarily negate the superlattice hypothesis.

The γ terminal solid solution has the carbazole structure, which is orthorhombic with four molecules in the unit cell arranged in two closely packed layers. The herringbone packing within the layers is very similar to that occurring in anthracene, and the γ phase may be regarded as derived from two layers of the α phase by shears on the (001) planes.[12]

The γ′ terminal solid solution which exists above 420 °K has, like α′, been identified only by calorimetric methods. Powder photographs of the high temperature phase were superficially identical with those of the low temperature form, making due allowance for thermal expansion, suggesting that there was no major structural change. However, the complicating factor of anisotropic thermal expansion, coupled with the poor quality of the high temperature photographs which is a consequence of recrystallization, precludes certainty on this point.

The β phase is very closely related to the γ phase. The structure is orthorhombic and the lattice parameters differ from those of pure carbazole only by a slight (*ca.* 2%) dilation of the *c*-axis. There are quite marked differences in the intensities of corresponding powder lines from the two phases which, together with the expansion of the *c*-axis, could arise from a different stacking of the two adjacent closely packed layers which comprise the unit cell.

It appears therefore that the X-ray data is consistent with the view that all phases in the anthracene–carbazole system are based on layers of molecules which are closely packed in herringbone fashion. The layers can then be stacked to give monoclinic or orthorhombic lattices, and further structures can arise from orientational or compositional order–disorder transformations.

Discussion

Prior to this investigation only the solidus and liquidus of the anthracene–carbazole system had been determined. Two of these earlier studies indicated that there was a complete series of solid solutions[1,2] while a third showed that the system had a peritectic point.[4] We have shown that, despite the similarities between the molecular dimensions and crystal structures of the two compounds,[12] five distinct solid phases α, α', β, γ and γ' are formed. The α, β and γ phases can be distinguished readily by X-ray diffraction, while the $\alpha \rightarrow \alpha'$ and $\gamma \rightarrow \gamma'$ transformations can be detected only by heat capacity measurements.

The heat capacity of pure carbazole as a function of temperature indicates that a transformation takes place at 420°K, with an associated entropy change of 0.15 cal/°K mole. A related transformation from γ to γ' occurs in the carbazole rich terminal solid solution at temperatures from 420° to 400°K. The transformation does not appear to be either a change in crystal symmetry or a free rotation of the molecules but it may represent an order–disorder reaction in which the molecules become orientationally disordered with respect to one another. The carbazole molecule has a polar diad symmetry axis which may be thought of as " up " or " down ", so that the transformation may be from an ordered array to one in which " up " and " down " molecules are randomly arranged among the molecular sites. Such an orientational order–disorder change would involve the flipping of the molecules rather than translational motion.

The entropy of such a transformation is given by $R\ln(N_2/N_1)$ where N_2 and N_1 are the average numbers of distinct orientations which the molecule can adopt above and below the transition temperature. Assuming a transformation from complete order to complete disorder with two distinct orientations, that is $N_2/N_1 = 2$, the expected entropy change is 1.38 cal/°K mole. The magnitude of the observed entropy change, 0.15 cal/°K mole, suggests that if this type of orientational disorder does occur in carbazole and the terminal solid solution, either the low temperature order or the high temperature disorder is incomplete.

The similarity in the crystal structures and lattice parameters of pure anthracene and the α' phase suggests that α' may be an ordered version of the α terminal solid solution. The transformation of α' to α or β is associated with a peak in the heat capacity-temperature curve, a maximum in the transformation temperature and a two phase region between the phases; all of which are consistent with a first order transformation due to a change in long range order. The absence of any rapid increase in the temperature dependence of the heat capacity of α' prior to the peak (Fig. 6) suggests that there is no change in short range order before the long range order–disorder change occurs on transformation.

There are two types of order–disorder transformation which may occur in alloys of molecular compounds. Orientational disorder of one of the molecular species may occur, as in pure compounds, or alternatively there may be compositional order-disorder in which the distribution of chemically distinct species among the molecular sites is either ordered or random. Orientational disorder may occur between the carbazole molecules in the α' phase, but a similar disordering is not possible between the anthracene molecules because the molecular symmetry precludes it without a marked change in lattice parameters. The calculated entropy change of 0.14 cal/°K mole due to orientational disordering of the carbazole molecules in the 10 pct carbazole α' phase alloy is much lower than the experimental value of 0.64 cal/°K mole. In addition, the orientational disorder of such a low percentage of the total number of molecules is unlikely to account for experimental observations such as the maximum values in the temperature, enthalpy and entropy of transformation of the α' phase at a composition of 10 pct carbazole.

It appears that the transformation of α' is probably due to compositional disordering. The entropy change associated with this mode of disordering is given by $R(f_1 \ln f_1 + f_2 \ln f_2)$ where f_1 and f_2 are the molecular proportions of the two species. For the 10 pct carbazole alloy this gives a value of 0.65 cal/°K mole which is in remarkably close agreement with the experimental value for the transformation. The existence of an ordered superlattice of anthracene and carbazole molecules centred on 10 pct carbazole and its transformation to a disordered structure at a critical temperature is consistent with the experimental results.

The transformation of α' to β involves a phase change from monoclinic to a related orthorhombic structure. However, the continuity of the temperature and the latent heat of transformation from compositions in which the α' to α transformation occurs to those in which the α' to β transformation occurs suggests that the latter may also be essentially a change in long range order.

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