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Studies on the Purification of Anthracene; Determination and Use of Segregation Coefficients

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Studies on the Purification of Anthracene; Determination and Use of Segregation Coefficients

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Abstract—Zone melting and normal freezing have been used in a study of the purification of anthracene. Of thirteen impurities concentrated by zone melting and gradient sublimation and isolated by chromatography, twelve have been identified as naphthalene, biphenyl, acenaphthene, fluorene, 9,10-dihydroanthracene, carbazole, phenanthrene, 2-methylanthracene, anthraquinone, pyrene, chrysene and tetracene. Effective segregation coefficients were measured at various rates of crystallization for fluorene, phenanthrene, carbazole, anthraquinone and tetracene. The effect of stirring on segregation was studied; by reducing the extent of constitutional supercooling, stirring gives greater segregation and smoother concentration profiles in normally frozen ingots.

Introduction

Extensive studies of the electrical properties of anthracene and other aromatic hydrocarbons have shown that they are critically dependent on purity.[1, 2, 3] Recrystallization, distillation, chromatography and zone melting have been used to purify anthracene for physical studies,[4, 5, 6] but little effort has been made to define even semiquantitatively the purity of a given sample, or the kind and number of impurities present. The goal of this work was to provide such samples and to gain insight into the mechanisms and effectiveness of various purification processes.

Unfortunately, there is no really good absolute criterion of purity for highly purified samples. Thermal analysis comes closest to providing such a criterion, but to detect impurities at concentrations below 10^{-2} mole % in this way is difficult (especially for air-sensitive materials) and not necessarily reliable.[7] An alternative

approach to the estimation of purity is to identify the impurities present in a sample and assay each of them. This method is tedious, but it has the advantage of providing information useful in relating specific physical effects to the presence of certain impurities.

Detection and Identification of Impurities

Zone melting and normal freezing[8] are very helpful not only in achieving purification but in measuring it. Zone melting can concentrate dilute impurities to detectable levels; once detected they may be isolated and identified. From normal freezing data it is possible to calculate an effective segregation coefficient, k, for an impurity; from k and published concentration profiles[9] the concentration of the impurity may be calculated at levels below analytical detectability.

Natural anthracene has been analyzed gas chromatographically, and numerous impurities have been detected and isolated, especially in the impurity-enriched ends of zone-melted ingots. Table 1 shows the relative retention times of a number of impurities. From the fact that the concentration of carbazole was higher at the top of zone-melted ingots (through which molten zones moved downward) it may be concluded that its k is greater than unity; this is consistent with published phase diagrams of the anthracene-carbazole system, which is said to consist of a continuous series of solid solutions.[10, 11] These data show that zone melting not only affords purified materials and concentrated impurities, but in addition provides information on the phase relationships of host and impurities.

Even in the impurity-enriched ends of the zone melted ingots, anthracene remained the major component. While repeated gas chromatography of material from ingot ends made possible the isolation of a number of impurities, the procedure was tedious and time consuming. A preliminary fractionation was therefore desired. Gradient sublimation[12] served well for this purpose. The gradient sublimation tubes were cut up, and the adherent films of sublimate were scavenged for further analysis. Gas chromatographic analysis

TABLE 1 Gas Chromatography of Anthracene

Chromatograph: F and M Scientific Corp., Model 500.

Column: 20% Apiezon L on 60–80 mesh acid-washed firebrick, 2 ft long, 0.25 in. diam.

Temperature: 175–255°, programmed at 5.6°/min.

		Area %		
T_R[a]	Assignment	Commercial	Zone melted top	Zone melted bottom
0.03				
0.07	Naphthalene			t
0.29	Biphenyl	t[b]	t	t
0.46	Acenaphthene	t		t
0.63	Fluorene			0.4
0.83	9,10-Dihydroanthracene			t
0.98	Carbazole	t	0.1	t
1.00	Anthracene, phenanthrene	99.5	99.9	97.3
1.20	2-Methylanthracene			t
1.31	Anthraquinone	0.2		2.3
1.65	Pyrene			t
2.31	Chrysene			t
3.16	Tetracene			t

[a] Retention time relative to anthracene taken as 1.00.

[b] t = trace.

was facilitated by a simple device for the introduction of solid samples directly into the chromatograph. By avoiding, or at least minimizing, the dilution and contamination effects of solvents, increased sensitivity and reliability were attained. Impurities isolated from anthracene were trapped preliminarily on adsorbents such as firebrick; the impurity-loaded adsorbent was then reinjected into the inlet of the chromatograph where organic material was quickly evaporated into the column. In this way, small amounts (tens of micrograms) were made sufficiently pure for identification by UV and IR spectrophotometry and/or by mass spectroscopy.

Phenanthrene was not separated from anthracene in any of numerous columns tried; however, it was readily detected spectrophotometrically after separation by elution chromatography.

Measurement of Effective Segregation Coefficients

Effective segregation coefficients, k, were measured by normal freezing of melts of anthracene containing known amounts of added impurity. In normal freezing a molten charge is allowed to solidify slowly from one end. The distribution of impurity produced by this process is described by the equation[8]

$$\log (c/c_0) = \log k + (k-1)\log (1-g), \tag{1}$$

where c is the impurity concentration in the solid ingot after fraction g of the original charge has solidified, c_0 is the initial,

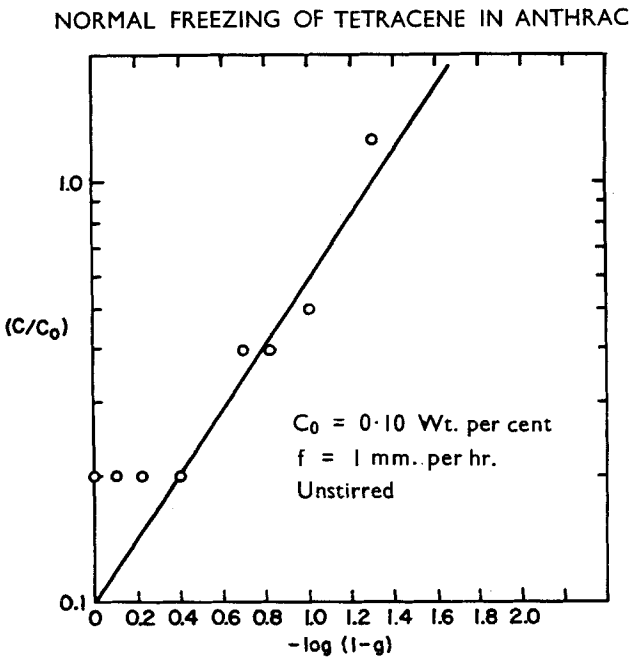


Figure 1.

uniform impurity concentration, and k is the effective segregation coefficient. A plot of log (c/c_0) against log $(1-g)$ should give a straight line of slope $(k-1)$ and intercept k.

A plot of log (c/c_0) against log $(1-g)$ for a 0.10 wt % solution of tetracene in anthracene, solidified at 1 mm/hr, is shown in Fig. 1. From the intercept, k is found to be 0.10 and from the slope, k is found to be 0.23. The reason for this discrepancy, which was observed at all rates of crystallization, is not known definitely, but it may indicate that k changes with concentration. Table 2 shows values of k measured in this way (from the intercepts) at various

TABLE 2 Effective Segregation Coefficients of Impurities in Anthracene from Normal Freezing Data

Rate of crystallization, f, mm/hr	Tetracene[a]	Anthraquinone[b]	Fluorene[b]	Phenanthrene[c]	Carbazole
1	0.10	0.021	0.23	0.10	0.9
2	0.15	0.084	0.30		0.9
4	0.23				
6	0.61				

[a] $C_0 = 0.10$ wt %. [b] $C_0 = 1.0$ wt %. [c] $C_0 = 0.017$ wt %.

rates of crystallization for several compounds in anthracene. In accord with theory and in agreement with earlier experimental work, k approaches unity with increasing rate of crystallization, f.

In early attempts to measure k by this method, it was found that c varied erratically with g; closer examination of the distribution showed that c went through numerous maxima and minima between the purer and less pure ends of the ingot (Fig. 2). The distribution described by Eq. (1) is based on the assumptions (*inter alia*) that the liquid is homogeneous throughout the solidification and that diffusion in the solid is negligible; under these conditions, the concentration profile resulting from partial solidification of an ingot containing an impurity of $k < 1$ would be that shown by the

dashed horizontal line in Fig. 3. In fact, however, the impurity is not distributed uniformly in the melt as it is segregated. Instead,

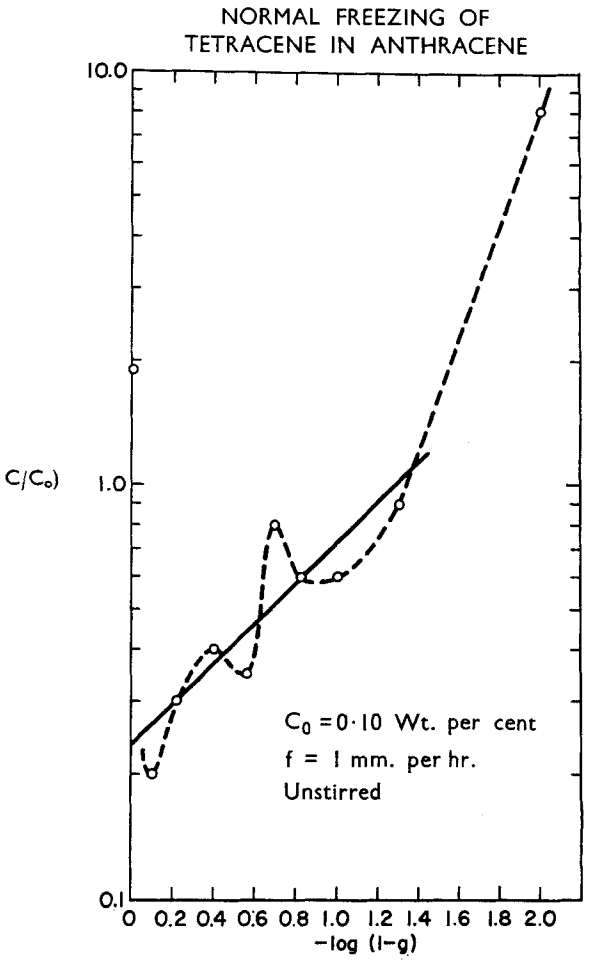


Figure 2.

a region of high impurity concentration is established at the solid-melt interface, in which impurity transport is diffusion-controlled, and the concentration profile is that shown by the solid line in

Fig. 3. In this case, constitutional supercooling[13] takes place. On attainment of some critical degree of supercooling in such a system, a relatively large body of highly impure liquid solidifies, entrapping the impurity contained near the interface. The next solid to form results from a liquid of lower impurity concentration and is itself purer than the solid resulting from the supercooled melt. This procedure is repeated cyclically, and the result is formation of a

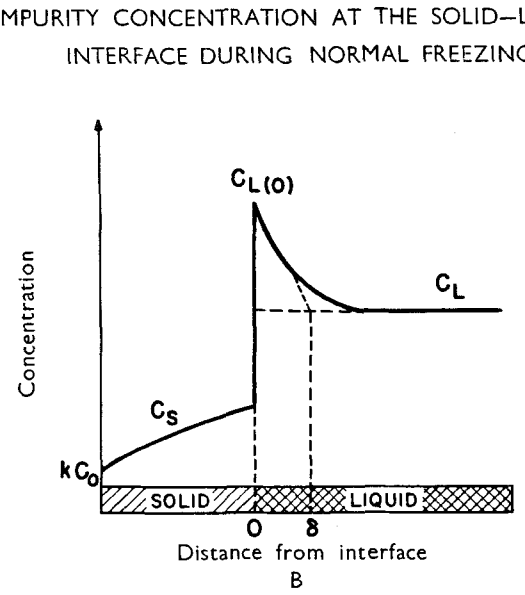


Figure 3.

system of alternating regions of high and low impurity concentration, reminiscent of the Liesegang phenomenon.[14]

The effects of constitutional supercooling were overcome by carrying out the normal freezing at low rates (<5 mm/hr) or, more effectively, by stirring the melt. A system was devised for rotation of the travelling normal freezing tube, with periodic reversal of the sense of rotation. In this way mechanical mixing was added to convective mixing, and constitutional supercooling was minimized, if not eliminated.

A plot of log (c/c_0) *vs.* log $(1-g)$ for a normally frozen 0.10 wt % solution of tetracene in anthracene, solidified at 1 mm/hr while rotating at 300 rev/min, is shown in Fig. 4. Stirred systems gave linear plots of log (c/c_0) against log $(1-g)$ for crystallizations at higher rates (Fig. 5).

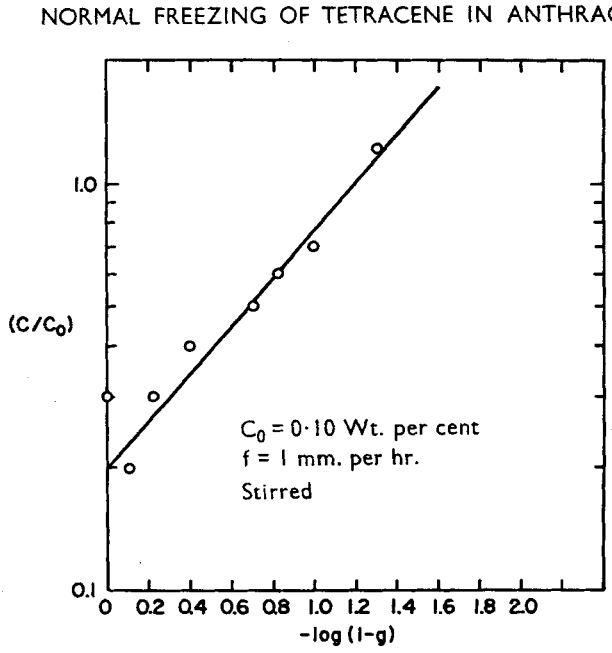


Figure 4.

Table 3 shows values of k measured for tetracene and anthraquinone in anthracene ingots that were stirred during normal freezing. Strikingly, the effectiveness of segregation at first increases with increasing f, for unknown reasons.

It is of primary interest to apply the results of the measurements of k to purification by zone melting. It might seem that values of k measured by normal freezing at $1 < f < 6$ mm/hr would not be relevant to zone melting carried out at 25 mm/hr. However, the temperature gradients applied to the liquid phase in zone

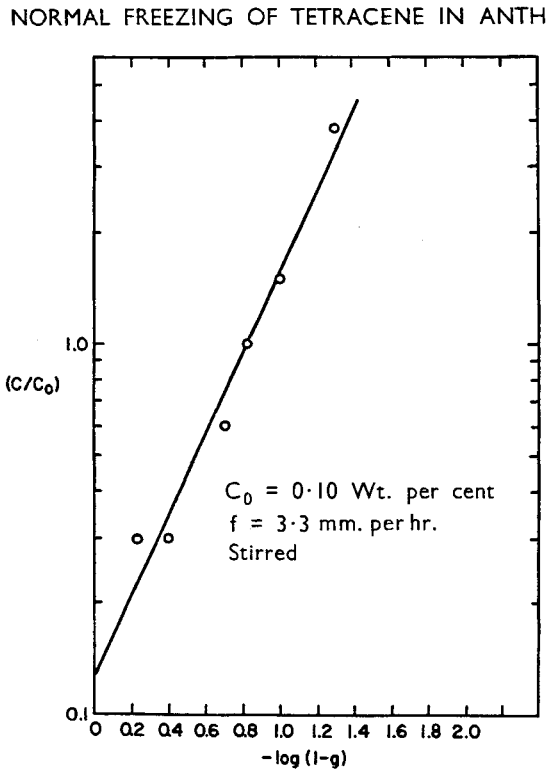


Figure 5.

TABLE 3 Effective Segregation Coefficients of Impurities in Anthracene from Normal Freezing with Stirring

Rate of crystallization, f, mm/hr	Tetracene[a]	Anthraquinone[b]
1	0.20	0.0080
2	0.07	0.0061
4	0.05	0.0058
6	0.12	

[a] $C_0 = 0.10$ wt %. [b] $C_0 = 0.017$ wt %.

melting are much greater than those applied in normal freezing. Consequently, convective mixing is much greater in zone melting and segregation is doubtless comparable with that attained in normal freezing at much lower f's. Assuming then that k measured at $f = 1$ mm/hr is applicable to evaluation of zone melting profiles, it is instructive to inquire what impurity concentrations may be achieved after some number of zone melting passes. In Table 4, C_0 is the initial concentration of the specified impurities in typical samples of commercially available natural anthracene, in mole per cent; $C_{0.50,\,10}$ is the average concentration in the purer half of an ingot after 10 passes. The values of $C_{0.50,\,10}$ were computed from published concentration profiles.[9]

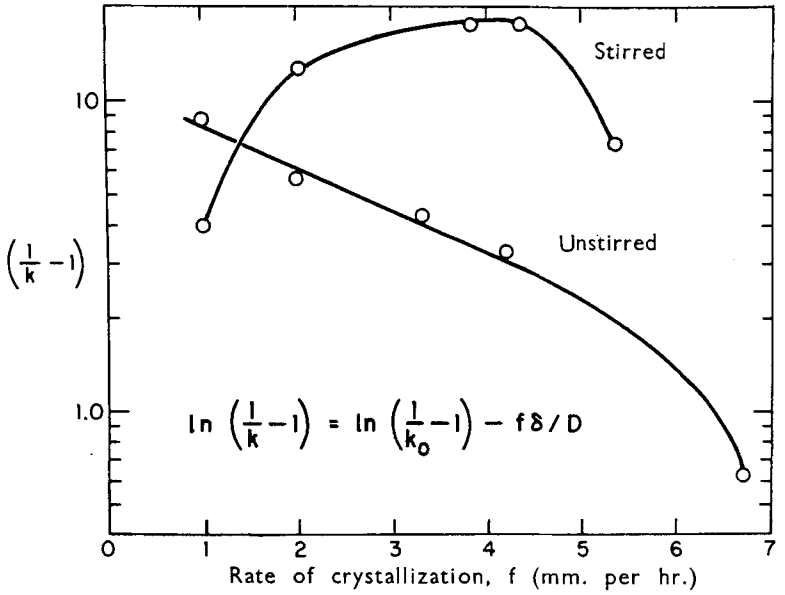
TABLE 4 Impurity Concentrations Attainable by Zone Melting

Impurity	k	C_0	$C_{0.50,\,10}$
Tetracene	0.10	5×10^{-3}	9×10^{-9}
Anthraquinone	0.02	2×10^{-1}	1×10^{-10}
Fluorene	0.2	5×10^{-2}	2×10^{-5}
Phenanthrene	0.1	5×10^{-2}	9×10^{-8}
Carbazole	0.9	1×10^{-1}	8×10^{-2}

It is evident that the concentrations of tetracene, anthraquinone, fluorene, and phenanthrene would be negligible after a simple 10-pass refinement. Carbazole must be removed by chromatography[15] or by repeated, multipass zone melting.[16] It is noteworthy that the segregation coefficient of carbazole in *purified* anthracene is less than unity. This result is not consistent with results of zone-melting crude anthracene nor with published phase diagrams of the anthracene-carbazole system.[10, 11] Assuming the correctness of both results, it may be argued that the segregation in commercial anthracene is the result of formation of a ternary (or higher-order) system involving anthracene, carbazole, and other impurities.[17]

Thickness of Layer of Diffusion-Controlled Impurity Transport

The effect of stirring was made visible by carrying out the normal freezing process with a strongly colored, added contaminant, alizarin. In the stirred system, only slight inhomogeneity was perceptible in the melt. In the unstirred system, a layer of high



Variation of segregation coefficient with rate of crystallization

Tetracene in anthracene

Figure 6.

impurity concentration could be seen after a small fraction of the molten charge had solidified. This layer attained a depth of about 5 mm.

According to the theory of Burton, Prim and Slichter[18] the thickness, δ, of the liquid layer in which impurity transport is diffusion-controlled can be calculated from the variation of k

with rate of crystallization f, if the diffusivity D of the impurity in the host is known, since

$$\log\left(\frac{1}{k}-1\right) = \log\left(\frac{1}{k_0}-1\right) - f\delta/D \qquad (2)$$

where k_0 is the equilibrium segregation coefficient.

Figure 6 shows a plot of $[(1/k)-1]$ against f for tetracene in anthracene; from the slope of the linear portion of the curve and an assumed diffusivity of 10^{-5} cm^2/sec, δ is found to be 5 mm. This value is in good agreement with the observed thickness of the interface layer in the anthracene-alizarin system.

Inorganic Contamination

A priori, it was thought that inorganic contaminants would be very rapidly segregated from anthracene by zone melting, since they would presumably be practically insoluble in both the solid and the melt. This expectation was not realized (see Table 5, Columns 1 and 2). An attempt was made to free anthracene of inorganic substances by sublimation. The product, while better than the zone-melted solid (Table 5, Column 3), still contained much inorganic material. The inorganics are of enormously lower volatility than anthracene, and yet are transferred from the gently heated surface of the sublimer to the condenser. This could mean that the metals are present as volatile organic complexes, but much more probably it indicates that the inorganics are carried to the condenser mechanically, as dust, in the stream of anthracene vapor. This suggestion explains too the failure of the inorganics to segregate or settle completely by gravity during zone melting, since such dust would doubtless be colloidally stable.

To test these ideas, mechanical removal was tried; by subliming anthracene through a layer of pure graphite, metal contamination was reduced to a lower level than was achieved by three conventional sublimations (Table 5, Column 4).

Another possibility for removal of metallic contaminants was

TABLE 5 Metal Contamination in Anthracene, in ppm

Element	(1) Top of zone-melted ingot	(2) Middle of zone-melted ingot	(3) Sublimed three times	(4) Sublimed through graphite	(5) Scavenged with phthalonitrile	(6) Scavenged with TCNQ[b]	(7) Commercial[a]
K	—	—	—	—	—	—	2–10
Ca	0.5–2	0.1–1	—	—	—	—	2–10
Cr	1–5	—	—	0.02–0.1	—	—	—
Na	—	—	—	—	—	—	2–10
Fe	5–25	—	0.2–1	0.1–0.5	0.5–2	0.2–1	2–10
Mg	0.2–2	0.05–0.2	0.1–0.5	0.05–0.2	0.2–1	0.02–0.1	0.05–0.2
Pb	0.05–0.2	—	0.05–0.2	0.02–0.1	0.1–0.5	—	0.1–0.5
Si	15–75	10–50	2–10	0.1–0.5	5–25	0.1–0.5	1–5
Mn	—	—	0.01–0.1	0.01–0.05	0.02–0.1	—	0.05–0.2
Zn	—	—	0.1–0.3	—	—	—	1–5
Cu	0.5–2	—	0.2–1	0.02–0.1	0.5–2	0.1–0.5	0.5–2
Ag	0.005–0.02	—	0.01–0.05	0.002–0.01	0.2–1	0.2–1	0.02–0.1
Al	0.5–2	0.1–1	0.1–0.5	0.02–0.1	0.2–1	0.2–1	0.2–1
Ni	0.05–0.3	—	0.01–0.1	—	—	—	—
Ti	—	—	0.05–0.2	—	0.2–1	—	—
Total	22–114	10–52	2.8–14	0.34–1.7	7–34	0.8–4	11–54

[a] Matheson, Coleman and Bell. [b] 7,7,8,8-Tetracyanoquinodimethan.

suggested by an observation made during zone melting of phthalonitrile. A sample of phthalonitrile, distilled through a column with a stainless-steel, spinning band was found to be slightly blue-green. When the solid was zone melted, a blue impurity segregated rapidly. Apparently the phthalonitrile had attacked the spinning band, with consequent formation of iron and/or chromium phthalocyanine(s). Addition of phthalonitrile to anthracene was therefore tried as a means of "scavenging" metals as phthalocyanines; chromium and iron levels were in fact reduced, but total metal contamination was still appreciable (Table 5, Column 5). A more general metal-scavenger was required, and 7,7,8,8-tetracyanoquinodimethan (TCNQ) was tried. The result was almost as favorable as that of sublimation through graphite (Table 5, Column 6).

The possibility exists that treatment with chemical scavengers may introduce organic impurities even as the inorganics are removed. This is probably not a serious problem, since the amounts of scavenger are small (about 0.1 wt %), and the scavengers differ sufficiently in molecular shape and size from anthracene to render formation of solid solutions very unlikely. The scavenger and complexes seem to be removed rapidly by zone melting.

A spectrographic analysis of a typical commercial anthracene is given in Column 7 of Table 5, for comparison with the other results.

Experimental

Zone Melting

A zone-melting tube (Fig. 7a lower section 15 mm OD × 50 cm long) was cleaned with a solution of a detergent in a dilute mixture of nitric and hydrofluoric acids,[19] then rinsed extensively with distilled water, dilute ammonia, distilled water, and finally with reagent-grade methanol. After the tube had drained dry (with its open ends protected against entry of dust by aluminum foil caps), its bottom was closed, and it was baked at 400° for 2 hr in a vacuum. The stopcock adapter b (Fig. 7) made it possible to

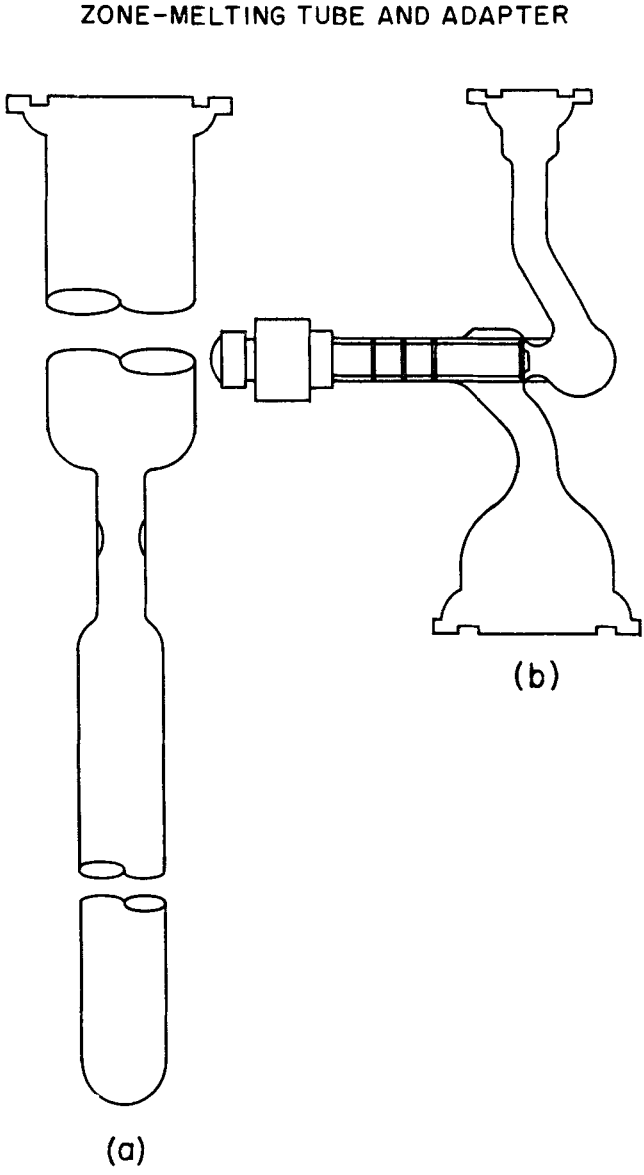


Figure 7.

remove the tube from the vacuum system, either evacuated or filled with nitrogen,† for loading in a dust-free, gloved bag.

The tube was charged with anthracene (Matheson, Coleman and Bell, AX 1590) and evacuated to 2×10^{-6} torr. The solid was melted by a cylindrical electrical heater whose temperature was controlled by a Pyr-O-Vane regulator (Minneapolis Honeywell Co.). The molten anthracene was allowed to solidify during about 0.5 hr. The tube was re-evacuated, and the constriction was heated gently with a flame to sublime away the adherent film in it. Finally, 4×10^{2} torr of nitrogen was admitted, the tube was sealed off at the constriction, and a length of 3 mm Pyrex glass rod was fused onto the tip. The rod was bent into a loop and annealed. The tube was suspended in an automatic zone melter[21] and subjected to 50 zone melting passes. The zone length was about 1/20 of the ingot length. Segment 0032/38‡ was white, and segment 3238/38 was yellow to dark brown.

Segments 3238/38 from two ingots of anthracene zone melted as above were charged into a clean tube, 9 mm OD × 45 cm long. The resulting ingot was subjected to 50 passes; segment 0025/33 was white and segment 2533/33 was brown to black.

Gradient Sublimation[12]

An effective, convenient gradient sublimer was simply fabricated as follows. A piece of aluminum pipe (30 in. long, 1.315 in. OD, 1.000 in. ID) was provided with a slot 6 in. long by 0.125 in. wide, for insertion of a thermocouple, then slipped into a combustion furnace (Hevi-Duty Type 70, 13 in. long overall, 1.25 in. diam. opening). The end of the aluminum pipe inside the furnace had been turned down to 1.250 in. diam. A coil of 0.25 in. OD copper tubing was wrapped tightly on the end of the exposed section of

† All nitrogen used in this work was freed from oxygen by passage through a tower of hot copper precipitated on kieselguhr[20] then dried by passage through Molecular Sieve, Type 5A (Fisher Scientific Co.).

‡ The first two digits give the distance in centimeters from the top of the ingot to the top of the segment, the second two digits give the distance to the bottom of the segment and the digits after the slant give the total length of the ingot.

pipe over a length of 4 in. The entire exposed section was covered with Fiberglas pipe insulation. Adapter plugs were made of Transite to center tubes of various diameters in the aluminum pipe. A thermocouple placed in the slot in the hot end of the pipe was used to actuate a Pyr-O-Vane Controller (Minneapolis Honeywell Company).

Segment 2333/33 of an ingot of twice zone-melted anthracene was placed in a porcelain boat (Coors No. 6A, 8.5 cm long) which was slipped into the end of a gradient sublimation tube 25 mm OD × 90 cm long, with a 35/25 O-ring joint. The tube was placed in the gradient sublimation heater and evacuated to 10^{-5} torr. It was heated for 1 hr at 50°, then for 1 hr at 100°, and finally for 1 hr at 150°. The furnace was cooled, and the tube removed. The boat contained a little orange material; a dense, pale-yellow sublimate started 9 cm "downstream" from the boat and extended for 17 cm, then gave way to a sparse, white sublimate that covered an additional 20 cm of the tube. The yellow sublimate showed a blue-white fluorescence in UV light (365 mμ), and the white sublimate showed a blue-violet fluorescence.

In earlier gradient sublimations, attempts to recover the sublimate by scraping failed because the thin films became charged and adhered to the glass. Solvent elution was undesirable because large amounts of solvent were required to wash the sublimate from the glass. It was found that the film of sublimate could be sublimed easily to the condenser of a modified McCarter sublimer[22] in which the condenser was provided with a drip-tip and the O-ring sample container was long enough to accommodate a segment of the gradient sublimation tube.

The gradient sublimation tube was cut into three sections, 9 to 11, 11 to 26, and 26 to 46 cm, respectively, from the sample boat. Section 1, from the hot end of the tube, was transferred to the McCarter sublimer and heated in vacuum until all the volatile solid had collected on the inner surface of the condenser cone. The sample container of the sublimer was replaced by one with a solvent well that contained 1.0 ml of purified benzene[23] that showed no impurities upon gas chromatographic analysis. The assembled

system was flushed with nitrogen. The benzene was heated gently until all the solid had been washed from the condenser. The resulting benzene solution was transferred from the well to a clean, plastic-capped vial by means of a hypodermic syringe, and the well was rinsed with about 0.2 ml of purified benzene; the rinse was added to the original solution.

The film from section 3 of the gradient sublimation tube was collected in the same way. Section 2 contained nearly pure anthracene.

Gas Chromatography

The benzene solutions of the gradient-sublimed samples were sampled for gas chromatographic analysis. The analytical system best suited to these samples was found to be Apiezon L (20%) on 60–80 mesh, acid-washed firebrick. This material was used in a 2-ft, stainless-steel column at temperatures programmed from 175° to 255° at 5.6°/min. The carrier gas was helium at 23 ml/min; thermal conductivity detection was used. The inlet pre-heater was maintained at about 230°. A chromatogram of cut 2 from the gradient sublimation is shown in Fig. 8.

In order to effect gas chromatographic separation of amounts sufficient for identification of the many peaks seen in Fig. 8, it was found necessary to inject the samples as solids. For this purpose, the sampler body A (Fig. 9) (15 mm OD, 105 mm long) was screwed onto the inlet fitting of the chromatograph (F and M Scientific Corp., Model 500); B is a Quick Vacuum Coupling (Vacuum Electronics Corp.) welded to A. Stainless steel rod C (0.1875 in. diam., 180 mm long) was provided with a milled cup D of about 150 mm^3 capacity, and a handle E.

A weighed sample (2 mg) of Cut 1 was placed in cup D and shaft C was passed through B into A. The outer nut of B was tightened to seal shaft C by means of a Viton fluoroelastomer O-ring. After the chromatographic column returned to equilibrium and a stable base-line was displayed on the recorder, handle E was pushed in completely, rotated 180°, and tapped to dump the contents of cup D into the hot inlet chamber.

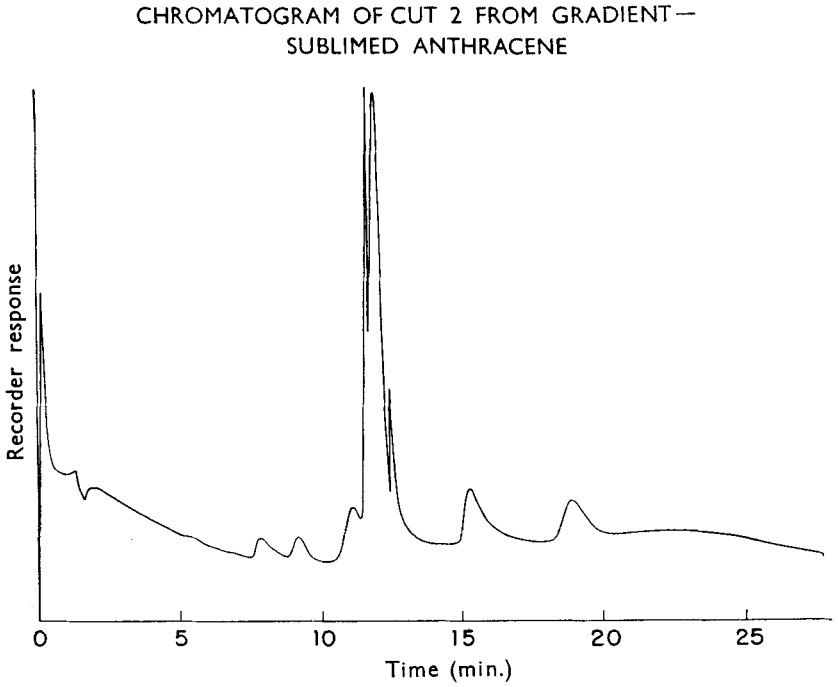


Figure 8.

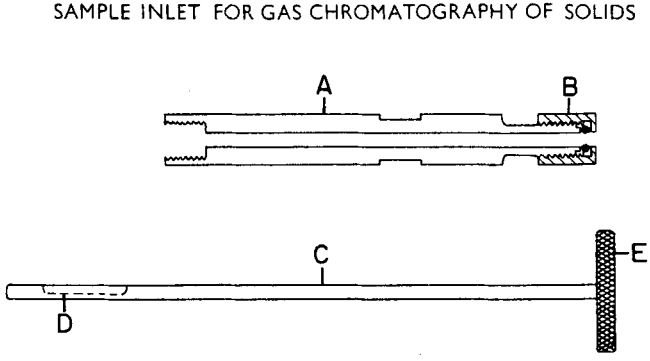


Figure 9.

To collect impurities as they emerged from the chromatograph, its outlet was modified somewhat (see Fig. 10). A stainless-steel, spherical joint B (size 12/5, inner) was welded to a threaded coupling that was then screwed into the outlet fitting. The stainless steel joint was surrounded by a heater C to prevent condensation of vapors in the outlet system.

The traps consisted of straight or U-shaped tubes attached to Pyrex glass spherical joints A (size 12/3, outer); they were used

TRAP FOR COLLECTING IMPURITIES
IN GAS CHROMATOGRAPHY

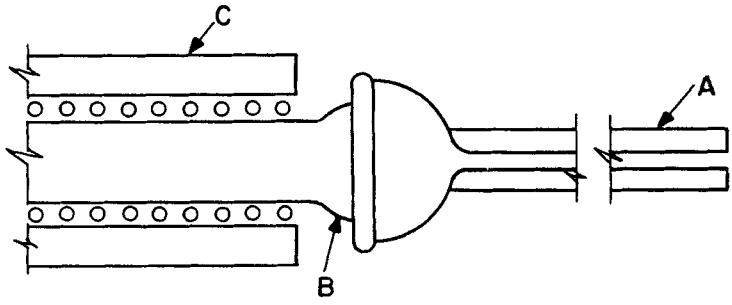


Figure 10.

empty or filled with an appropriate trapping medium. Empty tubes were used to trap impurities for UV-visible spectrophotometry. Sampling was carried out as follows: The trap was clamped horizontally, and a small wick of hardened filter paper (2 × 15 mm) moistened with 2,2,4-trimethylpentane was touched to the deposit in the trap. The wick was then suspended over a quartz optical cell of 1 cm path length and 0.8 ml capacity. It was washed with 2,2,4-trimethylpentane from a dropper, and the washings were collected directly in the cell. With a little practice it was possible to "scavenge" 5–15 μg of solid in this way; in most cases this was enough for measurement of the spectrum.

For IR spectrophotometry, the traps were packed with 10–50 mg

of potassium bromide. The potassium bromide was transferred to a micro-die for compaction;[24] IR spectra were measured on 10–50 μg of impurity.

In general it was possible to use the UV and/or IR samples for determination of molecular weight by mass spectrometry. The KBr was placed in a heated tube connected to the inlet of the spectrometer, and the sample was sublimed into the spectrometer. Alternatively, about 10 mg of ignited firebrick was added to the solution used for UV-visible spectrophotometry, and the solution was evaporated to dryness in a stream of dry, filtered nitrogen. The firebrick was then heated in the same way as KBr.

The assignments listed in Table 1 are based on equality of retention times with those of authentic samples and identity of UV and for IR spectra, along with molecular weight data from mass spectrometry.

Some of the peaks were not sharply separated by gas chromatography, and further purification was necessary. By packing a trap tube with 50–100 mg of ignited firebrick the difficulty of recovering a film of solid from the trap was obviated. The entire contents of the trap were returned to the cup of the solid sampler for re-injection into the chromatograph. The adsorbent accumulated in the inlet chamber, from which it was removed occasionally by washing with a solvent.

Determination of Effective Segregation Coefficients from Normal Freezing Data

Furnaces

The design requirements for a normal freezing furnace are essentially the same as for crystal growth.[3, 25] Two furnaces were used in this work; the first of these (F1) is shown in Fig. 11. A and B consisted of lengths of aluminum pipe of 3.5 in. outer diam. and $\frac{7}{32}$ in. wall thickness; they were wrapped with a thin layer of asbestos sheeting as electrical insulation, then with Nichrome heater wires of 58 and 110 Ω resistance, respectively. The heater coils were wound non-uniformly to provide a fairly uniform

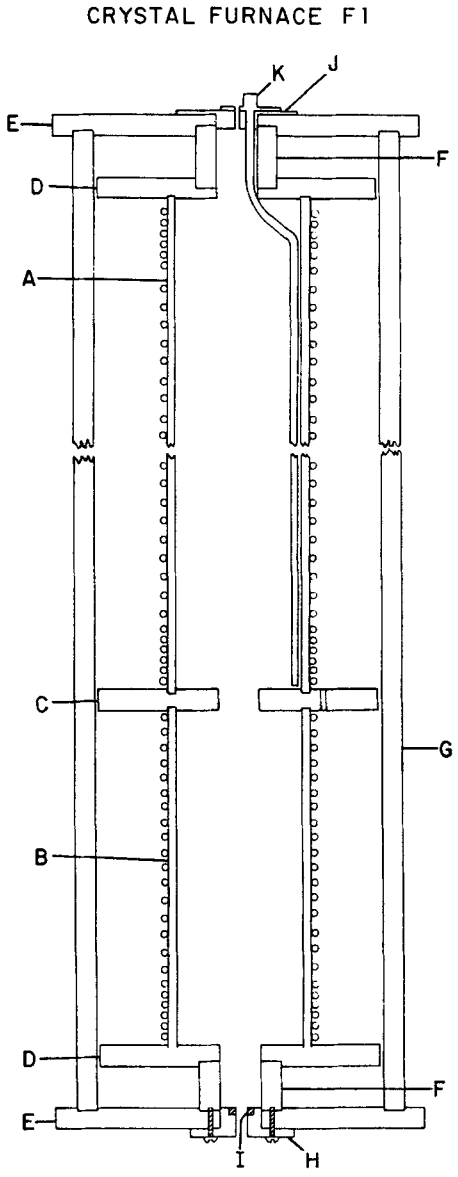


Figure 11.

temperature in each section of the furnace. The two sections were separated by a Transite baffle C, mounted in Transite discs D

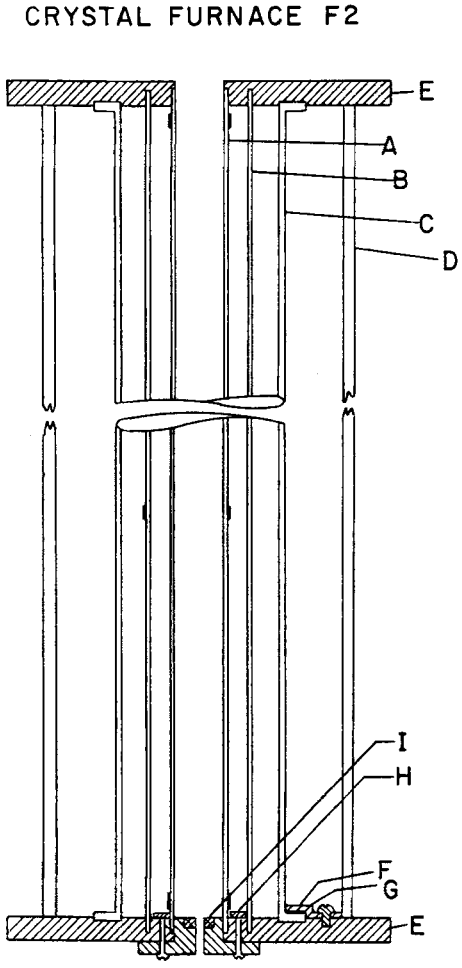


Figure 12.

which were separated from the aluminum end plates E by spacers F. The entire assembly was enclosed in a Transite pipe G; the ends and the annular spaces around A and B were filled with Fiberglas

insulation. A Phenolite plug H containing a press-fit ball bearing I was attached to the bottom of the furnace by machine screws. The top of the furnace was closed by Transite cap J which held resistance thermometer K.

Another furnace, F2, transparent over its entire length, is shown in Fig. 12. Part A is a conducting glass tube, 30 mm OD, with top, center and bottom terminal strips (Corning Glass Works); B and C are Pyrex tubes of 57 and 90 mm OD, respectively. D is a Lucite acrylic resin box that fits between Transite end plates E. The flanged ends of C were fastened to E by aluminum hold-down clamps G with rubber pads F. A steel ring H, screwed to E, allowed attachment of a Phenolite plug J that contained ball bearing I.

Temperature profiles were measured in F1 and F2 by raising thermocouples through them at 6 in/hr and recording the outputs continuously on a strip-chart recorder with a chart speed of 3 in/hr. The temperature gradients at the melting point of anthracene were 20° and 10°/cm during normal freezing in F1 and F2, respectively.

Stirring During Normal Freezing

A schematic diagram of the stirring apparatus is shown in Fig. 13. The rotation of threaded shaft A drives carriage B along guide rods C. Stirrer motor D (300 rev/min) was connected to the shaft of tube-holder E by a multi-jaw coupling F (Boston Gear Works). Shaft A was driven at zero to 0.25 rev/min by a Zero-Max variable speed reducer (Revco, Inc., Minneapolis, Minn.) which was in turn driven by a 1 rev/min synchronous motor. This arrangement gave linear travel at speeds from zero to about 18 mm/hr. To facilitate positioning of carriage B, the low-speed drive was disengaged by a change-gear mechanism that simultaneously engaged a 20 rev/min motor that drove carriage B at about 25 mm/min. The travel of carriage B was stopped at top and bottom by limit switches G.

Loading Tubes for Normal Freezing

Clean normal-freezing tubes were treated with a dilute hexane solution of a silicone fluid (Dri-Film SC-87, General Electric

PPARATUS FOR STIRRING DURING NORMAL FREEZING

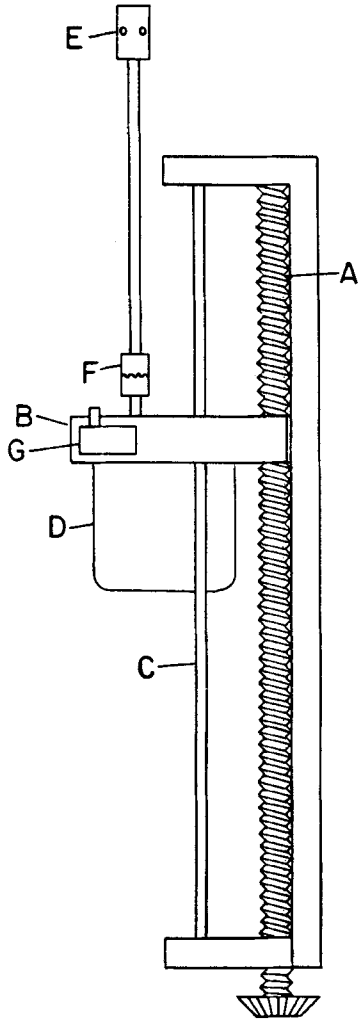
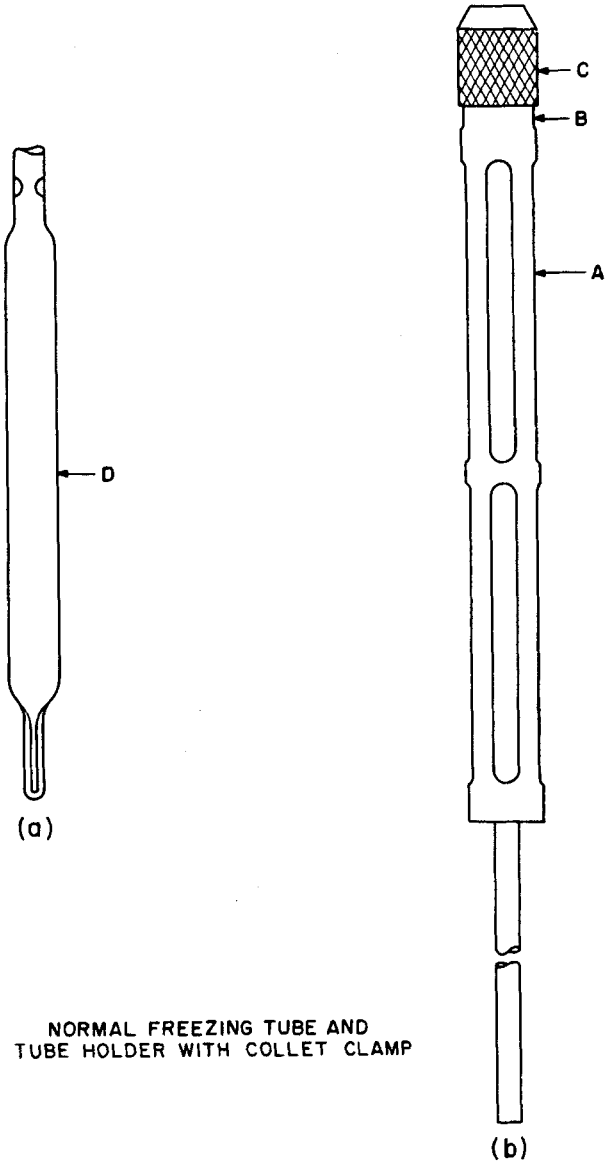


Figure 13.



NORMAL FREEZING TUBE AND
TUBE HOLDER WITH COLLET CLAMP

Figure 14.

Company, Silicone Products Department), then rinsed several times with hexane. The tubes were drained dry, evacuated, and baked for 2 hr at 400°. The silicone treatment facilitated removal of the normally frozen ingots from their tubes. The tube-charging procedure for normal freezing was essentially the same as for zone melting, except that a weighed sample of contaminant was first added to the tube and the tube was sealed off evacuated. After the tube was sealed off, its contents were melted and shaken vigorously to assure homogeneity at the start of normal freezing. Fig. 14a shows a normal freezing tube; the capillary appendage allows for some supercooling before the onset of crystallization in the body of the melt. Fig. 14b shows a tube holder; the tube is clamped in a collet at the top of the "cage" by means of a knurled, stainless-steel nut.

Normal Freezing—Without Stirring

For normal freezing without stirring the sealed tube was tied to a Fiberglas filament (1 mm diam.) that was attached to a drum on a clock motor. The tube was positioned in the lower (cooler) region of the furnace and then raised during 1 to 2 hr to melt the contents gradually. It was lowered slowly until the charge solidified. The solid was then cooled to room temperature during about two days.

Normal Freezing—With Stirring

The sealed tube was clamped carefully in a tube-holder (Figs. 13, 14b). The assembly was lowered through the furnace, and the stirrer shaft was slipped through the ball bearing whose mounting was then screwed in place in the bottom of the furnace. The upper section of coupling F (Fig. 13) was then affixed on the shaft. The tube was positioned in the same way as for normal freezing without stirring, and solidification was effected with rotation at 300 rev/min with reversal of sense of rotation every 60 sec.

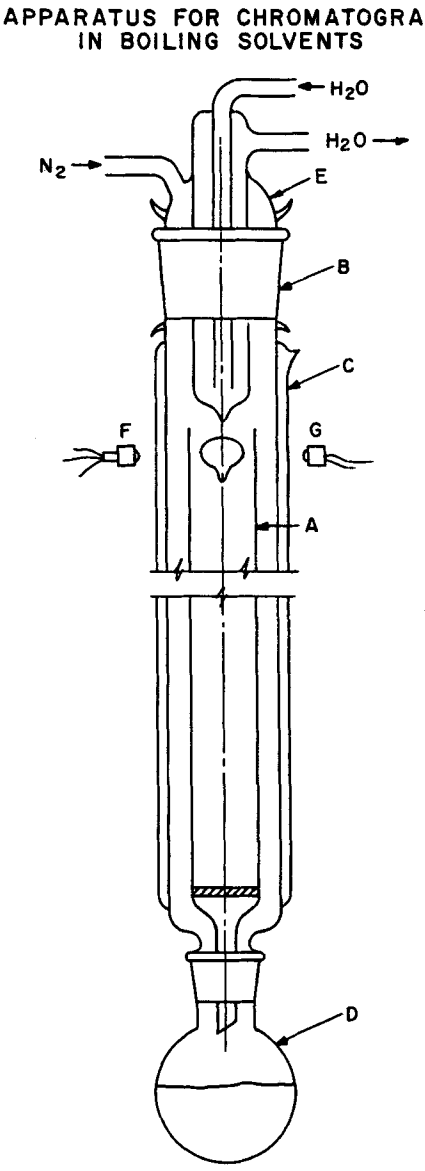


Figure 15.

Preparation of Materials for Normal Freezing

Anthracene was taken from the centers of ingots of commercial anthracene that had been chromatographed, sublimed and subjected to 50 passes in an automatic zone melter.[21] The chromatography was carried out primarily to remove materials more strongly adsorbed than anthracene on alumina, especially carbazole (which is only slightly segregated by zone melting).

A vapor-heated chromatography column[7, 26] was used. The chromatographic apparatus is shown in Fig. 15. Inner tube A (30 mm OD × 40 cm long) was packed with neutral alumina (Woelm, Activity I) to a depth of 25 cm; the column was covered with a disc of 100-mesh, stainless-steel screen, a layer of 4 mm diam. glass beads, 15 g of anthracene and a layer of glass beads, in order. A thin-walled, internally silvered, spherical Pyrex float was then placed in A, which was slipped into outer tube B; B was provided with an unsilvered, evacuated jacket C. A 500 ml flask D containing about 300 ml of hexane was attached to B, and condenser E, with a nitrogen-inlet sidearm, was inserted. The joints of the assembly were sealed with bonded Teflon tetrafluoroethylene sleeves (Ace Glass, Inc., Vineland, N.J.) to avoid the use of grease.

The hexane was heated at reflux, and extraction of the column with hot hexane was continued until the effluent was no longer fluorescent. Overflow of the column would introduce into the effluent unchromatographed material from the top of the column. To prevent this, heat applied to the flask was controlled by a liquid-level controller at the top of the column. The level detector consisted of a lamp F and a photo-diode G. As the hexane level rose, the opaque float interrupted the light beam and caused a reduction of heat input. A schematic diagram of the level controller is shown in Fig. 16.

When the effluent from A was no longer fluorescent, heating was discontinued and the column was allowed to drain for a few minutes. The hexane-filled flask was removed and replaced with a flask containing benzene. The extraction was again continued until no fluorescence was visible in the effluent. The process was repeated with acetone and methanol.

CIRCUIT OF LEVEL CONTROLLER

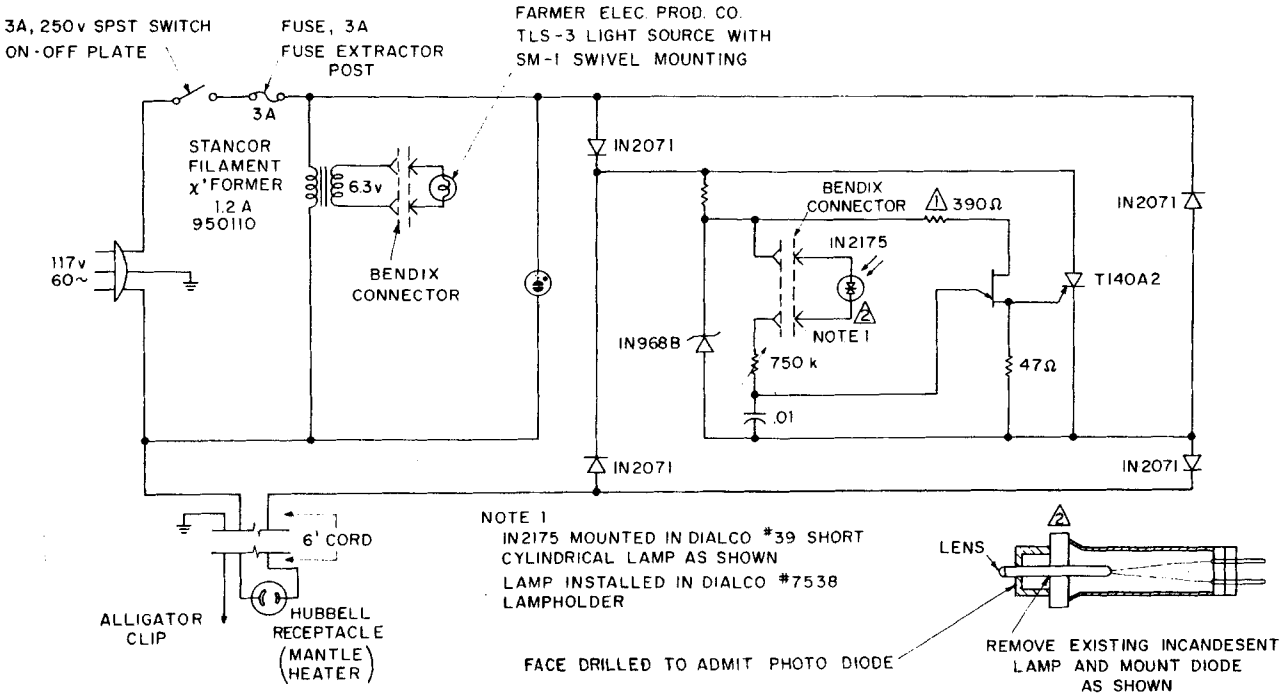


Figure 16.

The hexane eluate was evaporated, and the residue was sublimed and zone melted.

Fluorene (Eastman Organic Chemicals Dept., Eastman Kodak Company) was recrystallized twice from ethanol, sublimed in vacuum and zone melted (50 passes). The middle third of the ingot was gradient sublimed, and a pure center fraction was kept for use in normal freezing.

Carbazole (Reilly Coal Tar Company) was purified in the same way as fluorene, except that the recrystallization was omitted.

Tetracene (Rütterswerke AG, Frankfurt, Germany) was gradient sublimed, and a pure center fraction was used.

Phenanthrene-9-C^{14} (Nuclear Chicago Corp.) was diluted with phenanthrene that had been purified by the method of Bachmann,[27] then zone melted and finally gradient sublimed. The diluted material gave 1.045×10^6 decompositions/min/mg.

o-Benzoylbenzoic Acid-7-C.^{14} To 11.3 mg (0.076 mmole) of phthalic anhydride-7-C^{14} (Tracerlab, 0.67 mg/mmole) in a 5 ml flask was added 101.7 mg of phthalic anhydride and 0.60 ml of benzene. The flask was fitted with a condenser topped with a drying tube, and the benzene was frozen in an ice bath; 0.225 g (1.69 mmole) of anhydrous aluminum chloride was then added. The ice bath was removed, and the flask was heated 15 min on a steam bath. The reaction mixture was cooled in ice, then treated with 1 g of ice and 2 ml of 1.5 *N* HCl. The mixture was extracted with ether; the ethereal solution was in turn extracted twice with 0.5 ml of 10% sodium hydroxide solution. Concentrated hydrochloric acid was added slowly to the basic solution in a centrifuge tube until the pH was about 2. The centrifuged solid was washed with a little water, then dried in a vacuum desiccator to give 145 mg (84% of theory), m.p. 130–131°.

Anthraquinone-9-C.^{14} To 145 mg of *o*-benzoylbenzoic acid in a centrifuge tube was added 0.50 ml of concentrated H_2SO_4; the tube was heated gently with swirling to dissolve the acid. It was then heated 5 min at 155° ± 5°, cooled, and treated with 0.1 ml of H_2O. After addition of a further 3 ml of H_2O, the precipitate was isolated, washed with water, dilute ammonia, and water. The

anthraquinone was dried and sublimed to give 121 mg (86% of theory).

Analysis of Normally Frozen Ingots

Ingots of anthracene were easily removed in one piece from tubes that had been treated with silicone fluid. The surfaces of the ingots were covered with material that had sublimed from the upper to the lower parts of the tubes, since the former were at all times hotter than the latter. Thus, the impurity concentration at the surface was not representative of that in the interior. The surface of each ingot was therefore wiped with a soft paper tissue moistened with benzene. Each ingot was potted in a plastic matrix (Quickmount, Fulton Metallurgical Products Company, Pittsburgh, Pa.) in a boat of Teflon tetrafluoroethylene resin. Pencil marks were made defining 1 mm-thick slices of the ingot at $g = 0$, 0.2, 0.4, 0.6, 0.8, 0.9, 0.95, and 0.99, where g is the fraction of the ingot solidified. The sections were cut with a razor-saw (X-Acto Precision Tools, Inc.), and the anthracene slab was removed from its plastic matrix and analyzed.

Fluorene was determined gas chromatographically; its concentration was read from a calibration plot relating the fractional areas of the chromatogram to the known concentration of synthetic mixtures.

Carbazole was determined mass spectrometrically.

Tetracene was determined spectrophotometrically in dioxane solution from the intensity of the absorption at 473 mμ.

Phenanthrene and Anthraquinone. The contaminated anthracene samples were weighed and dissolved in dioxane in volumetric flasks; aliquots were removed for scintillation counting. Counting efficiency was determined for each sample.

Entrapment Sublimation

A Pyrex cup that fit closely in a McCarter sublimer[22] was charged with 10 g of anthracene (Matheson, Coleman and Bell); a layer of graphite (spectrographic grade, about 1 cm deep) was poured over the anthracene. The cup was slipped into the sublimer, which was

then evacuated very slowly. When the pressure was stable at about 10^{-5} torr, the sublimer was heated from room temperature to 150° during about 4 hr. Heating was continued until no more anthracene was visible in the cup. The sublimer was filled with nitrogen, removed from the vacuum system, and opened in a clean-room. The sublimate was collected with a stainless-steel spatula.

A sample of the sublimate was ashed with sulfuric acid, and the residue was scavenged with graphite for emission spectrographic analysis.

Zone Melting With Scavenging

Anthracene (Matheson, Coleman and Bell, 50 g) was charged into a Pyrex tube as described above. The solid was allowed to cool to room temperature, the tube was filled with nitrogen, and removed from the vacuum system. About 50 mg of phthalonitrile (sublimed, distilled in vacuum, zone melted) was added. The tube was re-evacuated, sealed off under 4×10^2 torr nitrogen pressure, then subjected to 50 zone melting passes. A composite sample was taken from the upper two-thirds of the tube for analysis.

The procedure with TCNQ was identical. In this case, a substantial amount of nearly black impurity was carried to the bottom of the tube during zone melting.

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