

AN INVESTIGATION OF THE STRUCTURAL PROBLEMS IN
RELATION TO SOME SYNTHETIC WAXES

by

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PUBLICATION

The Phase Behaviour of Fischer-Tropsch wax fractions under
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INTRODUCTION

Wax and wax-like substances have been defined in many ways. One reasonably extensive definition, by Hatt and Lamberton (1956) is given below :

"The term "wax" seems best used to denote a group of substances which qualitatively have certain physical properties in common. These properties are familiar ones, for in almost all countries some natural wax - beeswax, Japan wax, Chinese insect wax, the carnauba and candelilla waxes of the Americas - has been an important material in art and industry from prehistoric times.

Waxes are understood to be opaque or translucent solids, which melt without decomposition to form mobile liquids at temperatures in the region of 100°C. They differ in hardness, but are all essentially soft substances with poor mechanical strength. Most waxes can be easily shaped or kneaded at a little above ambient temperatures. In fact, the term could easily have been made to cover the whole class now named thermoplastics."

Pure n-paraffins would be too crystalline and brittle for use as waxes, whereas mixtures of n-paraffins have some valuable properties. The molecules bear such close resemblance to one another that they form mixed crystals of lowered crystallinity and the melting point is a function of the mean molecular weight. This is a desirable feature for it permits crystallinity and brittleness to be

reduced/...

reduced without a marked loss in the melting point or hardness. It also allows a mixture to simulate a pure compound very closely.

Waxes, in general, have been put to a large number of uses. They are used, for example, in candles, polishes, paper-coating, plastics, printing, matches, rust protectants and insulation. Each application requires its own appropriate range of wax properties.

CLASSIFICATION OF WAXES

Apart from the many natural waxes of plant, insect or animal origin, there exists a class of petroleum waxes which is composed of the solid non-aromatic hydrocarbons of petroleum. This latter class is subdivided into three groups :

- (1) n-Paraffin waxes comprising mainly mixtures of straight chain hydrocarbons of lower molecular weight.
- (2) Non n-paraffin waxes in the higher molecular weight range where branched-chain hydrocarbons become important.
- (3) Microcrystalline waxes where cyclic hydrocarbons with long side chains are predominant (Boeyens, 1964).

The crystallinity varies significantly among these groups, the n-paraffin waxes having a much higher degree of crystallinity than the microcrystalline waxes. This follows naturally, as branching and large cyclic groups are not easily accommodated in a regular crystal lattice.

One of the several types of synthetic waxes is a class known as the Fischer-Tropsch waxes. These waxes are very similar to the so-called paraffin waxes from petroleum, but are on the whole of higher average molecular weight. Most of the synthetic waxes are waxes only in the sense that they possess physical properties akin to the natural waxes. The synthetic waxes may be divided into many groups. A few of these are : the long-chain polymers of ethylene with OH or other end groups; halogenated hydrocarbons; hydrogenated waxes; wax esters, etc.

FISCHER-TROPSCH WAXES

Synthetic Fischer-Tropsch waxes are an important product of The South African Coal, Oil and Gas Corporation Limited (later referred to as Sasol), and have a variety of applications, some of the more significant ones being wax-paper technology, various wax blends, emulsions and polishes. Inevitably, many problems arise in their manufacture and application, and a fundamental understanding of wax properties is required for lasting solutions to these problems.

A. Fischer-Tropsch Synthesis

The Fischer Tropsch synthesis comprises essentially the reaction between carbon monoxide and hydrogen in the presence of a catalyst, yielding mainly hydrocarbons and a few oxygenated compounds (Le Roux, 1967; Rousseau, Van der Merwe and Louw, 1963). The choice of pressure, temperature and type of catalyst used has a large effect on the composition of the products formed.

Two processes are in operation at Sasol. One, the "Arge" synthesis developed in Germany, incorporates a

fixed-bed/...

fixed-bed catalyst which is in the form of pellets. The other, "Kellogg" synthesis developed in the U.S.A., has a fluidized-bed type catalyst in the form of a fine powder which is circulated through the reactor.

It is the "Arge" synthesis which provides the heavier products like oils and wax, whereas the "Kellogg" synthesis produces the bulk of the light products, mainly petrol. A more detailed description of the Fischer-Tropsch synthesis, reaction conditions, spectrum of products formed, and a brief discussion of the reaction mechanism has been given by Le Roux (1967).

B. Wax Recovery

There are four primary synthesis products obtained from the "Arge" synthesis :

- (i) Reactor wax is the heaviest product, containing a range of hydrocarbons from the high molecular weight hard wax down to small amounts of heavy Diesel oil.
- (ii) Reactor tail-gas is cooled and the hot condensate collected. It contains small amounts of hard wax, much medium wax and products within the Diesel range.
- (iii) The lightest product from the "Arge" synthesis, known as the cold condensate, contains small amounts of low-melting waxes suspended in hydrocarbons of the Diesel oil- and petrol-boiling range.
- (iv) The Rectisol condensate consists of hydrocarbons of the lower end of the petrol-boiling range, which are removed from the synthesis tail-gas by washing with cold heptane.

Hot/...

Hot and cold condensates, (ii) and (iii) are combined and distilled at atmospheric pressure to remove lighter components. The residue is added to the reactor wax (i) which is then cut into three fractions by vacuum distillation, with the following composition - C_{18} to C_{23} , C_{24} to C_{34} and greater than C_{34} .

The first cut, called "Gatsch", is not of much value and is usually cracked. The second cut is first hydrogenated, to remove traces of oxygenates and to convert unsaturated components to saturated ones. This process is followed by de-oiling the wax. After dissolution in a benzene-propanol mixture, the clear solution is cooled down in scraper coolers. The wax crystallizes out again leaving the bulk of unwanted oily material in solution. On cooling, medium wax crystallizes out first and then a smaller fraction, known as "soft wax". The third cut, called hard wax, is only hydrogenated. However, a further series of fractionations carried out on this latter cut results in many other useful waxes.

SCOPE AND AIM OF PROJECT

In molecular crystals of organic compounds, the intermolecular forces are of two weak kinds. Dipole association - including the hydrogen bond - is the stronger, and the other is the weak Van der Waals force. In paraffin waxes the Van der Waals forces are the essential attractive forces and, as these forces are nondirectional and also fall off rapidly with distance, the structure easily deforms (Hatt and Lamberton, 1956).

It/...

It has long been known that many waxes undergo a solid-solid transition similar to that observed in the pure n-paraffins. Barmby, Huston and Bostwick (1956) have shown that waxes melting below about 60°C exhibit two solid-solid transitions, whereas those melting between 60°C and 75°C have only a single transition. Waxes melting above 75°C do not have any solid-solid phase transitions. The solid phase transformation, several degrees below fusion, is accompanied by a relatively large volume change. This can cause stresses, cracks and voids in wax products which are generally undesirable.

Paraffin waxes are comprised of mainly n-paraffin hydrocarbons and are essentially crystalline masses containing variable quantities of amorphous material. The phase behaviour of the crystalline portion has a marked effect on the physical properties, particularly the density. The characteristics of the volume change with temperature and the magnitude of this change are also closely related to wax performance in many applications. One specific application depends directly on the thermal expansion of wax for the force required to operate an activating device. Of greater importance is the use of wax for numerous coating applications, particularly for paper and paperboard.

The structure and physical properties of petroleum waxes have been studied in some detail (Edwards, 1958; TAPPI, 1963). As Fischer-Tropsch waxes compete largely with the petroleum waxes, an investigation of the general phase behaviour of Sasol medium wax, which corresponds to some extent to fully refined paraffin wax from petroleum,

was/...

was undertaken. The polymorphism of the two classes was compared and also a more basic correlation of wax properties with those of the n-paraffins sought.

The behaviour of Sasol medium wax, which comprises essentially a mixture of straight chain n-paraffins containing a very small quantity of branched components, under the influence of two basic variables, temperature and pressure, was followed. In order that the results could be compared with those on the paraffinic hydrocarbons, the wax was split into a number of fractions. This also provided for the determination of the influence of molecular weight. Structural changes with temperature were followed by means of X-ray diffraction and the effect of pressure was observed with high pressure differential thermal analysis. Several other parameters were also determined and the results correlated.

A detailed survey of several structural and thermodynamic properties of the pure n-paraffins is given to provide for a comparison with the wax fraction data. The experimental procedures are then briefly described, followed by the results and subsequent discussions in the last chapter.

CHAPTER. I

Modern wax research has largely been based on relating wax quality to chemical composition of existing waxes. A more fundamental approach would be to study the physical properties of the pure components and to correlate these with wax properties.

1.1 Crystal Habit

The crystallization of n-paraffins in the "paraffin wax" range (viz. C_{20} to C_{40}) has been the subject of many studies, yet little agreement is found on many aspects of crystal growth. The three main crystal habits described are plates, needles, and an irregularly shaped habit of microscopically small crystals, commonly termed malcrystalline masses.

There are three independent processes involved in the growth of wax crystals. These are nucleation, lateral growth and crystal thickening. Each responds differently to composition changes, thermal history and other factors affecting wax crystallinity.

Clark (1951) studied the crystal types of 23 pure hydrocarbons comprising paraffinic, naphthenic and aromatic compounds crystallized at different rates both from the melt and from solutions over a wide range of temperatures. The two major factors in determining crystal habit are the rate of crystallization and the temperature difference between the melting point of the pure hydrocarbon and the cloud point (or the crystallization temperature of the solution).

The/...

The relation between crystal habit and polymorphic behaviour of long-chain paraffin hydrocarbons has been studied by Fontana (1953). The needle crystal habit originally thought characteristic of non-straight chain paraffins only, is also the natural crystal habit of the n-paraffins of the C_{25} to C_{38} range, when crystallized at temperatures above the solid state transition temperature. Fontana suggests that the nature of the paraffin needle crystal may be related to the free rotation about the long axes of the molecules which occurs in the solid above the transition point. Rhodes, Mason and Sutton (1927) claim that needles are, in fact, rolled plates. Below the transition temperature, the usual plate-like crystal forms. (Birdwell and Jessen, 1966; Chichakli and Jessen, 1967).

Consideration of the Van der Waals forces operative during crystallization of long-chain molecules indicates that the molecules prefer to line-up side-by-side like a bunch of pencils, rather than end to end, hence yielding a platy crystal habit. The plate-thickness depends on the number of monolayers stacked upon each other; however, spiral growth steps resulting from dislocations have also been mentioned as a cause of plate thickening (Dawson and Vand, 1951).

Bunn has pointed out that the shape of a crystal reflects the reciprocal unit cell and therefore crystals that possess long axes usually grow as plates.

1.2 General Configuration

Chainlike molecules tend to take up relative positions such that the chains are parallel when forming a condensed phase. The forces which keep the molecules in these

crystals/...

crystals together can be divided into two parts. One part of the cohesion can be ascribed to an interaction between the chains, the other between the atoms which form the end groups. For the normal paraffins the end groups all lie in the same plane called the end group planes. Bunn (1939) found that for chains of carbon number greater than 130 the end effects become negligible and the chains behave as if of infinite length.

n-Paraffins have been shown to lie with all the carbon atoms coplanar, to give a flat zig-zag shape with a repeat period of $2.54 \text{ \AA}$ (Shearer and Vand, 1956). This simple form can be distorted by substituents causing the carbon atoms to lie possibly on a spiral (Sakurai, 1958). One of the characteristics of the planar zig-zag chain configuration is the sub-cell structure. Basically this constitutes two CH_2 -groups. However, symmetry relations depending on the actual structure may require more CH_2 - units per sub-cell.

Even carbon number molecules from C_{22} to C_{44} , and odd carbon number molecules from C_9 through to approximately C_{43} , show a solid-solid transition, with a latent heat, several degrees below the melting temperature.

Above the transition temperature the molecules are considered as rotating about their long axes and this rotational phase is designated by α . Below the transition point the molecules stop rotating and settle to fixed positions in an orthorhombic lattice

which/...

which may further transform slowly to a more stable structure. The non-rotating phase is designated by β .

1.3 Phase behaviour of the n-paraffins

Crystals of paraffin chain molecules are known to have a large variety of polymorphic forms. The forms depend upon the temperature, the number of carbon atoms and the purity (Piper et al, 1931).

Many different phase notation systems are found in the literature. Broadhurst (1962) has adequately correlated several previous ones and introduces his own notation for the known stable modifications. These are shown in table 1.

TABLE I

	NOTATION
<u>Hexagonal</u> Chains are perpendicular to the end group planes. Molecules rotate about long-chain axes.	α_H
<u>Orthorhombic</u> Chains are perpendicular to the end group planes. Rotation is greatly restricted. Sub-cell is orthorhombic.	β_0
<u>Triclinic</u> Chains make an angle of about 73° with the end group planes. Rotation is very greatly restricted. Sub-cell is triclinic.	β_T
<u>Monoclinic</u> Chains make an angle of about 61° with the end group planes. Rotation is very greatly restricted. Sub-cell is orthorhombic.	β_M

A correlation between the number of carbon atoms comprising an n-paraffin chain and the respective melting and transition temperatures shown in figure 1, reveals the relationship amongst the different phases listed in table 1.

Hoffman and Decker (1953) discuss three types of phase changes in paraffinic compounds:

- (a) the thermodynamically reversible rotational transitions between α_H and β type phases which take place just below the freezing point;
- (b) the slow irreversible $\alpha_H - \beta_M$ and $\beta_0 - \beta_T$ transformations which take place on prolonged storage at constant temperature; and
- (c) the λ -transitions which extend well below the freezing or rotational transition points.

The rotational transitions are of the first order and the entropy of transition is shown to be independent of chain length between 22 and 30 carbon atoms.

Broadhurst (1962) discusses the anomalous double solid-solid transition reported in n-C₃₆H₇₄. The double transition is interpreted as $\beta_M - \beta_0$ and $\beta_0 - \alpha_H$ on increasing the temperature. Extrapolation of the melting and transition temperatures for the even n-paraffins (see Figure 1) indicates that a double transition should occur in all even paraffins from C₃₄ to C₄₄ and that the longer even paraffins should be subject to a single solid-solid $\beta_M - \beta_0$ transition. The fact that the $\beta_M - \beta_0$ transition, if real, is so seldom observed is probably due to the known stabilizing influence which even small quantities of impurities impose on the orthorhombic- β_0 phase/...

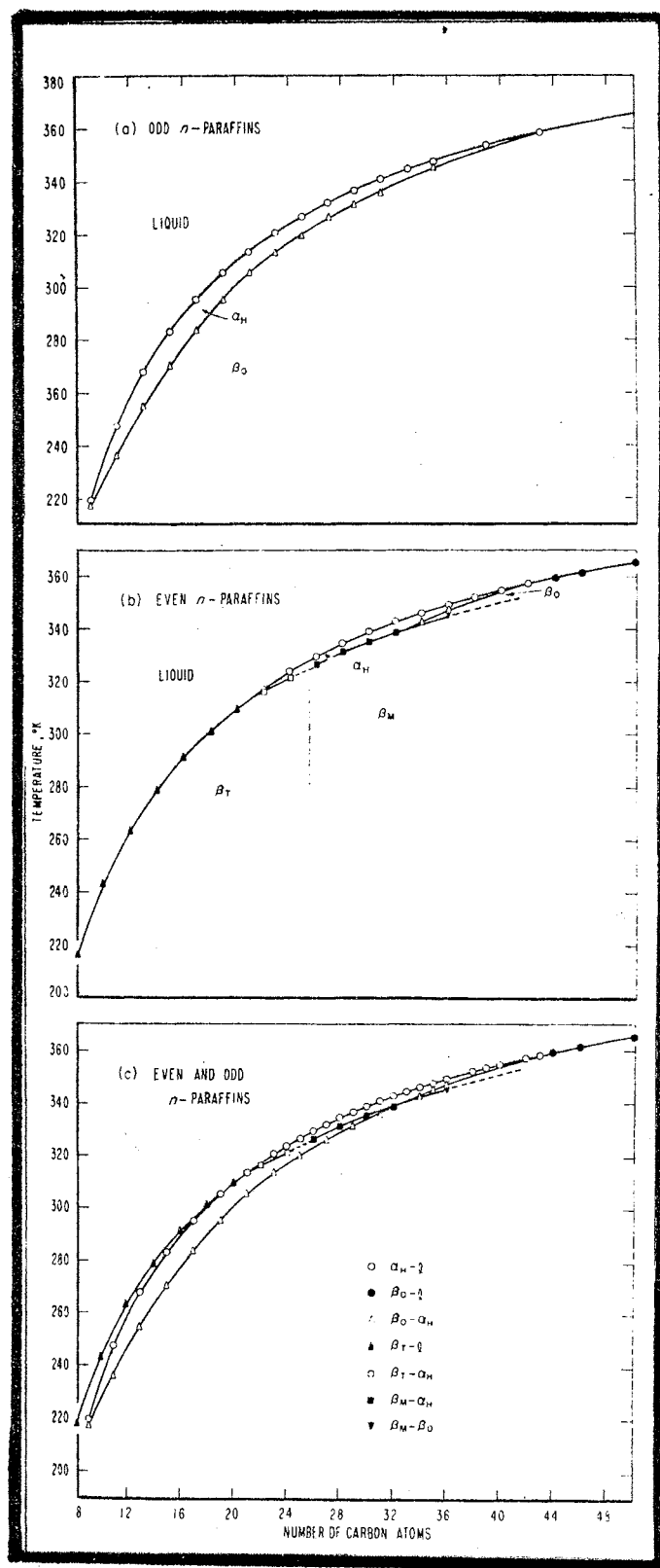


FIGURE 1

Experimental melting and transition temperatures for the *n*-paraffins containing from 8 to 50 carbon atoms per molecule (Broadhurst, 1962).

*Perhaps "perpendicular" (with respect to the packing planes) would be better than "vertical".

phase of the longer paraffins and also the kinetic difficulties which would appear to be associated with the mutual tilting of a large number of long, densely packed chains (Broadhurst, 1962).

For the hydrocarbons C_{18} through to C_{24} , some confusion exists as to whether a first-order phase transition does occur. Kitaigorodskii, Mnyukh and Nechitailo (1959) claim that for very pure C_{18} and C_{20} no solid-solid phase transition is observed. In some early work, Müller (1932) found that C_{21} and C_{23} showed two forms, ~~but~~ the transformation of one to the other being continuous and not abrupt as is the case for C_{24} through to about C_{44} .

Hoffman (1952) has made an interesting suggestion on the n-paraffins in the C_{18} to C_{24} range. Often broadening of the melting and transition points are observed for the above range. A possible reason for this is that a transformation of an entirely different character from that due to molecular rotation may interfere with the measurements. This transformation is between the vertical and tilted packing arrangements of long chain hydrocarbons. Compounds which exceed a chain length of 24 carbon atoms usually remain in the vertical or near vertical configuration in the solid state, and only vertical phases undergo rotational transitions. In the even numbered molecules the vertical form slowly converts to the tilted form, which results in a non-equilibrium mixture of the two forms. This often leads to the observation of unsharp melting and transition processes.

From studies on the growth features on crystals

of/...

of long chain compounds, another type of polymorphism known as polytypism was observed. Polytypism can be regarded as a one-dimensional polymorphism. Amelinckx (1956) studied the packing possibilities of the monolayers for the monoclinic form of $n\text{-C}_{34}\text{H}_{70}$. The results indicate that at least seven separate polytypic forms are possible.

Traces of impurities affect not only the magnitude of the latent heat, but may also change the character of the phase change. In some cases impurities seem capable of altering a first-order transformation into one of second order. Obviously the kinetics of the transition will also be influenced. Even at a fixed temperature, different forms of one compound sometimes appear by changing the method of crystallization. Teare (1959) has described his work on $\text{C}_{36}\text{H}_{74}$ where monoclinic crystals were obtained by crystallization from benzene while the orthorhombic form was usually obtained from petroleum ether.

1.4 Structure of the n-Paraffins

Work on the structural elucidation of the n-paraffins and related compounds has been in progress over the past fifty years. However, a lack of appreciation of the effect of impurities, mainly neighbouring homologues, has resulted in poor agreement in published work. A useful summary of the structural position at the present time is given by McClure (1968) and is presented in table 2.

TABLE /...

TABLE . 2

FORM	Odd n-Paraffins	Even n-Paraffins		
	$>C_9$	$C_{18} - C_{24}$	C_{26}	$C_{28} - C_{40}$
Stable	Ortho-	Triclinic	Triclinic	Monoclinic
Modification	rhombic		or	
Modification			Monoclinic	
a few de-				
grees below	Hexagonal	Hexagonal	Hexagonal	Hexagonal
the melting		?		
point				

1.4.1 Effect of Impurities

A general effect of impurities is to stabilize the vertical α_H or β_0 structures, presumably by removing rotational constraints and by interfering with the orderly end-group packing necessary in the tilted β_T and β_M structures. An excellent example of the effect of a small trace of impurity is furnished by the work on hexatriacontane, $C_{36}H_{74}$. The first analysis by Vand (1953) gave an orthorhombic form, whereas a later determination on recrystallized material, from the same initial batch, by Shearer and Vand (1956) showed the crystals belonged to the monoclinic system.

The importance of very highly purified compounds has been clearly demonstrated by the work of Smith (referred to by McClure, 1968) on mixtures

of/...

of paraffins in which he showed that small amounts of impurities were sufficient to cause a transformation from (for even numbered n-paraffins) either a monoclinic or a triclinic ~~pure~~ structure $\sqrt{}$ to an orthorhombic one. Furthermore, if the difference in chain length between the paraffin and its impurity exceeded four carbons, phase separation occurred.

1.4.2 The Odd n-Paraffins

The first complete structural analysis on an n-paraffin was undertaken by Müller (1928) on a single crystal of the normal hydrocarbon, $C_{29}H_{60}$. X-ray examination led to a rectangular prism-shaped unit cell, containing four molecules and belonging to the orthorhombic space group Pnam. The CH_2 -groups of the chain molecule lie equally spaced on two parallel rows, the lines between successive centres thus forming a zig-zag. Considering the xy section, there is a paraffin chain in the centre of the cell with four other chains at each corner, a quarter of each being assigned to that unit cell. To accommodate four molecules in the unit cell, two chains are placed end to end at each of the above positions with a gap of about $3\overset{\circ}{A}$ between the end groups. The distance of nearest approach between two centres on two neighbouring molecules is about $3.7\overset{\circ}{A}$. All the molecular chains are vertical with respect to the basal plane of the rectangular prism.

Smith's (1953) analysis of the same compound many years later, led to the orthorhombic space/...

space group Pbcm and he attributed the discrepancy to the presence of ^{traces of} ~~slight~~ impurities in Müller's crystals. The above orthorhombic form was studied in detail by Smith (1953) who used a single crystal of $n\text{-C}_{23}\text{H}_{48}$. He found the chains to line up in a quasihexagonal array like a bunch of pencils, with the ends perfectly aligned. This permits the length of the chains to be measured from the (00ℓ) spacings. The odd numbered members in the range C_{21} to C_{29} were all shown to be orthorhombic, belonging to the space group Pbcm (D_{2h}^{11}). In this range the $(h00)$ and $(0k0)$ spacings remained constant.

1.4.3 The Even n-Paraffins

Ohlberg (1959) discusses the stable crystal structures of the even numbered n-paraffins ranging from C_{20} through to C_{36} .

Several polymorphic forms for the even n-paraffins have been reported (McCrone, 1954). The three most common phases noted were originally designated types A, B and C by Müller (1930). These are distinguished by their different long-spacings and correspond to orthorhombic, triclinic and monoclinic crystal systems, respectively. Incubation for three years at 37.5°C permitted the characterization of the stable crystalline modification for each compound and substantiated the purity of their samples as well. This was achieved by intermittently examining the stored samples with an x-ray diffractometer. At the end of six months the existence of more than one phase could still be detected in each sample. At the end of three years each sample exhibited/...

exhibited the diffraction pattern of a single phase, characteristic of a high purity material.

Correlation of the long-spacing with carbon number for the series of compounds examined, shows that the points for different forms lie on separate straight lines. Besides the three common forms they detected another, D, which is metastable.

The stable form of the even n-paraffins is either monoclinic or triclinic, depending on the number of carbon atoms in the particular n-paraffin. On cooling the orthorhombic form first appears below the transition temperature, but as this form is unstable for the pure even n-paraffins, transformation to the triclinic or monoclinic structure takes place. An important parameter differentiating these forms is the angle of tilt, $\bar{\beta}$, defined as that angle which the n-paraffin chain makes with the basal plane. Since the change in the angle of tilt accompanies a change in the number of CH_2 -groups in the chain, it must be a change in the Van der Waals forces which is responsible for the variation of the abovementioned angle.

The additivity of the Van der Waals forces between CH_2 -groups on neighbouring chains for odd n-paraffins is described by Vand and De Boer (1947). For these compounds, the additivity results in a decrease in the cross-sectional area of the chain with an increase in chain length. Ohlberg's (1959) results show that the additivity for even n-paraffins causes a decrease in the angle of tilt and that this angle does not change continuously with chain length. Thus it is suggested by Ohlberg that energy barriers could be correlated with angles of tilt, and this probably accounts for the

sudden/...

sudden change in structure from triclinic to monoclinic at C_{26} for the even paraffin series.

1.4.4 A Theoretical Geometric Approach

An interesting approach is the deduction of possible structures for the normal alkanes from the molecular shape (Kitaigorodskii and Mnyukh, 1959).

The concept that organic crystals are constructed of closest packed molecules, the forms of which are described with the aid of universal intermolecular radii, was expressed as early as 1945.

For the n-paraffins the above concept is seen to be sufficient for the theoretical analysis of the regularity of the packing of the molecules. It has been shown that crystals of n-paraffins are made up by closest packing of layers of molecules. One characteristic of the layer is its sub-cell, which refers to the CH_2 -sub-cell structure. The naturally occurring packings are found amongst those indicated by geometrical analysis, but other geometrically possible structures may exist under other thermodynamic conditions. This deduction explains the existing polymorphic forms, predicts other modifications as possible and ultimately enables one to establish reliable empirical rules relating the changes in packing type to the rise or fall in energy or entropy (Kitaigorodskii, 1955).

Three types of sub-cells are possible for n-paraffins - triclinic, monoclinic and orthorhombic. From the sub-cells, cells are defined, built upon the repeat vectors of the methylene groups of layer molecules. One

of/...

of these vectors is always directed along the chains of the molecules and is of length $2.54\text{\AA}$. Each type of layer may be oblique or ~~straight~~ perpendicular and there are several types of oblique layers. Again the important parameter of the oblique layer is ~~its angle or slope,~~ the angle of tilt of the molecules relative β . As a result of ~~mutual~~ the perpendicular displacement in the laying down of ~~straight~~ layers, it is possible to obtain orthorhombic, monoclinic and triclinic structures. Only the most densely packed of these may be realized in nature. Subsequent analysis has shown that for the most densely-packed orthorhombic form only two space groups are possible, viz. Pbcm and Pnam.

1.5 Effect of Temperature on Structure

When normal paraffins crystallize from the melt, the molecules arrange themselves in the hexagonal lattice. Under these conditions the molecules are rotating about their long axes and fill almost cylindrical space. This modification is easily recognised by x-ray examination since the prominent (110) and (200) reflections of the ^{orthorhombic} paraffin structure coincide in this case (Boeyens, 1964). On cooling through the solid-solid transition point, from the hexagonal structure, the molecules stop rotating and settle in fixed positions in an orthorhombic lattice. On cooling, tilting occurs in the even n-paraffins, giving rise to the observed triclinic or monoclinic lattice. The effect of the transition is for the molecules to move closer together whereby the a-dimension decreases by almost 10% from $8.24\text{\AA}$ to $7.45\text{\AA}$ while the b-dimension increases from $4.76\text{\AA}$ to $4.97\text{\AA}$ (the d_{110} and d_{200} are no longer identical). This contraction causes the crystal

to pull apart and sometimes fragment (Edwards, 1958). As this can cause visible voids in the waxes, known as mottling, it is not commercially desirable.

1.6 Nature of the Phase Behaviour in Paraffinic Materials

The nature of the solid-solid phase change has been the subject of considerable study (Andrew, 1950; Hoffman and Smyth, 1950; Hoffman, 1952; Al-Mahdi and Ubbelohde, 1953; Hoffman and Decker, 1953; Aranow, Witten and Andrews, 1958; and McClure, 1968).

Müller (1932) first made the suggestion, based on x-ray data, that paraffin molecules ^{above} ~~at~~ some transition temperature, T_t , were in a state of hindered rotation. Much work since has served to confirm Müller's original idea.

A number of attempts have been made to explain this rotational transition theoretically. Various authors have calculated the thermodynamic properties of the transition in terms of models for a system of co-operatively rotating rigid rods. These models are of the order-disorder type and difficult to analyse in terms of their fundamental assumptions.

Hoffman (1952) assumed that the potential energy barrier hindering the rotation of chain molecules about their long axes in the solid state has one deep minimum and Ω other minima with a potential energy ∇ above that of the deeper well. Molecular models suggest that Ω should be between 8 and 18.

The high entropy of fusion of long-chain hydrocarbons was measured by Aranow, Witten and Andrews

1958). /...

(1958). They attributed these high entropies of fusion to the onset at melting of freedom of the molecule to undergo hindered rotation about each carbon-to-carbon bond. The entropy of fusion of long-chain paraffins increased by a factor very close to $R \ln 3$ for each additional CH_2 -group added to the chain. For the even paraffins the theory checks well, but deviations occur for the odd paraffins. However, if the entropy of the solid-solid transition, which occurs in these compounds, is added to the entropy of fusion good agreement with the theory is observed. Lately, McClure (1968) has described the nature of the rotational phase transition in paraffin crystals. He attempts to calculate the change in lattice energy accompanying the rotational phase transition. This is based on the assumption that the change in lattice energy corresponding to the discontinuous change in the crystal structure may be approximated by the difference in the theoretical lattice potential energies of the crystal before and after the transition has occurred. His results indicate that the change in lattice energy is of the same order as the experimental heat of transition.

The construction of a proper ~~co-operative~~ law which includes co-operative effects between all structural changes as well as between molecules undergoing a particular co-operative change is needed. Therefore, cognizance should be taken of the fact that the onset of rotation and the discontinuous change in structure are not independent, but rather in themselves co-operative.

1.7 Effect of Pressure on the Phase Behaviour

The property of polymorphism under high pressure inherent in n-paraffins and related substances, is one of the aspects of this investigation. Study of fusion curves may give some better understanding of the melting process, as well as yield indications of any polymorphic phase transitions that exist in the crystalline substance.

Previous work on ^{P-T} fusion curves is described by Dudley (1960) and some common characteristics appear. The curves exhibit a universal direction of curvature, being concave towards the pressure axis. It is generally found that the fusion temperature rises with increasing pressure, corresponding to the fact that the liquid phase has a larger volume than the solid. For all normal curves (positive slope) the curvature decreases at high pressures. The volume change on fusion for most curves was found to decrease in magnitude with increasing pressure, the rate of decrease itself becoming less at higher pressures. Hence ΔV against P is concave towards the pressure axis.

At an early stage Simon became interested in this field and approached it by using methods of low temperature physics. He studied empirically the results of Tammann and Bridgman on a range of inorganic substances and developed, more or less by analogy with the Van der Waals vapour pressure formula, the following equation:

$$\log (P + a) = c \log T + b$$

where T is the melting temperature at pressure P and a, b, and c are constants dependent on the

material/...

material (Simon and Glatzel, 1929).

The constant b is usually evaluated by defining the temperature T_0 as that at which the pressure $P = 0$. Actually b was first evaluated in terms of the triple point pressure. However, the triple point pressure is generally only a few tenths of an atmosphere, and the fusion curve is considered over a range of thousands of atmospheres, so no appreciable error is introduced by letting T_0 be the temperature at which the curve intercepts the temperature axis, i.e. $P = 0$.

The equation may be re-arranged (Babb, 1963) :

$$P/a = (T/T_0)^c - 1$$

The constant ' a ' has been interpreted as the "internal pressure". Every solid body is supposedly subjected to a powerful internal pressure resulting from the interatomic forces that hold the crystal lattice together. The total pressure was to be the sum of the internal and external pressures, $(P + a)$. From the equation it can be seen that ' a ' could be regarded as the negative pressure under which the substance would melt at a temperature of absolute zero.

By calling P/a the reduced pressure π and expressing T/T_0 as the reduced temperature, τ , the Simon equation becomes :

$$\pi = \tau^c - 1$$

which could be considered as a law of corresponding states/...

states, if c were constant for all substances concerned. This is almost the case for certain classes of substances (Dudley, 1960).

There does not exist much work on hydrocarbon systems at elevated pressures. That which has appeared shows that the transitions observable at atmospheric pressure disappear rapidly as the pressure is increased. No high-pressure phases for paraffin systems have been noted, but for the possible high-pressure phase detected in this work (Stokhuyzen and Pistorius, 1969).

Cuttler et al. (1958) have studied the compression of several high molecular weight hydrocarbons, a few being *n*-paraffins, to a pressure of 10 kilobars. They found that compressibility is strongly dependent on molecular structure, and that the pressure-volume isotherms could be described by the Tait equation:

$$V_0 - V = C \log (1 + P/B)$$

or, for pressures above a certain minimum, whose value depends on the compound, by the Hudleston equation:

$$\log \left[V^{2/3} P / (V_0^{1/3} - V^{1/3}) \right] = A + B (V_0^{1/3} - V^{1/3})$$

where A , B and C are constants, V_0 is the specific volume at atmospheric pressure and V the specific volume at pressure.

Nelson, Webb and Dixon (1960) examined the phase behaviour of a series of *n*-paraffins to 10 kilobars. The heaviest, $n\text{-C}_{24}\text{H}_{50}$, showed the presence of a solid-solid transition till only about a kilobar. They concluded that the melting curves of pure $n\text{-C}_9$, $n\text{-C}_{12}$,

$n\text{-C}_{13}/\dots$

$n\text{-C}_{13}$ and $n\text{-C}_{24}$ could not be satisfactorily fitted by the Simon equation, while that of $n\text{-C}_{18}$ could.

An investigation of the lattice parameters of pure $n\text{-C}_{30}\text{H}_{62}$ and $n\text{-C}_{32}\text{H}_{64}$ at high pressures by Kabalkina (1959) appeared to reveal a solid-phase transition at 7.3 kilobars for both substances. It appears, however, that the measurements have been misinterpreted. Kabalkina's figure shows a pressure-induced phase transition to a less dense state. This is thermodynamically impossible.

CHAPTER II2.1 Materials and their Characterisation2.1.1 Materials

Sasol medium wax derived from the Fischer-Tropsch synthesis described earlier (see introduction) comprises part of the hydrogenated second distillation cut of crude reactor wax from the 'Arge' process. The wax is white in colour, homogeneous in composition and relatively soft, giving a penetration* of ~ 18 at 25°C (Stokhuyzen, 1966).

It is essentially made up of n-paraffin chains which are saturated and vary in length. X-ray powder diffraction yielding an average chain length of $39.5\text{\AA}$ and an average number molecular weight of 420 ± 25 , which is determined ebullioscopically, was found (see Appendix I).

As the wax has been de-oiled, the iso-paraffin content is very low. A Debye-Sherrer diffraction photograph (Plate 1), readily shows that the wax exhibits a high degree of crystallinity. A method (Le Roux, 1969a), based on the difference in infrared absorption of the amorphous and crystalline phases, shows a crystallinity of over 80%.

The range of composition in medium wax is rather broad. This has the effect of broadening out many properties/...

* The penetration of a wax is the depth, in tenths of a millimeter, to which a standard needle penetrates into the wax under defined conditions (ASTM Designation : D 1321 - 55T p*760, 1955).



27a.

PLATE 1.

Debye-Scherrer diffraction pattern,
(filtered cobalt radiation).

properties, like transition phenomena, and also obscuring others. The wax was split into five fractions under vacuum distillation in order to relate its properties more closely to the n-paraffins. By this means the structural origins of the properties might be more readily ascertained. The temperature ranges and percentage of each fraction collected are shown in table 3. These temperatures are empirically corrected to a pressure of 760 mmHg, using a nomogram constructed by United Oil Products.

TABLE 3

FRACTION	LIMITS OF DISTILLATION (°C)	WEIGHT % COLLECTED
1	<405	5.3
2	405 - 430	31.9
3	430 - 455	24.3
4	455 - 480	25.1
5	>480	13.4

2.1.2 Characterisation

Several basic parameters have been determined to achieve a more complete characterisation.

2.1.2.1 Molecular Weight

The common ebullioscopic technique, which is based upon the elevation of the boiling point of a solvent by a non-volatile solute,

was/...

was used. Kennedy et al, (1959) made a thorough study of the method, particularly the effect of different solvents on polar and nonpolar materials, and claim under optimum conditions an average value to within 2.5%.

After the apparatus has been calibrated using a series of pure hydrocarbons of known molecular weight and the ebullioscopic constant determined, the apparent molecular weight is calculated from a series of concentrations of the unknown. Toluene was used in place of Benzene because of its higher boiling point. Three determinations were carried out on each fraction and their mean values are shown in table 4. However, the nature of the system and experimental difficulties encountered resulted in lower accuracies than 2.5%. Probably the error ranges between about 5% for the low molecular weight fractions and about 10% for the highest molecular weight fraction. For details on the construction of the basic apparatus, the reader is referred to Van Nes and Van Weston (1951).

2.1.2.2 Density

As part of the structural investigation of the wax fractions, accurate density values are needed. A number of attempts were made to obtain reproducible results, but these were unsuccessful. The main cause of this difficulty was the inclusion of air bubbles. The samples have cylindrical forms, obtained by pouring the molten wax into a glass tube about 3 mm.

in/...

in diameter and 25 mm. long. Generally air bubbles form along the axis of the cylindrical sample. However, cutting the sample lengthwise along its centre, eliminates this. To regain smooth surfaces, the wax pieces were warmed till they just began to melt and were then allowed to cool again. These wax pieces are easily inserted into a standard specific gravity bottle. Usually a wetting agent, in this case Triton X, is used to reduce the adherence of air bubbles to the surface of the wax.

The determinations were carried out in triplicate in a constant temperature waterbath at 25°C, applying the standard pycnometric method (Stokhuyzen, 1967). Mean values are tabulated in table 4.

TABLE 4

FRACTION	EBULLIOSCOPIC MOLECULAR WEIGHT	DENSITY AT 25°C g/ml
1	366	0.882
2	384	0.910
3	398	0.919
4	451	0.926
5	514	0.931
Error	± 30	± 0.002

2.1.2.3 Gas Chromatography

The compositional distribution of each fraction was determined by gas chromatographic analysis. Ludwig (1965) resolved the hydrocarbon components of four

microcrystalline/...

microcrystalline waxes in the range C_{25} to C_{68} on dual 2-foot columns packed with a stationary phase, SE-52, on Chromosorb G.

A similar method was employed by the Analytical Research Group at Sasol on the medium wax fractions. There were only a few minor changes. Xylene replaced iso-octane as a solvent and this avoided having to heat the syringe for sample introduction. Also the concentration of wax in solvent (5 to 15%) used, was lower than in Ludwig's case. The analysis was carried out on a Microtek G.C. 2500 - R II apparatus.

The peaks on the chromatogram are identified by mixing the given wax fraction with a pure n-paraffin within the probable range of composition. In each case one of the peaks increased strongly in intensity. The percent by weight of a given component in the homologous series, was taken as the ratio of its peak area to the summation of the areas of all the peaks. Relative response factors for each component have not been included in the calculation, but are not expected to be very different. The essential results are given in table 5.

TABLE 5

FRACTION	RANGE OF COMPONENTS	MAIN COMPONENTS i.e. $\geq 5\%$ (WEIGHT %)	MINOR COMPONENTS $\leq 5\%$ (WEIGHT %)	AVERAGE CARBON NUMBER
1	$C_{15} - C_{31}$	$C_{21} - C_{26}$	11.5	23.0
2	$C_{20} - C_{31}$	$C_{23} - C_{28}$	5.9	25.0
3	$C_{23} - C_{34}$	$C_{26} - C_{31}$	6.7	28.4
4	$C_{27} - C_{36}$	$C_{29} - C_{34}$	7.5	30.5
5	$C_{31} - C_{39}$	$C_{33} - C_{37}$	6.3	34.4

The gas chromatograms of the wax fractions are shown in figures 2a to 2e.

2.2 X-Ray Analysis

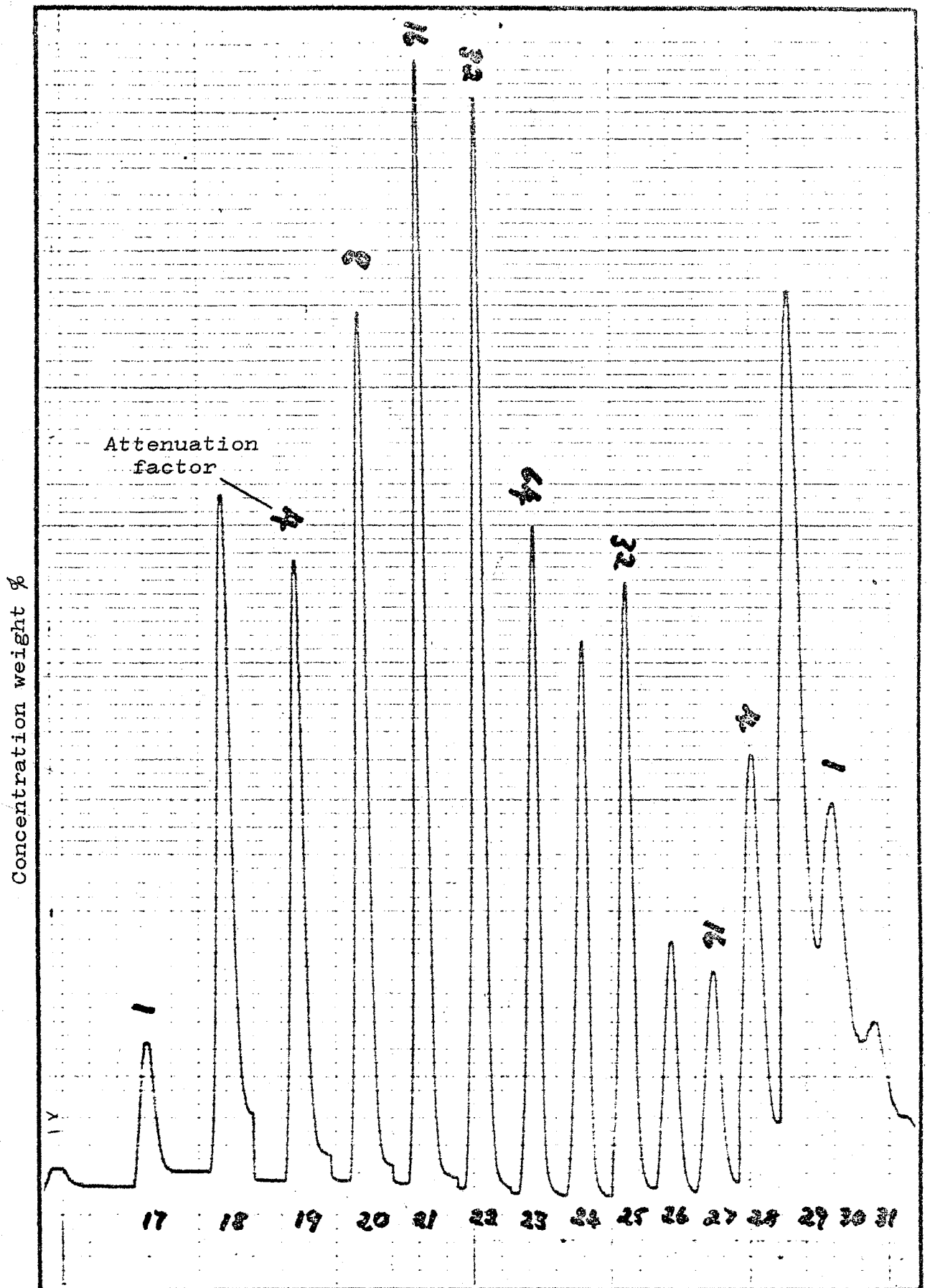
A one kilowatt North American Philips (Norelco), water-cooled x-ray diffraction unit was used, employing copper, cobalt and iron radiation interchangeably. Some of the initial work was carried out at the C.S.I.R.

2.2.1 Diffraction by Single Crystals

Single crystals were grown from toluene and petroleum ether solutions using concentrations of wax of about 4 grams per 100 ml. The wax sample was dissolved in hot solvent and cooled at a steady rate in a tube contained in a thermos half-filled with initially boiling water. Crystallization was usually achieved overnight and the bulk of the crystalline material comprised the well-known plate-like crystal habit. However, the particular solvent appeared to affect the size of crystals formed - crystallization from petroleum ether produced smaller crystals than those grown from toluene. Malcrystalline masses quickly formed on the surface of the crystal plates as solvent evaporated.

Individual single crystals were extremely difficult to obtain. Draining off the excess solvent was tried, but the plates then tended to stick together and were practically impossible to separate. The drained crystals were washed with cold solvent and an attempt to separate the crystals by using an ultrasonic separator was also unsuccessful. The

most/...



Carbon Number.

FIGURE 2

Gas chromatograph - fraction 1.

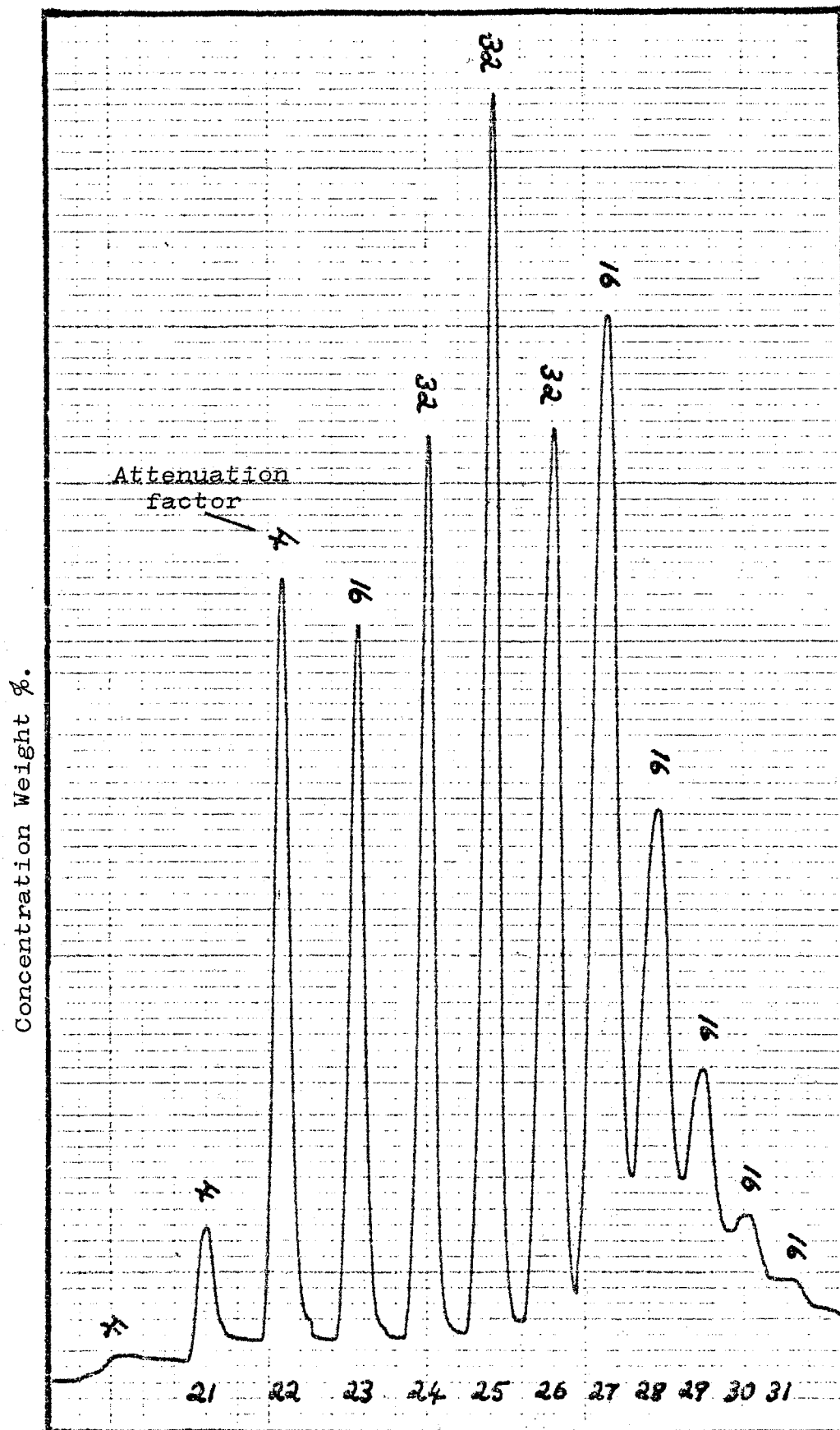
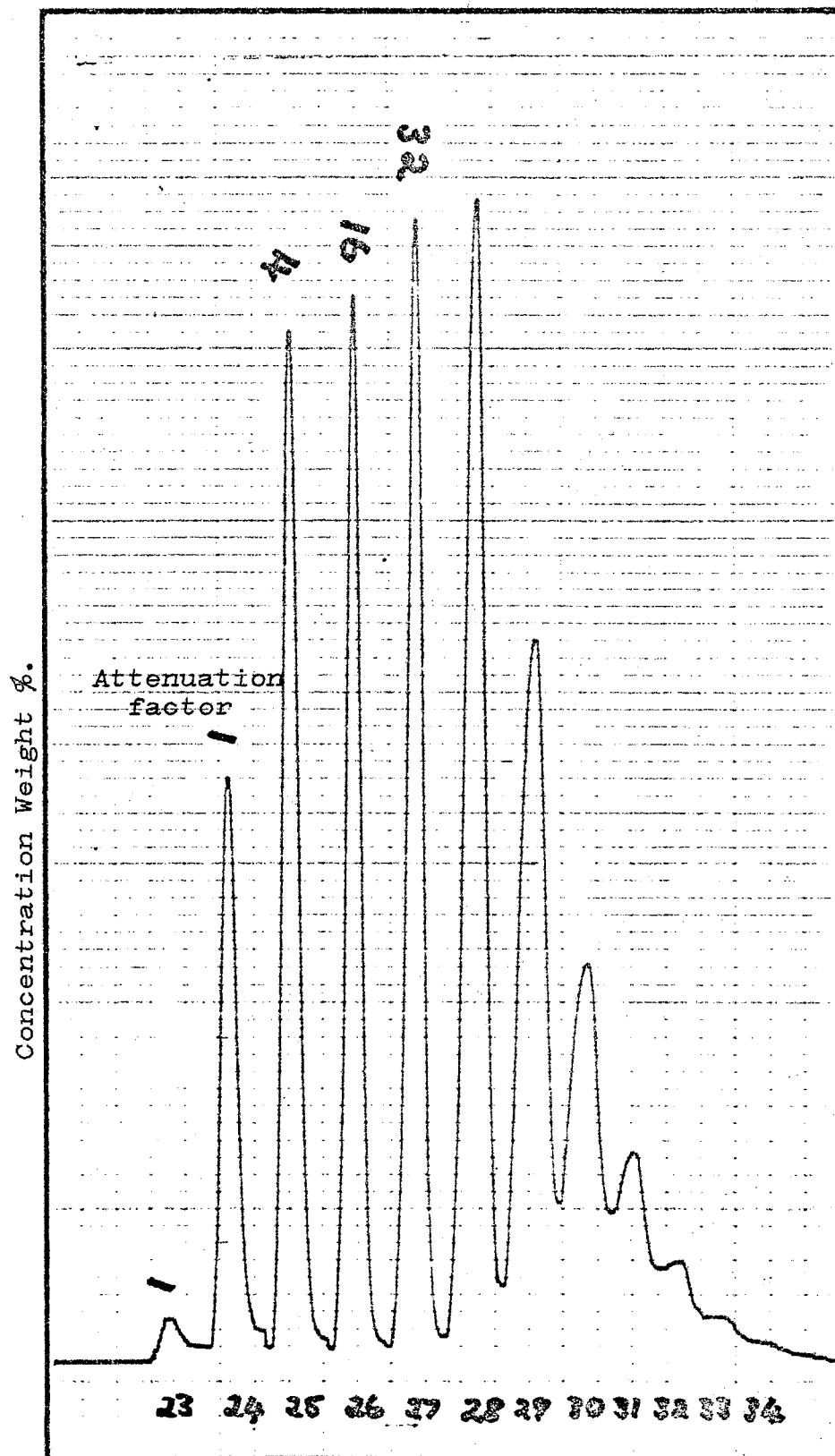


FIGURE 2b.

Gas chromatograph - fraction 2.

52c



Carbon Number.

FIGURE 2c.

Gas chromatograph - fraction 3.

32 d

Concentration Weight %

Attenuation
factor

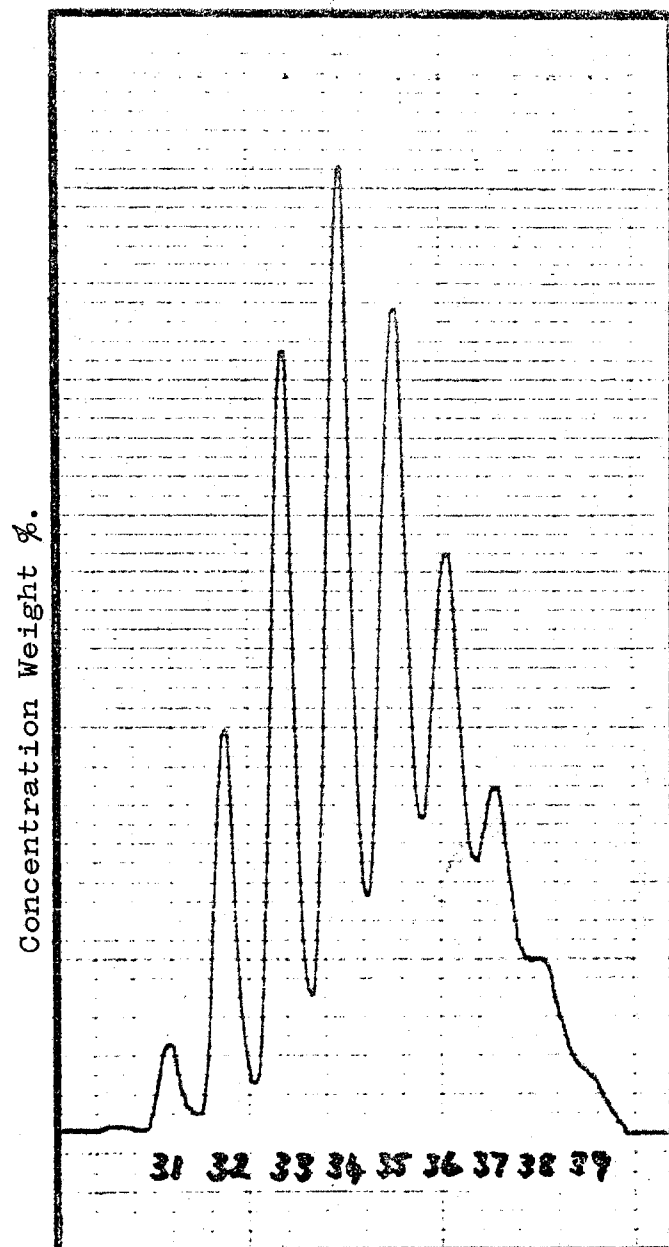
27 28 29 30 31 32 33 34 35 36

Carbon Number.

FIGURE 2d.

Gas chromatograph - fraction 4.

32 e



Carbon Number.

FIGURE 2e.

Gas chromatograph - fraction 5.

most successful procedure was to leave the tube unstoppered and undisturbed for several weeks.

Suitable crystals were observed under polarized light which immediately provided information as to whether the crystal was single or whether several plates were stuck together; on rotation of a single crystal, two extinction directions were found at right angles to each other, but, if the sample consisted of more than one plate, complete extinction was not observed and often a spectrum of colours was seen.

A crystal closest to single crystal characteristics was sorted out and usually cut to a rectangular form with a sharp blade so that its edges were parallel to the extinction directions. The crystal was either mounted with its axis of rotation parallel to one of the extinction directions, or normal to the crystal surface. The crystal was glued to the end of a 0.3 mm. (Lindemann glass) capillary with ordinary mucilage.

Oscillation photographs taken on a Nonius Weissenberg camera with a cylindrical film diameter of 57.3 mm., usually provided the information for accurate alignment of the crystal. For filtered radiation, exposure times varied between two and five hours in the case of oscillation and rotation photographs and, in most cases, three days for the different layer-line Weissenberg patterns. Standard development procedures were followed.

2.2.2 Diffraction by Powder

Powder diffraction patterns were obtained on a wide-angle Philips diffractometer having a scintillation counter as detector. To provide the facility of temperature variation over the range ambient to about 100°C, the safety cover of the diffractometer was modified into an oven, following the basic design given by Barmby, Huston and Bostwick (1956).

Heating was affected by passing pre-heated nitrogen over the sample at a constant flow rate. The gas temperature was controlled by a thermocouple situated very near to the sample, and connected to the temperature control unit. Temperature measurements were made at two points with iron-constantan thermocouples. One was positioned about one millimeter above the sample surface and the other directly below the sample, along the axis of rotation of the sample holder. Neither of the thermocouples interfered with the passage of the x-ray beam. A reference junction of melting ice (0°C) was incorporated in the temperature measurements.

The sample container made from stainless steel was 1 mm. deep and 10 mm. in diameter. After having been thoroughly cleaned and then prewarmed, molten wax was poured into the metal container till the surface was quite convex, and then allowed to cool at room temperature. Before use, the surface was flattened on a mechanical lathe, but for the softer waxes a smooth, flat surface was achieved by scraping with a sharp blade or rubbing gently on a piece of rough paper. The flat sample surface was aligned so as to lie in the plane containing the axis of

of/...

of rotation of the diffractometer.

The sample container was clamped in an insulating block and this fixture was then screwed into the sample holder, which was able to rotate. The insulating block was necessary to avoid heat losses because the rotatable sample holder itself provided a large heat sink. A diagram of the essential oven components and sample fixture is shown in figures 3 and 4.

The effect of a change in the flow rate is seen to be far more pronounced in the high temperature range. However, constant flow rates were reasonably well maintained. Temperature constancy was followed on a millivolt recorder and the average temperature drift over a scanning period of about one hour, was $\pm 0.5^{\circ}\text{C}$. There was a significant temperature difference between the top and bottom measuring thermocouples. However, the bottom thermocouple was found to represent the true wax temperature within a degree or so if the wax was given at least half an hour to obtain equilibrium. This was deduced by comparing the transition temperatures given by the x-ray results and the Differential Scanning Calorimeter (DSC) thermogram.

For the low temperature region, viz. 5° to 10°C below room temperature, required for the investigation of fraction 1, the nitrogen was pre-cooled through a coil immersed in ice-water, enabling measurements to begin at about 15°C . Nitrogen

(dried/...

OVEN ATTACHMENT.

(Photograph on Plate 10)

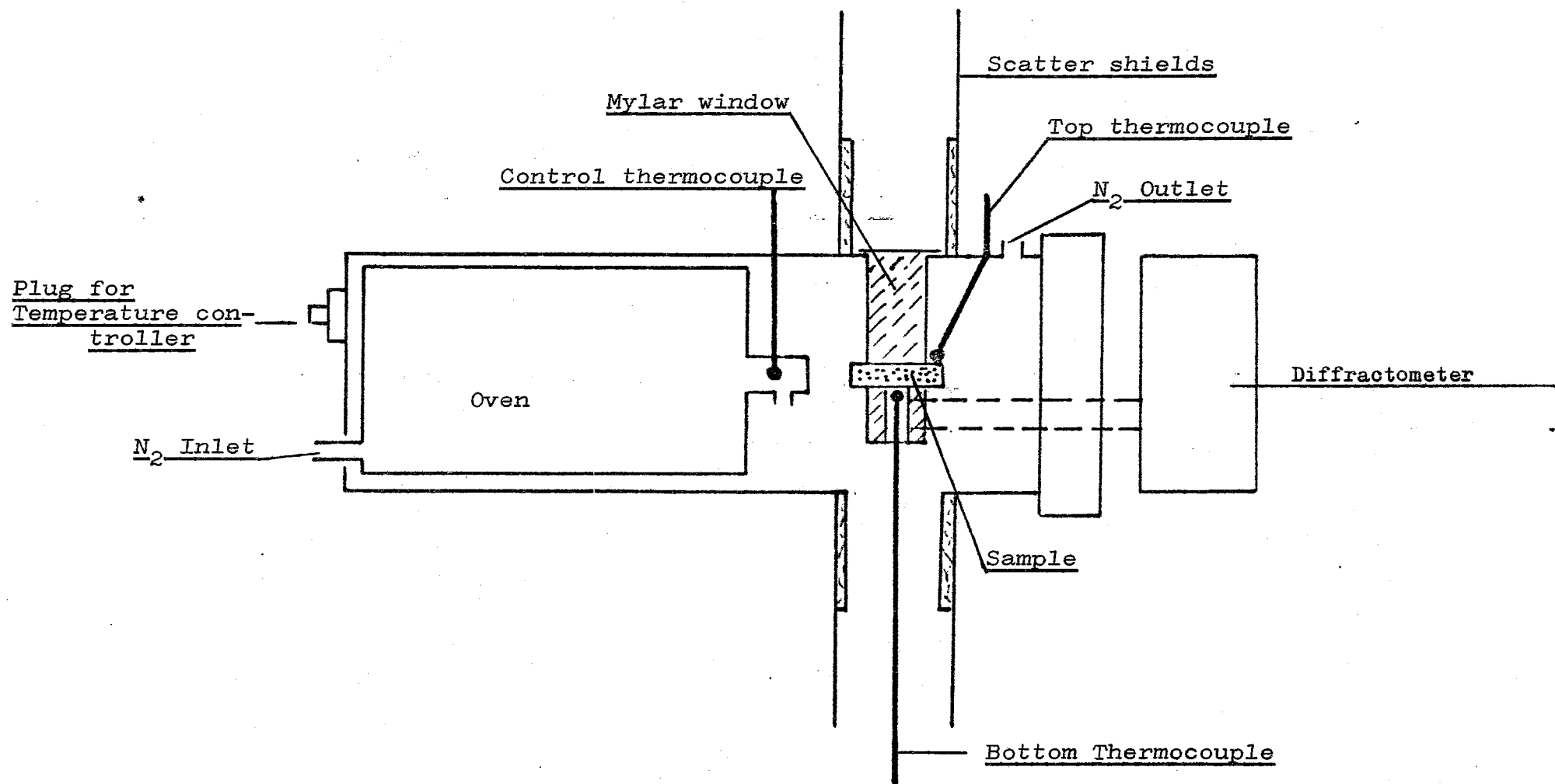
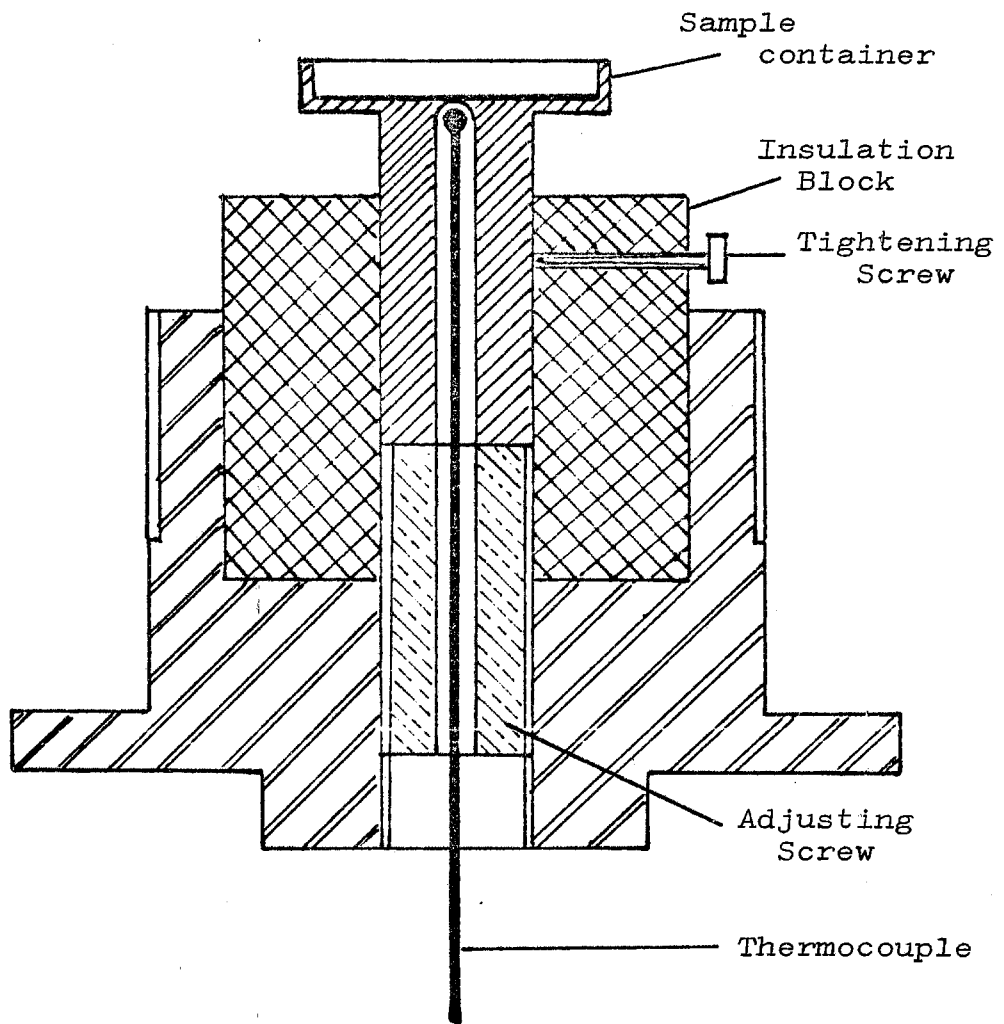


FIGURE 3.

SAMPLE FIXTUREFIGURE 4.

35 c

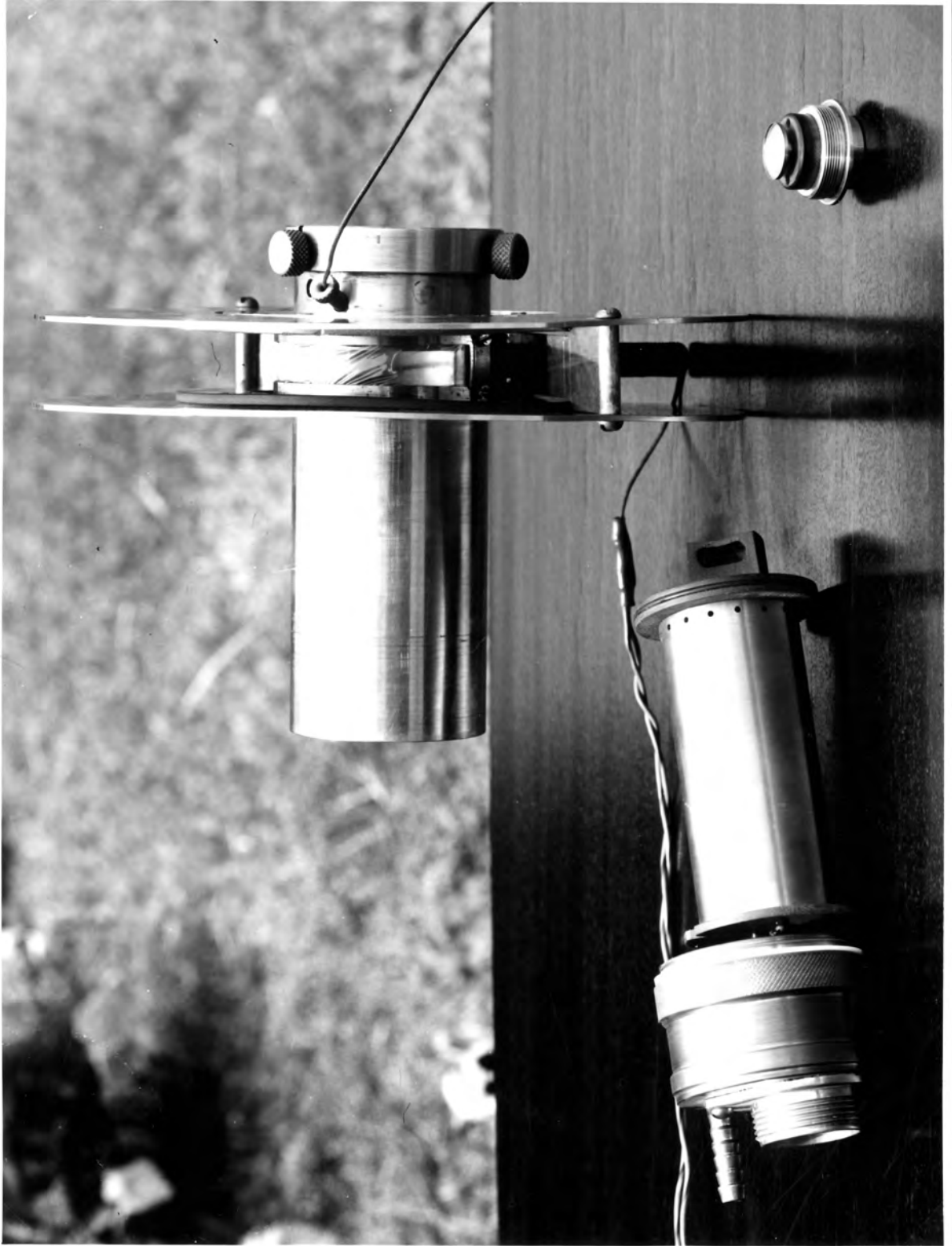


PLATE 10. Oven attachment and sample fixture.

(dried by passing over silica gel) was used to avoid oxidation of the wax, particularly at the higher temperatures.

The waxes were scanned over a range of $70^\circ 2\theta$, where θ is the Bragg angle. All the waxes were run at room temperature and only fractions 1 and 4, plus a hard wax fraction, were scanned at different temperatures.

The usual conditions under which the diffractometer was operated were :

Tube radiation :	Cobalt	Divergence slit, 1° or 2°
λ	$= 1.7902 \text{ \AA}$	Receiving slit, 0.2 mm.
mA	$= 10$	Scanning rate, generally 1° per min.
kV	$= 35$	Multiplier setting, 1
		Time constant, 4 sec.

A discriminator unit was also used, and usually operated at a channel width of 12 volts.

2.3 Thermodynamic Analysis

The thermodynamic parameters were obtained from two complementary experimental techniques, differential thermal analysis at atmospheric and at very high pressures. The latter experiments were carried out in the National Physical Research Laboratory of the C.S.I.R. under the guidance of Dr C.W.F.T. Pistorius, head of the High Pressure Physics division. Differential Scanning Calorimeter thermograms were provided by S. Pretorius in the Wax research Laboratory at Sasol.

2.3.1 Differential Scanning Calorimetry (DSC)

2.3.1.1 Instrument

The Perkin-Elmer Differential Scanning Calorimeter, DSC - 1B, is based on the temperature control of two miniature sample holders, the former for average temperature control and the latter for differential temperature control.

As the temperature is programmed, the sample and reference temperatures are continually maintained at the same level. This is accomplished by closed-loop, negative feedback control of the power which is supplied to the sample and reference holders.

Since power is energy-per-unit-time, the DSC records the rate of energy absorption as a function of sample temperature. Consequently, on a linear time base recorder, a peak area represents the energy of the associated transition.

Standard substances of high purity (99.999%) like indium and benzoic acid are used to calibrate the instrument for a particular range.

2.3.1.2 Sample preparation and operation

Several milligrams of a given sample were accurately weighed into a small aluminium sample-pan which was then transferred to the sample holder. The sample analyser was flushed with dry nitrogen at atmospheric pressure to avoid oxidation of the material.

The/...

The apparatus was operated in the low range region using heating and cooling rates of 8° per minute. All the fractions were run, as well as a few single crystals obtained from fraction 4. That significant fractionation had taken place during crystallisation in the latter case, was clearly seen from the shape of the thermogram. The crystal endotherms on melting, were sharper and better defined. Complete reproducibility was found with a re-run of fraction 1 about fifteen months later. For each run the first melt thermogram was usually discarded, as the sample tended to melt non-homogeneously.

The energy changes are easily determinable from the freezing exotherm and melting endotherm. A difference of approximately 8° between the end of melting and the beginning of freezing is ascribed to inherent thermal lags and possibly to a certain amount of super-cooling within the sample.

2.3.2 High Pressure Differential Thermal Analysis

Pressures to just over 40 kilobars were generated in a piston-cylinder device. The details of the apparatus are described by Kennedy and Lamori (1961), and the furnace assembly was similar to that used by Cohen, Klement and Kennedy (1966). Phase changes were detected by differential thermal analysis (DTA), using Chromel-Alumel thermocouples, and corrections were made for the effect of pressure on the thermocouples.

The samples were contained in copper capsules

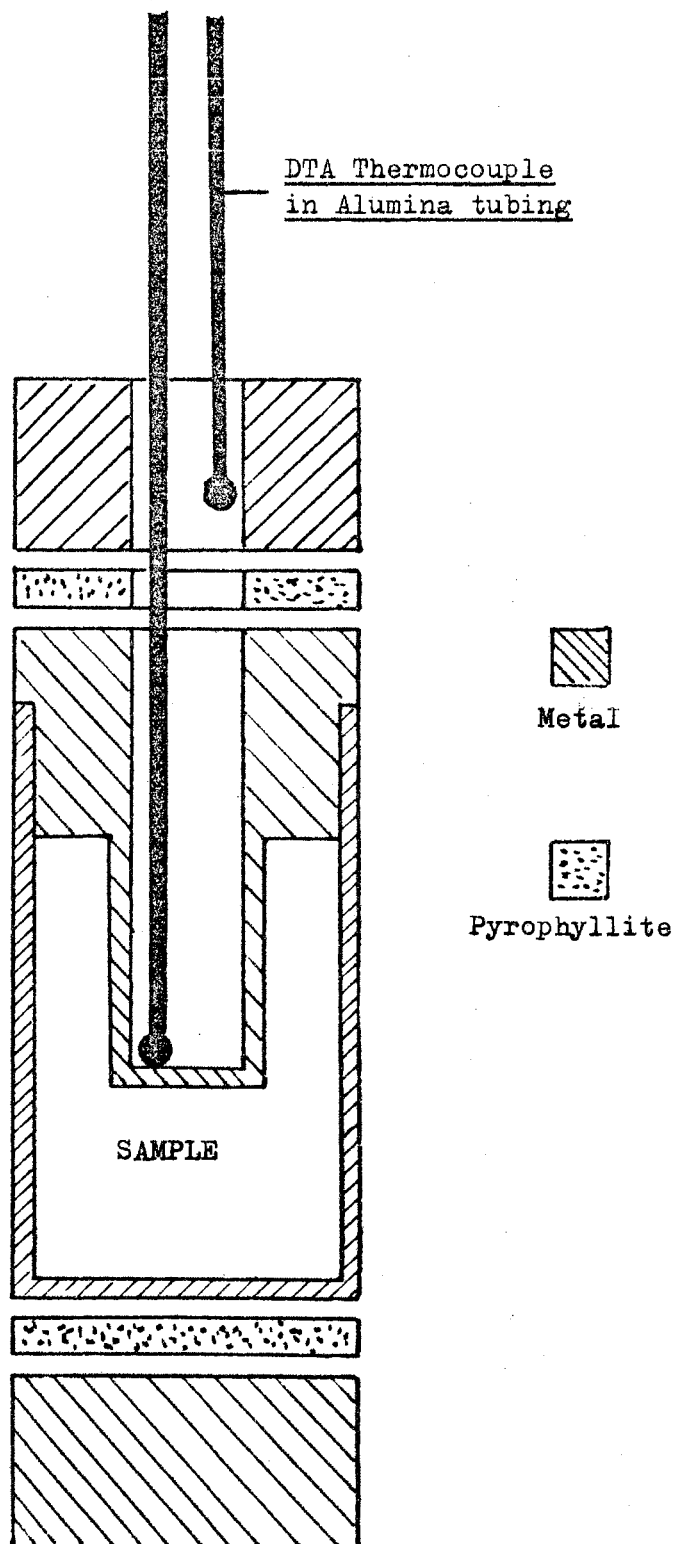
which/...

which incorporated thermocouple wells (Pistorius, 1965), a design which intensified the DTA signals. A sandwich-like arrangement of additional copper pieces above and below the capsules, was used to diminish axial thermal gradients; this design also allows higher amplification of the DTA signals (Rapoport, 1966). The modified capsule arrangement is shown in figure 5.

The capsules were first sealed by subjecting them to a pressure of about 20 kilobars in situ before starting the measurements and no contamination or leakage was observed in such cases. Failure to pre-seal the capsule invariably permitted leakage of the sample upon melting.

The heating/cooling rates ranged from 0.3 to 1.3°C per second and temperatures could be determined to $\pm 2^\circ\text{C}$. Sliding friction was eliminated by comparing the results on increasing and decreasing pressure. The double value of friction was typically about 4 kilobars. The resulting pressures were further corrected for non-symmetrical pressure losses. Pistorius, Rapoport and Clark (1967) have shown that the procedure of evaluating pressure losses in internally-heated piston-cylinder devices by assuming symmetrical friction is in error below about 500°C, and an error as much as about 5 kilobars at 40 kilobars and 25°C may result. The corrected pressures are assumed to be accurate to better than ± 0.5 kilobar.

Each phase diagram is based on only one run, except for fraction 5 which was repeated qualitatively, using a stainless steel capsule in place of a copper one in order to obtain stronger DTA signals. Treatment and tabulation of experimental data are given in Appendix III(c).

SAMPLE CAPSULE USED IN DTA STUDIESFIGURE 5.

CHAPTER III3.1 Results3.1.1 Single Crystal Analysis

To provide the necessary basis for and to justify the indexing of the powder diffraction patterns, an examination of single crystals of the different wax fractions was needed. Similarity among all the powder patterns just below ambient temperatures (i.e. about 15°C) suggested that the analysis of diffraction by single crystals of only one fraction was necessary. Reasonable crystals were successfully obtained for fractions 3 and 4, but as fraction 4 had the narrower range of composition, it was chosen for analysis.

Several types of diffraction photographs were taken to reveal the symmetry conditions and gave the magnitudes of the cell constants. The different diffraction patterns are shown in plates 2 - 9, with their respective indexing below, where applicable.

Cell parameters were measured from rotation, zero-layer Weissenberg and precession photographs in the standard way. The mean values with their estimated errors are shown in table 6. These parameters are compared with the n-paraffin $C_{32}H_{66}$ which has a carbon number* closest to that of the wax fraction.

Table 6/...

*By carbon number is meant, the number of carbon atoms in a straight, saturated hydrocarbon chain.

TABLE 6'

CELL CONSTANT	FRACTION 4	n-C ₃₂ H ₆₆
b	7.50 ± 0.04 Å	[⊗] 7.478 ± 0.005 Å
a	5.00 ± 0.04 Å	[⊗] 4.970 ± 0.005 Å
c	42.5 ± 0.3 Å	42.7 ± 0.2 Å

([⊗]Data from Smith, 1958).

Interpretation of diffraction patterns with the crystal mounted perpendicularly to its surface (i.e. normal to the (00 ℓ) planes) is not straight-forward. The reciprocal lattice planes are very closely spaced and isolation of a single layer line is extremely difficult (see plate 6). A good zero-layer Weissenberg diffraction pattern, plate 7, was obtained with this orientation of the crystal, but it is possible that reflections from the first layer are also superimposed. The presence of the sub-cell is clearly seen from the oscillation photograph in this orientation (plate 6), and also from the precession photograph (plate 9).

Crystal deformation and experimental difficulties prevented the examination of the single crystals in the more symmetrical hexagonal state.

3.1.1.1 Symmetry Conditions

The rotation and zero-layer Weissenberg photographs clearly show the presence of mirror planes. These are perpendicular

to/...

to one another and therefore indicate the orthorhombic class mmm.

Zero-layer Weissenberg and the precession patterns (plates 3, 7 - 9) show that the reflections $(h00)$ and $(0k0)$ are present only for h and k both even. Comparison of the zero-, first- and second-layer lines (plates 3, 4 and 5) show that $(h0\ell)$ reflections are present only for h even and $(0k\ell)$ reflections only appear for $(k + \ell)$ even. This latter condition implies (00ℓ) reflections are absent for ℓ odd, and hence doubles the long spacing. Because of the magnitude of the long spacing, the spots are rather close together, thereby making the last condition not immediately obvious. No absences exist for $(hk0)$ and $(hk\ell)$ reflections.

Combination of the symmetry information leads unequivocally to the orthorhombic space group Pnam (or D_{2h}^{16}) consistent with the densely-packed structure postulated by Kitaigorodskii (1955) on geometrical grounds.

3.1.1.2 Number of Molecules per unit cell

The density of the single crystals was determined experimentally by the flotation method, using a water-methanol mixture. An average value of 0.915 ± 0.005 g/cc. was obtained, Average molecular weights were calculated from

the/...

42 a



PLATE 2. Rotation photograph about b , (filtered cobalt radiation).

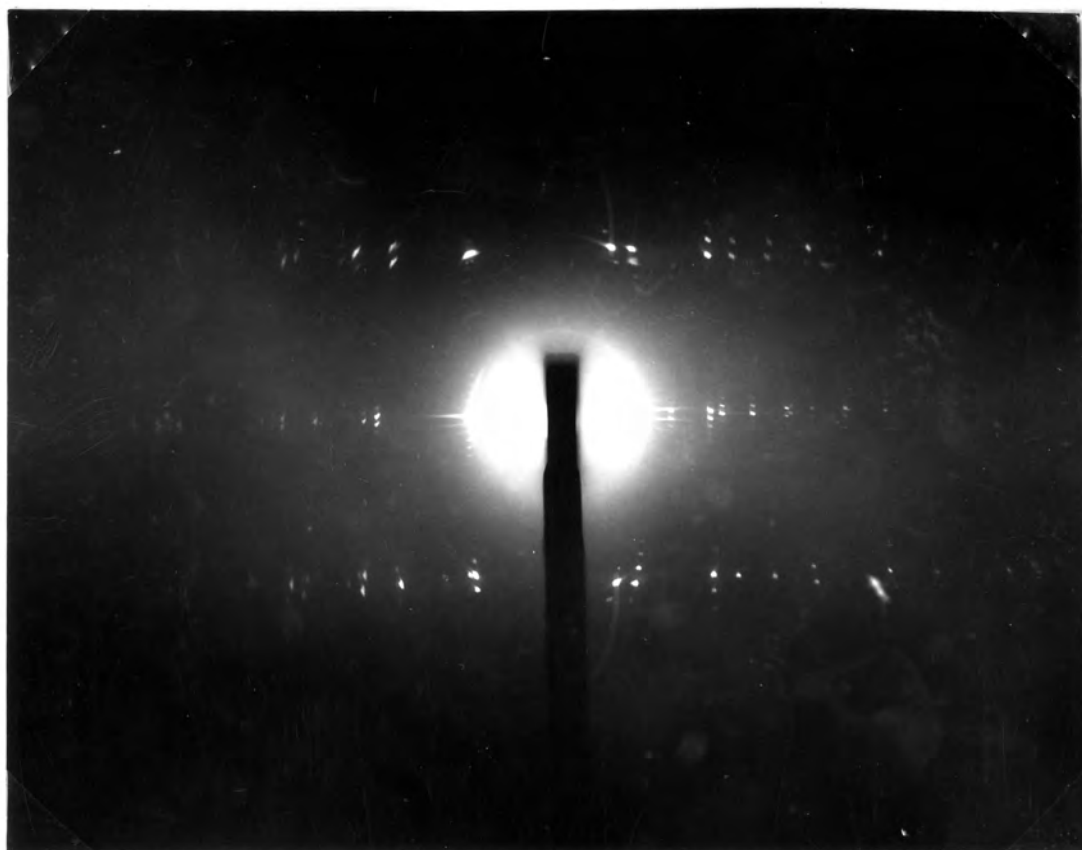
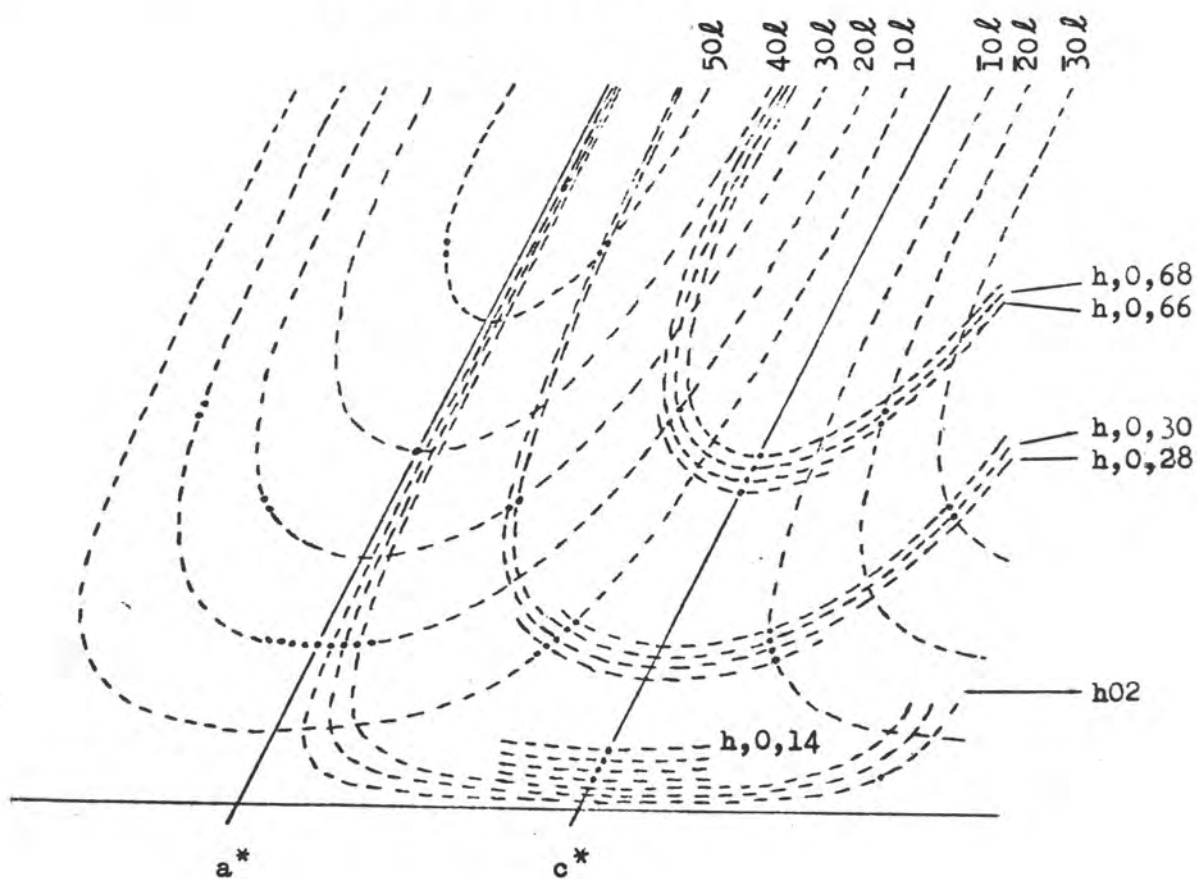


PLATE 6. Oscillation photograph about c , (filtered copper radiation).



PLATE 3. Zero-layer Weissenberg photograph. Crystal mounted along b , (filtered cobalt radiation).



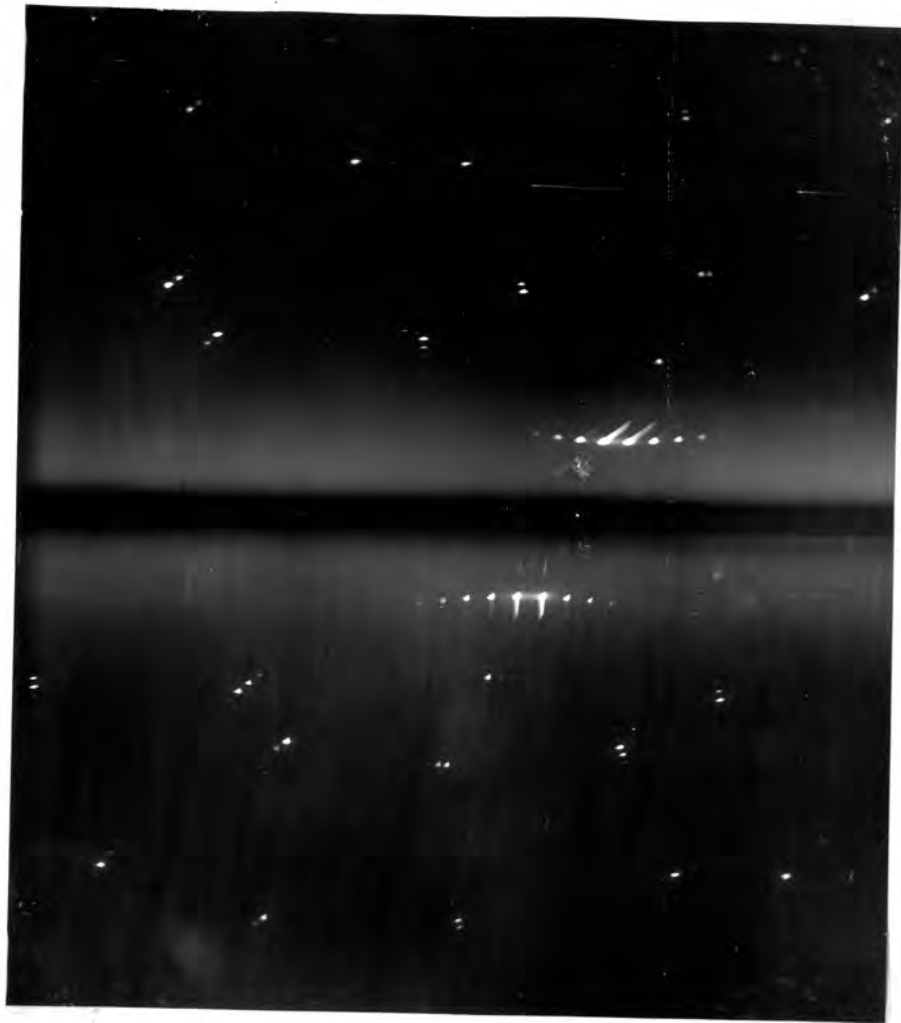
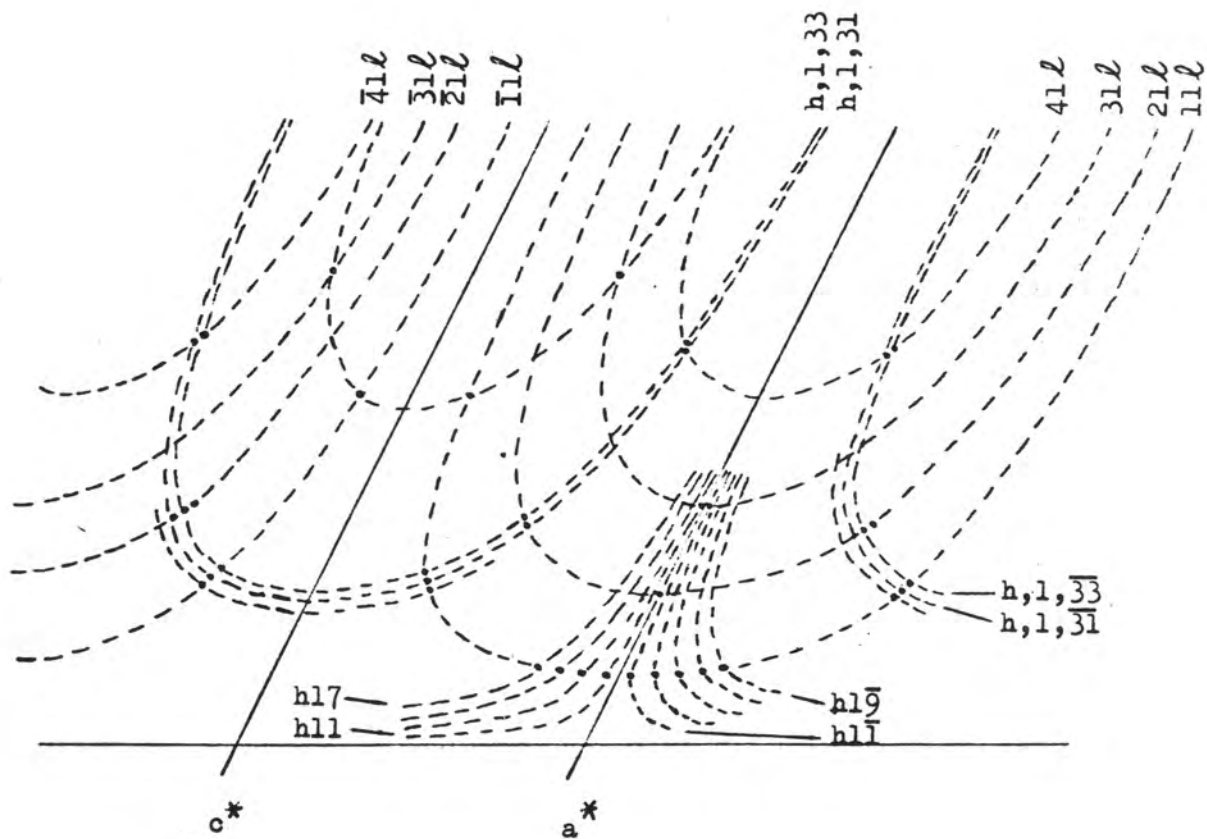


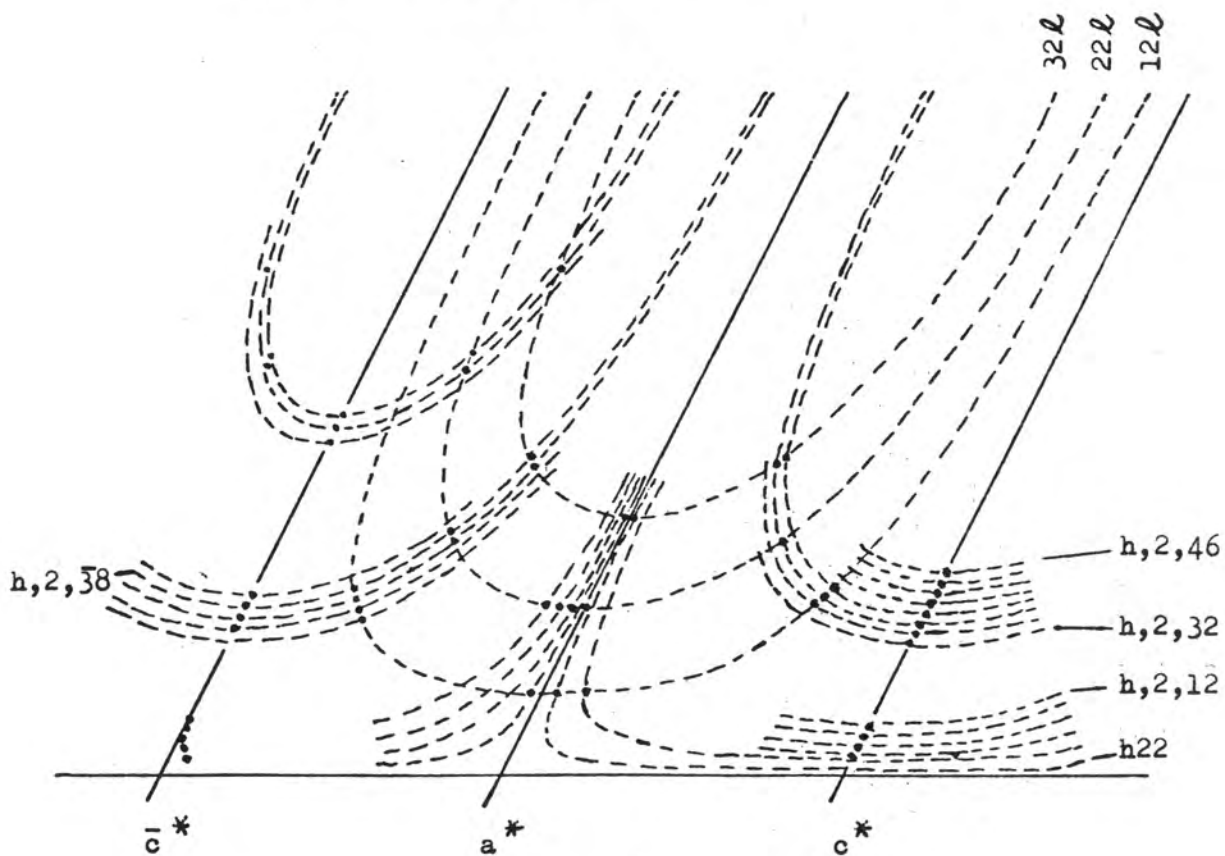
PLATE 4. First-layer Weissenberg photograph; crystal mounted along b , (filtered cobalt radiation).



42 d



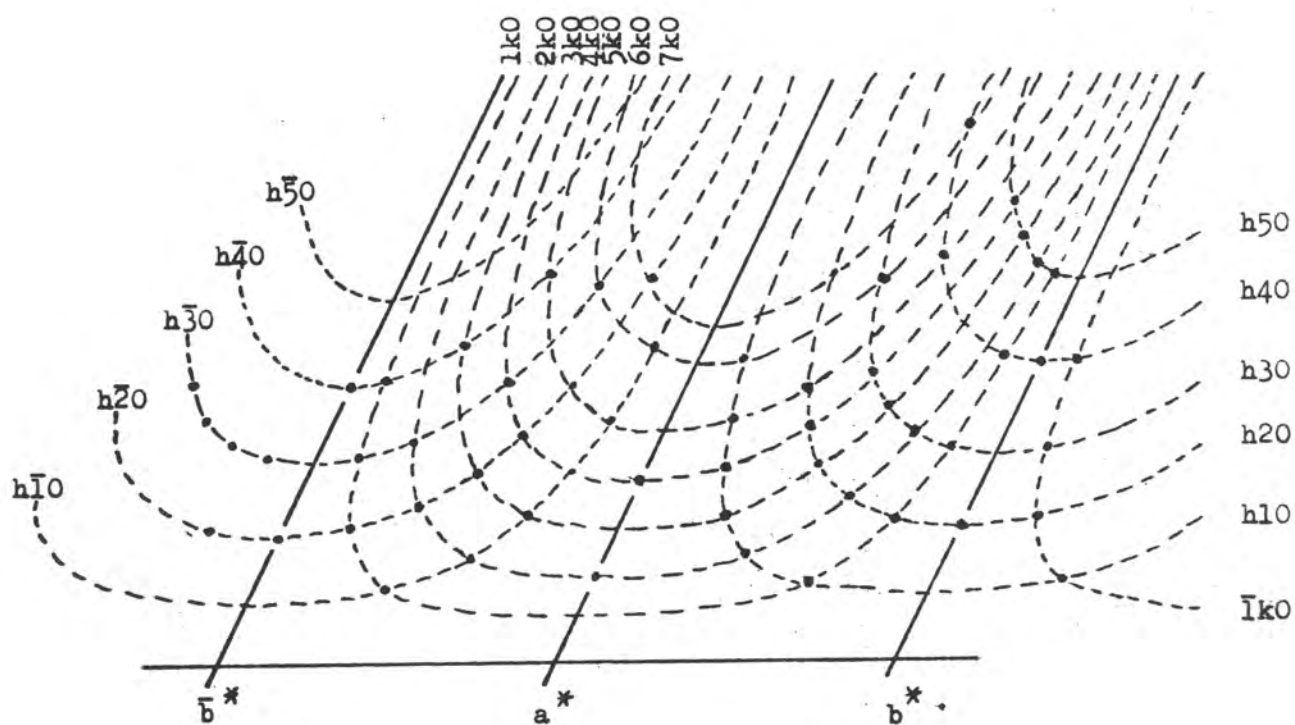
PLATE 5. Second-layer Weissberg photograph. Crystal mounted along b , (filtered cobalt radiation).



422



PLATE 7. Zero-layer Weissberg photograph. Crystal mounted along c , (filtered copper radiation).



ERRATA: a^* and b^* INTERCHANGED.

42f

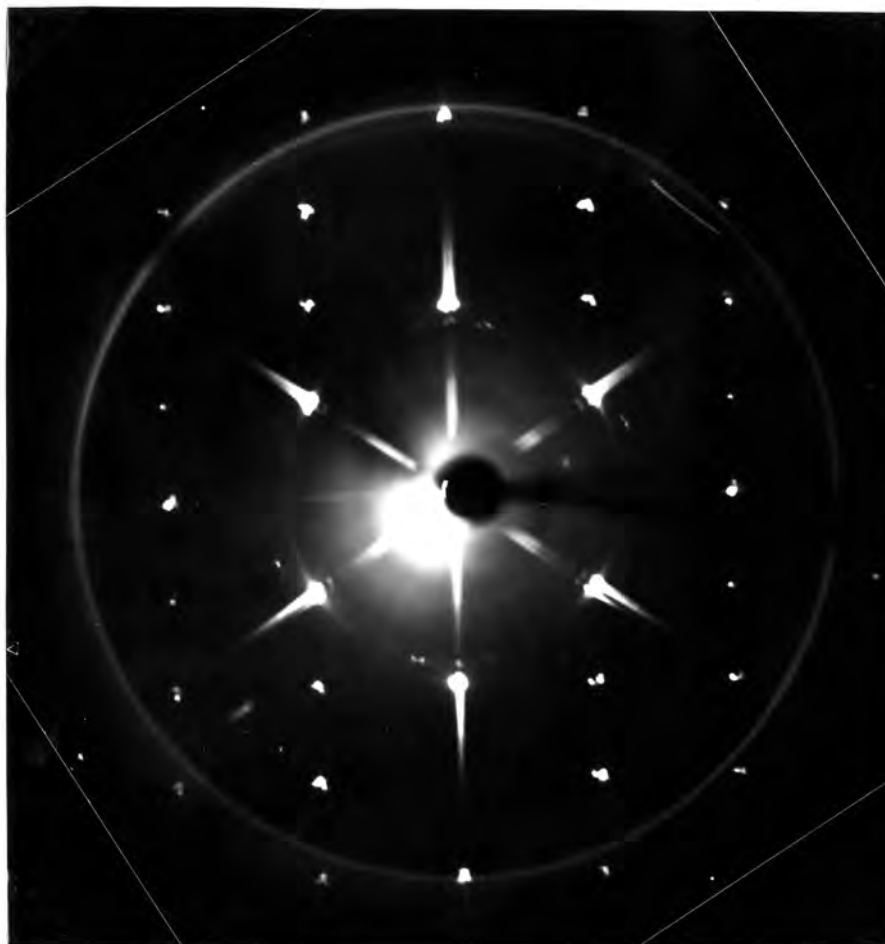
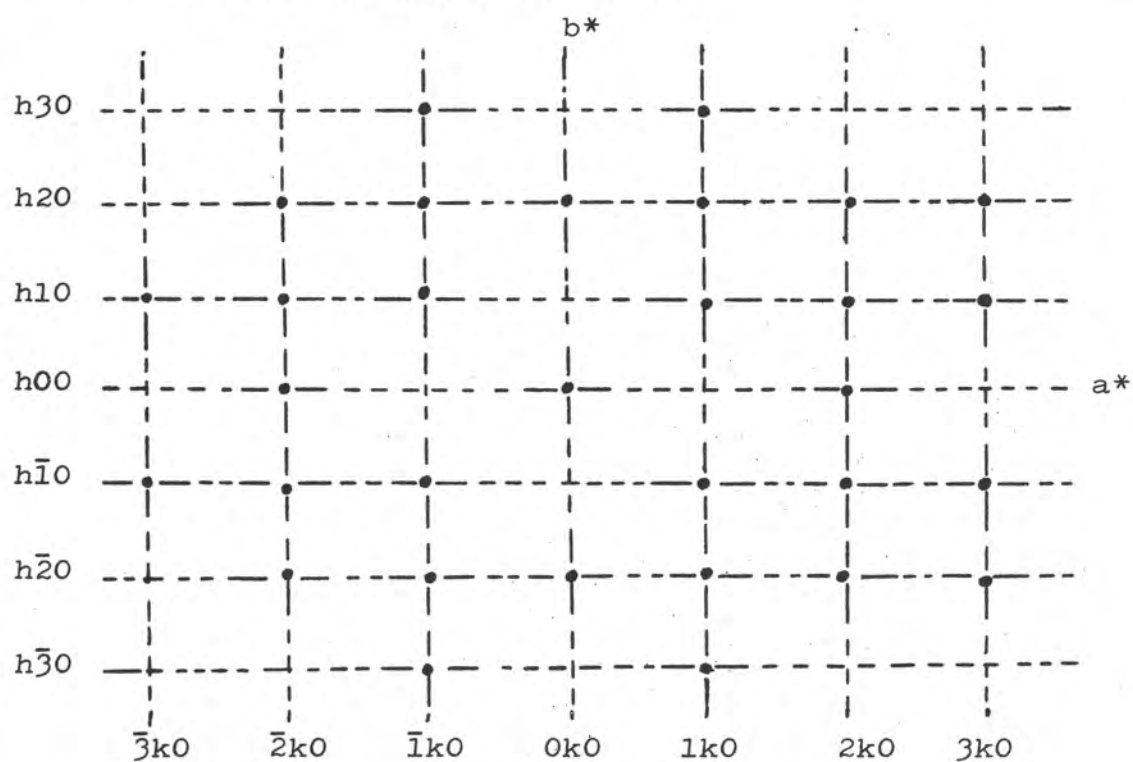


PLATE 8. Precession photograph. Crystal mounted along a ,
(filtered copper radiation).



42g.

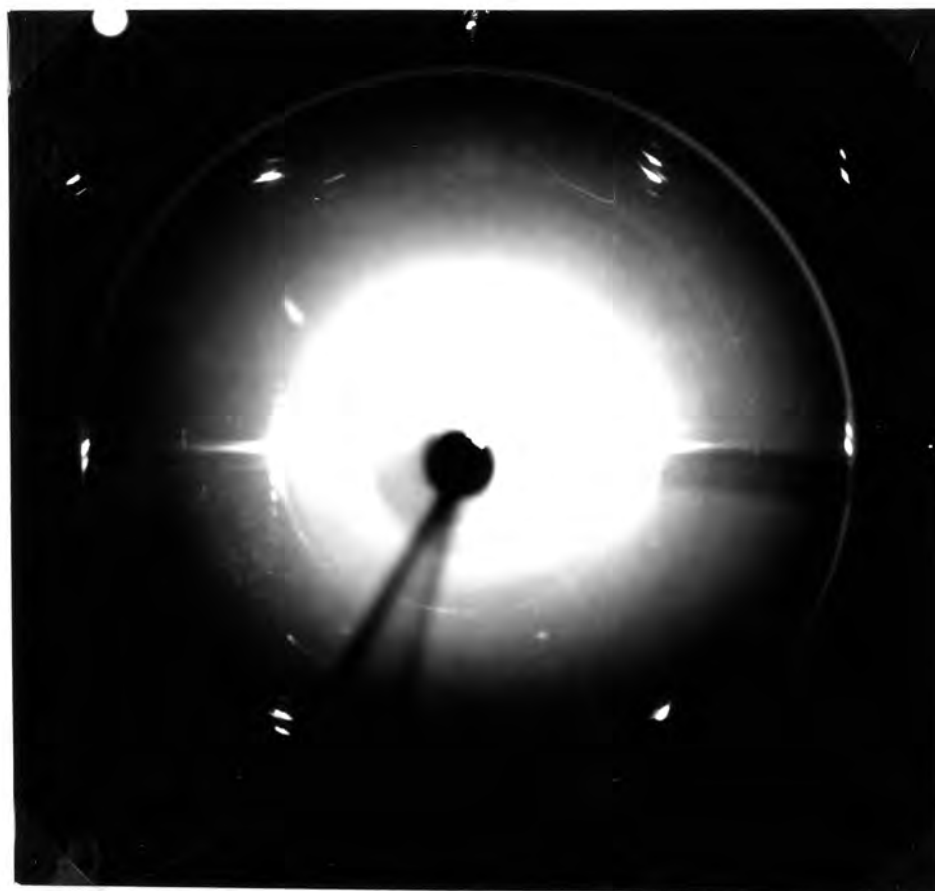
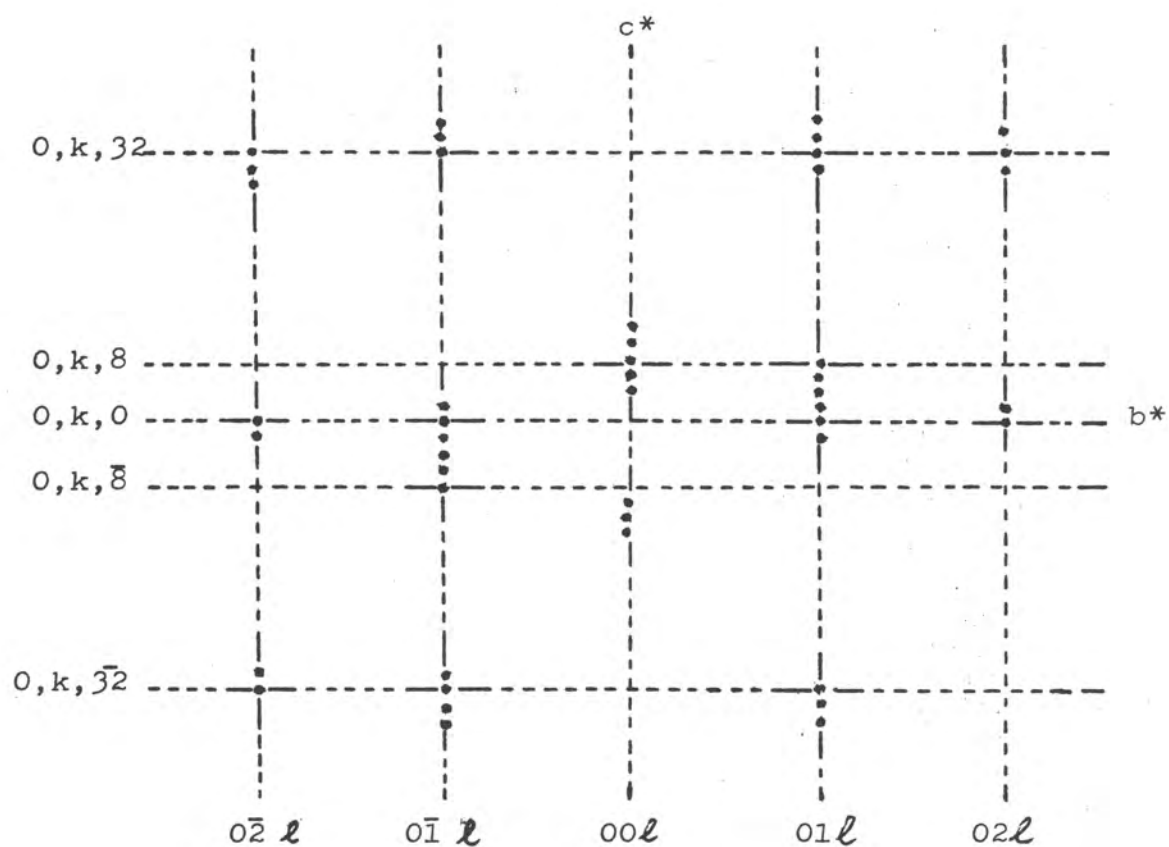


PLATE 9. Precession photograph. Crystal mounted along c ,
(filtered copper radiation).



the average carbon numbers obtained from powder diffraction results (see section 3.1.2) and the number of molecules within the unit cell was derived from

$$n = \frac{\rho V N}{M}$$

where ρ is the crystal density, V the unit cell volume, M the average molecular weight and N, Avogadro's constant ($6.024 \times 10^{23} \text{ mole}^{-1}$). The value of n was found to be four (3.94).

3.1.2 Powder Analysis

From single crystal data and using a computer programme, all the possible reflections from the derived orthorhombic lattice were generated. The main powder reflections observed were identified; a typical diffraction trace at ambient temperature is shown in figure 6. By means of an iterative process using a least-squares computer programme in conjunction with the above programme, the cell constants were refined. The indexing of the main reflections agrees with that found in the literature (Müller, 1932). The two strongest reflections, (110) and (200), are directly related to the short spacings of the unit cell (see figure 7) and are of great significance as their variation provides information on changes in the a and b lattice dimensions. Because of the rectangular prism-shaped unit cell, the (00l) reflections provide a direct measure of the/...

439

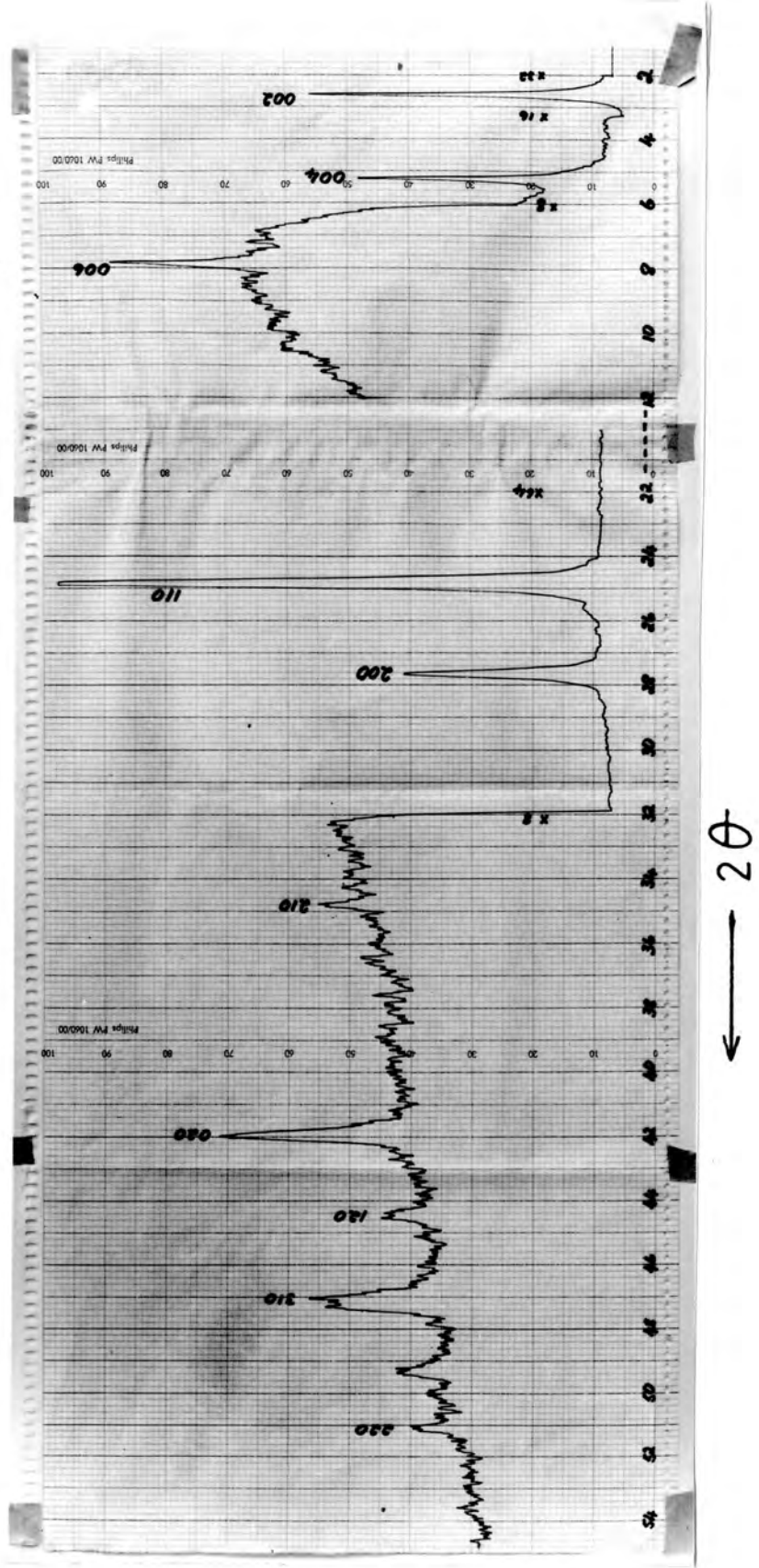


FIGURE 6.

Diffraction trace - fraction 3.

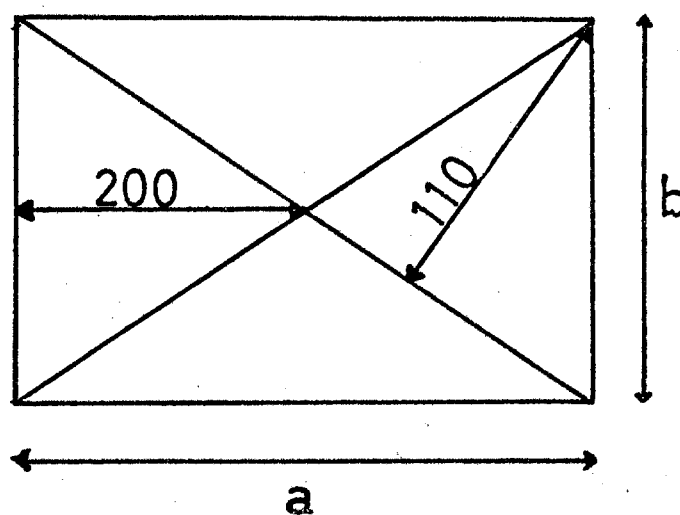


FIGURE 7.

Short-spacings of unit cell in relation to d_{110}
and d_{200} .

the chain length.

The variation of chain length with the number of carbon atoms in the chain for the n-paraffins in the C_{15} to C_{35} range, is well represented by the equation

$$\frac{c/2}{\text{\AA}} = 1.27 (n - 1) + 3.27 \text{ ----- (1).}$$

Using this relationship and the measured c-spacings, the x-ray average carbon number of each wax fraction was calculated and hence the x-ray average molecular weight found. If the latter parameter is incorporated into the expression used for calculating the number of molecules per unit cell given in 3.1.1.2, with $n = 4$, a set of crystal densities may be obtained.

Further powder diffraction data was collected from flat plate transmission photographs. From these the unit cell dimensions could be measured and the values quoted in table 7 are mean values determined from both diffractometer and film methods. No corrections for absorption, film shrinkage or Lorentz polarization have been made.

At about 15°C all the wax fractions show similar diffraction patterns and, by comparison with the single crystal data of fraction 4, are considered to be in the stable low-temperature modification, having the orthorhombic form with the space group Pnam. In the high pressure work this polymorph has been called the δ -phase.

TABLE 7

PARAMETER	FRACTION 1	FRACTION 2	FRACTION 3	FRACTION 4	FRACTION 5
c $\pm$ 0.5 Å	32.5	35.8	38.8	42.5	46.4
b $\pm$ 0.02 Å	4.91	4.93	4.96	5.00	5.00
a $\pm$ 0.02 Å	7.50	7.48	7.47	7.50	7.52
X-ray average carbon number	24.0	26.6	29.0	31.9	35.0
X-ray average molecular weight	338	374	408	448	492
Crystal density	0.935	0.948	0.941	0.934	0.936

3.1.2.1 Powder Diffraction at elevated temperatures

DSC analysis indicated that all the fractions undergo a solid-solid phase transformation several degrees below melting and, in addition, for fraction 1 and possibly for fraction 2, a second solid-solid phase change was evident. The similarity of the diffraction patterns only necessitated examination of two fractions, viz. 1 and 4, over a wide temperature range. However, to provide a little more information about the 'high pressure-phase (δ)' detected in the high pressure analysis (see section 3.1.3), a hard wax fraction of high molecular weight was also examined.

The hard wax fraction investigated has a DSC melting point at 117°C and the thermogram also shows/...

shows the presence of a second peak a few degrees lower at about 114°C . It is anticipated that the hard wax has a carbon number in the vicinity of 100. Chains of up to 300 carbon atoms have been detected in a Sasol wax by gel permeation chromatography. A high carbon number implies a long chain length resulting in the (00ℓ) reflections occurring at such low Bragg angles that they could not be detected. However, comparison of the rest of the diffraction pattern with that of fraction 4, indicates that the stable modification of the hard wax at room temperature probably is also the orthorhombic phase (P_{nam}).

A description of the temperature variation attachment is given in section 2.2.2. As mentioned before, the significant changes in the diffraction patterns occur in the 2θ range 20° to 30° , (where θ is the Bragg angle). Low angle reflections do not provide accurate lattice dimensions and the small variations observed for the long-spacing (00ℓ) reflections are not statistically significant in terms of the experimental error. This suggests that the thermal expansion along the chain axis is negligibly small in cases where it has been measured (Müller, 1930).

Over the ambient to melting point temperature range, the three wax fractions exhibited distinctly different behaviour. Plots of the

d-spacing/...

d-spacing (d_{110} and d_{200}) against temperature shown in figures 8 - 10, provide a comparison of the behaviour of the three waxes. The experimental data are tabulated in appendix III(A).

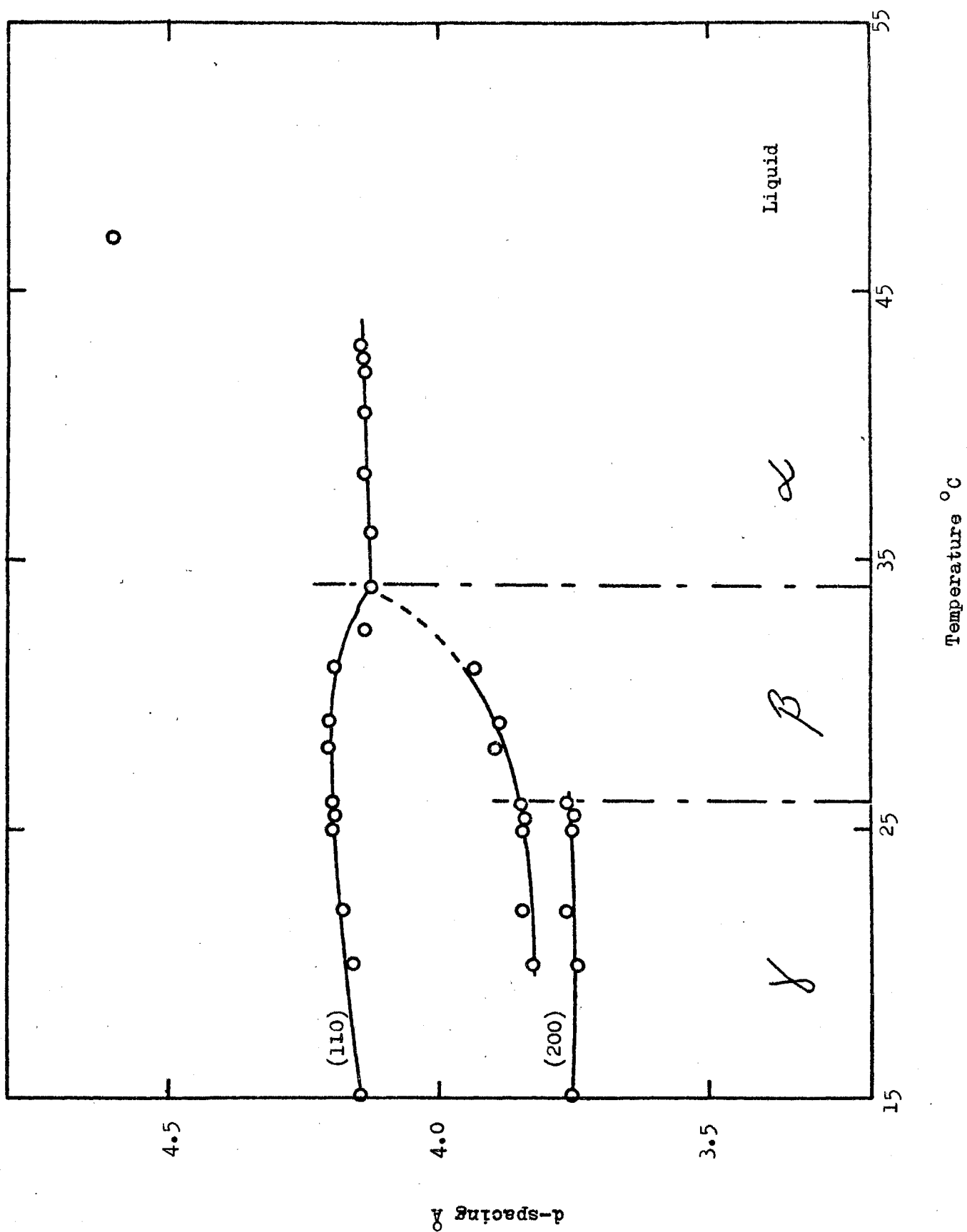
On increasing the temperature, fraction 1 shows three distinct diffraction patterns; fraction 4 two; and the hard wax fraction only one. It is obvious that the nature of the two solid-solid phase changes in fraction 1 is different. The first encountered on raising the temperature is abrupt and discontinuous and hence first order, while the second transition is continuous and probably of the second order. Fraction 4 shows only a discontinuous transition, and the hard wax shows no solid-solid transformation at all. These results are in complete accord with those published by Barmby, Huston and Bostwick (1958) on the petroleum waxes.

The actual temperature of the wax was not known but assumed to be represented by that of the diffractometer sample container. However, wax thermal conductivity is extremely low, so that long periods are required for achievement of equilibrium in the sample. For experimental purposes equilibrium was assumed once the sample holder had been at a steady temperature for at least 15 minutes. The possibility that the wax
was/...

47 a

FIGURE 8.

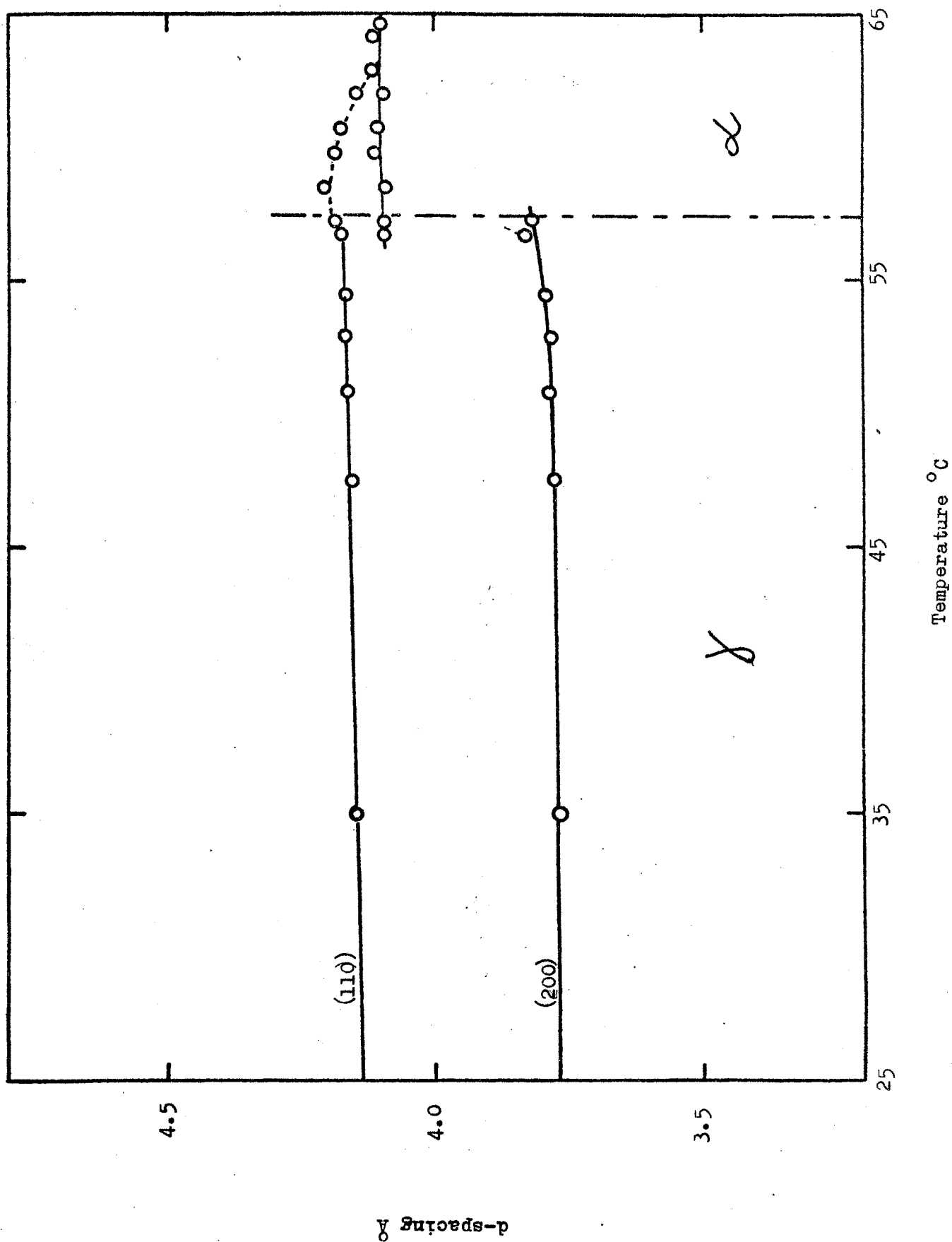
Variation of d_{110} and d_{200} with temperature for
fraction 1.



47 b

FIGURE 9.

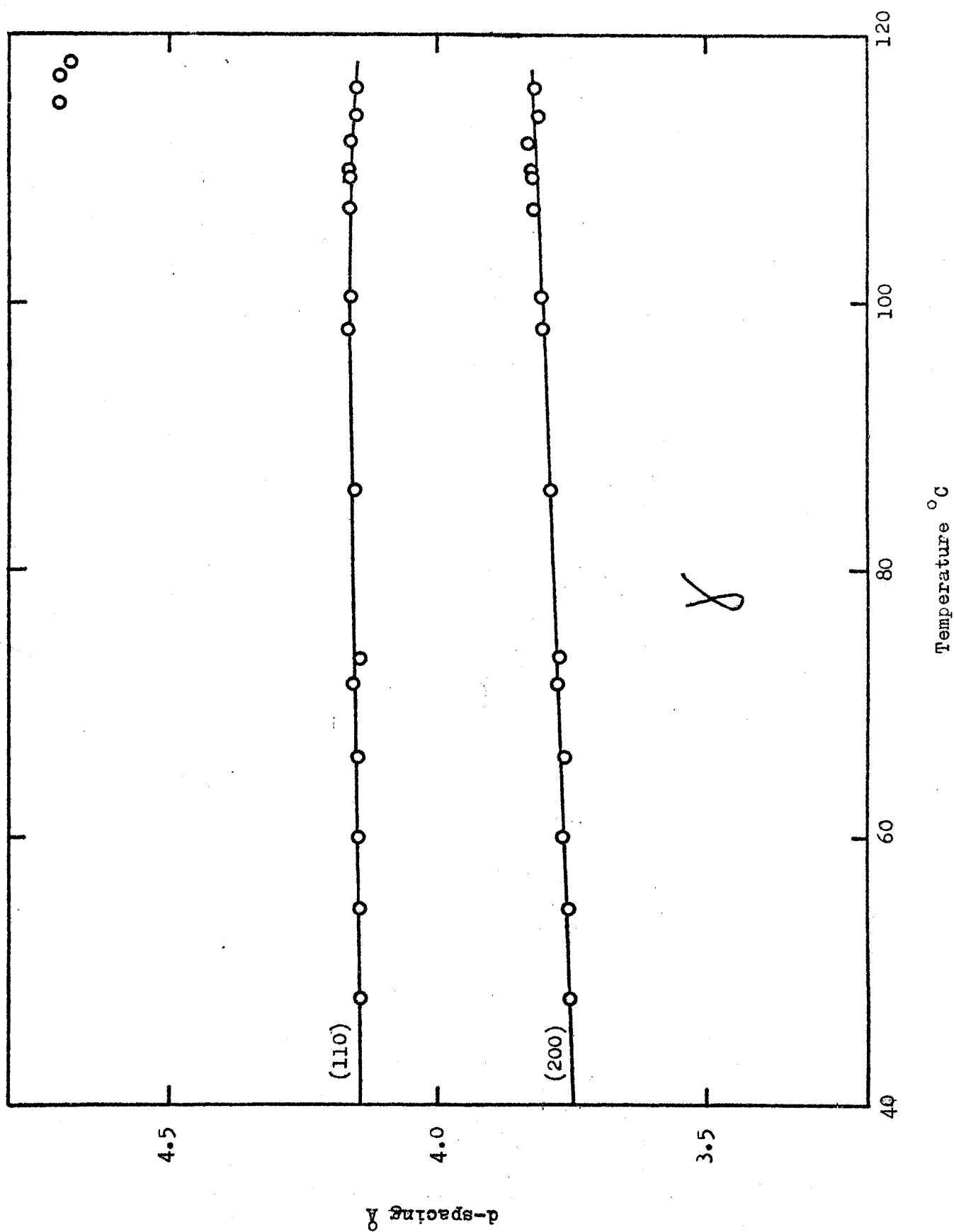
Variation of d_{110} and d_{200} with temperature
for fraction 4.



47c

FIGURE 10.

Variation of d_{110} and d_{200} with temperature
for the hard wax fraction.



was not at equilibrium is very likely and the wax probably possessed significant thermal gradients which were responsible for the overlapping of two phases in the transition region.

The transition temperatures indicated by the x-ray data are more accurate for fraction 1, where agreement is found with the DSC values to approximately one degree, than for fraction 4, where the temperature differs by several degrees from that indicated by DSC. This results from the experimental work being done at two stages with different modifications to the oven attachment. The latter modification effected much better temperature control and measurement.

3.1.3 Calorimetric properties

3.1.3.1 Parameters at atmospheric pressure

Accurate enthalpy values as well as transition and fusion temperatures at atmospheric pressure were obtained using differential scanning calorimetry (DSC). The thermal data listed in table 8 were determined from the DSC-traces as follows :

A planimeter was used to obtain accurate values of the areas under the transition and fusion peaks, and the total area. The sample weight and respective endotherm areas are tabulated in appendix III(B). The transition and fusion endotherms were separated by a vertical line as shown in figure 11; no appreciable

error/...

48 a

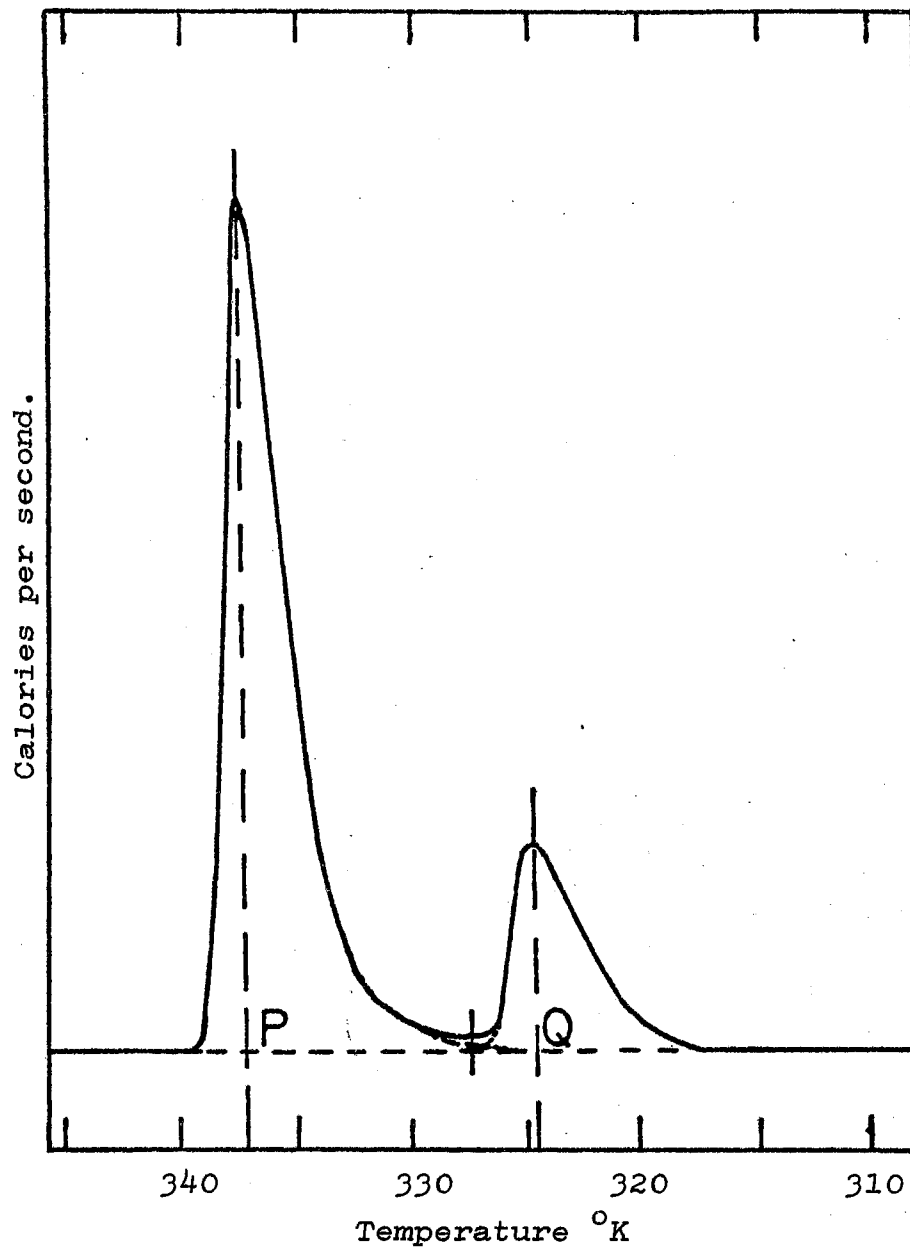


FIGURE 11.

Typical DSC trace - fraction 3.

TABLE 8

Calorimetric Properties characterising the wax fractions

Parameters	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Error
Melting Point °C	48	58	63	69	75	± 2
Transition Point °C	34; 27	40; 37	52	61	70	± 2
ΔH_{tr} Kcal/mole	0.89; 2.37	3.98	4.61	5.84	6.69	± 0.2
ΔH_f Kcal/mole	11.12	13.98	15.80	16.72	18.64	± 0.2
ΔH_{tot} Kcal/mole	14.48	17.96	20.41	22.56	25.33	± 0.4
ΔS_{tr} cal/mole deg.	3.0; 7.7	12.8	14.2	17.0	19.3	± 0.25
ΔS_f cal/mole deg.	34.7	42.8	47.0	48.9	53.5	± 0.25
ΔS_{tot} cal/mole deg.	45.4	55.0	61.2	65.9	72.8	± 0.5

error is incurred by not completing the curves (as shown by the dotted lines) and then measuring the areas. However, this is only valid if the fusion and transition peaks are well separated. In cases such as fractions 4 and 5, where the transition peak merges somewhat with the fusion peak, a large error can result by just separating the two endotherms with a vertical line. The transition area is taken to be too large (particularly in the case of fraction 5) and the fusion area too small. Fractions 4 and 5 have been corrected by superimposing the fusion peak of fraction 3 (which is well separated from the transition peak) upon them.

Enthalpy values were calculated from

$$\frac{\Delta H}{\text{cal.g}^{-1}} = \frac{1.09 \times \text{area} \times \text{range} \times 60}{9.74 \times \text{weight}}$$

where 1.09 is a calibration constant and 9.74 is the rectangular area on the chart which is equal to the chart in width and in length equal to one minute of run.

The entropies, $\Delta H/T$, were subsequently calculated using the absolute transition and melting temperatures (points P and Q in figure 11). Points P and Q are obtained by laying a calibrated slope, which was obtained with one of the standard substances used, upon the endotherm, so that the line passes through the peak maximum and intersects the interpolated baseline

as/...

as shown in the figure.

DSC showed the transition endotherms to be broad. Fractions 1 and 2 exhibit two solid-solid transitions while the other fractions have only one. In the former two fractions, the solid-solid transitions merge with increasing molecular weight; also an overlap between the transition and fusion endotherms was observed as the melting points of the fractions increased.

Correlation of the total entropy change ΔS_T (which is the sum of the entropy of transition ΔS_{tr} and the entropy of fusion ΔS_f), with carbon number yielded linear relationships for both the odd n-paraffins and the wax fractions as shown in figure 12. Comparison between the odd n-paraffin and wax fraction points shows that they can be drawn with the same slope, but the wax line falls significantly below that of the odd n-paraffins. Assuming the entropy change to be entirely a property of the crystalline portion of the material and considering the pure paraffins to be 100% crystalline, the wax points may be corrected by shifting them to coincide with the values for the pure compounds. From the relative values of ΔS_T at a given carbon number the crystallinity of each wax fraction may be calculated

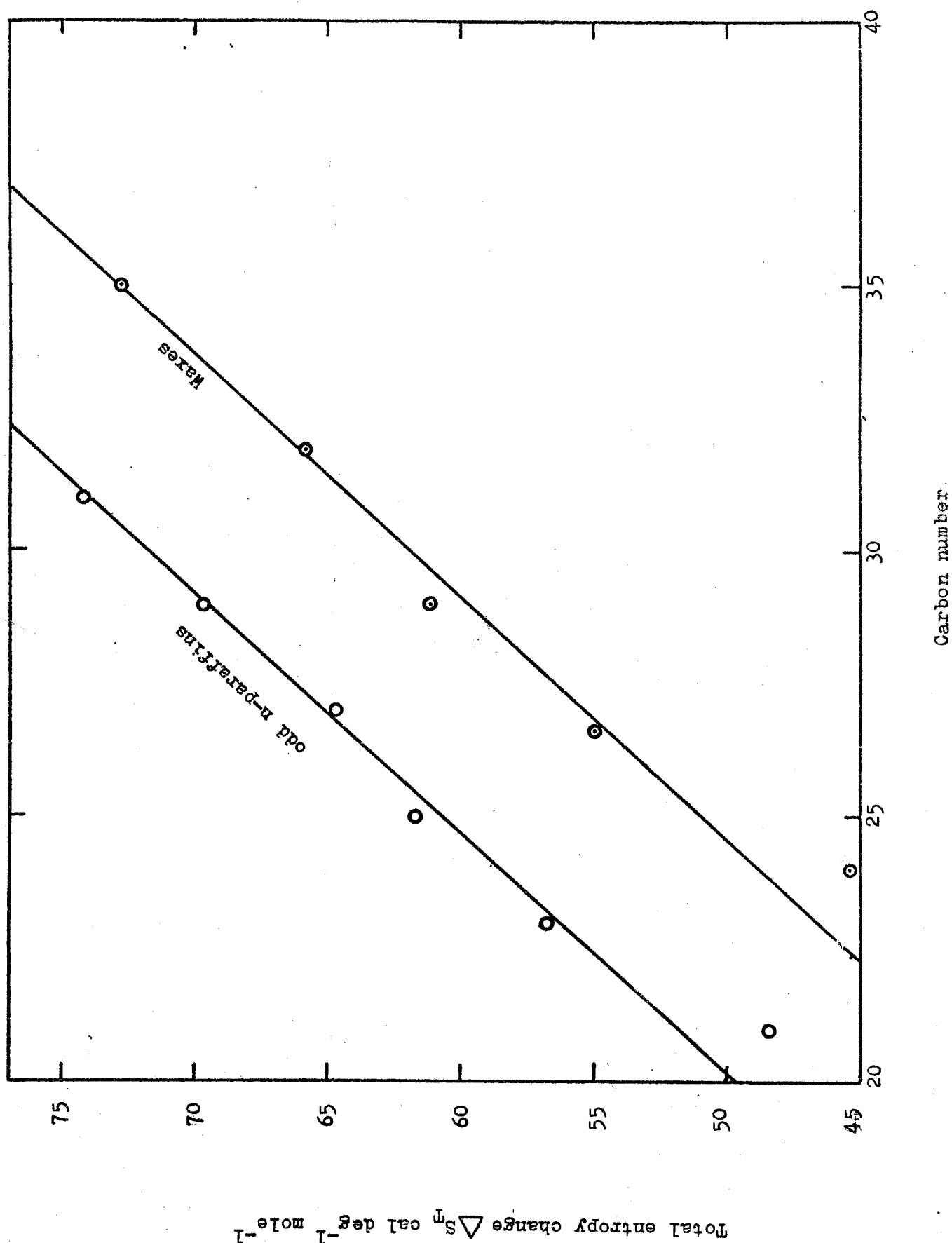
$$\text{Crystallinity \%} = \frac{\Delta S_T}{\Delta S_T^\circ} \times 100$$

where ΔS_T° refers to the corresponding n-paraffin value.

S/a

FIGURE 12.

Correlation between total entropy change and carbon number.



A similar process may be followed for the total enthalpy change ΔH_T . Crystallinities from these two calculations differ by about a percent or two, but as the former takes into account the effect of different melting points of wax and pure paraffin, the entropy calculation would appear to give the more appropriate values. However, both methods are listed in table 9 and the average value was used for correcting the wax data.

Gas chromatographic results indicated that fractionation was more complete for the lower molecular weight fractions (see figures 2a to 2e). However, there was no difficulty in identifying the main components and, choosing an arbitrary lower limit of less than 5% by weight as insignificant, each wax fraction was seen to comprise six main components. This uniformity probably resulted in the waxes behaving like a series. A knowledge of the number of components and mole fraction of each component (table 10) in a given wax fraction, from the gas chromatographic data, allows the entropy of mixing to be determined from

$$\Delta S_{\text{mix}} = -R \sum_{i=1}^N x_i \ln x_i$$

where x_i refers to the i^{th} mole fraction, R is the gas constant, and N is the number of components in each wax fraction. The values

averaged/...

TABLE 10Composition of wax fractions

Carbon number	Mole fraction ($\pm 5\%$) in fraction				
	1	2	3	4	5
17	0.000	0.000	0.000	0.000	0.000
18	0.002	0.000	0.000	0.000	0.000
19	0.019	0.000	0.000	0.000	0.000
20	0.051	0.002	0.000	0.000	0.000
21	0.059	0.006	0.000	0.000	0.000
22	0.195	0.023	0.000	0.000	0.000
23	0.249	0.091	0.001	0.000	0.000
24	0.200	0.217	0.003	0.000	0.000
25	0.120	0.272	0.022	0.000	0.000
26	0.060	0.207	0.084	0.000	0.000
27	0.024	0.102	0.199	0.005	0.000
28	0.012	0.053	0.245	0.035	0.000
29	0.006	0.020	0.223	0.111	0.000
30	0.002	0.006	0.104	0.218	0.000
31	0.001	0.002	0.077	0.219	0.019
32	0.000	0.000	0.023	0.187	0.085
33	0.000	0.000	0.015	0.125	0.175
34	0.000	0.000	0.006	0.066	0.217
35	0.000	0.000	0.000	0.029	0.210
36	0.000	0.000	0.000	0.005	0.174
37	0.000	0.000	0.000	0.000	0.081
38	0.000	0.000	0.000	0.000	0.032
39	0.000	0.000	0.000	0.000	0.009

averaged about $3.8 \text{ cal. deg.}^{-1}, \text{ mole}^{-1}$ and are shown in table 9. It has been assumed that the entropy of mixing is the same for the solid as for the liquid if the components are completely mixed in both phases; therefore this factor was not included in the correlations.

TABLE 9

FRACTION	PERCENT CRYSTALLINITY		ΔS_{mix} cal.deg. ⁻¹ mole
	METHOD 1 (ΔS_T)	METHOD 2 (ΔH_T)	
1	77.5	76.4	4.00
2	86.0	85.0	3.71
3	88.0	87.6	3.83
4	86.7	87.6	3.85
5	88.0	88.8	3.79

3.1.3.2 High Pressure DTA

The transition signals were broad (as found with the DSC) except for the γ/δ signals in fraction 5 (see figure 13(iii)). The freezing signals were fairly sharp and remained measurable throughout the pressure range, whereas the melting signals lost their sharpness and became virtually immeasurable after a few melting/freezing cycles. The shape of the signals were, however, once again improved if the temperature of the system was lowered to $\sim 25^\circ\text{C}$ and then left for ~ 10 minutes. Examples of the type of signals

obtained/...

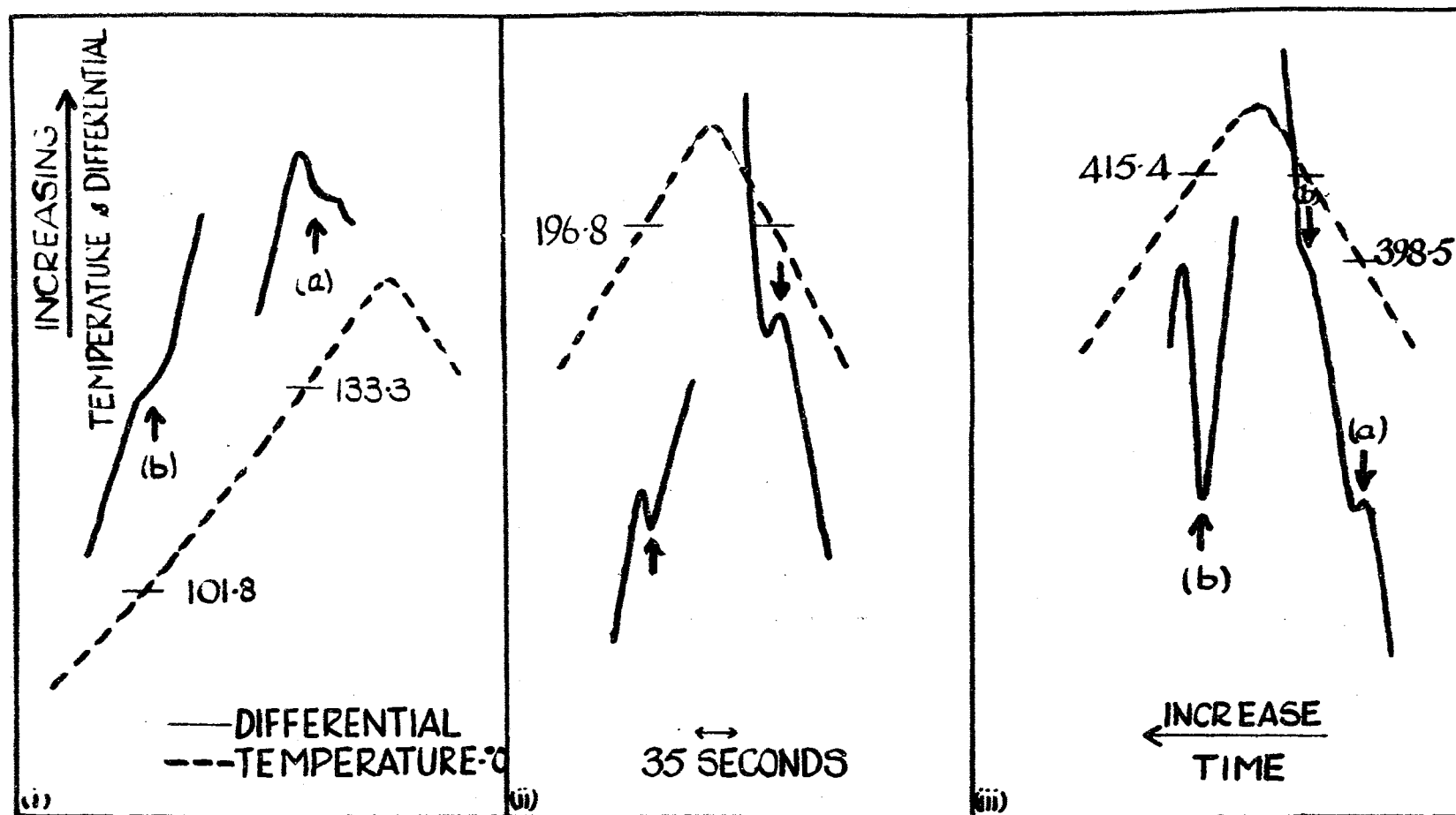


FIG. 13

Typical DTA signals

- (i) (a) Fraction 2 Liquid/ α at 3.3 k bar;
 (b) Fraction 2 γ/α at 3.3 k bar;
- (ii) Fraction 4 melting/freezing at 7.8 k bar;
- (iii) (a) Fraction γ/δ at 39.5 k bar
 (b) Fraction 5 melting/freezing at 40.9 k bar.

0.75

obtained can be seen from figure 13.

The phase diagram of fraction 1 is shown in figure 14. The γ/β and β/α transition lines meet at the $\alpha/\gamma/\beta$ triple point at 3.7 kbar, 82°C. No DTA signals corresponding to the resulting γ/α transition line could be observed, but the liquid/ γ/α triple point was marked by an inflection on the melting curve at 15.5 kbar. The transition signals could not be observed on the releasing pressure cycle, due to their low latent heats and the inevitable deterioration of thermal contact between the thermocouple and the sample on decrease of pressure. The melting curve of the α -phase initially rises sharply with pressure, but has considerable curvature. The DTA signals corresponding to both melting and freezing were sharp. No supercooling on freezing was evident but, due to the range of composition, the beginning of freezing was consistently $\sim 15^\circ\text{C}$ above the beginning of melting. The points plotted are the means of melting and freezing. The freezing points of the γ -phase were only $\sim 2^\circ\text{C}$ above the melting points.

The melting/freezing DTA signals decreased in intensity over the pressure range 10 to 30 kbar. The melting signals almost disappeared and the freezing signals became small. Above ~ 30 kbar the signal shape improved once again, the melting signals being observable but not accurately measurable. Where melting and freezing signals/...

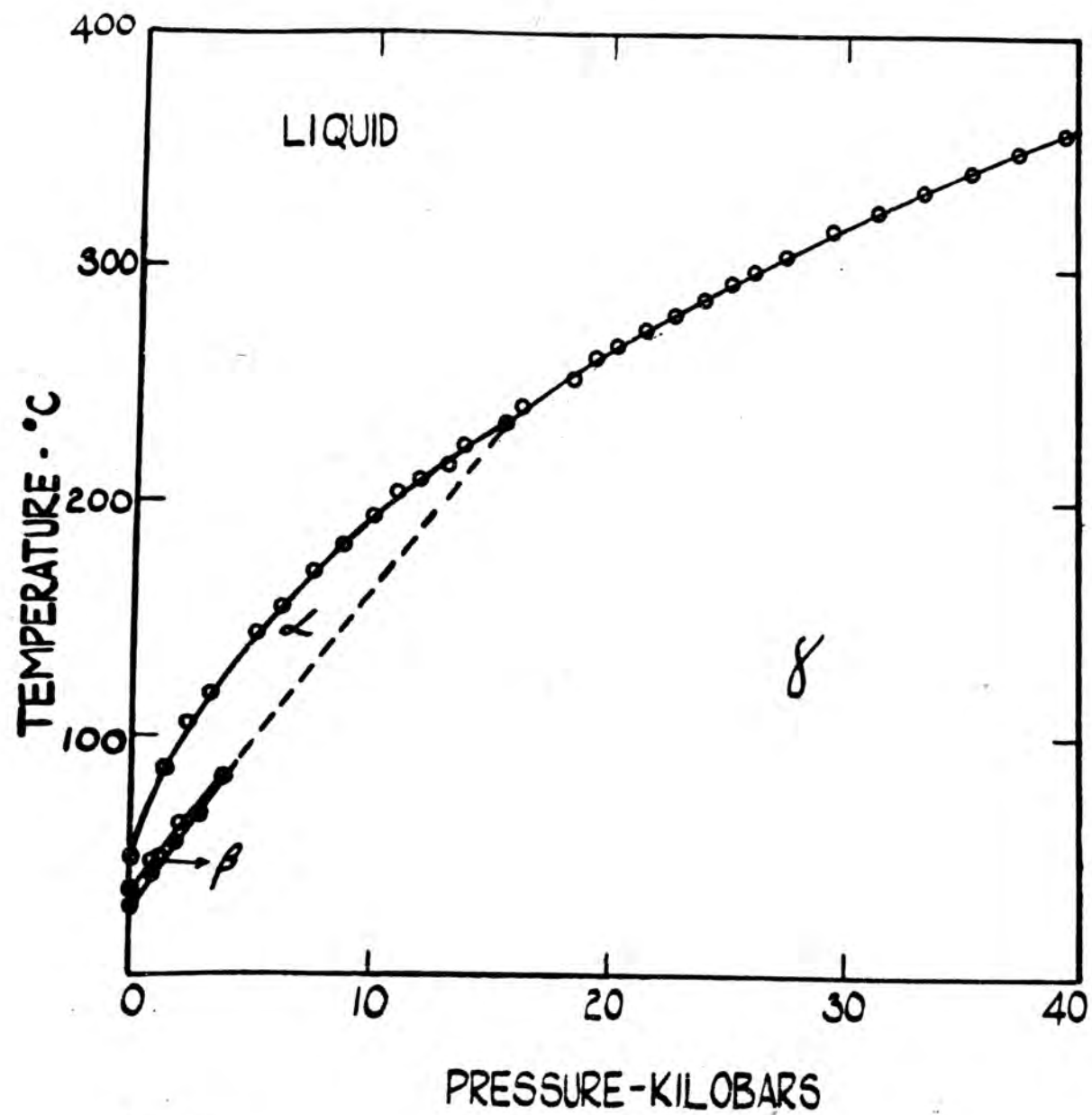


FIG. 14

Phase diagram - fraction 1.

955

SS b

*This has not been shown in figure 15 as its value is too small in relation to the scale used.

signals could be clearly detected, freezing still occurred consistently $\sim 2^{\circ}\text{C}$ above melting.

The phase diagrams of the other fractions are shown in figures 15 - 18. The general behaviour is quite similar to that of fraction 1. The β -phase occurs only in fractions 1 and 2, the $\alpha/\gamma/\beta$ triple point* for fraction 2 lying at $\sim 50^{\circ}\text{C}$, 0.5 ± 0.5 kbar, so that its region of stability is very small. A new high-pressure form was found in fraction 5, i.e., the fraction studied with the highest mean molecular weight. This γ/δ transition line (figure 18) branches off from the melting curve of the γ -phase at a triple point liquid/ δ/γ near ~ 26.5 kbar and $\sim 355^{\circ}\text{C}$. The DTA signals in this region (figure 13(iii)) are quite reproducible.

The phase relations of the various wax fractions are summarized in tables 11 and 12. The polymorphic transition lines have been fitted to simple polynomials, and the melting curves to the Simon equation (Simon and Glatzel, 1929).

$$P - P_0/a = (T/T_0)^c - 1$$

where $T^{\circ}\text{K}$ and $T_0^{\circ}\text{K}$ are the melting points at P and P_0 kilobar, respectively, P_0 and T_0 being the parameters of the triple point of the phase in question; a and c are adjustable constants, determined by Babb's (1963) method.

The/...

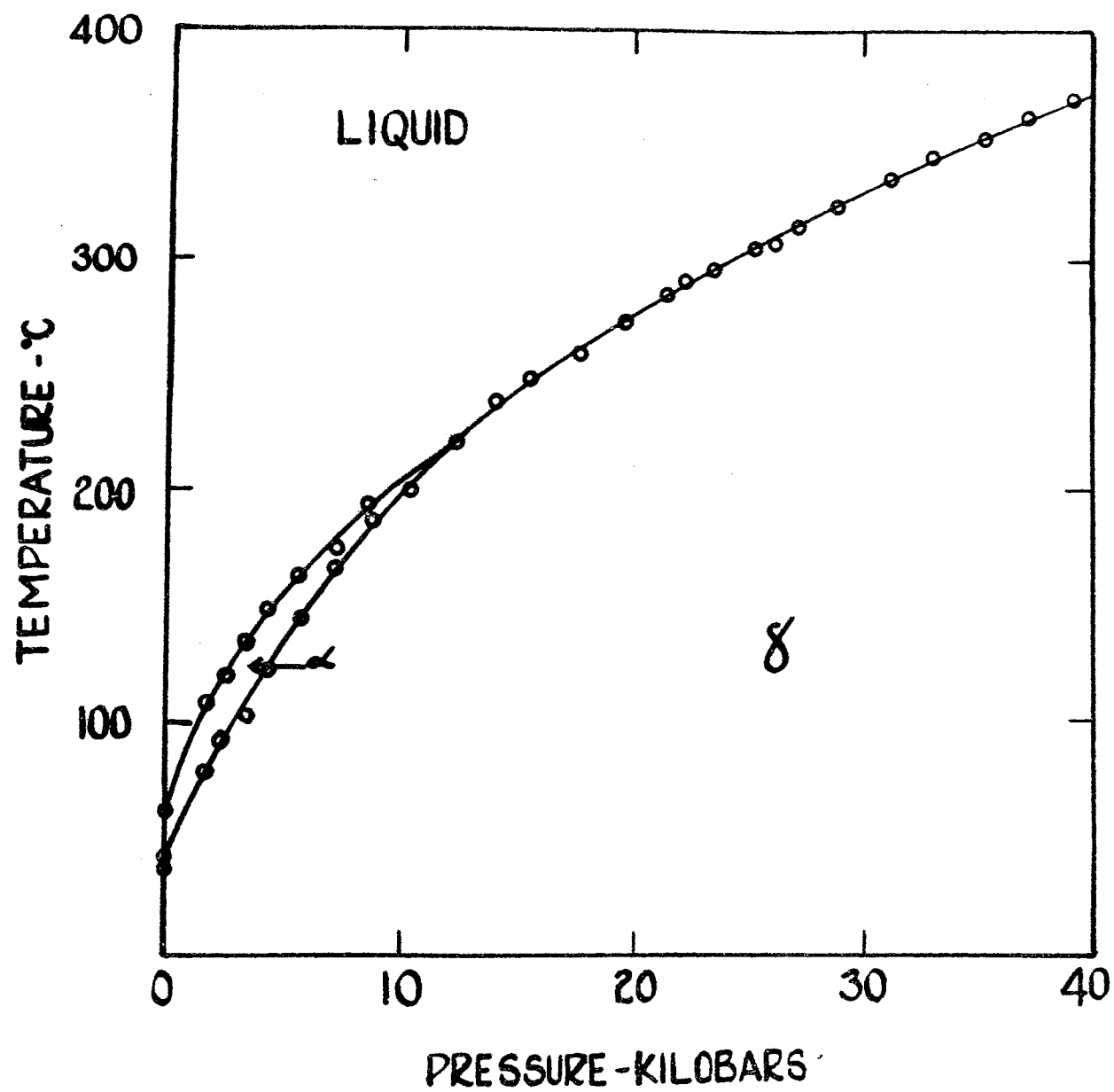


FIG. 15

Phase diagram - fraction 2.

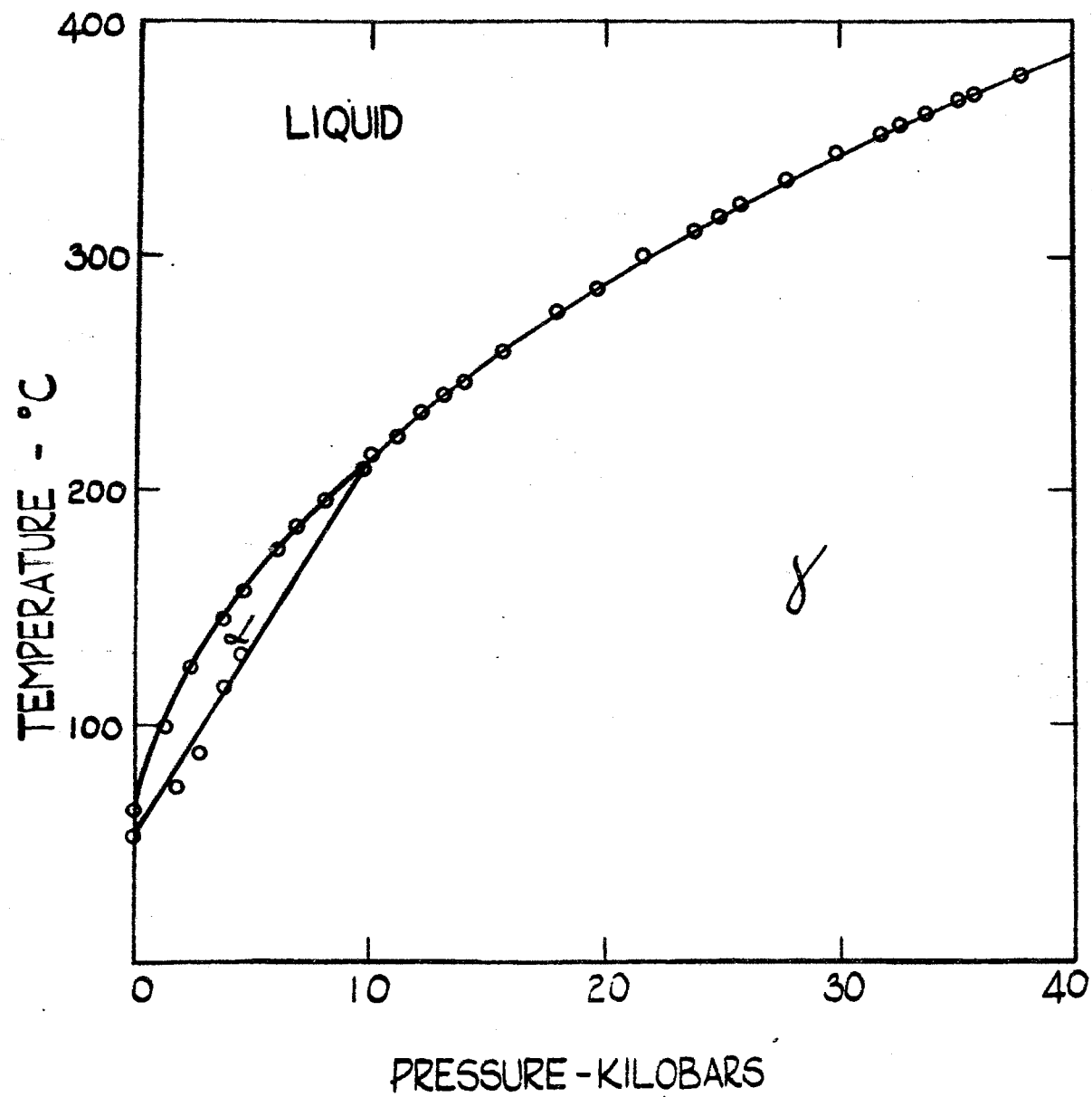


FIG. 16 Phase diagram - fraction 3.

995

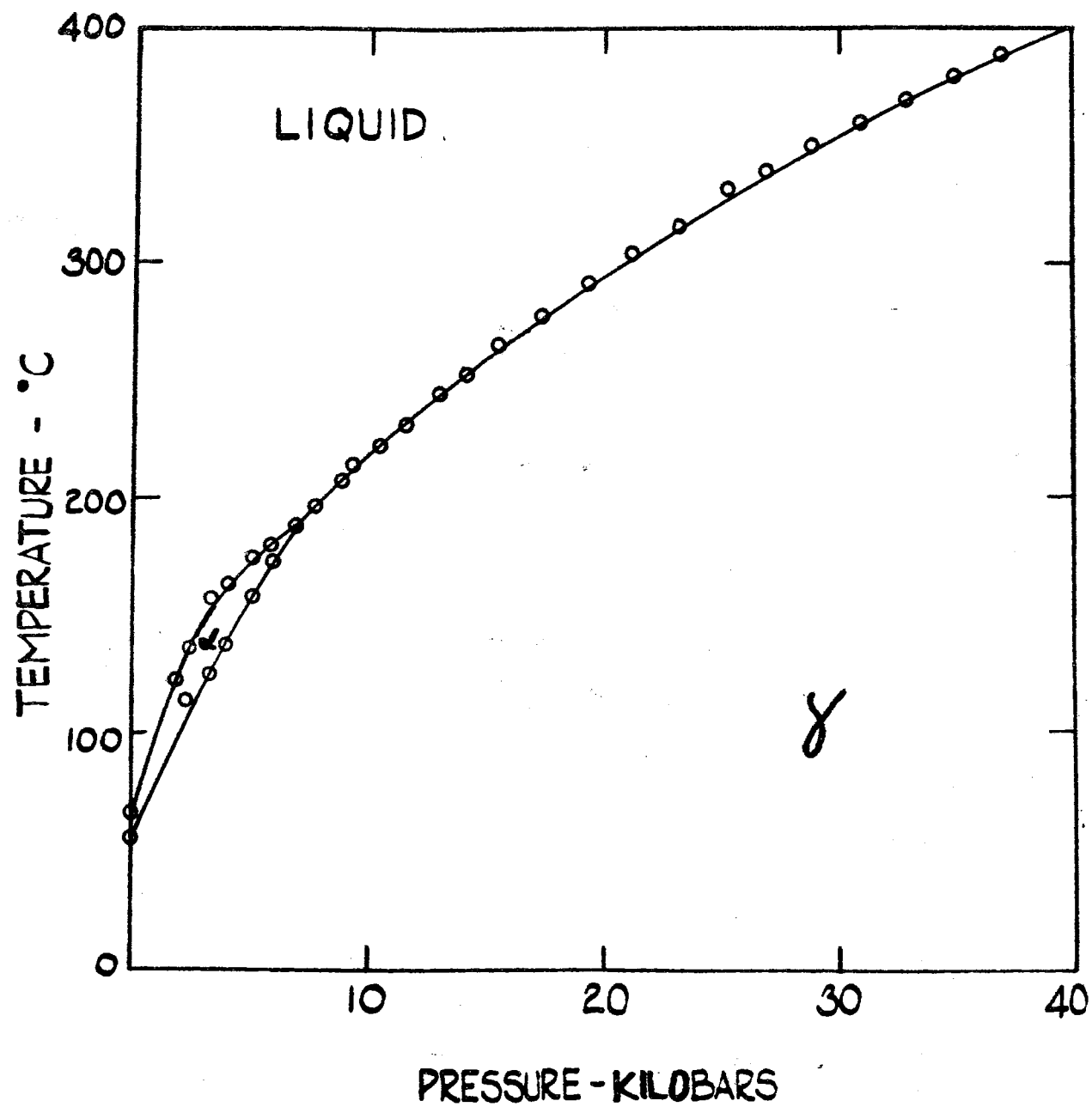


FIG. 17

Phase diagram - fraction 4.

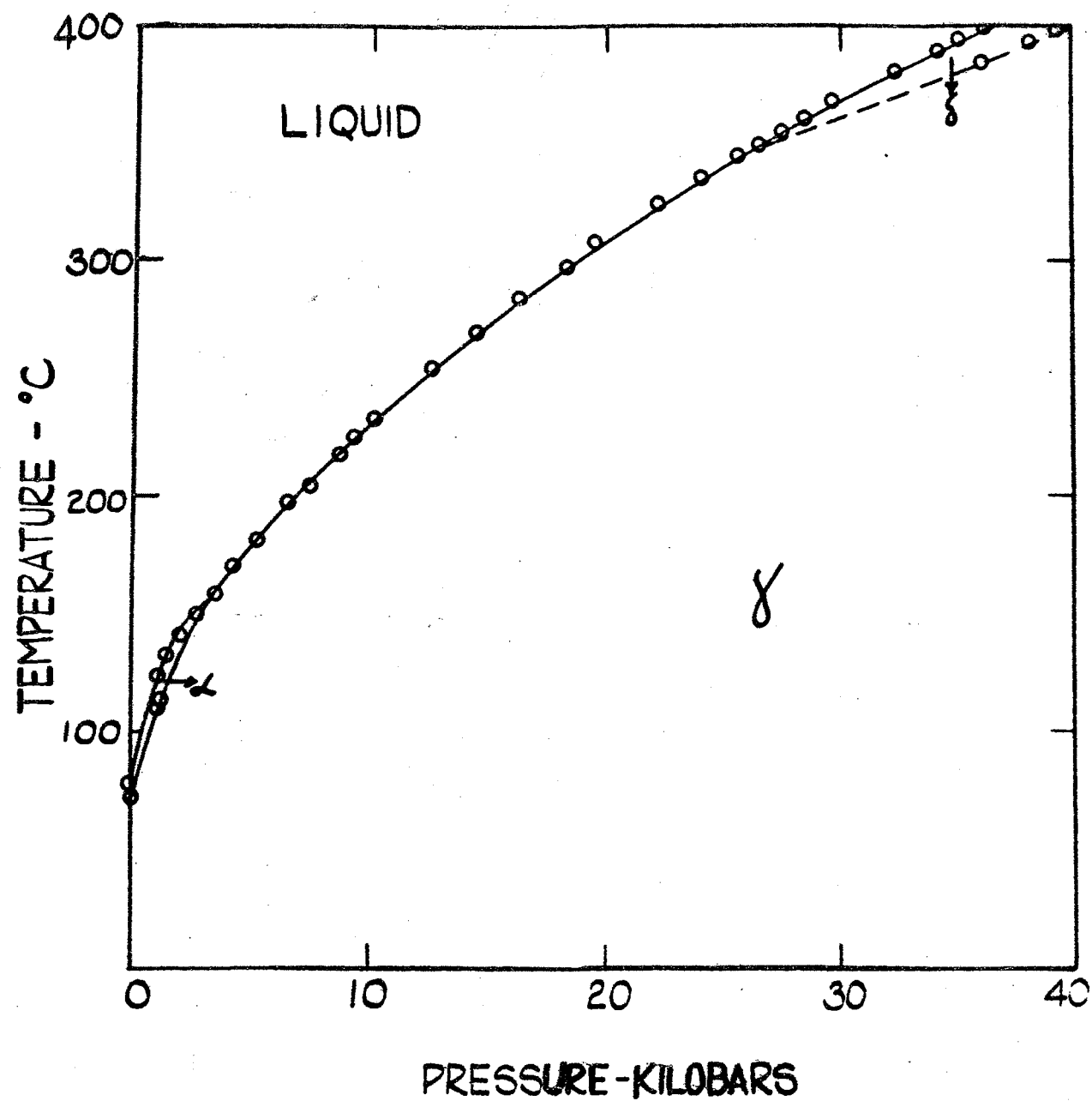


FIG 18

Phase diagram - fraction 5.

TABLE 11

Phase Behaviour of Wax Fractions at High pressure

WAX	PHASE BOUNDARY	EQUATION TO PHASE BOUNDARY (P = Kilobar)	Δt °C
FRACTION 1	v/β	$t(^{\circ}\text{C}) = 14.6P + 28.5$	0.4
	β/α	$t(^{\circ}\text{C}) = 12.3P + 36$	1.6
	v/α	$t(^{\circ}\text{C}) = 12.9(P-3.7) + 82$	1.0
	α/liquid	$P/2.69 = (T/322.2)^{4.204} - 1$	2.9
	v/liquid	$(P-16.5)/19.12 = (T/515)^{3.842} - 1$	0.7
FRACTION 2	v/α	$t(^{\circ}\text{C}) = 41.5 + 20.24P - 0.48 P^2$	2.8
	α/liquid	$P/2.17 = (T/333)^{4.845} - 1$	2.4
	v/liquid	$(P - 12.3)/16.29 = (T/493)^{3.685} - 1$	1.5
FRACTION 3	v/α	$t(^{\circ}\text{C}) = 16.1 P + 53.0$	5.2
	α/liquid	$P/1.99 = (T/337.3)^{4.943} - 1$	2.5
	v/liquid	$(P - 9.7)/12.84 = (T/483)^{3.894} - 1$	0.7
FRACTION 4	v/α	$t(^{\circ}\text{C}) = 56.0 + 22.8 P - 0.6 P^2$	1.8
	α/liquid	$P/0.94 = (T/338)^{6.833} - 1$	3.3
	v/liquid	$(P - 7.2)/14.46 = (T/464)^{3.154} - 1$	2.7
FRACTION 5	v/α	$t(^{\circ}\text{C}) = 72.0 + 33.6 P - 2.6 P^2$	0.3
	v/δ	$t(^{\circ}\text{C}) = 3.84(P - 26.5) + 348.5$	0.4
	α/liquid	$P/0.39 = (T/349.8)^{11.052} - 1$	1.3
	v/liquid	$(P - 3.5)/9.56 = (T/431)^{3.354} - 1$	1.1
	δ/liquid	$(P - 26.5)/39.17 = (T/621.5)^{2.864} - 1$	0.6

TABLE 12

Triple Points

INVARIANT POINTS	SYSTEM	PRESSURE ($\pm$ 0.5 KBAR)	TEMPERATURE ($\pm$ 2°C)
$\nu/\beta/\alpha$	FRACTION 1	3.7	82
$\nu/\alpha/\text{liquid}$	FRACTION 1	15.5	234
$\nu/\beta/\alpha$	FRACTION 2	0.5	51
$\nu/\alpha/\text{liquid}$	FRACTION 2	12.3	220
$\nu/\alpha/\text{liquid}$	FRACTION 3	9.8	210
$\nu/\alpha/\text{liquid}$	FRACTION 4	7.0	187.5
$\nu/\alpha/\text{liquid}$	FRACTION 5	3.5	158
$\delta/\nu/\text{liquid}$	FRACTION 5	26.5	348.5

The initial slopes of the melting curves at $P = 0$ are

$$\left(\frac{dT}{dP}\right)_{P=0} = T_0 / \alpha_c$$

by differentiation of the Simon equation.

Table 13 lists the changes in molar volume at the transition and fusion points at atmospheric pressure, as well as the changes of volume at the triple points. The latter values were calculated on the reasonable assumption of the approximate constancy of the total entropy change, ΔS_T , along the fusion curve, using the Clapeyron-Clausius equation. This assumption is generally borne out by experiment wherever it is possible to check it (Bridgman, 1949). The slopes of the phase boundaries at the specified points are also tabulated.

3.2 Discussion

3.2.1 Diffraction by Single Crystals and Powders

The diffraction photographs show that the reflections occur in groups and vary in intensity. This intensity distribution results essentially from the existence of a sub-cell and may be explained by considering the chain configuration within the crystal lattice.

For a completely ordered arrangement of atoms within a unit cell, for example a regularly spaced row of atoms, as shown in figure 19(a), a spacing on the film equivalent to the interatomic,

i.e./...

TABLE 13

Melting parameters at zero and triple point pressures

Parameter	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5
Initial slope of transition line ($^{\circ}\text{C}/\text{kbar}$)	12.3 (β/α) 14.6 (γ/β)	20.2 (γ/α)	16.1 (γ/α)	22.8 (γ/α)	33.6 (γ/α)
Initial slope of melting curve of α -phase ($^{\circ}\text{C}/\text{kbar}$)	29.	32.	34.	53.	80.
Initial slope of melting curve of γ -phase at the triple point ($^{\circ}\text{C}/\text{kbar}$)	7.0	8.2	9.6	10.2	13.5
Δv_{tr} at $P=0$ (cm^3/mole)	0.2 (β/α) 4.0 (γ/β)	10.9 (γ/α)	9.6 (γ/α)	16.2 (γ/α)	27.2 (γ/α)
Δv_{f} at $P=0$ (cm^3/mole)	41.4	56.0	67.1	108.0	180.0
$\Delta v_{\text{f}(\gamma)}$ at triple point (cm^3/mole)	13.3	18.9	24.7	27.6	41.3

i.e. the sub-cell, distance d is obtained. However, for a random distribution of atoms within the crystal structure, the spacing of the spots on the film refers to the unit cell length D , see figure 19(b). In the case of the waxes a compromise between the above situations occurs, figure 19 (c), thus producing a partially ordered arrangement. Intensities of spots of spacing d , are no longer equivalent.

Single crystal diffraction showed strong reflections for 0, 0, 66 and 0, 0, 68. These were not observed on the diffractometer patterns, one possible reason being that the Lorentz polarization and absorption factors are significantly different for the powder and the crystal. The Lorentz polarization factor for the powder as given by:

$$\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

is about three times larger than the factor for the crystal, which is given by :

$$\frac{1 + \cos^2 2\theta}{\sin 2\theta}$$

where θ is the Bragg angle. Another possibility is that of θ -angle integration. In single crystal diffraction patterns the reflections of a particular layer line are spread over the whole film. But with the powder patterns, all the reflections are superimposed on a common baseline. Hence resolution is significantly reduced and many of the

weaker/...

An alternate interpretation of the diffraction
intensity distribution

Consider two n-paraffin chains end to end in the unit cell as described before. The separation between the methyl end groups (measured along the chain axis) is slightly longer than the distance between neighbouring methylene groups in the chain (also measured along the chain axis). This small difference in the above mentioned spacings results in a slight phase difference in the reflections from the various planes in the two chains.

Consider the $00l$ reflections which are directly related to the spacings along the chain axis between the carbon atoms. Call the spacing between neighbouring carbon atoms d . It is easily seen that there are many more reflections from planes with spacing d than those with spacing $2d$ and in turn those with spacing $3d$ etc. The combination of this multiplicity factor and to a lesser extent the small phase difference, results in the observed intensity pattern. This may be confirmed by measuring the distance between the strongest reflections along the c-axis----- the value found relates to the subcell spacing d .

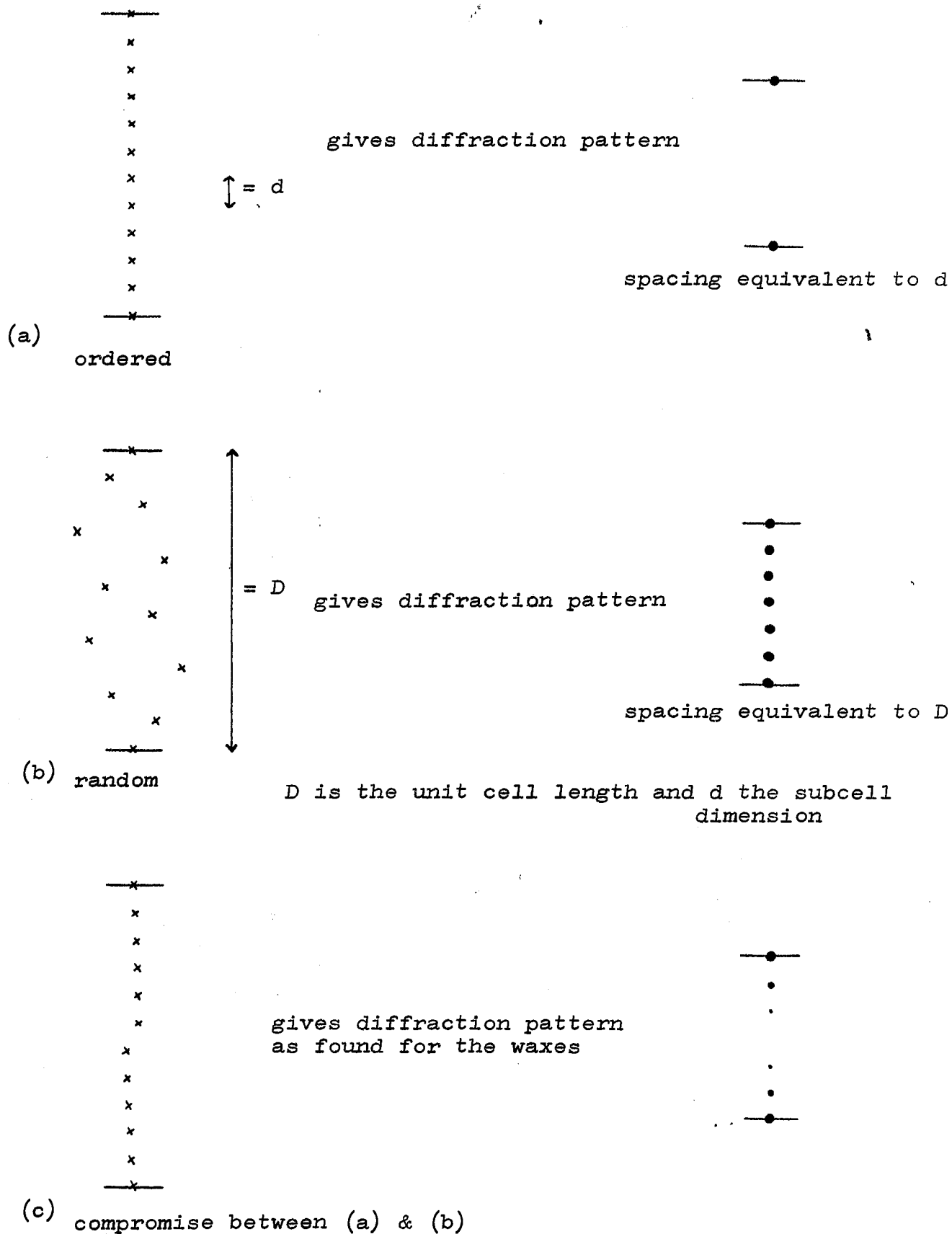


FIGURE 19.

Diffraction intensity distribution.

are
weaker high-angle reflections, obscured.

Low crystallinity also leads to low intensity at high 2θ -angles.

The powder diffraction pattern is greatly simplified above the rotational solid-solid phase transition and shows only two strong reflections, the (110) and (220) peaks of the hexagonal form. It was also observed that the (110) reflection persisted even after the sample appeared molten. This supports the infrared work of Le Roux (1969) which indicates considerable order just above the melting region. Mnzyukh (1959) detected a solid amorphous phase of "liquid" type, previously found to be characteristic only of high polymers, in straight chain paraffins. This suggests that the pure paraffins are not 100% crystalline and questions the earlier assumption (section 3.1.3.1). However, the influence of the amorphous material in the pure paraffins is considered to be negligible.

3.2.2 Molecular Configuration

The arrangement of the molecular units in the unit cell is shown schematically in figure 20(i). Müller (1932) suggested that the cross-sectional molecular volume is of elliptical shape and that the molecules oscillate about their chain axes, the amplitude of oscillation increasing as the temperature is raised. In order to accommodate four chain molecules within the unit cell, two paraffin chains are placed end to end at the positions indicated, resulting/...

which results in twice the chain length being measured.

At the transition temperature the long-chain molecules begin to rotate and describe cylindrical volumes, figure 20(b). The molecules move apart along the a-axis and slightly together in the b-direction. The schematic diagram (figure 20) clearly shows how the higher symmetry of the rotational phase (α_H) is attained.

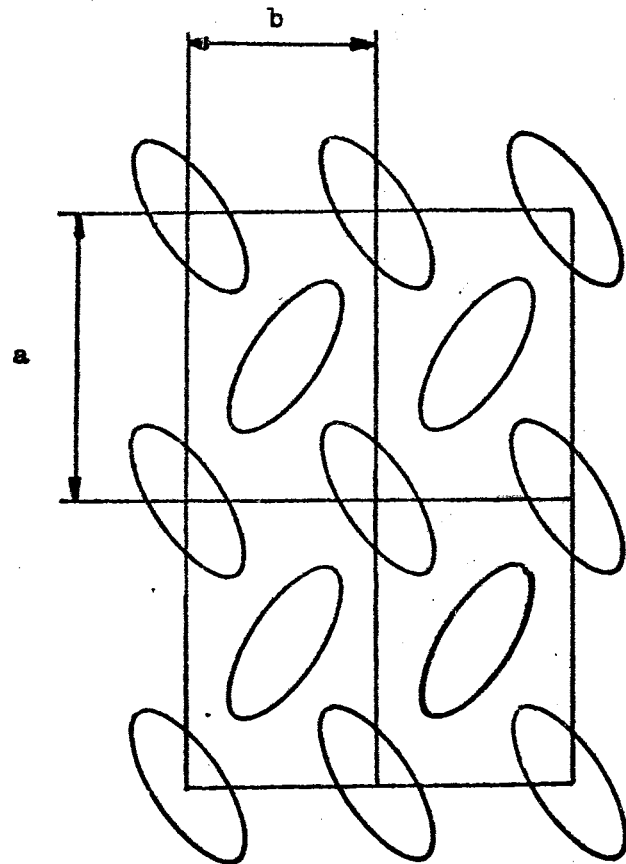
Recently a new theory for the rotational transition has been described (Blasenbrey and Pechold, 1967). The rotational transition is treated theoretically as a transition of a paraffin crystal with a 2gl-kink⁽¹⁾ acting as a dislocation in a kinked lattice crystal. For the short paraffin chains (i.e. $< C_{11}$) only a single kink is considered. However, for the longer paraffins several kinks must be accounted for. This is achieved by splitting the long chain into segments. Good agreement between theory and experiment was obtained.

Previous theories all deal with the rotation of a paraffin chain as a whole about the chain axis. The proposed kink model makes provision for rotation about individual carbon-carbon bonds, thus destroying the planar zig-zag shape. Below the transition point the density of kinks is very low, whereas above the transition temperature the kink density increases significantly. The formation of these kinks must lower the packing density.

3.2.3/...

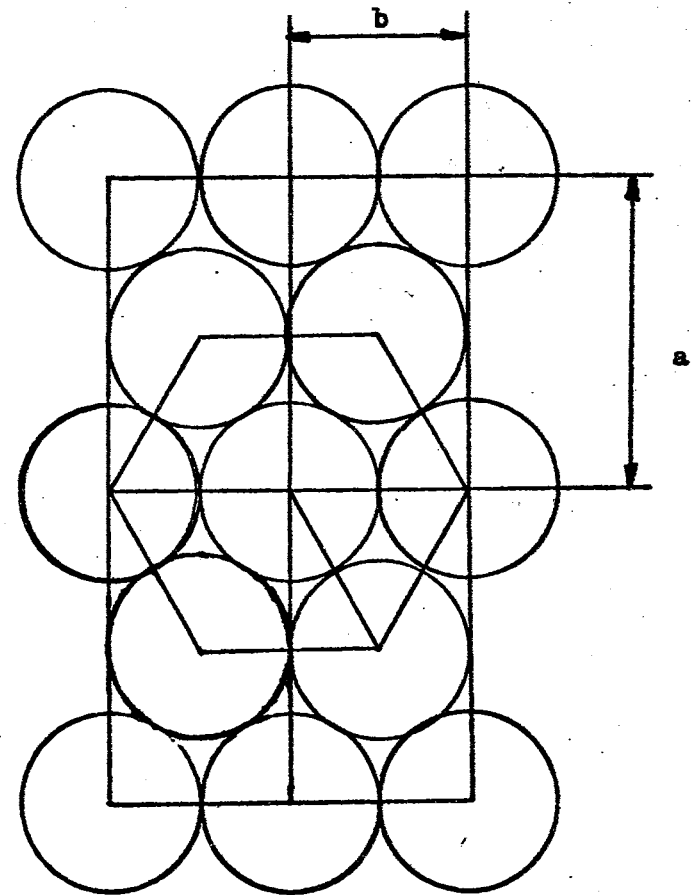
(1) A 2gl-kink comprises 2 gauche-sequences with a trans-sequence sandwiched between them.

orthorhombic



(1)

hexagonal



(11)

FIGURE 20.

Schematic configuration of molecules.

63 a

3.2.3 Chain length and Carbon number

For a homologous series of 'vertical chain' normal aliphatic compounds the relation between chain length and carbon number is given by (MacArthur, 1944) :

$$c/2 = k(n - 1) + \delta$$

where k represents the increment per CH_2 group, and δ the end gap (measured along c) between terminal carbon atoms of adjacent molecules.

MacArthur mentions several minor factors which may modify the standard interpretation of the linear relationship :

- (i) real modification in molecular chain structure;
- (ii) slight non-alignment of chain and cell axes;
- (iii) temperature
- (iv) variation in end gap between chains;
- (v) rotation or torsion of chain.

Factor (iv) is particularly relevant when considering the wax fractions. Müller (personal communication from MacArthur) suggests that linearity, beyond a first approximation for the different homologous series, will depend on what function the δ 's are of carbon number, polarity and temperature. Deviations are expected to be larger for the lower members of the series, where the melting points approach room temperature, as the effect of temperature will be quite significant for these materials.

The/...

The extrapolated relation for very pure n-paraffins is given by (Kurtz and Lipkin, 1941)

$$\frac{c/2}{\text{\AA}} = 1.27 (n - 1) + 3.27 \text{ ----- (2)}$$

Comparison with other published data indicates that the end constant actually varies from 3.27 $\text{\AA}$ to about 4.77 $\text{\AA}$, depending on how the sample was prepared. The lowest values, approaching 3.27, were obtained when the n-paraffin was allowed to crystallize on a glass plate. Mechanical disturbance after crystallization resulted in higher values.

The n-paraffin (data : Broadhurst, 1962) and wax fraction relationships are shown in figure 21. For the latter, the average carbon numbers from gas chromatography results were used as the other average carbon numbers were determined from the long spacing using equation (2), and thus provided no independent correlation. The equations representing the linear relationships are

$$\text{n-paraffins} \quad \frac{c/2}{\text{\AA}} = 1.286(n - 1) + 2.8$$

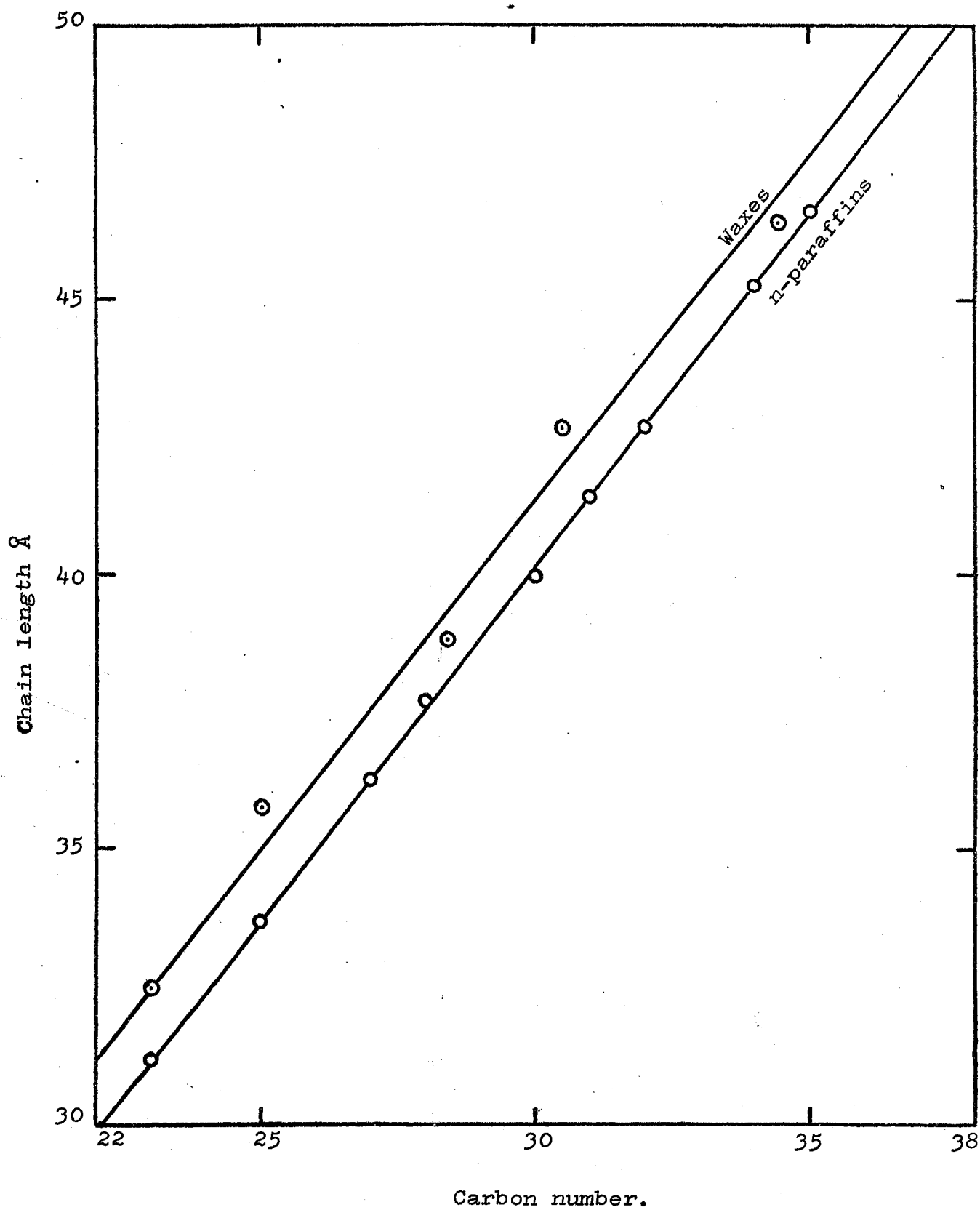
$$\text{wax fractions} \quad \frac{c/2}{\text{\AA}} = 1.27(n - 1) + 4.5$$

In the case of the n-paraffins, deviation from equation (2) is probably caused by correlation over the limited C_{20} to C_{40} range, yielding a slightly different slope which obviously affects the end constant significantly. For the wax fractions most of

the/...

FIGURE 21.

Correlation between chain length and carbon number.



the points that influence the standard linear relation listed by MacArthur are relevant and hence, ^{*}~~if a line with the correct slope is drawn through the wax values~~, it is not surprising to find that the end constant is noticeably larger than is the case for the n-paraffins.

The waxes are not completely crystalline, therefore it should be remembered that the x-ray data refer to the crystalline regions only. However, on comparing the average carbon numbers derived from x-ray and gas chromatographic data, there is no marked difference (see tables 5 and 7). The reason the x-ray values are slightly higher can be explained by assuming the amorphous portion of the sample to be composed of essentially the shorter components. This is expected to be significant for fraction 1. The molecular weight distribution of the amorphous and crystalline phases is thus not symmetric and slightly different averages arise.

3.2.4 Crystallinity

A knowledge of the percentage crystallinity of each wax fraction was necessary for adequate correlation with the n-paraffins. Because the paraffin waxes are orthorhombic in structure, comparison is only made with the pure odd n-paraffins as these are also orthorhombic (although of a different space group) and exhibit the rotational order-disorder solid phase change of the waxes. Reliable data for
the/...

* such as enthalpy, entropy and density

the pure odd n-paraffins in the wax range (i.e. C_{20} to C_{40}) are presented in Broadhurst's paper (1962) on the phase behaviour of the n-paraffins. Properties dependent essentially on the proportion of crystalline material may be corrected by the appropriate factor before comparisons with the pure odd n-paraffins are made.

Crystallinity determinations indicate that fraction 1 has a value ~~far~~ lower than the rest of the fractions. This results from the former having a much wider range of composition than the other fractions and being probably the only fraction containing the very small percentage of iso-components usually present in the medium wax. Deoiling never removes all isoparaffins. Branched chains greatly hinder crystallization and although each fraction has six main components, the postulated iso-content in fraction 1, though small, ~~greatly~~ reduces its crystallinity.

Some properties* were measured on the whole wax and in each case, using an average carbon number, the data did not fit in with that of the wax fractions. This suggests that the range of composition and compositional distribution have a marked effect on the properties and, hence, the crystallinity of the substance.

3.2.5 Measurements from DSC

The validity of certain parameters obtained from DSC thermograms is not well established; in particular/...

particular the melting or transition temperatures are uncertain. It should be stressed that it is not strictly accurate to speak of a melting point, but rather of a melting range (especially in the case of the mixtures which are of concern here). Even in pure compounds crystal defects result in a range of melting, although small. A theoretical justification for the points chosen is given in appendix II.

Recently, Brennon, Miller and Whitwell (1969) have described a new technique for analysing DSC data where there is a shifting heat capacity base-line for a system undergoing a thermal event, allowing enthalpy change to be isolated from heat capacity contributions. However, since the base-line in the case of the wax fractions is not displaced before and after the total endothermic change, their analysis is not required.

3.2.6 Enthalpy and Entropy Changes

3.2.6.1 Enthalpy

The relationship between the total enthalpy difference in the two states of aggregation (viz. the solid and liquid phases) and carbon number, is given by the general form

$$\Delta H_T = \Delta h_T (n - 1) - \Delta H_E$$

The first term in this equation may be considered to represent the Van der Waals attraction and implies a constant increment
per/...

per mole for each additional carbon-carbon bond added to the chain. The constant term refers to the repulsive contribution from the end groups. The wax fractions and odd n-paraffins are correlated in figure 22 and the equations representing the linear relations are :

$$\Delta H_T = 0.858(n - 1) - 0.72 \text{ k cal. mole}^{-1} \quad (3)$$

for the odd n-paraffins, and

$$\Delta H_T = 0.858(n - 1) - 3.85 \text{ k cal. mole}^{-1} \quad (4)$$

for the wax fractions.

A reason why the constant term is larger in the case of the waxes could be the irregular alignment between different layers which results from the crystal being a hybrid of several chain lengths.

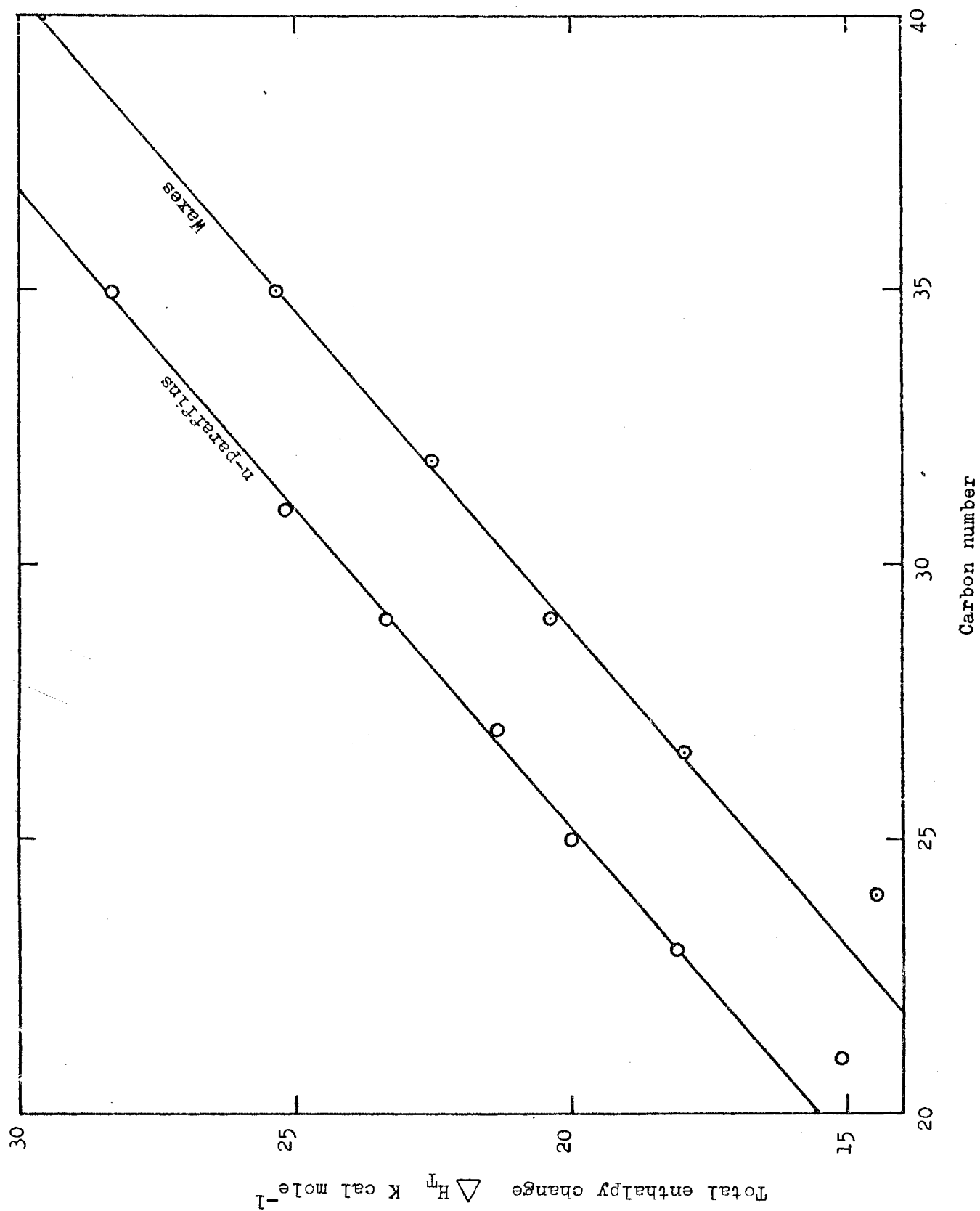
Muller (1941) has shown that the repulsive forces between paraffin chains have their origin essentially in the hydrogen shells that surround the carbon chain. The forces are of the same order as those existing between helium atoms.

It must be remembered that the structures are slightly different for the two cases and the lattice parameters indicate that the molecules are slightly closer together, both end-to-end and sideways-on, for the n-paraffins. The former leads to a larger negative/...

FIGURE 22.

69 a

Correlation between total enthalpy change and carbon number.



negative constant while the latter should alter the slope. This would imply a larger repulsive contribution for the pure compounds, but the opposite is found. However, end group repulsion is likely to be significantly larger than repulsion between the chains and, hence, will override the above discrepancy.

The depression of the freezing point derived using the Chapeyron-Clausius equation is given by :

$$\frac{d \ln x_1}{dT} = \frac{\Delta H}{RT^2}$$

where x_1 is the mole fraction of solvent, T the absolute freezing temperature, ΔH the enthalpy change on freezing and R the molar gas constant.

When x_1 is unity, i.e., pure solvent, the freezing point is T_0 and integration between T and T_0 , assuming ΔH to remain constant, gives

$$\ln x_1 = -\frac{\Delta H_F}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

or $\ln x_1 \sim -\frac{\Delta H_F}{R} \cdot \frac{\Delta T_F}{T_0^2},$

where ΔT_F is substituted for $T_0 - T$, and $T_0 T$ is put equal to T_0^2 , which is justifiable if the solution is dilute. Since $x_1 + x_2 = 1$, $\ln x_1$ is equal to $\ln(1 - x_2)$, and for dilute solution, i.e., when x_2 is very small, $\ln(1 - x_2)$ is approximately equal to $-x_2$, so that

$$\Delta T_F / \dots$$

(71)

$$\Delta T_F = \frac{RT_o^2}{\Delta H_F} x_2 \text{ ----- (5)}$$

where x_2 represents the mole fraction impurity, i.e. the solute.

A similar expression holds for the solid-solid transition process, viz.

$$\Delta T_t = \frac{R T_o^2}{\Delta H_t} x_2 \text{ ----- (6)}$$

These equations are based on the assumption that the impurity is insoluble in the solid. Therefore the mole fraction of impurity will be the same for the solid as for the liquid, and expressions (5) and (6) may be combined to yield

$$\frac{\Delta H_t}{\Delta H_F} = \frac{\Delta T_F}{\Delta T_t} \cdot \frac{(T_o^2)_t}{(T_o^2)_F} \text{ ----- (7)}$$

where ΔT_F is the depression of the freezing point and ΔT_t the depression of the transition point. The equation may be approximated to

$$\frac{\Delta H_t}{\Delta H_F} \approx \frac{\Delta T_F}{\Delta T_t}$$

The impurity, which should lower the crystallinity, will have the same relative effect on both the transition and fusion processes. However, the magnitude of the

enthalpy/...

enthalpy change is a factor of two or more smaller for the former transformation.

This will cause a significantly larger absolute influence on ΔH_t and hence the depression of the transition point. Therefore the transition points are a far more sensitive measure for the presence of impurities. This is borne out in the correlation of the melting point and transition point data for the n-paraffins and wax fractions as shown in figure 27.

Equation (7) does not hold if solid solutions form between the impurity and major component. For the wax fractions significant deviations from the equality, represented by equation (7), were found. This indicates the possible presence of solid solutions for the waxes which is not an unreasonable deduction, as the impurity is in the form of neighbouring homologues. Formation of solid solutions may actually raise the melting point of a sample above that of the pure material.

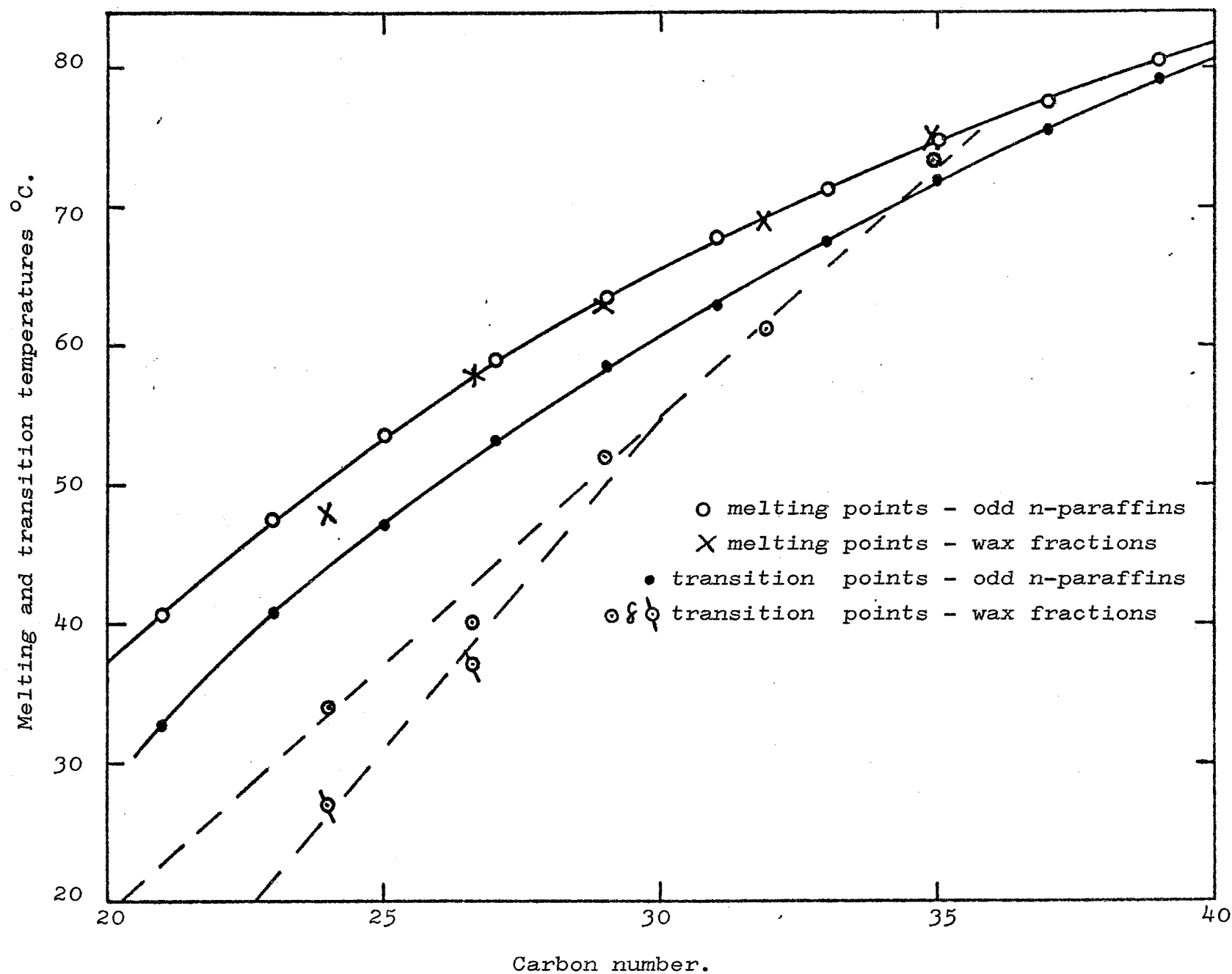
The equation for the freezing point depression when solid solutions are formed is given by :

$$\Delta T'_f = \frac{R T_o^2}{\Delta H_f} (x_2 - x_2')$$

where x_2' is the mole fraction of solute in the dilute solid solution. The equation may be rewritten in the form

$$\Delta T'_f / \dots$$

7a9



$$\Delta T_f' = \frac{R T_o^2}{\Delta H_f} x_2 \left(1 - \frac{x_2'}{x_2} \right),$$

where x_2'/x_2 is the ratio of the mole fraction of the solute in the solid to that in the liquid solution.

Replacing the fraction, x_2'/x_2 , by the distribution coefficient, represented by k , the equation becomes

$$\Delta T_f' = \frac{R T_o^2}{\Delta H_f} x_2 (1 - k) \text{ ----- (8)}$$

If the impurity does not dissolve appreciably in the solid solvent, then k is almost zero and equation (8) reduces to (5). From the present data the extent of solid solutions formed in the wax fractions could not be determined.

Within experimental error the ratios $\Delta H_t/\Delta H_F$ for the wax fractions were found to be almost constant, at about 0.3. Barmby, Huston and Bostwick (1956) found a constant ratio of about 0.66 for the petroleum waxes. The reason why the latter is just about twice the value found for the wax fractions is not clear, but implies that their measured heats of transition are significantly larger than those found in this work. For the n-paraffins, calorimetric studies indicate that the latent heats of transition are approximately half the heat of fusion, which gives a ratio of about 0.5. Waxes which have a range of composition and hence a lower crystallinity, are expected to/...

to yield a lower ratio than the pure paraffins. This suggests a probable error in the calorimetric measurements of Barmby et al.

3.2.7.2 Entropy

Aranow, Andrews and Witten (1958) have shown that for the n-paraffins, the total entropy change ΔS_T (i.e. the entropy change of fusion ΔS_f plus the entropy change of transition ΔS_{tr}) is related to the carbon number by the approximate relation

$$\Delta S_T / (\text{cal. deg.}^{-1} \text{mole}^{-1}) = R \ln 3(n-1) + 5.31 \quad (9)$$

In their fusion model of paraffins there are three potential minima for rotation about each carbon-to-carbon bond and this yields a factor of $R \ln 3$ for the entropy increase per mole on addition of a carbon-carbon bond. The constant 5.31 was calculated for ethane from their fuller expression for the fusion model.

The odd n-paraffin and wax fraction relationships are shown in figure 12, and the points may be represented by :

$$\Delta S_T (\text{cal. deg.}^{-1} \text{mole}^{-1}) = 2.2(n-1) + 8 \quad (10)$$

for the odd n-paraffins; and

$$\Delta S_T (\text{cal. deg.}^{-1} \text{mole}^{-1}) = 2.2(n-1) - 1.8 \quad (11)$$

for the wax fractions.

The odd n-paraffin data (Broadhurst, 1962) could be fitted to the approximate relation given in equation (9), but with a different

intercept/...

intercept. Obviously a certain error is involved in extrapolation to zero, for the relationships have only been considered over a range of 20 to 40 carbon atoms. The relative errors in the slope and intercept are assumed to be about five percent. However, a five percent error in the slope gives a significant absolute error in the intercept, i.e. ± 3 .

The degree of "randomization" introduced during a change of phase from solid to liquid is represented by the ΔS_T . For a crystalline material this will have a certain value composed of a chain contribution and an end-group contribution. On consideration of both the n-paraffins and wax fractions, it is expected that the chain contribution remains unaltered. Mixtures of aligned molecules are represented by an average carbon number. The end-group contribution will be significantly altered by the non-uniformity of the system, and will be affected so that the end-group contribution will be lowered because of the already randomized situation in the solid. The negative value in equation (11) indicates that this effect perhaps extends into the chain region, reducing the contribution from the aligned chains.

The entropy of transition, ΔS_{tr} , comprises the sum of the entropy of expansion and the configurational entropy change, $R \ln \Omega$. Ω is the number of equivalent positions which a molecule may occupy in the rotational (α_H)-phase as it rotates through an angle 2π about its/...

its long axis. Ω is expected to lie in the range 8 to 18, but if the molecule twists severely, Ω would increase markedly with increasing chain length (Hoffman and Decker, 1953).

The entropy of expansion is given by

$$\Delta S_{\text{exp}} = 2.34 \times 10^{-5} \Delta V \alpha' / \beta'$$

where α' is the coefficient of cubic expansion in deg.^{-1} , β' the cubical compressibility in $\text{cm}^2 \text{g}^{-1}$ and ΔV the change in molar volume at the transition point in ml. per mole; 2.34×10^{-5} is a conversion factor.

Hoffman and Decker give the value for α in the C_{20} to C_{30} n-paraffin range as $60 \times 10^{-5} \text{deg.}^{-1}$. Müller (1941) has found the compressibility of a paraffin wax to be $1.7 \times 10^{-8} \text{cm}^2 \text{g}^{-1}$. Using these values and the volume changes found from the high pressure analysis (table 13), expansion entropies for each wax fraction were calculated and hence Ω determined calculations were carried out both with and without corrections for crystallinity and the values listed in table 14.

$$R \ln \Omega = \Delta S_{\text{tr}} - \Delta S_{\text{exp}}$$

$$\therefore \Omega = \text{antilog} \frac{\Delta S_{\text{tr}} - \Delta S_{\text{exp}}}{2.303 R}$$

TABLE 14/...

TABLE 14

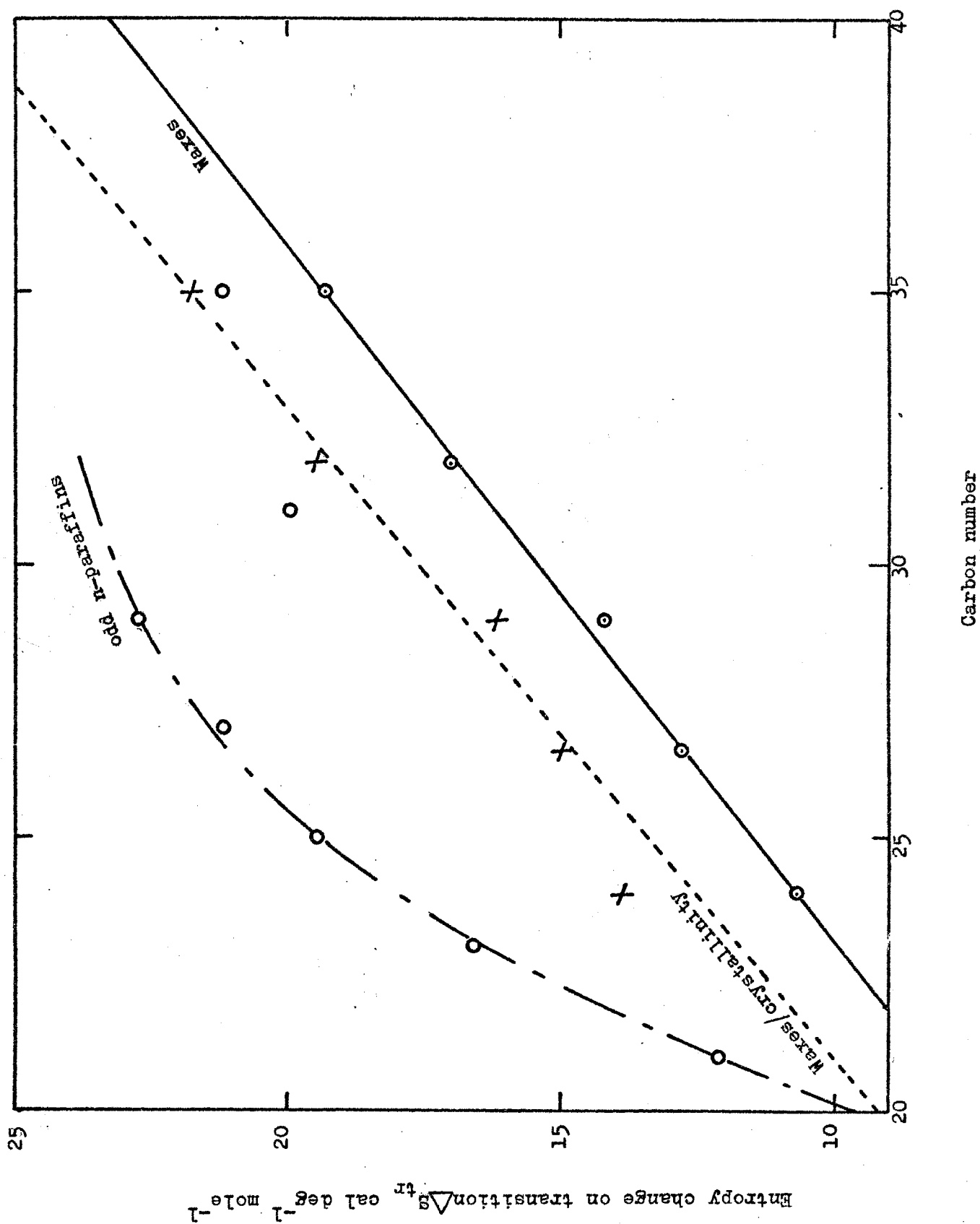
FRACTION	Ω corrected for crystallinity	Ω not corrected for crystallinity
1	49	21
2	10	9
3	40	24
4	8	6
5	-6	-8

As seen from the table, values of Ω have a rather random appearance. Experimental error should greatly affect Ω for it is a logarithmic function. The high values could mean torsional twisting of chain molecules but no definite conclusion can be made. In the case where crystallinity factors were ignored and the value for fraction 5 discarded, an average $\Omega = 15$ was found which is remarkably close to the value ($\Omega = 14$) found by Hoffman and Decker (1953) for their transition model.

For the wax fractions the entropy of transition was found to exhibit a nearly linear relation with average carbon number (see figure 23). No such relationship occurs for the odd n-paraffins, also shown in the figure. Hoffman and Decker (1953) found the transitional entropy to be independent of chain length for the even n-paraffin in the

77a
FIGURE 23.

Correlation between entropy of transition and carbon number.



C_{20} to C_{30} range. The difference in behaviour between the even and odd n-paraffins is not unexpected as the even-odd effect, resulting from different end group packings is well established (Müller, 1929; Broadhurst, 1962). However, the dissimilar behaviour of the odd n-paraffins and wax fractions can only be related to the presence of impurities in the latter. Small amounts of impurity are known to stabilize the orthorhombic form.

3.2.7 High Pressure Phase Behaviour

All the fusion curves have normal concave curvature towards the pressure axis, with the melting temperatures rising considerably with increasing pressure. The volume changes on fusion decrease normally with increasing pressure, and the rate of decrease also becomes less at higher pressures.

Barmby, Huston and Bostwick (1956) suggested that the γ/β transition is of the first order and involves the transformation of one orthorhombic lattice into another by discrete changes in the cell constants, while the β/α transition, although from an orthorhombic to a hexagonal lattice, is of the second order. The DTA signals observed in the present work for the β/α transition of fraction 1 were considerably smaller and less well-defined than those for the γ/β transition. It should be borne in mind that, if either of the γ/β or β/α transitions is of the first order, the γ/α transition will also be of the first order.

The/...

The β -phase cannot exist at positive pressures for wax fractions higher than the present fraction two ($\sim C_{27}$). The stability region of the α -phase also decreases considerably with increasing molecular weight, and is quite small for fraction 5 ($\sim C_{35}$). The liquid/ γ / α triple points move towards lower pressures with increasing mean molecular weight of the wax fractions, while at atmospheric pressure the γ/α transition points simultaneously approach the melting points. The initial slopes of the liquid/ α phase boundaries increase with molecular weight (see figures 14 - 18).

The various phase diagrams can therefore be combined into a "master" diagram as shown in figure 24. The broken lines refer to the atmospheric pressure ordinates of the various fractions. This diagram clearly illustrates the dependence of the phase behaviour on the molecular weight and hence on the carbon number for n-paraffin waxes. It is apparent that increasing pressure simulates a longer chain-length. This master diagram can therefore be used to predict the approximate phase behaviour of other n-paraffin waxes.

The considerable decrease in the size of the DTA signals in the pressure range 10-30 kbar can be ascribed to the failure of the samples to recrystallize fully upon freezing. A run in which ~ 20 kbar was reached after ~ 30 melting/freezing cycles yielded very small signals, while a similar run in which pressure was directly taken to ~ 20

kbar/...

79a

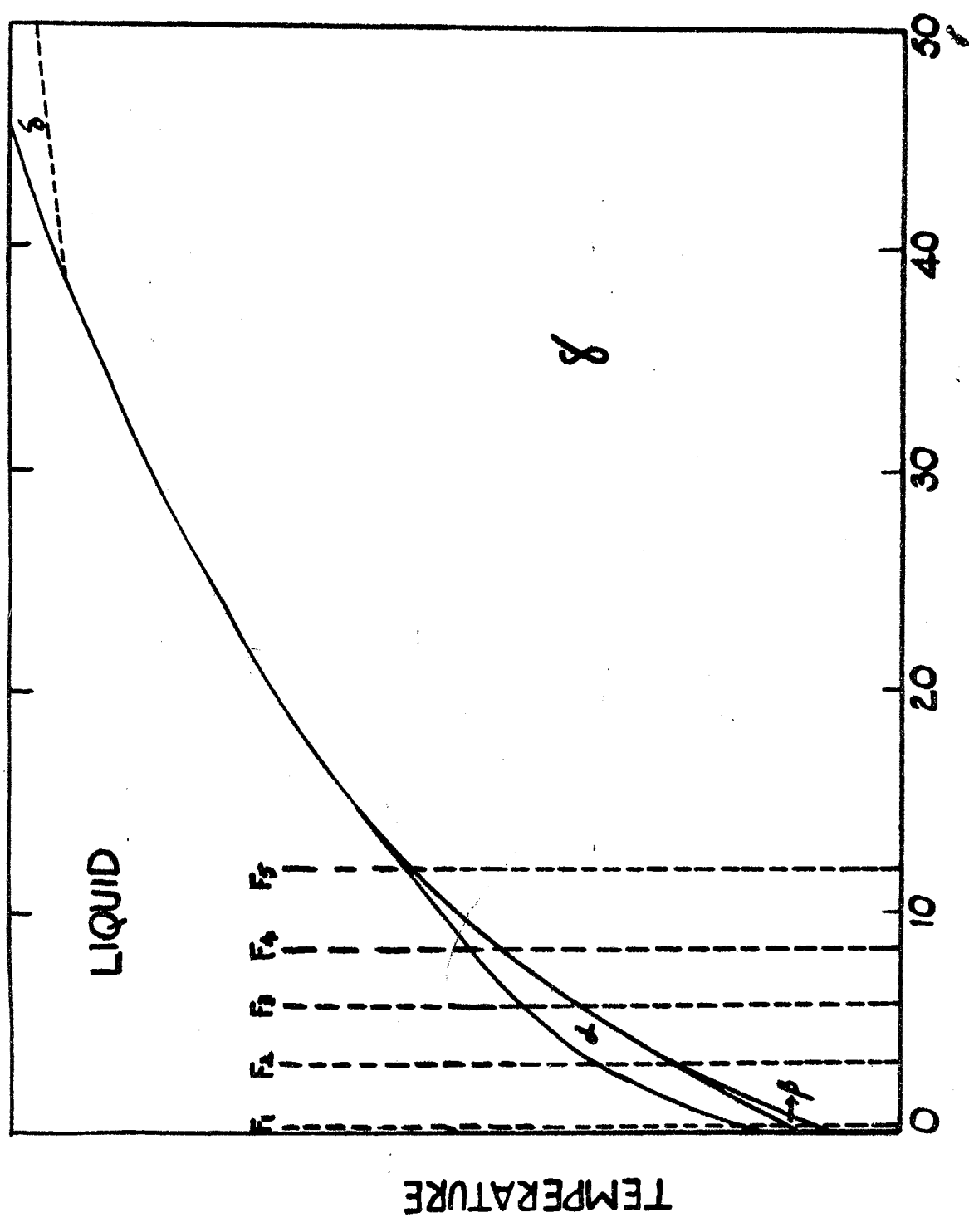


FIG. 24

'master' phase diagram.

kbar yielded large signals. Furthermore, the signal size could be improved to some extent by "annealing" the sample at a low temperature for 10 minutes or more. The increase in the signal size at pressures above ~ 30 kbar can be simply explained by taking into account the higher rate of recrystallization at the higher temperatures of the melting curve in this pressure range. Another possibility is the description by Cuttler et al. (1958) of the variation of internal energy with pressure and volume. The physical interpretation suggests that the resultant forces under low pressure are attractive and as the volume decreases the potential energy of the mutual forces decreases. When the volume has undergone a sufficient decrease, the repulsive forces become predominant and a further decrease in volume results in an increase of the internal energy.

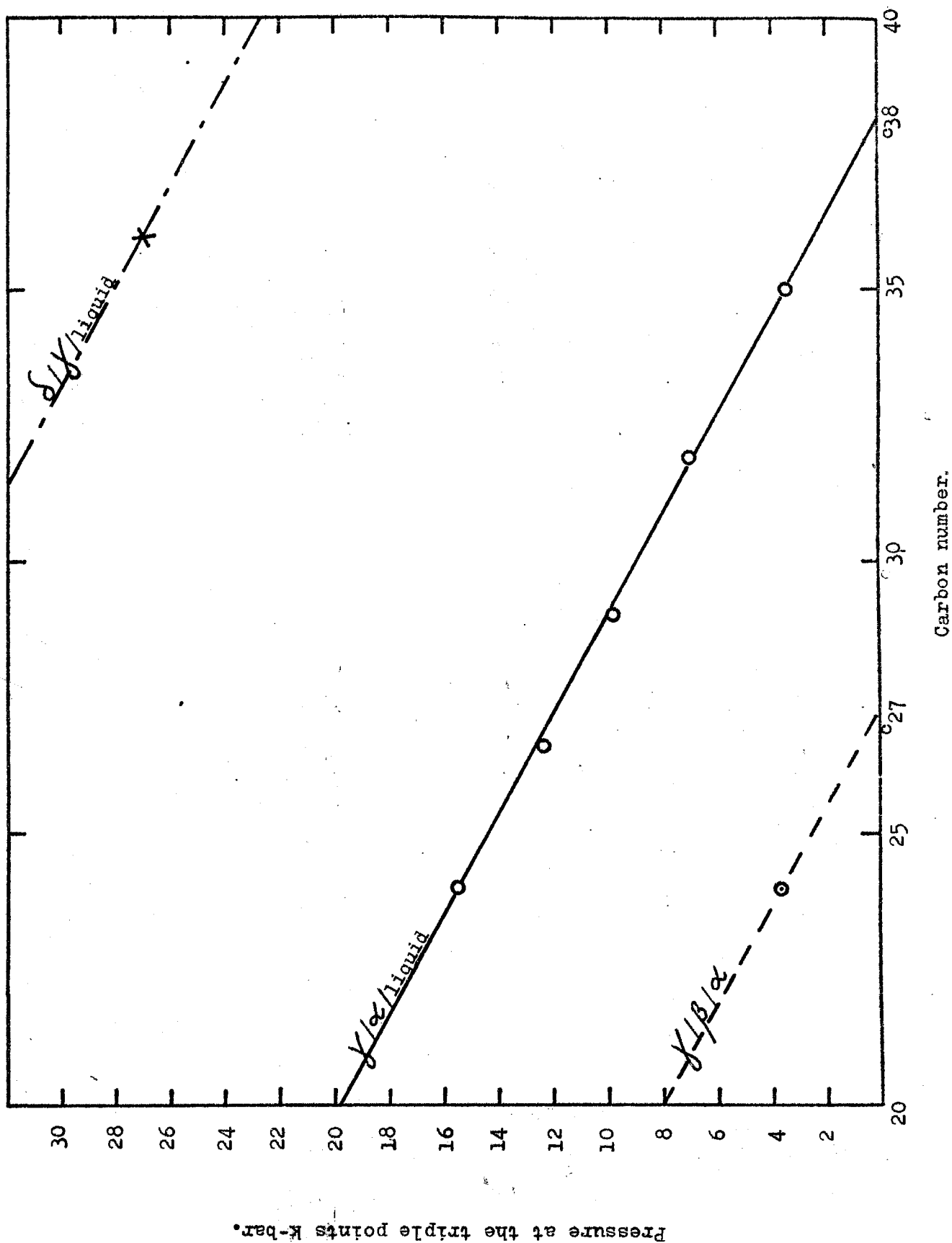
If the γ/α phase transition is considered as being an order-disorder transition involving rotation of the n-paraffin chains, the phase diagrams show that, at high pressures, the rotation of the chains is inhibited. When the molecules have enough thermal energy to overcome this effect, the entropy is already large enough to cause disintegration of the crystal lattice, and melting occurs.

It is interesting to note that the linear relationship between the liquid/ γ/α triple points and their carbon numbers (figure 25) implies that
the/...

FIGURE 25.

80 q

Correlation of triple point pressures with carbon number.



the orthorhombic/hexagonal (γ/α) transition no longer occurs for mean carbon numbers above n_{39} . A similar line for the β/α transition suggests that this transition will be absent beyond $n_{C_{27}}$, as is known (Barmby, Huston and Bostwick, 1956).

Except for possible phase separation at higher pressures or carbon numbers there is no even-odd effect in the present waxes. In fact, even one or two percent of impurities suffice to destroy even-odd effects characteristic of pure n-paraffins (McClure, 1968). The nature of the transitions and of the phases occurring is also changed. It is, therefore, clear that a comparison of the present work with earlier high-pressure studies on pure n-paraffins is, although instructive and possibly reasonable for the odd n-paraffins, not completely valid. Deffet (1935) measured the melting and transition curves of n-C₃₂ to 1 kbar. This n-paraffin is closely related to this fraction 4. The slopes of his boundaries agree with ours to ~ 0.25 kbar, well within the combined experimental error. Nelson, Webb and Dixon (1960), working on a series of n-paraffins, examined their phase behaviour to 10 kbar. The longest chain substance studied by them, viz., n-C₂₄, is close to that for fraction 1, but shows, even at atmospheric pressure, completely different transition phenomena. They concluded that the melting curves of pure n-C₉, n-C₁₂, n-C₁₃ and n-C₂₄ could not be satisfactorily fitted by the Simon equation, while that of n-C₁₈ could/...

could. The present melting curves of the wax fractions are fitted by the Simon equation within the experimental error, but it is probable that, had the experiments over a large pressure range been as accurate as those of Nelson et al. over a restricted pressure range, the fit might have been less satisfactory.

3.2.7.1 Fractions from Hard Wax

X-ray diffraction of the hard wax fraction was undertaken for the possible elucidation of the double endotherm shown on its DSC thermogram. As the d-spacings remain essentially constant (figure 10) and no transformation to the more symmetrical hexagonal form takes place, the result lends support to the suggestion that the DSC peaks represent phase separation. The possibility of a solid-solid transition from one orthorhombic to another closely related orthorhombic form cannot, however, be excluded.

Many of the crystallized fractions from hard wax exhibit this double endotherm phenomenon. One significant effect is the progressive separation of the two endotherms with increasing molecular weight, whereas with the medium wax fractions the transition and fusion peaks merge with increasing molecular weight. It is suspected/...

suspected that the appearance of the induced high pressure ' δ -phase' in fraction 5 is closely related to the two peaks observed with the hard wax fractions. Both observations might mean the same thing.

Kitaigorodskii, Mniukh and Nechitailo (1959) have shown that continuous solid solutions do not form between even and odd n-paraffins and under identical conditions it was found that molecules with greater chain lengths have lower solubility than molecules with shorter chain lengths. Pressure has the effect of simulating longer chains and if the difference in chain lengths exceeds four carbon atoms for the components of the mixture, phase separation is known to result. (Piper et al, 1931). All these factors contribute to the suggestion that phase separation is a reasonable explanation for the observed phenomenon. The two endotherms produced by the hard wax fractions then represent the melting of two components, one rich in even n-C_n chains and the other in odd n-C_n chains.

If the high-pressure high-temperature phase δ found above ~ 30 kbar for fraction 5 is, in fact, a new solid phase, then, on the basis of the "master" phase diagram (figure 24), a similar phase may be expected to occur in

the/...

the phase diagrams of the other wax fractions at pressures above 40 kbar. Furthermore, such a phase might occur at atmospheric pressure below the melting point of a wax fraction with a sufficiently high mean carbon number. The estimation of the necessary carbon number is necessarily crude. A linear relationship exists between the present liquid/ γ/α triple point and their respective carbon numbers (see figure 25). If a similar relationship with the same slope for the liquid/ δ/γ triple points is assumed, the high-pressure form of fraction 5 simulates the atmospheric pressure behaviour of a fraction with a mean carbon number of at least 60.

For the homologous series of n-paraffins the essential variable is chain length and the short-spacings are seen to remain practically constant. It has been shown that chain length and carbon number bear a linear relation to one another (see section 3.2.3). Noting the fact that pressure simulates longer chain lengths, it is not unexpected that pressure should exhibit a linear relation with carbon number. It is also not entirely unreasonable to assume that the different triple point pressures will show a similar relation, having in common the same slope. For, when drawn with the same slope, the $\alpha/\beta/\gamma$ triple point pressure line intersects the horizontal axis at $\sim C_{27}$, which/...

which is approximately at the boundary differentiating waxes with two and one solid-solid transition, respectively (Barmby, Huston and Bostwick, 1956).

3.2.7.2 The Simon Equation

The reduced form of the Simon equation has the form

$$\pi = \tau^c - 1 \text{ ----- (12)}$$

where $\pi = (P/a)$ is the reduced pressure and $\tau = (T/T_0)$, the reduced temperature.

Dudley (1960) suggests that if the parameter c in the Simon equation is constant for all substances concerned (section 1.7), expression (12) may be considered as a law of corresponding states. For a class of substances this is almost true. For example, for diatomic gases $C \sim 1.8$ and for the alkali metals $C \sim 4.0$. In the case of the wax fractions, which can be regarded as part of a homologous series, $C \sim 3.6$. This is only applicable for the γ /liquid portion of the curve. Over the α /liquid portion the constant varies between 4 and 11. Large errors inherent in the Simon constants 'a' and 'c' make any conclusions or deductions difficult. It should be remembered that the Simon equation is to be considered only as a very useful and simple interpolation equation and/...

and it should not be considered as an exact representation of the melting curve (Babb, 1963).

Recalling the general form of the Simon equation, it may be rearranged to

$$T^c = \frac{P - P_o + a}{a} T_o^c$$

P_o is usually neglected as it is only a few tenths of an atmosphere. Differentiation with respect to pressure gives

$$\frac{d(T^c)}{dP} = \frac{T_o^c}{a} = cT^{c-1} \frac{dT}{dP}$$

$$\text{since } \frac{dT^c}{dP} = cT^{c-1} \frac{dT}{dP}$$

Hence,

$$\frac{dT}{dP} = \frac{T_o^c}{acT^{c-1}} \text{-----(13)}$$

and further rearrangement yields

$$\frac{dT}{dP} = \frac{T_o}{ac} \left(\frac{a}{P+a} \right)^{\frac{c-1}{c}}$$

Now at zero applied pressure, the usual form for the initial slope of the melting curve is obtained, viz.

$$\frac{dT}{dP}, P=0 = \frac{T_o}{ac} \text{-----(14)}$$

The Clapeyron-Clausius equation is given by

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \text{-----(15)}$$

where ΔH is the enthalpy change and ΔV the volume change of the particular process. T is the absolute temperature

at/...

at which the process occurs.

Equations (13) and (15) may be equated providing an expression for ΔH :

$$\Delta H = T \Delta V \cdot \frac{acT^{c-1}}{T_o^c}$$

i.e. $\Delta H = ac \Delta V \left(\frac{T}{T_o} \right)^c$ ----- (16)

but $\left(\frac{T}{T_o} \right)^c = \frac{P}{a} + 1$ and it has been shown that the total enthalpy change varies linearly with carbon number over the range investigated in this work (section 3.2.6.1). Therefore, equation (16) becomes

$$\Delta H = c \Delta V (P + a) = x(n-1) + y \text{---} (17)$$

where x and y are constants.

At zero applied pressure, the latter expression is simplified to

$$\Delta H = c \Delta V a \text{-----} (18)$$

However, it is probably more correct not to ignore the effect of atmospheric pressure and therefore the more accurate expression is given by

$$H = c \Delta V (1 + a) \text{-----} (19)$$

Equation (18) represents a relationship between the work done against the lattice forces on expansion multiplied by an "intensification" factor (c) and the carbon number

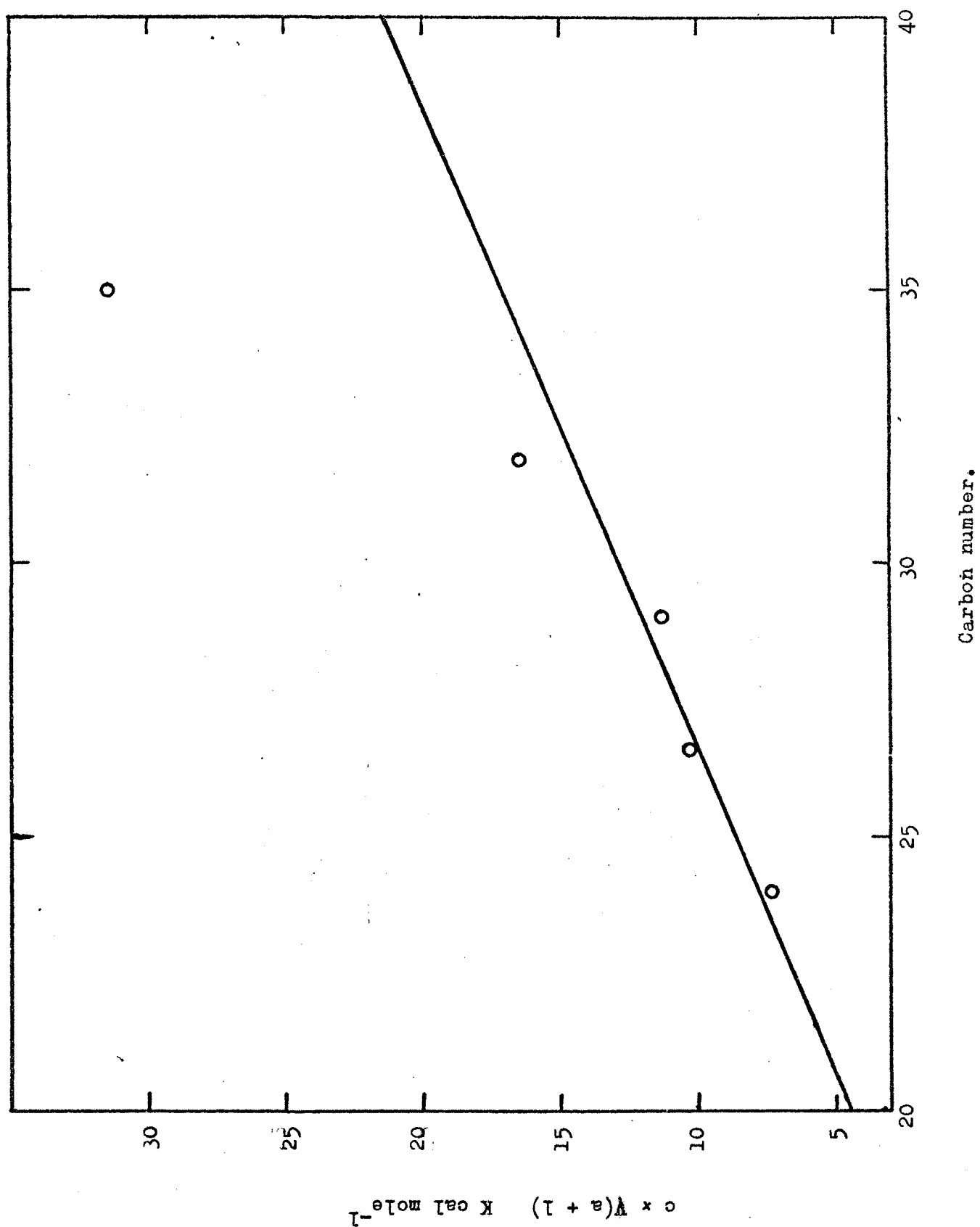
related/...

related linearly to the enthalpy change. A plot of $c\Delta V(1 + a)$ against carbon number is shown in figure 26. The slope of the line should be the same as for the $(\Delta H_T, n)$ relation. If a line with the correct slope is drawn through the calculated values, reasonable agreement is obtained, except for fraction 5. However, large errors are inherent in the volume determinations and as the total volume change, ΔV_T , for fractions 4 and particularly 5 are significantly larger than for the other fractions, the deviations are most marked. The volume change calculations incorporate the initial slopes of the melting curves and the estimated error in the slope is assumed to vary between about 5% for the smaller slopes to about 15% for the largest slope.

FIGURE 26.

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Correlation between work of expansion and carbon number.

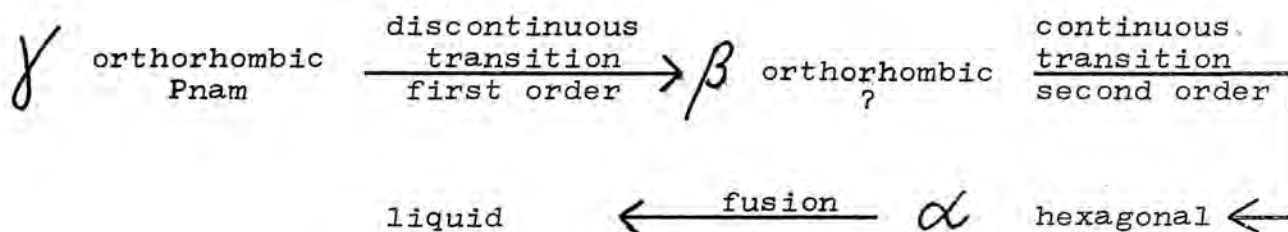


3.3 Principal Conclusions

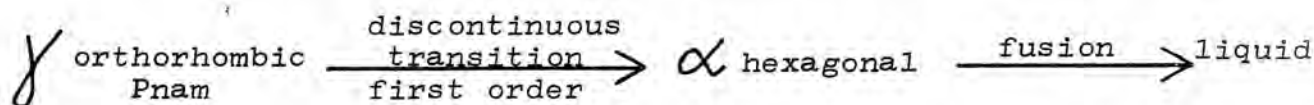
3.3.1 Phase Behaviour

The general phase behaviour of the synthetic Fischer-Tropsch waxes has been shown to be very similar to that reported on the paraffinic waxes from petroleum. The essential features are :

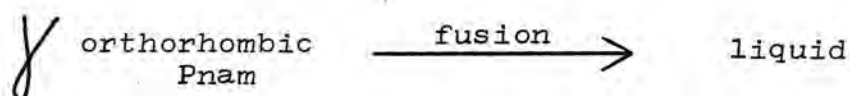
- (i) Waxes showing two solid-solid transitions have, on the average, carbon numbers less than approximately 27. On increasing the temperature, the stable modification passes through the following phases :-



- (ii) Waxes showing a single solid-solid phase transformation have average carbon numbers between about C_{27} and C_{39} . On raising the temperature to melting, the following was observed :-



- (iii) For the wax range of about C_{40} to C_{60} , no solid-solid phase changes were detected. Temperature increase indicated only :-

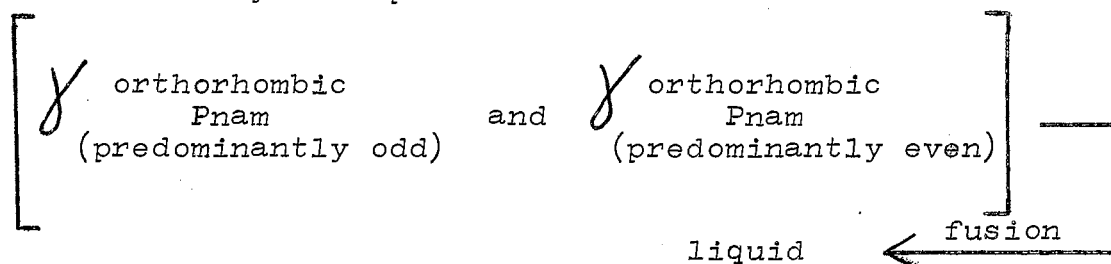


(iv) Above/...

*

From the 'master-phase diagram' it can be deduced that a wax showing no polymorphism may be obtained by limiting the carbon number range to between 40 and 60. This is desirable, for solid phase changes greatly influence wax quality.

- (iv) Above an average carbon number of approximately C_{60} , waxes exhibited a double melting endotherm. This phenomenon has not been reported for the related long-chain waxes. Experimental evidence suggests that phase separation rather than a solid-solid transformation has taken place and may be represented as :-



The solid phase transitions rapidly disappear under the influence of pressure, except for the 'high pressure phase - δ ' which increases its range of stability as the higher pressure simulates longer chains. Similarity of the phase behaviour of the different wax fractions provides for the construction of a 'master-phase diagram' which can be used qualitatively to describe the phase behaviour of an unknown paraffinic or closely related wax.

* ~~One significant deduction is that a wax free from all polymorphism, and this is desirable, for solid phase changes greatly influence wax quality, may be made by limiting the carbon number range to between C_{40} and C_{60} .~~

Experimental evidence from x-ray diffraction has shown that the structure of the waxes in their stable modification is orthorhombic, with space group Pnam. This is consistent with the reported

structure/...

structure for the impure n-paraffins and Kitai-gorodskii's analysis on a geometrical basis.

3.3.2 Calorimetric Properties

A relationship between the properties of the wax fractions and those of the n-paraffins has been determined. Over the medium wax range, comprising essentially chain lengths between C_{20} and C_{40} , certain relationships were shown to exist. Within experimental error, these relationships hold for both the odd n-paraffins and the wax fractions, but it should be remembered that these correlations are not necessarily obeyed below or beyond the range of carbon number of the present waxes.

In the correlations of the thermodynamic parameters, enthalpy and entropy, with carbon number, the values of the quantities pertaining to the wax fractions were significantly lower than those for the corresponding odd n-paraffins, but the parameters exhibited similar relationships. The difference between the two sets of results has been ascribed to a lack of complete crystallinity of the wax fractions. On comparing the wax and n-paraffin values it has been assumed that for the former the entropy of mixing may be neglected and that for the latter the material is 100% crystalline.

The percentage crystallinity of each wax fraction has been derived by incorporating the above observed difference. The values compare

well/...

well with an independent' infra-red determination. A knowledge of the crystallinity allows the appropriate properties, dependent essentially on the crystalline portion of the material, to be corrected before comparison with the n-paraffin data is made. By this means, semi-quantitative information about the properties of an unknown wax may be derived. From a DSC thermogram it is possible to derive melting and transition points, enthalpy changes, entropy changes and the crystallinity. The latter is calculated from a comparison of either the enthalpy or entropy values with the corresponding odd n-paraffin data.

The wax fractions each have six major components and this results in their behaving like a series. Compositional distribution and type of impurity influence the crystallinity in different ways. For example, iso-components significantly reduce the crystallinity. The influence of the range of composition is shown by the fact that the unfractionated wax does not fit in with the related wax fraction correlations.

Experimental evidence qualitatively suggests the formation of solid solutions which result in the wax fractions closely simulating the pure compounds. The extent of solid solutions formed could not be determined.

A relationship between the total enthalpy change and the differential form of the Simon
equation/...

equation was derived. Within the limits of experimental error the work of expansion against the lattice forces multiplied by some constant, varies nearly linearly with carbon number.

SUGGESTIONS FOR FURTHER WORK

A knowledge of the complete structure of the wax will provide useful information on active and inhibited sites particularly in relation to chemical reactions. Closely related to this is a clearer understanding of the influence of branching on the structure as well as a full structure analysis of an isoparaffin.

The orthorhombic β -phase, exhibited by waxes having two solid-solid transitions, and also the rotating hexagonal α -phase require further structural elucidation. These will greatly aid the necessary further study on the nature of the transition and melting processes.

Additional work on the effect of substituents and blends on wax phase behaviour is required in wax applications.

The "long-chain" or "high pressure" phase indicated by DSC and high pressure DTA data needs further clarification. Study of the structure and phase behaviour of hard wax and its fractions will assist with this investigation.

An interesting field requiring more work is the crystallization of waxes. Connected subjects are crystal habit, solid solutions and polytypism.

In/...

In the light of recent literature the interpretation of DSC thermograms needs to be put on a sound basis.

Further high pressure work on the n-paraffins and related substances needs to be undertaken.

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APPENDIX INUMBER AND WEIGHT AVERAGE MOLECULAR WEIGHT

An average molecular weight $\bar{M}$ may be defined by

$$\bar{M} = \frac{\sum N_i M_i^a}{\sum N_i M_i^{a-1}}$$

where N_i is the number of molecules with molecular weight M_i and the index 'a' may have any real value. Two cases are of interest :

- (i) $a = 1$, which gives the number average $\bar{M}_n$ and is defined by -

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{W}{N}$$

where W is the total weight and N the total number of molecules in the sample;

- (ii) $a = 2$, which gives the weight average $\bar{M}_w$ and is defined by -

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum W_i N_i}{W}$$

where W_i is the weight of polymer of molecular weight M_i (Meares, 1965).

APPENDIX IIDSC MELTING PARAMETERS

The Differential Scanning Calorimeter measures the thermal energy per unit time, dq/dt , transferred to or from the sample as the temperature of the sample holder is changed at a linear rate, dT/dt . Without thermal lags, the instrument readout would be directly proportional to dq/dT_s , the energy change in the sample per degree, the proportionality constant being the scanning rate.

$$dq/dt = dT_s/dt \times dq/dT_s \text{ -----(1)}$$

In the range where no transition occurs, dq/dT_s is the ordinary heat capacity of the sample. In the transition region it may be considered to represent the effective heat capacity of the sample due to the energy required to accomplish the transition.

For an absolutely pure compound, having a melting point T_o and essentially zero melting range:

$$dq/dT_s \longrightarrow \infty \text{ as } T_s \longrightarrow T_o \text{ (See Figure 1)}$$

For an impure material, however, dq/dT_s is finite and a function of the sample temperature, such that:

$$dq/dT_s = \frac{\Delta q (T_o - T_m)}{(T_o - T_s)^2} \text{ -----(2)}$$

where the melting point depression due to impurity is

$$T_o - T_m = \frac{R T_o^2 x_2}{\Delta H_f} \text{ (Van't Hoff equation) -----(3)}$$

and T_s is the sample temperature

T_o is the theoretical melting point

T_m is the actual melting temperature

$$\Delta q = \text{total/...}$$

Δq = total heat of fusion of sample, calories.

ΔH_f = Molar heat of fusion of sample, calories/mole.

R = Molar gas constant.

x_2 = Mole fraction of the impurity.

From the above, a theoretical melting peak shape can be drawn (sample 99.5% pure), (Figure 1).

An actual DSC peak differs from Fig. 1 mainly because of thermal resistance in the system. Under proper experimental conditions the only significant thermal resistance in the system is that between the sample pan and sample holder, which is designated R_o .

The effect of this thermal resistance is to impede the flow of thermal energy from the holder at programme temperature T_p , to the sample at temperature T_s .

The relationship between the heat flow rate, the thermal resistance and the temperature difference between the holder and the sample is the thermal analog of Ohm's law:

$$R_o \, dq/dt = T_p - T_s \text{ ----- (4)}$$

This equation states that the difference between the sample and programme temperatures is proportional to the DSC signal and that the proportionality constant is R_o .

A very pure sample, 99.9999% pure indium, is supplied as a standard with the calorimeter. This melts over an extremely narrow temperature range so that, during melting, as the programme temperature increases, the sample temperature is essentially constant (Figure 2):

$$\text{i.e.,} \quad dT_s/dt = 0$$

Differentiation of equation (4) gives:

$$R_o \, d\dot{q} = \dot{T}_p - \dot{T}_s$$

Since/...

Since $\dot{q}$ represents the ordinate reading of the DSC, $\dot{q}$ represents the slope of the curve at any point. During the melting of high purity indium, the equation implies that, since T_s is constant, the slope of the DSC curve is also constant, and equal to T_p/R_o .

R_o can easily be evaluated from the slope of a high-purity melt and scanning rate.

The area in the tail of the peak represents the energy required for the sample to catch up to the programme temperature after melting is completed and hence is ordinary "heat capacity energy". This must be included for ΔH measurements.

Ultrapure samples will seldom be encountered. It is clear from Fig. 1 that the point at which the peak rises significantly from the base line will not, in general, be the correct melting point. The proper melting point is obtained by correcting the peak temperature for thermal lag by drawing a line through the peak of slope $\dot{T}_p/R_o$ and reading the temperature at the point where this line intersects the interpolated base line (Figure 3).

The correct melting point is at B rather than A, which only represents a correction of a few tenths of a degree.

The simplest way to make the correction is to run a series of indium samples at different scanning rates and sensitivities, for reference. The sample is then run and simply overlaid on the appropriate indium scan with the indium leading edge passing through the sample peak maximum. The melting point is then read at the intersection point with the baseline (Perkin-Elmer).

THEORETICAL MELTING PEAK SHAPE 99.5 % PURE.

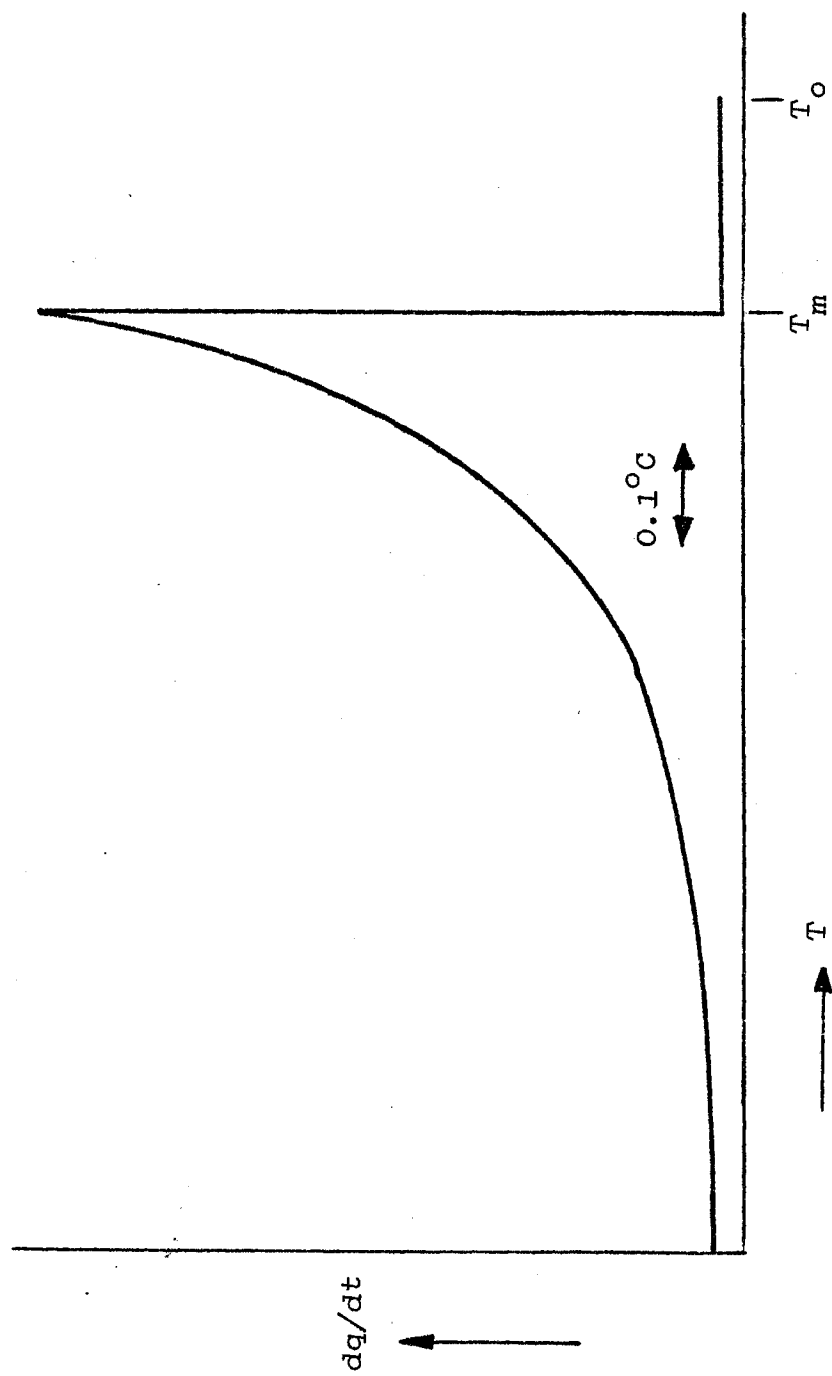


FIGURE 1.

102 b

HIGH PURITY INDIUM MELT.

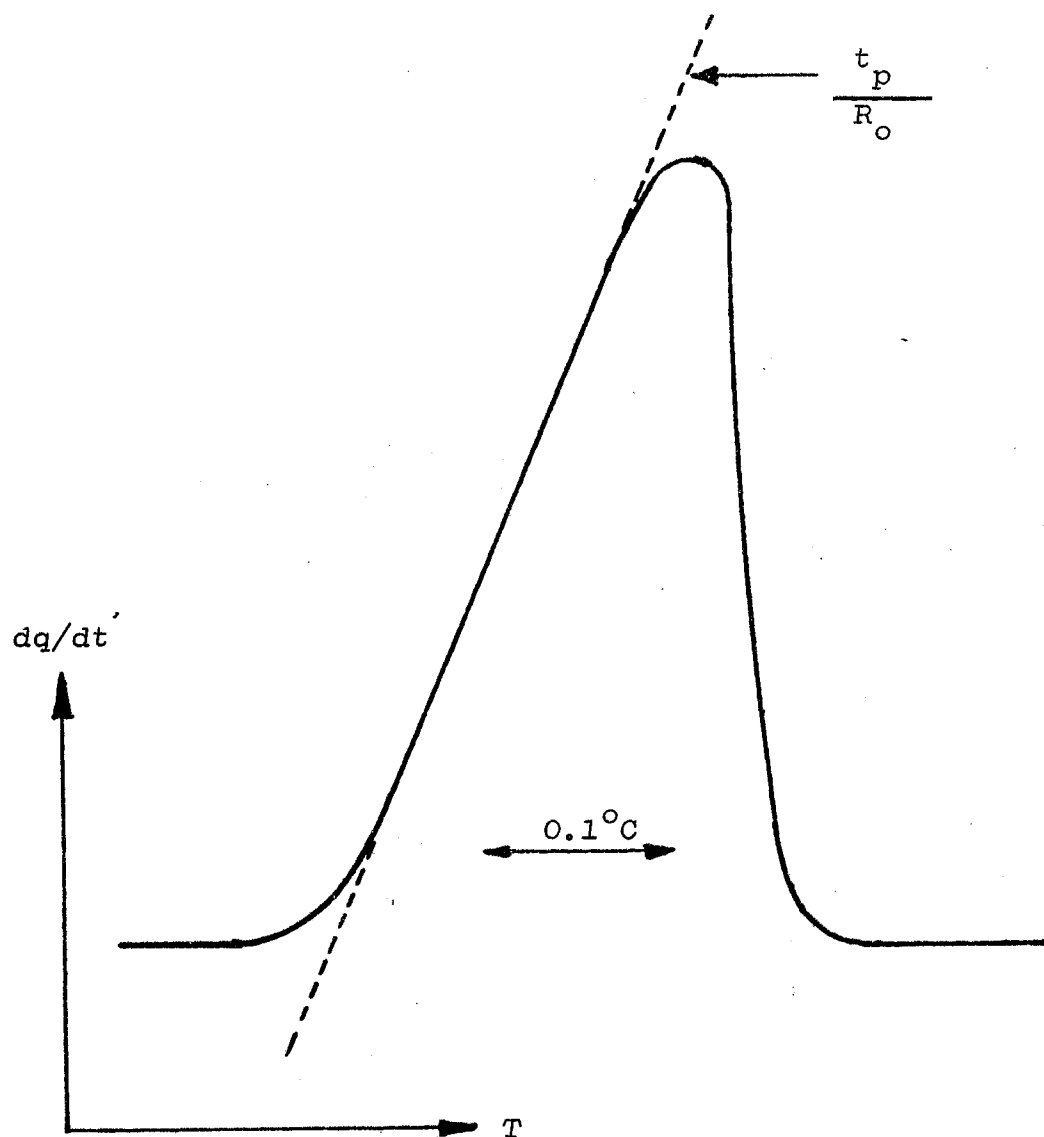


FIGURE 2.

TRIPHENYLMETHANE MELT 99.9%.

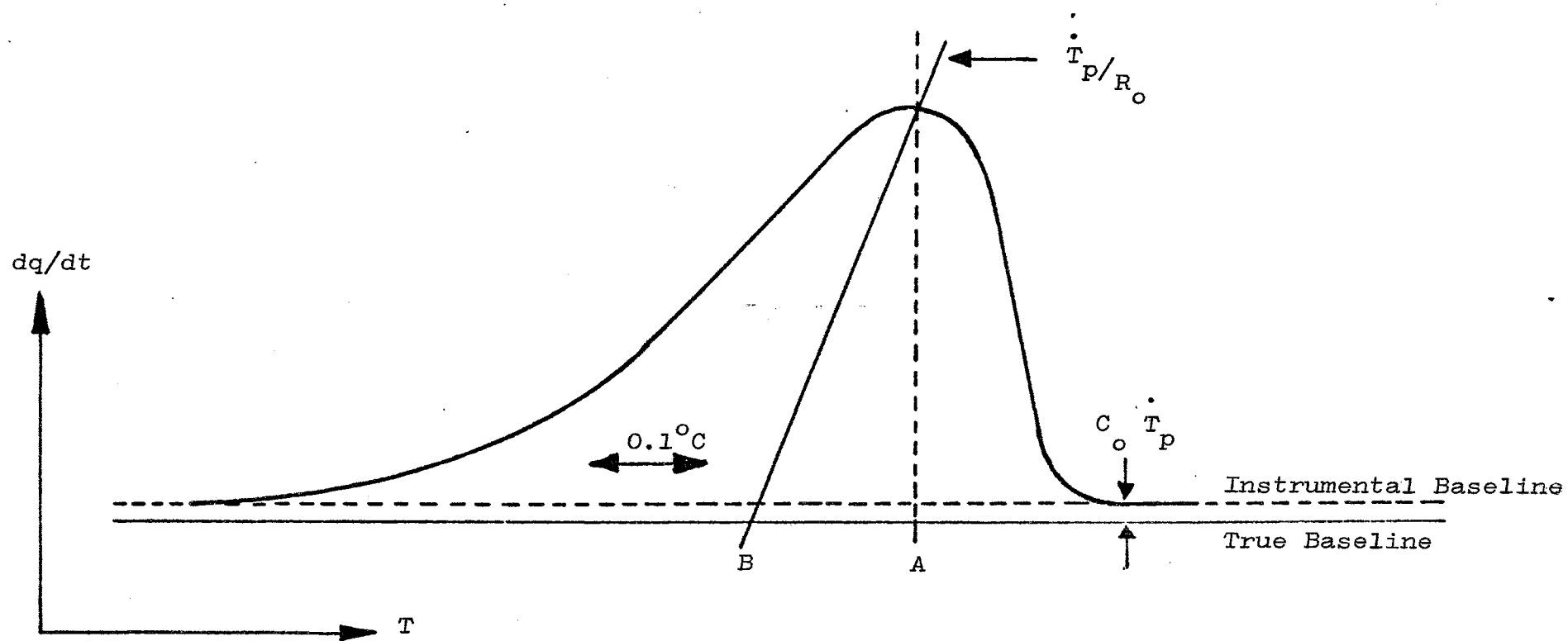


FIGURE 3.

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APPENDIX III.EXPERIMENTAL DATA.A. X-Ray Powder Analysis :

The variation of the Bragg angles and corresponding d-spacings, in the 2θ range 20° - 30° , with temperature, are tabulated below :

(1) Fraction 1 : (Cobalt $\lambda = 1.7889\text{\AA}$)

Temperature $^\circ\text{C}$	θ_1	θ_2	θ_3	d_1	d_2	d_3
15.0	24.90	-	27.60	4.150	-	3.750
20.0	24.84	27.08	27.65	4.159	3.821	3.742
23.0	24.72	26.92	27.52	4.179	3.843	3.761
24.4	24.59	26.95	27.58	4.199	3.837	3.753
25.0	24.59	26.92	27.59	4.199	3.843	3.750
25.5	24.62	26.93	27.60	4.195	3.840	3.750
26.0	24.59	26.87	27.50	4.199	3.848	3.763
26.7	24.62	26.63	-	4.195	3.882	-
27.8	24.54	26.64	-	4.209	3.882	-
28.0	24.55	26.54	-	4.205	3.897	-
29.0	24.55	26.60	-	4.205	3.888	-
30.5	24.66	26.25	-	4.189	3.938	-
31.0	24.62	26.27	-	4.195	3.935	-
31.5	24.72	26.10	-	4.179	3.961	-
32.4	24.99	-	-	4.133	-	-
33.0	25.10	-	-	4.116	-	-
34.0	25.03	-	-	4.126	-	-
34.5	25.05	-	-	4.123	-	-
35.7	24.58	-	-	4.202	-	-
36.2	25.01	-	-	4.129	-	-

(2)/...

Temperature °C	θ_1	θ_2	θ_3	d_1	d_2	d_3
37.2	25.03	-	-	4.127	-	-
38.1	24.95	-	-	4.139	-	-
39.7	25.01	-	-	4.131	-	-
40.5	24.97	-	-	4.136	-	-
42.0	25.00	-	-	4.133	-	-
43.0	24.92	-	-	4.146	-	-
44.7	~ 22.6			~ 4.565		
47.0	~ 22.4			~ 4.605		

(2) Fraction 4 : (Copper $\lambda = 1.5405\text{\AA}$)

Temperature °C	θ_1	θ_2	θ_3	d_1	d_2	d_3
35.0	21.40	-	23.60	4.149	-	3.767
47.5	21.38	-	23.54	4.153	-	3.776
50.8	21.33	-	23.47	4.162	-	3.787
52.9	21.30	-	23.50	4.168	-	3.783
54.4	21.32	-	23.43	4.164	-	3.794
55.8	21.20	-	23.30	4.187	-	3.815
56.7	21.28	21.69	23.37	4.172	4.094	3.831
57.2	21.20	21.70	23.30	4.187	4.092	3.815
57.8	21.30	21.81	-	4.168	4.075	-
58.5	21.10	21.70	-	4.207	4.092	-
59.1	21.27	21.68	-	4.174	4.096	-
59.8	21.23	21.60	-	4.186	4.111	-
60.1	21.28	21.65	-	4.172	4.101	-
60.7	21.25	21.63	-	4.178	4.105	-
61.3	21.25	21.58	-	4.178	4.114	-

(3)/...

Fraction 4 (contd.)

Temperature °C	θ_1	θ_2	θ_3	d_1	d_2	d_3
62.0	21.42	21.70	-	4.145	4.092	-
62.5	21.25	21.50	-	4.178	4.130	-
62.9	21.25	21.55	-	4.178	4.120	-
63.2	21.52	-	-	4.126	-	-
64.1	21.58	-	-	4.114	-	-
64.6	21.70	-	-	4.092	-	-

(3) Hard Wax Fraction (Cobalt $\lambda = 1.7889\text{\AA}$)

Temperature °C	θ_1		θ_2	d_1	d_3
48.0	24.93		27.58	4.146	3.753
54.5	24.92		27.54	4.146	3.758
60.0	24.90		27.48	4.149	3.769
66.0	24.91		27.50	4.149	3.763
71.6	24.85		27.43	4.159	3.774
73.5	24.90		27.43	4.149	3.774
86.0	24.87		27.31	4.156	3.790
98.0	24.78		27.18	4.169	3.807
100.3	24.82		27.18	4.162	3.807
107.0	24.81		27.09	4.165	3.821
109.5	24.80		27.06	4.165	3.823
110.0	24.79		27.02	4.169	3.829
112.0	24.82		27.00	4.162	3.832
114.0	24.89		27.14	4.152	3.812
116.0	24.89		27.10	4.152	3.818
117.0	~ 21.9		~ 4.709		
118.0	~ 22.0		$\sim 4.688.$		

For the stable orthorhombic modification (γ Pnam)

θ_1 and θ_3 refer to the (110) and (200) reflections, respectively.

B./...

B. Differential Scanning Calorimetry (DSC) :

For fractions 1 to 3 the transition and fusion endotherms were separated by a vertical line as described in the text. However, in the case of fractions 4 and 5 the endotherms were separated by superimposing the fusion peak of fraction 3 upon them. Listed below are the areas (in square inches) of the transition and fusion peaks, respectively, and also the weight of each sample used :

Fraction	Weight of sample mg.	Area of transition endotherm	Area of fusion endotherm
1	5.68	0.14 & 0.39	1.74
2	5.35	0.53	1.86
3	4.77	0.50	1.72
4	4.95	0.60	1.72
5	4.74	0.60	1.67

C. High Pressure DTA :

Oil pressure is read directly from a Bourdon guage and converted to piston load by a factor dependent on the ratio of the diameters of the high-pressure piston and ram piston. Temperature values for discontinuities in the DTA-curve are directly read off the recorder trace in millivolts (small corrections for the difference in position between the temperature and differential pens, and for the 0.5 second time constant of the differential D.C. amplifier were taken into account) and these readings subsequently converted to °C from tables.

Friction corrections were made by taking readings for both increasing and decreasing pressure. The difference

in/...

in the two curves yields twice the magnitude of sliding friction at various pressures and hence each pressure reading can be appropriately corrected. The observed temperature values are the means of the heating and cooling readings.

These initially corrected observed pressure and temperature readings are further corrected for the following factors by means of a computer programme (POINTCOR) :

- (i) Pressure effect on thermocouple calibration;
- (ii) unsymmetrical friction correction;
- (iii) weight of main ram;
- (iv) thermal expansion and elastic deformation of the piston.

Another computer programme (CURVFIT) was then employed to ascertain the best fit of the experimental data to polynomials and/or the Simon equation.

(N.B. Both computer programmes were written by Mrs Martha C. Pistorius and are available from Dr C.W.F.T. Pistorius of the National Physical Research Laboratory of the Council for Scientific and Industrial Research - Pretoria.)

The data listed below give the observed and corrected readings (i.e. before and after the application of POINTCOR) of the two parameters, temperature and pressure. It is the finally corrected points that have been plotted in the phase diagrams, and it must be stressed that not all the points have been plotted.

$P_{\text{obs}}/\dots$

(108)

P_{obs} - observed pressure, Kilobars

P_{cor} - corrected pressure, Kilobars

T_{obs} - observed temperature, $^{\circ}C$

T_{cor} - corrected temperature, $^{\circ}C$.

FRACTION 1 :

	P_{obs}	P_{cor}	T_{obs}	T_{cor}
Transition β/α	0.00	0.00	36.0	35.9
	1.08	0.85	46.5	46.4
	1.45	1.18	49.3	49.2
	2.41	2.03	63.8	63.7
	3.14	2.68	67.3	67.2
	-	3.70	-	82.0
Transition γ/β	0.00	0.00	28.5	28.4
	1.08	0.85	41.3	41.2
	2.10	1.76	54.8	54.7
	-	3.70	-	82.0
Melt from Hexagonal phase	0.00	0.00	49.2	49.1
	1.21	0.97	83.8	83.6
	1.61	1.33	86.2	86.0
	2.62	2.23	104.8	104.6
	3.69	3.19	118.3	118.1
	4.18	3.63	122.5	122.3
	4.47	3.90	125.5	125.3
	5.79	5.09	142.5	142.3
	5.84	5.14	141.8	141.6
	6.94	6.14	154.8	154.6

(109)

Fraction 1 (continued)

	P _{obs}	P _{cor}	T _{obs}	T _{cor}
Melt from Hexagonal phase (Contd.)	7.29	6.46	156.5	156.3
	8.32	7.41	169.5	169.3
	8.95	7.98	173.5	173.3
	9.45	8.44	177.0	176.8
	9.79	8.76	180.8	180.6
	10.96	9.85	192.3	192.1
	11.08	9.96	192.8	192.6
	12.13	10.94	204.0	203.8
	12.65	11.41	203.0	202.9
	13.11	11.85	210.0	209.9
	14.46	13.10	215.0	214.9
	15.17	13.78	224.0	223.9
	16.28	14.81	227.8	227.7
	15.5		234.0	
Melt from Orthorhombic phase	17.58	16.07	240.8	240.8
	17.94	16.39	240.3	240.3
	19.93	18.29	253.3	253.4
	20.00	18.36	254.0	254.1
	20.98	19.31	262.0	262.1
	21.85	20.14	265.8	266.0
	23.18	21.43	273.8	274.0
	23.71	21.94	276.5	276.7
	24.56	22.75	280.3	280.6
	25.71	23.87	286.5	286.8
	25.73	23.90	288.3	288.6
	26.97	25.10	294.0	294.4

(110)

Fraction 1 (continued)

	P _{obs}	P _{cor}	T _{obs}	T _{cor}
Melt from Orthorhombic phase (continued)	27.49	25.61	296.8	297.2
	27.91	26.02	299.0	299.4
	28.05	26.16	299.8	300.2
	29.28	27.36	305.5	306.0
	29.62	27.69	306.8	307.3
	31.38	29.43	316.5	317.2
	33.27	31.29	324.3	325.1
	33.38	31.39	324.0	324.8
	35.35	33.35	333.5	334.4
	35.60	33.58	333.3	334.2
	37.39	35.38	342.3	343.3
	38.02	35.98	342.5	343.6
	39.44	37.42	350.6	351.8
	41.43	39.41	358.5	359.8

FRACTION 2 :

Transition

γ/α

	P _{obs}	P _{cor}	T _{obs}	T _{cor}
	0.00	0.00	41.3	41.2
	1.93	1.61	77.5	77.3
	2.77	2.36	81.6	81.4
	3.80	3.28	102.0	101.8
	4.97	4.34	120.8	120.6
	6.50	5.73	142.5	142.3
	8.08	7.18	165.5	165.3
	9.84	8.80	180.8	180.6
	11.72	10.56	200.0	199.8
	13.60	12.33	220.0	219.9.

(111)

Fraction 2 (contd.) :

	P _{obs}	P _{cor}	T _{obs}	T _{cor}
Melt from Hexagonal phase	0.00	0.00	60.3	60.2
	2.02	1.70	107.3	107.1
	2.84	2.43	119.3	119.1
	3.85	3.34	133.5	133.3
	5.00	4.39	147.3	147.1
	6.41	5.67	161.5	161.3
	8.12	7.23	173.3	173.1
	9.69	8.70	193.5	193.3
	10.06	9.03	194.0	193.8
	11.82	10.67	208.5	208.3
	11.82	10.67	207.8	207.6
	13.53	12.28	221.8	221.7
	13.60	12.33	220.0	219.9

Melt from Orthorhombic
phase

13.60	12.33	220.0	219.9
13.66	12.40	223.8	223.7
15.56	14.20	237.8	237.7
17.12	15.68	248.0	248.0
17.44	15.97	247.5	247.5
19.31	17.75	259.0	259.1
21.33	19.70	272.8	273.0
21.66	20.04	277.0	277.2
23.21	21.53	284.3	284.5
24.05	22.35	290.3	290.6
25.28	23.53	295.0	295.3
27.20	25.40	304.3	304.7

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Fraction 2 (contd.)Melt from Orthorhombic
phase (contd.)

P _{obs}	P _{cor}	T _{obs}	T _{cor}
28.06	26.23	306.5	307.0
29.13	27.30	313.8	314.3
30.81	28.96	323.0	323.7
31.12	29.27	324.8	325.5
33.13	31.26	334.0	334.8
35.05	33.18	343.8	344.7
35.60	33.72	345.3	346.3
37.17	35.28	352.0	353.1
39.23	37.35	360.6	361.8
41.20	39.33	368.8	370.2
0.00	0.00	53.0	52.9
2.16	1.81	75.6	75.4
3.17	2.72	89.5	89.3
4.32	3.76	117.0	116.8
5.18	4.54	131.3	131.1
10.80	9.75	210.0	209.8
0.00	0.00	64.3	64.2
1.58	1.30	100.0	99.8
1.68	1.39	100.5	100.3
2.65	2.26	126.5	126.3
3.33	2.87	127.0	126.8
4.38	3.83	145.8	145.6
5.26	4.63	157.0	156.8
6.92	6.15	175.3	175.1
7.78	6.95	185.0	184.8
9.11	8.17	195.3	195.1
10.80	9.75	210.0	209.8

FRACTION 3 :
Transition γ/α

Melt from Hexagonal Phase

Fraction 3 (contd) :Melt from Orthorhombic
phase

P _{obs}	P _{cor}	T _{obs}	T _{cor}
10.80	9.75	210.0	209.8
10.84	9.78	210.3	210.1
11.23	10.15	215.5	215.3
11.98	10.86	222.0	221.9
12.40	11.25	223.5	223.4
13.40	12.19	232.8	232.7
14.35	13.09	240.0	239.9
15.30	13.99	246.3	246.2
17.01	15.63	259.2	259.2
17.31	15.92	261.8	261.8
19.51	18.03	276.0	276.1
21.19	19.67	287.2	287.4
21.39	19.85	286.5	286.7
23.35	21.77	299.8	300.1
23.62	22.03	301.0	301.3
25.56	23.92	310.5	310.9
26.55	24.90	317.3	317.7
27.57	25.90	321.8	322.3
29.56	27.87	331.8	332.4
31.74	30.04	343.5	344.3
32.45	30.74	346.0	346.8
33.66	31.96	352.3	353.2
34.48	32.78	356.0	357.0
35.70	33.99	360.8	361.8
35.88	34.18	362.0	363.1
37.04	35.33	365.8	366.9
37.79	36.07	368.3	369.5
39.74	38.04	376.5	377.8

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FRACTION 4 :

Transition

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P _{obs}	P _{cor}	T _{obs}	T _{cor}
0.00	0.00	55.0	54.9
2.80	2.38	110.6	110.4
3.80	3.28	124.4	124.2
4.63	4.04	136.9	136.7
5.82	5.14	156.5	156.3
6.72	5.98	172.0	171.8

Melt from Hexagonal
phase

0.00	0.00	65.0	64.8
2.36	1.99	121.7	121.5
2.84	2.43	134.6	134.4
3.87	3.38	156.8	156.6
4.37	3.83	153.6	153.4
4.68	4.12	162.5	162.3
5.35	4.73	165.0	164.8
5.84	5.18	170.5	170.3
6.13	5.46	180.0	179.8
6.28	5.58	174.0	173.8
6.70	5.97	178.4	178.2

Melt from Orthorhombic
phase

7.63	6.84	188.0	187.8
7.81	7.02	196.2	196.0
7.82	7.01	187.7	187.5
8.64	7.78	194.9	194.7
9.37	8.46	202.7	202.5
9.50	8.60	208.7	208.5
9.69	8.77	205.6	205.4
10.37	9.40	210.5	210.3

10.81/...

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Fraction 4 (contd) :Melt from Orthorhombic
phase (contd)

P _{obs}	P _{cor}	T _{obs}	T _{cor}
10.81	9.83	216.2	216.0
11.25	10.25	221.2	221.0
11.55	10.52	220.7	220.6
12.61	11.53	229.7	229.6
12.74	11.65	229.9	229.8
13.14	12.05	236.5	236.4
13.33	12.22	234.8	234.7
13.38	12.26	235.0	234.9
14.08	12.93	240.2	240.1
14.31	13.16	243.0	242.9
15.11	13.93	250.7	250.6
15.16	13.96	246.7	246.6
15.42	14.22	250.2	250.2
16.08	14.86	254.6	254.6
16.57	15.31	254.4	254.4
16.92	15.69	265.2	265.2
18.82	17.53	277.2	277.3
20.78	19.45	290.5	290.7
22.66	21.32	304.0	304.3
23.88	22.56	317.0	317.4
24.61	23.25	315.5	315.9
25.76	23.63	320.7	320.9
26.86	25.51	331.5	332.0
28.38	27.02	339.0	339.6
30.36	29.01	349.0	349.7
30.91	29.55	350.0	350.8
32.43	31.09	358.5	359.4
32.82	31.48	360.0	360.9
33.83	32.50	364.4	365.4

34.43/...

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Fraction 4 (continued) :P_{obs} P_{cor} T_{obs} T_{cor}Melt from Orthorhombic
phase (contd)

34.43	33.12	368.7	369.7
35.37	34.07	372.2	373.3
36.42	35.13	377.0	378.2
36.53	35.23	376.2	377.4
38.40	37.18	387.7	389.0

FRACTION 5 :

Transition A

γ/α

0.00	0.00	71.9	71.7
1.28	1.03	104.4	104.2
1.37	1.11	106.4	106.2
1.75	1.46	115.2	115.0
4.00	3.50	158.0	157.8

Transition B

γ/δ

28.00	26.54	348.0	348.6
37.64	36.11	383.6	384.9
39.68	38.18	392.4	393.8
41.00	39.51	397.0	398.5

Melt from Hexagonal
phase

0.00	0.00	76.8	76.6
1.33	1.08	123.9	123.7
1.37	1.12	122.7	122.5
1.80	1.50	131.2	131.0
2.42	2.06	139.1	138.9
3.19	2.76	147.5	147.3
3.90	3.41	157.3	157.1
4.00	3.50	158.0	157.8

Melt/...

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Fraction 5 (contd) :Melt from Orthorhombic
phase

P _{obs}	P _{cor}	T _{obs}	T _{cor}
4.00	3.50	158.0	157.8
4.87	4.29	169.7	169.5
5.86	5.20	180.8	180.6
7.32	6.55	195.7	195.5
7.46	6.67	193.3	193.1
8.36	7.51	203.7	203.5
8.64	7.78	210.3	210.1
9.68	8.74	216.6	216.4
10.22	9.25	223.4	223.2
11.21	10.18	231.8	231.7
11.96	10.89	238.8	238.7
13.80	12.64	253.8	253.7
13.80	12.64	254.1	254.0
15.77	14.53	269.1	269.1
16.37	15.11	273.4	273.4
17.67	16.36	282.5	282.6
18.42	17.09	289.1	289.2
19.78	18.41	296.5	296.7
20.98	19.59	306.5	306.7
21.77	20.36	309.6	309.9
23.75	22.31	322.6	323.0
25.62	24.17	334.4	334.9
26.43	24.97	338.5	339.0
27.26	25.79	343.2	343.8
27.69	26.23	346.1	346.7
28.00	26.54	348.0	348.6

Melt/...

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Fraction 5 (contd) :

Melt from 'Phase δ '

P _{obs}	P _{cor}	T _{obs}	T _{cor}
28.00	26.54	348.0	348.6
28.02	26.56	348.1	348.7
28.97	27.51	353.2	353.9
29.67	28.22	358.1	358.8
29.97	28.52	359.1	359.9
31.24	29.79	365.9	366.7
31.7	30.24	366.8	367.7
33.75	32.32	378.3	379.3
34.49	33.08	382.1	383.2
35.66	34.26	387.9	389.1
36.69	35.32	393.1	394.4
37.60	36.25	397.8	399.1
39.05	37.71	403.0	404.4
39.64	38.32	406.6	408.1
40.94	39.67	413.8	415.4

THE PHASE BEHAVIOUR OF FISCHER-TROPSCH WAX
FRACTIONS UNDER HIGH PRESSURE

By R. STOKHUYZEN^{*} and C.W.F.T. PISTORIUS^{**}

The phase behaviour of five distillation fractions of a Fischer-Tropsch wax were investigated at pressures up to 40 kilobars by means of differential thermal analysis. The approximate constancy in the number of significant components (i.e., greater than 5% by weight) in each wax fraction is probably responsible for the fact that they appear to behave like a series. Similarity of the phase diagrams of the individual wax fractions give rise to the construction of a "master" phase diagram. A possible new high pressure phase was detected in the heaviest fraction, but the possibility of phase separation cannot be excluded.

Introduction

Pure n-paraffin crystals are known to exist in four crystal modifications. Paraffins with even carbon numbers from C_{18} to C_{24} are triclinic, C_{26} can either be monoclinic or triclinic, whereas those from C_{28} to at least C_{36} are monoclinic. The odd carbon numbered paraffins are all orthorhombic at room temperature. The fourth modification is that of the hexagonal or quasihexagonal state which results from the occurrence of the first-order phase transition at a temperature several degrees below the melting point. Reference to the crystallographic, structural and thermal studies concerning the pure n-paraffins have been given elsewhere.¹

n-Paraffins containing more than one or two percent impurities cannot exist in the monoclinic, triclinic or orthorhombic modifications mentioned above. Instead, they are orthorhombic with a different space group,²⁻⁴ irrespective of whether the main component of the wax has an even or odd chain length. Waxes melting below ca 60°C exhibit two solid-solid transitions, whereas those melting between ca 60°C and ca 75°C have only a single transition. Waxes melting above 75°C do not have any solid-solid phase transitions. The phase just below the melting point is invariably hexagonal^{4,5} as is the corresponding phase of the pure n-paraffins. The intermediate phase (β) occurring for low melting waxes is orthorhombic, but with a structure differing from that of the orthorhombic phase present in waxes showing only one transition. The first transition encountered in the low melting waxes involves discrete changes/...

changes in lattice dimensions and is therefore regarded as first order, while the second transition is gradual and assumed to be of the second order. The phase behaviour is observed to be first order⁵ in the higher melting waxes involving only one transition.

Few similar studies on the very different transition phenomena of the somewhat impure n-paraffin waxes have been reported.⁶ The only melting curves of high-melting n-paraffins reported are those of n-dotriacontane to 1 kbar, and n-tetracosane up to 10 kbar.⁸

The sum of the entropies of fusion and transition of long-chain n-paraffins increases by ca $R \ln 3$ for each additional CH_2 -group.⁹ This high entropy appears to be due to the onset of hindered rotation about the C-C bonds. The entropy of the transition just below the melting point is very nearly independent of the chain length for pure n-paraffins.¹⁰ In the case of the somewhat impure waxes the low-temperature form is different, however, and the entropy of the higher transition is therefore not necessarily independent of the chain length. The entropy of mixing should be taken into consideration.

Experimental

Sasol medium wax comprises part of the hydrogenated second distillation cut of crude reactor wax from the Arge synthesis.^{11,12} The wax is relatively soft and homogeneous and is made up of essentially n-paraffin chains which are saturated and vary in length. Medium wax has an average chain length of $39.5\text{\AA}$ and average molecular weight of 420 ± 25 . As the wax has been de-oiled, the iso-paraffin content is very low. A Debye-Sherrer diffraction photograph showed the wax to be highly crystalline. An infrared method shows a crystallinity of 83%.¹³ The wax was split into five fractions under vacuum distillation (see table I). Gas chromatographic analysis was carried out on the separate fractions following Ludwig's method,¹⁴ and the compositional distribution of each fraction is given in table II.

Accurate enthalpy values as well as transition and fusion temperatures at atmospheric pressure were obtained using a Perkin-Elmer Differential Scanning Calorimeter (DSC-1B). The instrument was calibrated using standards of benzoic acid and indium (99.999% pure). The area of each peak (see Fig. 1) is directly related to the enthalpy change. The thermal data listed in table I were obtained from the DSC-traces as follows: A planimeter was used to obtain accurate values of the areas under the transition and fusion peaks and the total area. The transition and fusion peaks were separated by a vertical line as shown in Fig.1, and no appreciable error was incurred by not completing the curves (as shown by the dotted lines) and then measuring the areas. However, this is only valid if the fusion and transition peaks are well

separated/...

separated. For fractions 4 and 5, where the fusion and transition peaks are somewhat merged, the fusion peak of fraction 3 was superimposed upon them to give the correct separation. The respective entropies, $\frac{\Delta H}{T}$, were subsequently calculated using the absolute transition and melting temperatures (points Q, P in Fig. 1). The points are given using the calibrated slope obtained with one of the standard substances used.¹⁵

Accurate density values were obtained by means of standard methods at 25°C. Approximate molecular weights were obtained using the elevated boiling point method. Making use of the crystallographic data (see below) and the above molecular weights and densities, values for the average molecular weights were determined in the usual manner.

Crystallography

Powder diffraction patterns were obtained on a wide-angle Phillips diffractometer. Single crystals of fraction 3 and 4 were grown from either toluene or petroleum ether solution. Large plate-like crystals readily formed. However, separation of single plates was extremely difficult. Oscillation and zero, first and second layer Weissenberg photographs were taken using filtered copper radiation ($\lambda = 1.5405\text{\AA}$). A number of precession photographs were also taken as well as a number of flat-plate transmission patterns. The powder diffraction traces show up the first few orders (00 ℓ) directly related to the long spacing of the crystal lattice. These give the average chain length of the wax and its fractions. The average carbon number

is/...

is readily found by assuming the planar zigzag structure of the n-paraffin chain. The mean C-C bond distance is 1.534 Å and the mean C-C bond angle is $112^{\circ}1'$. From these figures the mean period of the zigzag chain is 2.546 Å.¹⁶ The approximate carbon number may be found from the molecular weight. The values quoted in table I are the average of the above.

High pressure analysis

Pressures to just over 40 kbar were generated in a piston-cylinder device previously described.¹⁷ The furnace assembly was similar to that used by Cohen et al.¹⁸ Phase changes were detected by means of differential thermal analysis (DTA), using Chromel-Alumel thermocouples. Corrections were made for the effect of pressure on the thermocouples.

The samples were contained in copper capsules which incorporated thermocouple wells.¹⁹ A sandwich-like arrangement of additional copper pieces above and below the capsules was used to diminish axial thermal gradients.²⁰ The capsules were first sealed by subjecting them to a pressure of ~ 20 kbar in situ before starting the measurements. No contamination or leakage was observed in such cases. Failure to preseat the capsule invariably caused leakage of the sample upon melting. Each individual phase diagram is based on only one run, except for fraction 5 which was repeated using a stainless steel capsule yielding stronger DTA signals. The heating/cooling rate ranged from 0.3 to 1.3 °C/second. Temperatures could be determined to $\pm 2^{\circ}\text{C}$. Sliding

friction/...

friction was eliminated by comparing the results on increasing and decreasing pressure. The resulting pressures were further corrected for non-symmetrical pressure losses as described by Pistorius et al.²¹ The corrected pressures are assumed to be accurate to better than ± 0.5 kbar.

The transition signals were broad except for the γ/δ signals in fraction 5 (see Fig. 2). The freezing signals were fairly sharp and remained measurable throughout the pressure range, whereas the melting signals lost their sharpness and became virtually unmeasurable after a few melting/freezing cycles. The shape of the signals was, however, once again improved if the temperature of the system was lowered to $\sim 25^\circ\text{C}$ and the sample left for ~ 10 mins. Examples of the type of signals obtained can be seen from figure 2.

Results

Differential scanning calorimetry showed the transition endotherms to be broad (see Fig. 1). Fractions 1 and 2 have two solid-solid transitions while the others have only one. The sharpness of the peaks provided some measure of the range of composition of each fraction. The results are listed in table I.

Fractions 3 and 4 are orthorhombic at room temperature as shown by single crystal x-ray diffraction (unpublished), as well as by the analogy with previously published work.^{1-6,22,23} The data are consistent with the space group Pnam. The powder patterns of fractions 2 and 5 were closely similar to those of fractions 3 and 4. Work on fraction 1 is in progress. There is no reason to expect fraction 1 at low temperatures not/...

not to be similar to the other fractions.

The phase diagram of fraction 1 is shown in Fig. 3. The γ/β and β/α transition lines meet at the $\alpha/\gamma/\beta$ triple point at 3.7 kbar, 82°C. No DTA signals corresponding to the resulting γ/α transition line could be observed, but the liquid/ γ/α triple point was marked by an inflection on the melting curve at 15.5 kbar. The transition signals could not be observed on the releasing pressure cycle, due to their low latent heats and the inevitable deterioration of thermal contact between the thermocouple and the sample on decrease of pressure. The melting curve of the α -phase initially rises sharply with pressure, but has considerable curvature. The DTA signals corresponding to both melting and freezing were sharp. No supercooling on freezing was evident, but, due to the range of composition, the beginning of freezing was consistently $\sim 15^\circ\text{C}$ above the beginning of melting. The points plotted are the means of melting and freezing. The freezing points of the γ -phase were only $\sim 2^\circ\text{C}$ above the melting points.

The melting/freezing DTA signals decreased in intensity over the pressure range 10 to 30 kbar. The melting signals almost disappeared and the freezing signals became small. Above ~ 30 kbar the signal shape improved once again, the melting signals being observable but not accurately measurable. Where melting and freezing signals could clearly be detected, freezing still occurred consistently $\sim 2^\circ\text{C}$ above melting.

The/...

The phase diagrams of the other fractions are shown in Figs 4 - 7. The general behaviour is quite similar to that of fraction 1. The β -phase occurs, apart from fraction 1, only in fraction 2, but the $\alpha/\gamma/\beta$ triple point is here estimated to be at $\sim 50^\circ\text{C}$, 0.5 ± 0.5 kbar, so that its region of stability is very small. A new high-pressure form was found in fraction 5, i.e., the fraction studied with the highest mean molecular weight. This γ/δ transition line (see Fig. 7) branches off from the melting curve of the γ -phase at a triple point liquid/ δ/γ near ~ 26.5 kbar, $\sim 355^\circ\text{C}$. The DTA signals in this region (Fig. 2(iii)) are quite reproducible.

The phase relations of the various wax fractions are summarized in tables III and IV. The polymorphic transition lines have been fitted to simple polynomials, and the melting curves to the Simon equation²⁴

$$(P - P_0)/A = (T/T_0)^c - 1,$$

where $T^\circ\text{K}$ and $T_0^\circ\text{K}$ are the melting points at P and P_0 kbar, respectively, P_0 and T_0 being the parameters of the triple point of the phase in question. A and c are adjustable constants, determined by means of Babb's method.²⁵

The initial slopes of the melting curves

$$(dT/dP)_P = P_0 = T_0/Ac$$

by differentiation of the Simon equation.

Table V lists the changes in molar volume at the transition and fusion points at atmospheric pressure, as well as the changes of volume at the triple points. The latter

values/...

values were calculated on the reasonable assumption of approximate constancy of the total entropy of fusion ΔS_{tot} along the fusion curve, using the Clapeyron-Clausius equation. This assumption is generally borne out by experiment wherever it is possible to check it.²⁶ The slopes of the phase boundaries at the specified points are also tabulated.

Discussion

All the fusion curves have normal concave curvature towards the pressure axis with the melting temperatures rising considerably with increasing pressure. The volume changes on fusion decrease normally with increasing pressure, and the rate of decrease also becomes less at higher pressures.

Barmby et al.⁵ suggested that the γ/β transition is of the first order and involves the transformation of one orthorhombic lattice into another by discrete changes in the cell constants, while the β/α transition, although from an orthorhombic to a hexagonal lattice, is of the second order. The DTA signals observed in the present work for the β/α transition of fraction 1 were considerably smaller and less well defined than those for the γ/β transition. It should be borne in mind that if either of the γ/β or β/α transitions is of the first order, the γ/α transition also will be of the first order.

The β -phase cannot exist at positive pressures for wax fractions higher than the present fraction two ($\sim C_{27}$). The stability region of the α -phase also decreases considerably with increasing molecular weight, and is quite small/...

small for fraction 5 ($\sim C_{35}$). The liquid/ γ/α triple points move towards lower pressures with increasing mean molecular weight of the wax fractions, while at atmospheric pressure the γ/α transition points simultaneously approach the melting points. The initial slopes of the liquid/ α phase boundaries increase with molecular weight (see Figs 3 - 7).

The various phase diagrams can therefore be combined into a master diagram as shown in Fig. 8. The broken lines refer to the atmospheric pressure co-ordinates of the various fractions. This diagram clearly illustrates the dependence of the phase behaviour on the molecular weight and hence the carbon number for n-paraffin waxes. It is quite obvious that increasing pressure simulates a longer chain-length. This master diagram can therefore be used to predict the approximate phase behaviour of other n-paraffin waxes.

The considerable decrease in the size of the DTA signals in the pressure range 10 - 30 kbar can be ascribed to the failure of the samples to recrystallize fully upon freezing. A run in which ~ 20 kbar was reached after ~ 30 melting/freezing cycles yielded very small signals, while a similar run in which pressure was directly taken to ~ 20 kbar yielded large signals. Furthermore, the signal size could be improved to some extent by "annealing" the sample at a low temperature for 10 minutes or more. The increase in the signal size at pressures above ~ 30 kbar can be simply explained by taking into account the high rate of recrystallization at the higher temperatures of the melting curve in this pressure range.

If the γ/α phase transition is considered as being an
order/...

order-disorder transition involving rotation of the n-paraffin chains, the phase diagrams show that, at high pressures, the rotation of the chains is inhibited. When the molecules have enough thermal energy to overcome this effect, the entropy is already large enough to cause disintegration of the crystal lattice, and melting occurs.

If the high-pressure high-temperature phase δ found above ~ 30 kbar for fraction 5 is, in fact, a new solid phase, one can, on the basis of the "master" phase diagram (Fig. 8), expect a similar phase to occur in the phase diagrams of the other wax fractions at pressures above 40 kbar. Furthermore, one can expect such a phase to occur at atmospheric pressure below the melting point of a wax fraction with a sufficiently high mean carbon number. The estimation of the necessary carbon number is necessarily crude. A linear relationship exists between the present liquid/ γ/α triple points and their respective carbon numbers. If one can assume a similar relationship with the same slope for the liquid/ δ/γ triple points, the high-pressure form of fraction 5 simulates the atmospheric pressure behaviour of a fraction with a mean carbon number of at least 68. Unpublished DSC work on wax fractions containing appreciable amounts of n-paraffins with carbon numbers near 100 have shown that separate peaks do, in fact, occur near the melting point.²⁷ However, it should be borne in mind that there is a definite possibility that the two sets of signals obtained for fraction 5 above ~ 30 kbar are due to phase separation. It is known that even and odd n-paraffins are not miscible in all proportions,²⁸ and that the miscibility

gap increases with chain length, or, on the basis of the present work, with pressure. It is therefore possible that the present fraction 5, consisting of both even and odd n-paraffins, at high pressures separate into two phases, of which one will be rich in odd n-paraffins, and the other in even n-paraffins. Once again the same will apply to the lower fractions at pressures above 40 kbar, and to even higher fractions at pressures below ~ 30 kbar. Phase separation may occur when the difference in carbon number of the components of a mixture exceeds four.¹

It is interesting to note that the linear relationship between the liquid/ γ/α triple points and their carbon numbers implies that the orthorhombic/hexagonal (γ/α) transition no longer occurs for mean carbon numbers above ~ 39 . A similar line for the β/α transition suggests that this transition will be absent beyond $\sim C_{28}$, as is known.

Except for possible phase separation at higher pressures or carbon numbers there is no even-odd effect in the present waxes. In fact, even one or two percent impurities suffice to destroy the even-odd effects characteristic of pure n-paraffins.¹ The nature of the transitions and of the phases occurring is also changed. It is, therefore, clear that a comparison of the present work with earlier high-pressure studies on pure n-paraffins is, although instructive, not completely valid. Deffet⁷ measured the melting and transition curves of n-C₃₂ to 1 kbar. This n-paraffin is closely related to our fraction 4. The slopes of his boundaries agree with ours to ~ 0.25 kbar,

well/...

well within the combined experimental error. Nelson et al.,⁸ working on a series of n-paraffins, examined their phase behaviour to 10 kbar. The heaviest substance studied by them, viz., n-C₂₄, is close to our fraction 1, but shows, even at atmospheric pressure, completely different transition phenomena. They concluded that the melting curves of pure n-C₉, n-C₁₂, n-C₁₃ and n-C₂₄ could not be satisfactorily fitted by the Simon equation, while that of n-C₁₈ could. The present melting curves of the wax fraction are fitted by the Simon equation within the experimental error, but it is probable that, had our experiments over a large pressure range been as accurate as those of Nelson et al. over a restricted pressure range, the fit would have been slightly less satisfactory.

An investigation of the lattice constants of pure n-C₃₀ and n-C₃₂ at high pressures appeared to reveal a phase transition at 7.3 kbar for both substances.²⁹ It appears to us, however, that the measurements have been misinterpreted. Kabalkina's figure shows a pressure-induced phase transition to a less dense state. This is thermodynamically impossible. The actual data can, in fact, within the expected experimental error, be fitted quite well by a single smooth curve without any discontinuity.

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Figure 1. Typical DSC melting and transition endotherms on heating fraction 4. P and Q are the melting and transition temperatures, respectively.

Figure 2. Typical DTA signals

- (i) (a) Fraction 2 liquid/ α at 3.3 kbar;
(b) Fraction 2 α/γ at 3.5 kbar;
- (ii) Fraction 4 melting/freezing at 7.8 kbar;
- (iii) (a) Fraction 5 γ/δ at 39.5 kbar;
(b) Fraction 5 melting/freezing at 40.9 kbar.

Figure 3. Phase diagram of fraction 1 to 40 kbar.

Figure 4. Phase diagram of fraction 2 to 40 kbar.

Figure 5. Phase diagram of fraction 3 to 40 kbar.

Figure 6. Phase diagram of fraction 4 to 40 kbar.

Figure 7. Phase diagram of fraction 5 to 40 kbar.

Figure 8. Master phase diagram to 50 kbar of fractions from Fischer-Tropsch paraffin wax.

TABLE I

Properties characterising the wax fractions

Parameters	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Error
Melting point °C	48	58	63	69	75	± 2
Transition Point °C	34; 27	40; 37	52	61	70	± 2
Density g/ml	0.882	0.910	0.919	0.926	0.931	± 0.002
ΔH_{tr} Kcal/mole	0.89; 2.37	3.98	4.61	5.84	6.69	± 0.2
ΔH_f Kcal/mole	11.12	13.98	15.80	16.72	18.64	± 0.2
ΔH_{tot} Kcal/mole	14.48	17.96	20.41	22.56	25.33	± 0.4
ΔS_{tr} cal/mole deg	3.0; 7.7	12.8	14.2	17.0	19.3	± 0.25
ΔS_f cal/mole deg	34.7	42.2	47.0	48.9	53.5	± 0.25
ΔS_{tot} cal/mole deg	45.4	55.0	61.2	65.9	72.8	± 0.5
Average chain length ^o	32.5	35.8	38.8	42.3	46.4	± 0.5
Average mol. weight	318	362	398	442	490	± 5
Average carbon number	24	27	29	32	35	± 1
Limits of distillation °C*	<405	405-430	430-455	455-480	>480	
Range of composition (≥5% weight)	C ₂₁ -C ₂₆	C ₂₃ -C ₂₈	C ₂₆ -C ₃₁	C ₂₉ -C ₃₄	C ₃₃ -C ₃₇	
Most abundant component	C ₂₃	C ₂₅	C ₂₈	C ₃₁	C ₃₄ & C ₃₅	

*Temperatures corrected to 760 mm mercury.

TABLE II
Composition of wax fractions

Carbon number	Mole fraction ($\pm 5\%$) in fraction				
	1	2	3	4	5
17	0.000	0.000	0.000	0.000	0.000
18	0.002	0.000	0.000	0.000	0.000
19	0.019	0.000	0.000	0.000	0.000
20	0.051	0.002	0.000	0.000	0.000
21	0.059	0.006	0.000	0.000	0.000
22	0.195	0.023	0.000	0.000	0.000
23	0.249	0.091	0.001	0.000	0.000
24	0.200	0.217	0.003	0.000	0.000
25	0.120	0.272	0.022	0.000	0.000
26	0.060	0.207	0.084	0.000	0.000
27	0.024	0.102	0.199	0.005	0.000
28	0.012	0.053	0.245	0.035	0.000
29	0.006	0.020	0.223	0.111	0.000
30	0.002	0.006	0.104	0.218	0.000
31	0.001	0.002	0.077	0.219	0.019
32	0.000	0.000	0.023	0.187	0.085
33	0.000	0.000	0.015	0.125	0.175
34	0.000	0.000	0.006	0.066	0.217
35	0.000	0.000	0.000	0.029	0.210
36	0.000	0.000	0.000	0.005	0.174
37	0.000	0.000	0.000	0.000	0.081
38	0.000	0.000	0.000	0.000	0.032
39	0.000	0.000	0.000	0.000	0.009

TABLE III.

Phase Behaviour of Wax Fractions at High pressure

WAX	PHASE BOUNDARY	FIT	Δt °C
FRACTION 1	γ/β	$t(^{\circ}\text{C}) = 14.6P + 28.5$	0.4
	β/α	$t(^{\circ}\text{C}) = 12.3P + 36$	1.6
	α/γ	$t(^{\circ}\text{C}) = 12.9(P-3.7) + 82$	1.0
	α/liquid	$P/2.69 = (T/322.2)^{4.204} - 1$	2.9
	γ/liquid	$(P-16.5)/19.12 = (T/515)^{3.842} - 1$	0.7
FRACTION 2	γ/α	$t(^{\circ}\text{C}) = 41.5 + 20.24P - 0.48 P^2$	2.8
	α/liquid	$P/2.17 = (T/333)^{4.845} - 1$	2.4
	γ/liquid	$(P - 12.3)/16.29 = (T/493)^{3.685} - 1$	1.5
FRACTION 3	γ/α	$t(^{\circ}\text{C}) = 16.1 P + 53.0$	5.2
	α/liquid	$P/1.99 = (T/337.3)^{4.943} - 1$	2.5
	γ/liquid	$(P - 9.7)/12.84 = (T/483)^{3.894} - 1$	0.7
FRACTION 4	γ/α	$t(^{\circ}\text{C}) = 56.0 + 22.8 P - 0.6 P^2$	1.8
	α/liquid	$P/0.94 = (T/338)^{6.833} - 1$	3.3
	γ/liquid	$(P - 7.2)/14.46 = (T/464)^{3.154} - 1$	2.7
FRACTION 5	γ/α	$t(^{\circ}\text{C}) = 72.0 + 33.6 P - 2.6 P^2$	0.3
	γ/δ	$t(^{\circ}\text{C}) = 3.84(P - 26.5) + 348.5$	0.4
	α/liquid	$P/0.39 = (T/349.8)^{11.052} - 1$	1.3
	γ/liquid	$(P - 3.5)/9.56 = (T/431)^{3.354} - 1$	1.1
	δ/liquid	$(P - 26.5)/39.17 = (T/621.5)^{2.864} - 1$	0.6

TABLE IV

Triple Points

INVARIANT POINTS	SYSTEM	PRESSURE (± 0.5 KBAR)	TEMPERATURE ($\pm 2^{\circ}\text{C}$)
$\gamma/\beta/\alpha$	FRACTION 1	3.7	82
$\gamma/\alpha/\text{liquid}$	FRACTION 1	15.5	234
$\gamma/\beta/\alpha$	FRACTION 2	0.5	51
$\gamma/\alpha/\text{liquid}$	FRACTION 2	12.3	220
$\gamma/\alpha/\text{liquid}$	FRACTION 3	9.8	210
$\gamma/\alpha/\text{liquid}$	FRACTION 4	7.0	187.5
$\gamma/\alpha/\text{liquid}$	FRACTION 5	3.5	158
$\delta/\gamma/\text{liquid}$	FRACTION 5	26.5	348.5

TABLE V

Melting parameters at zero and triple point pressures

Parameter	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5
Initial slope of transition line ($^{\circ}\text{C}/\text{kbar}$)	12.3 (β/α) 14.6 (γ/β)	20.2 (γ/α)	16.1 (γ/α)	22.8 (γ/α)	33.6 (γ/α)
Initial slope of melting curve of α -phase ($^{\circ}\text{C}/\text{kbar}$)	29.	32.	34.	53.	80.
Initial slope of melting curve of γ -phase at the triple point ($^{\circ}\text{C}/\text{kbar}$)	7.0	8.2	9.6	10.2	13.5
ΔV_{tr} at $P=0$ (cm^3/mole)	0.2 (β/α) 4.0 (γ/β)	10.9 (γ/α)	9.6 (γ/α)	16.2 (γ/α)	27.2 (γ/α)
ΔV_{f} at $P=0$ (cm^3/mole)	41.4	56.0	67.1	108.0	180.0
$\Delta V_{\text{f}}(\gamma)$ at triple point (cm^3/mole)	13.3	18.9	24.7	27.6	41.3

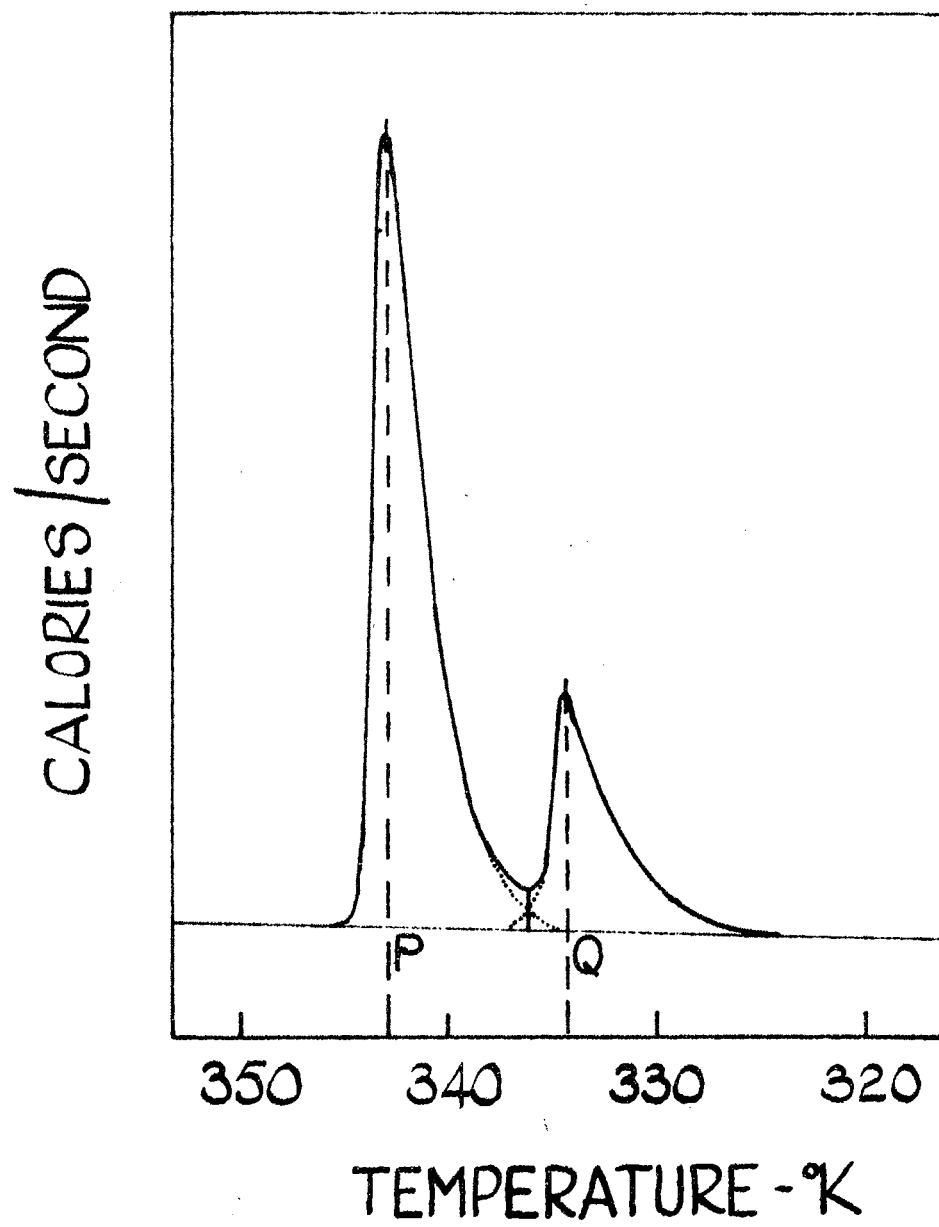


FIG.1

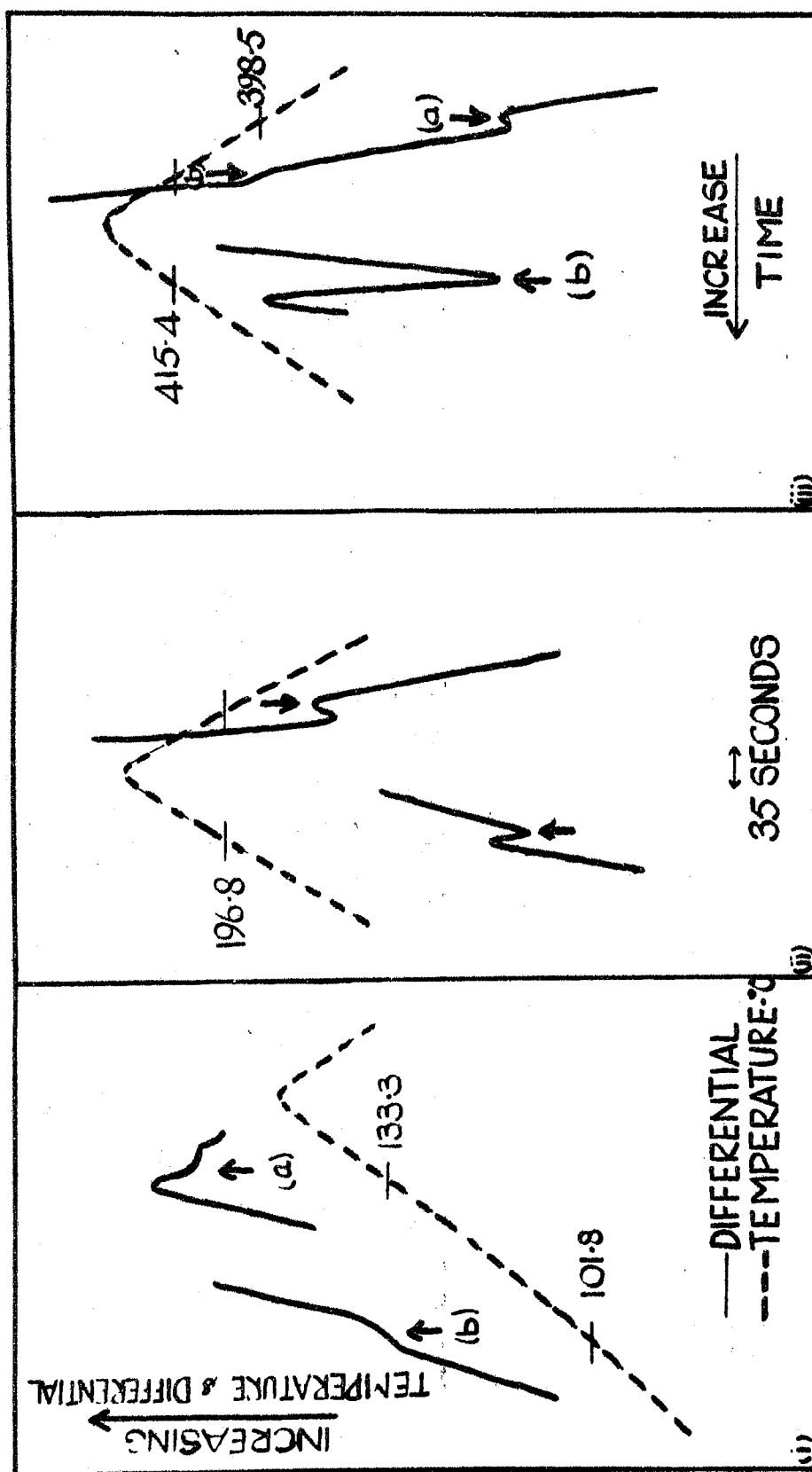


FIG. 2

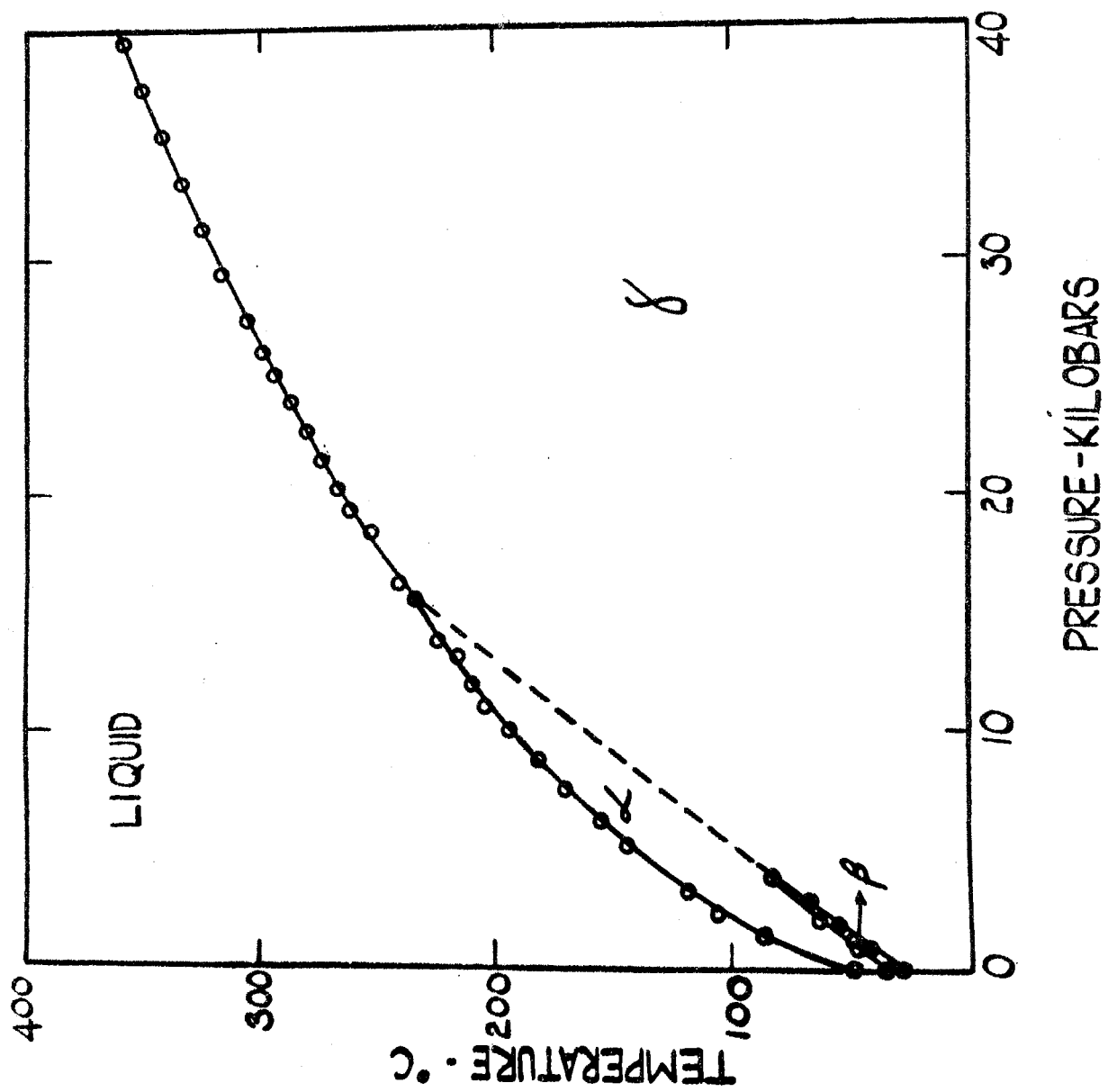


FIG. 3

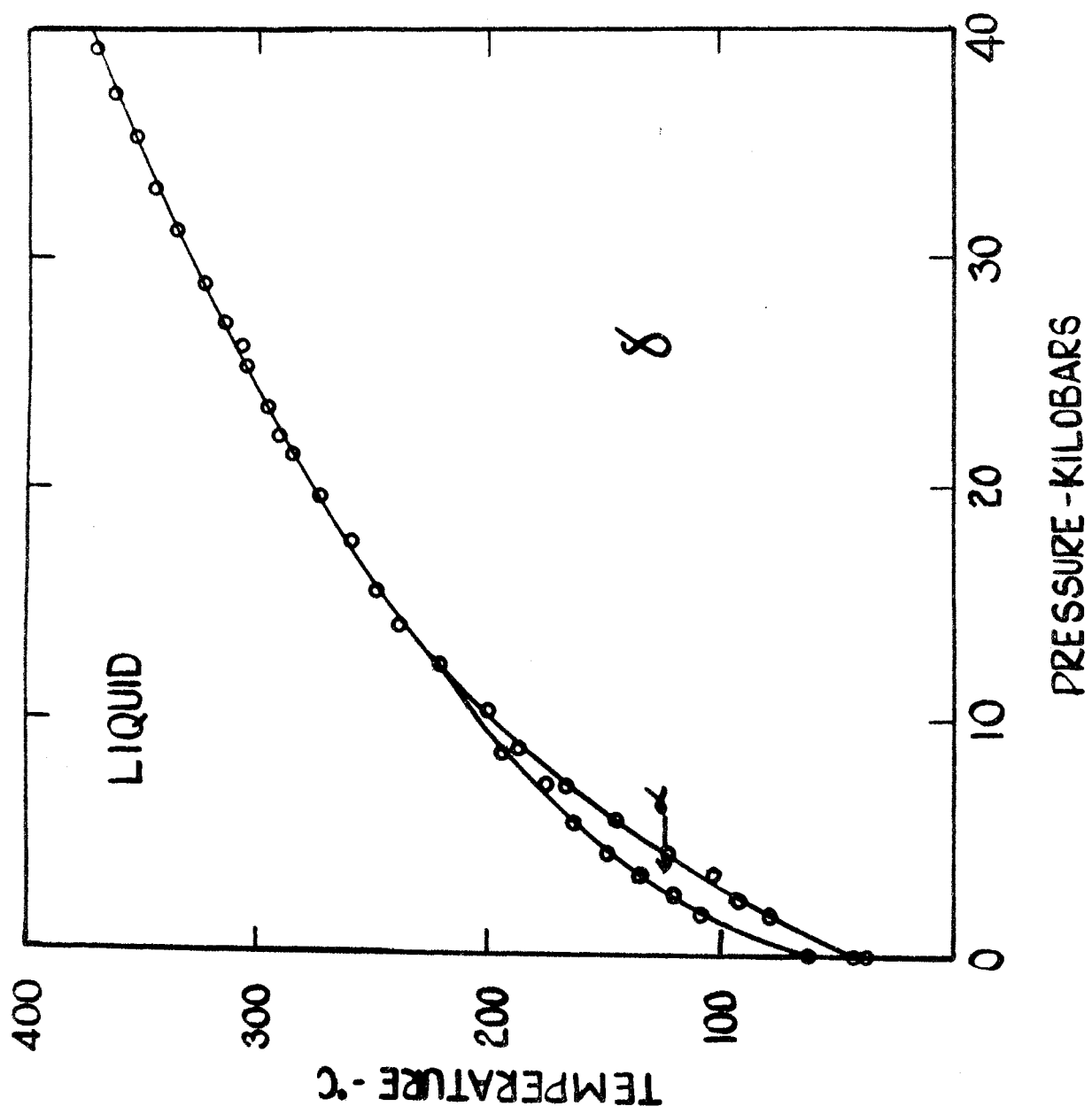


FIG. 4

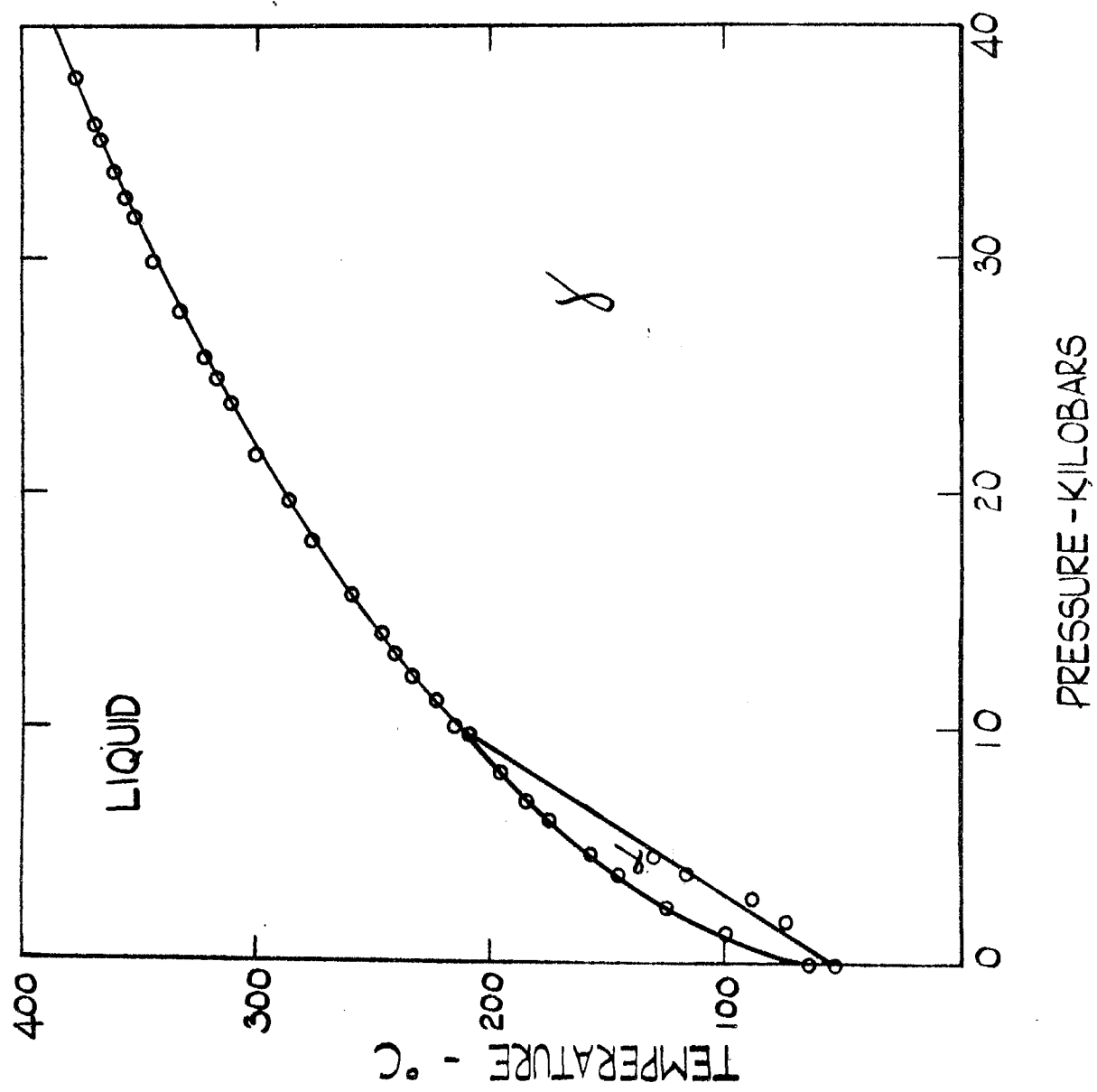


FIG 5.

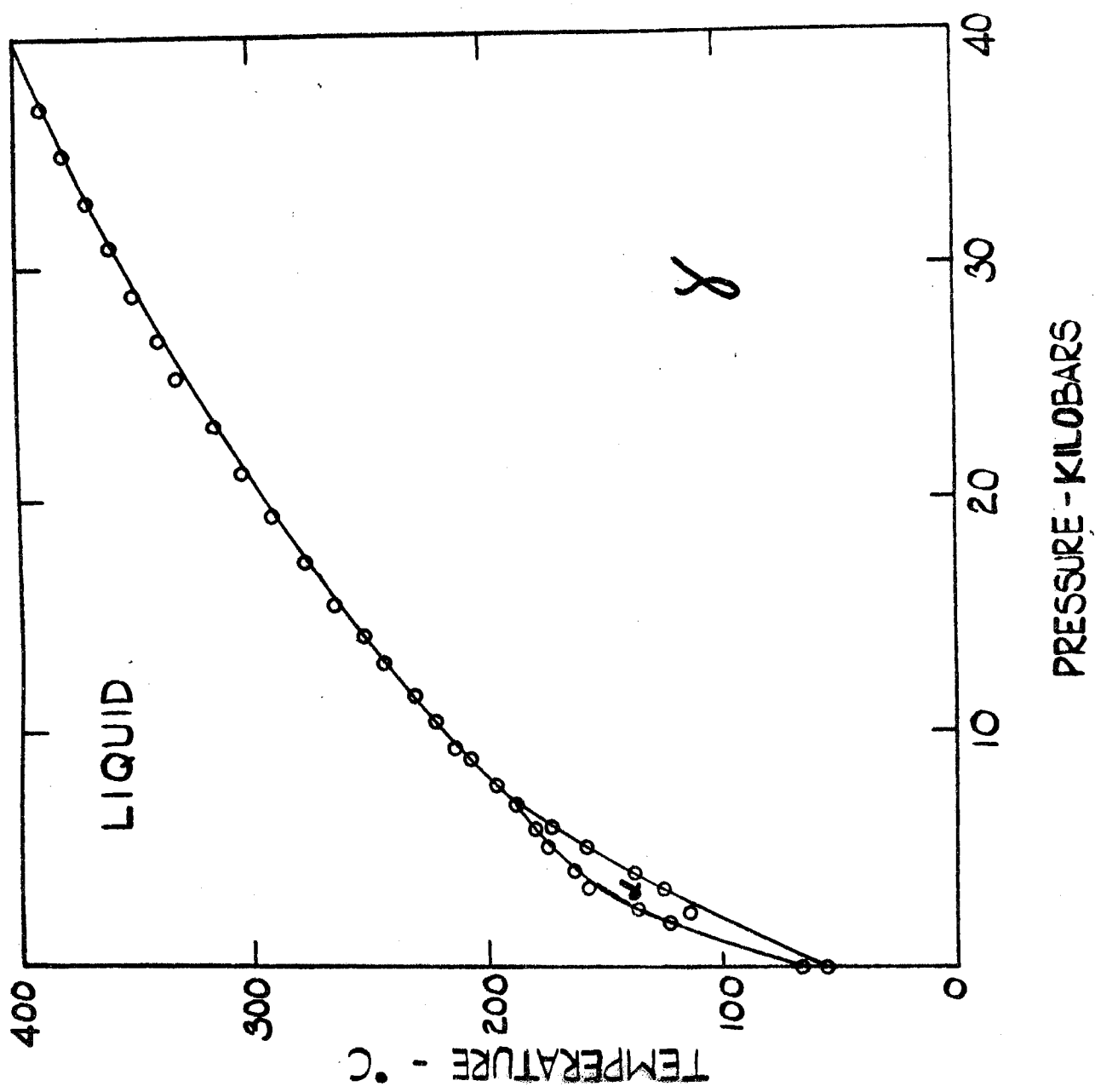


FIG. 6

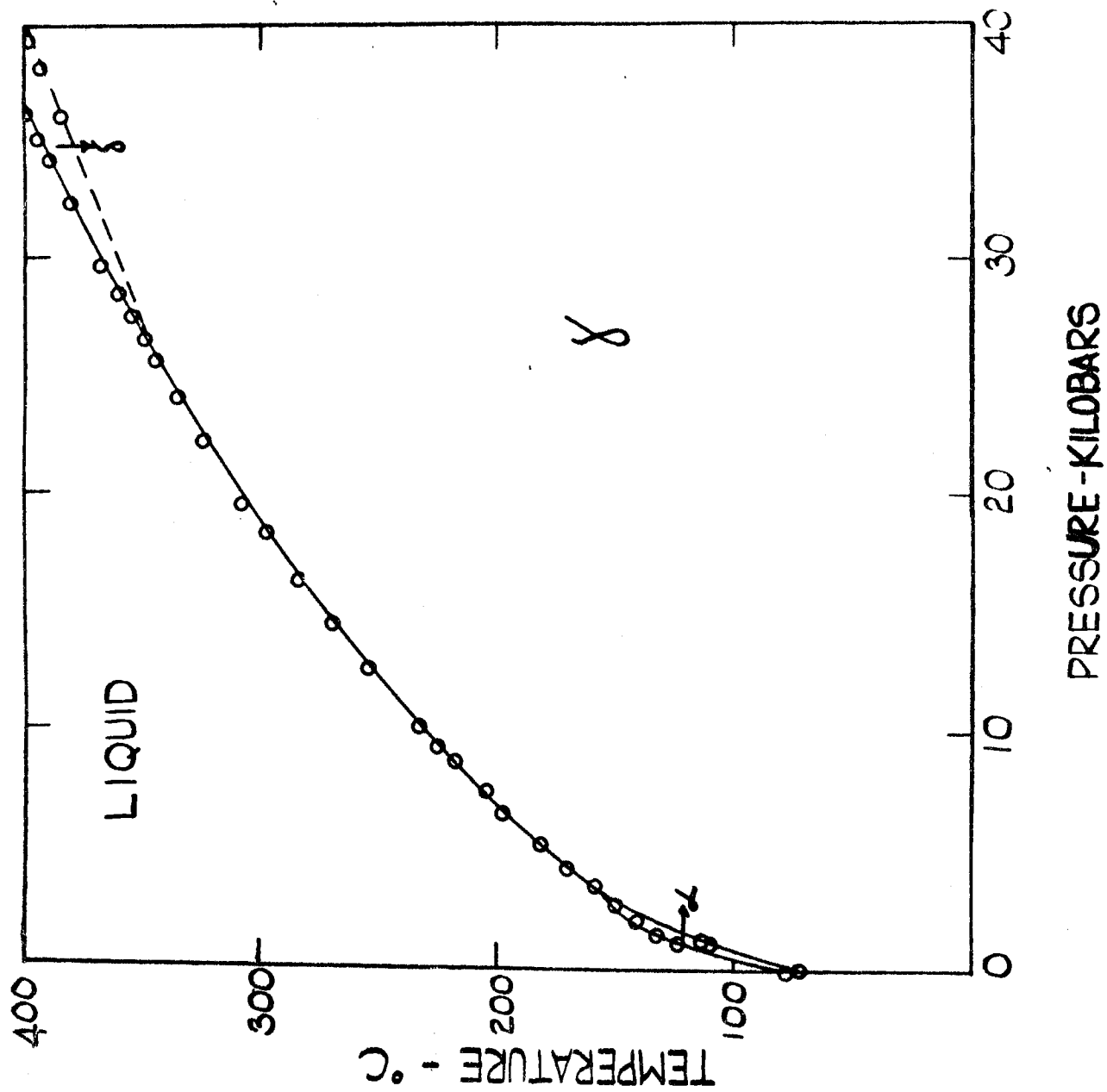


FIG. 7.

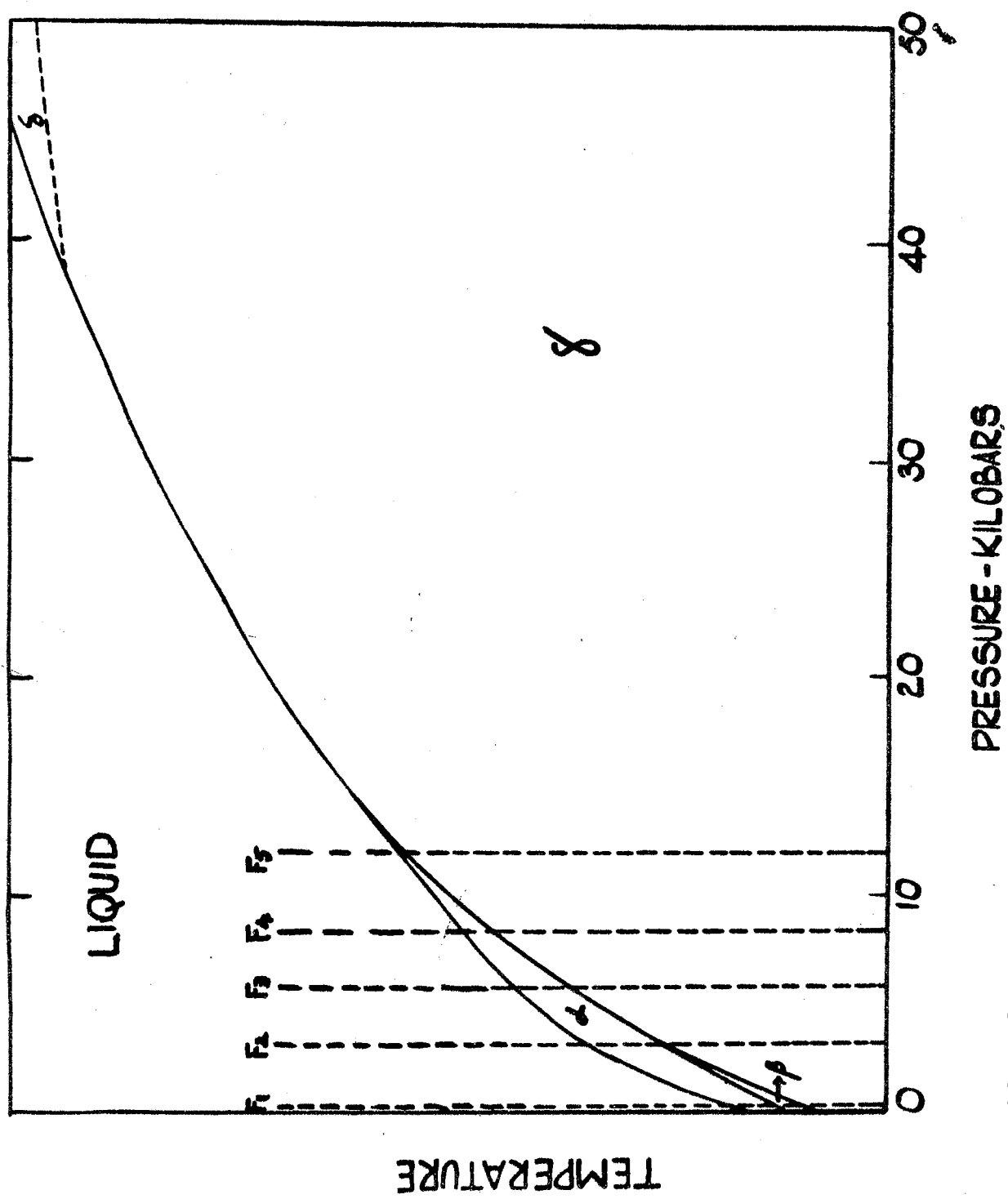


FIG. 8

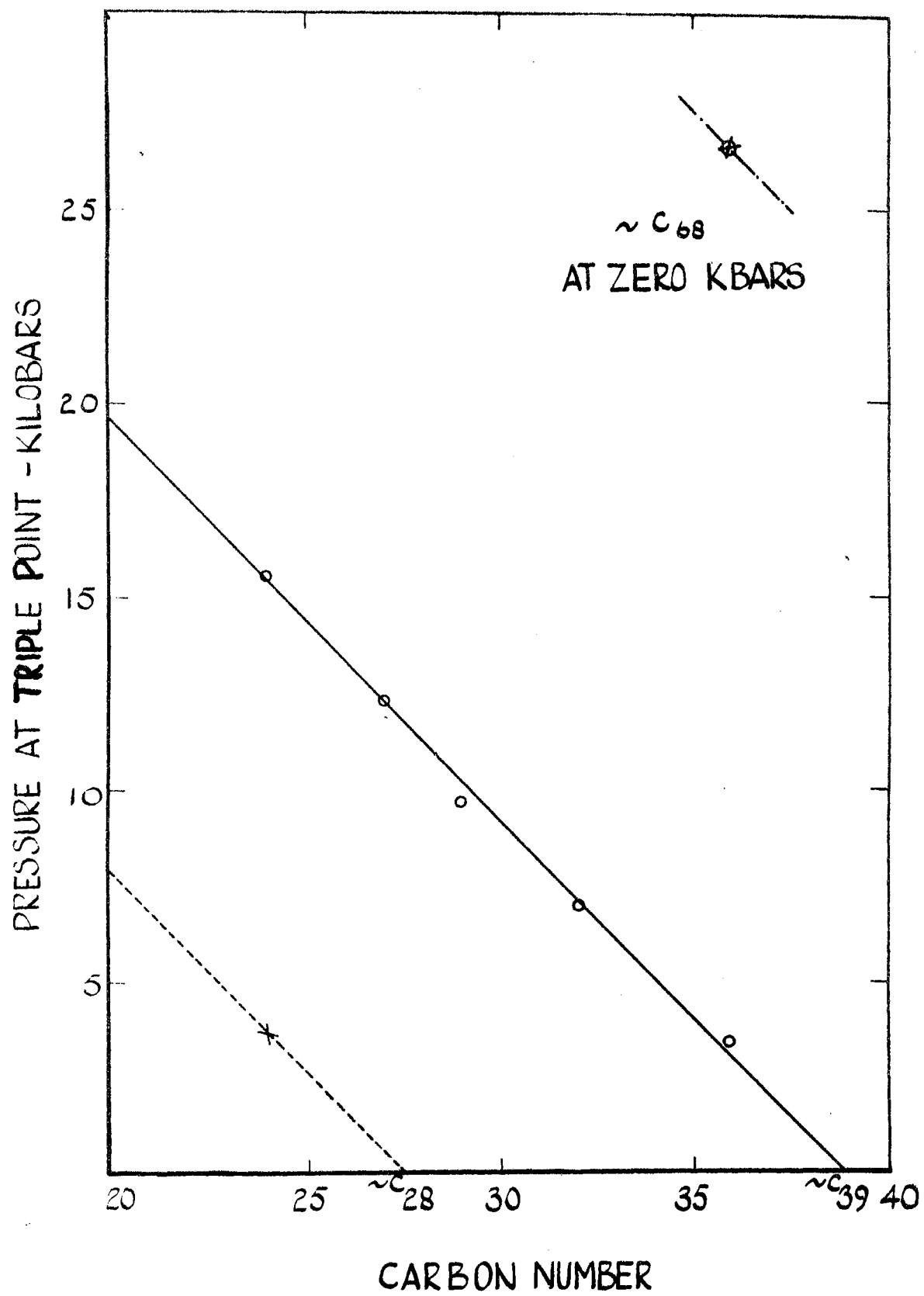


FIG.9