"Low Temperature Calorimetric Studies of Inclusion Compounds"

A thesis submitted for the Degree of Doctor of Philosophy
of the University of London

by

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October 1967

to my parents

ACKNOWLEDGEMENTS

I would like to record my gratitude for the most enthusiastic and considerate manner in which Dr. N.G. Parsonage has supervised the work of this thesis.

In addition I thank my colleagues in the laboratory, Preedeeporn Limcharoen, Henry Stroud and Barry Utting, for enlightening discussions, and Preedee and Henry in particular for many hours of assistance during the heat capacity measurements. I am also indebted to Dudley May and David Blythin for help in the investigation of the purity of some of the compounds used.

I would like to record my appreciation for assistance from the college technical staff and the staff of the stores, and to Janet, my sister, for typing the stencils, to Mrs. Pat Fox for duplicating them, and to Mr. G. Millhouse for assistance with the diagrams and photographs.

Finally I acknowledge a grant from the Science Research Council over the period October 1964 - September 1967 which made this work possible.

ABSTRACT

The heat capacities of the urea -n- undecane, urea -1- decene, urea -1- hexadecene and urea -1- eicosene adducts have been measured in the temperature range 12-300°K. For each the smooth heat capacity and the entropy per mole of urea has been calculated at various temperatures.

In all except the urea -1- decene adduct strongly co-operative anomalies in the heat capacity were observed. The heat capacities in the anomalous regions were investigated in greater detail and the excess enthalpies and entropies involved were calculated in each case. Although a co-operative anomaly was absent in the urea -1-decene adduct heat capacity, several regions of anomalously high heat absorption were observed. The excess entropy involved was calculated and found to be comparable with the entropies of the co-operative anomalies of the other adducts.

The heat capacity anomaly in the urea - n- undecane adduct was compared with similar anomalies previously reported in other urea -n- alkane adducts, and with a heat capacity calculated using a statistical mechanical model that had been developed for this system by earlier workers. This model incorporates the Ising and Weiss treatments of co-operative phenomena.

An attempt is made to explain the different natures of the anomalies in the heat capacites of the 1- alkene adducts by postulating a different head-tail arrangement in the urea channels for each of the 1- alkenes studied. The configurational heat capacities of these arrangements of alkene molecules have been calculated using an Ising model and applying the Monte Carlo technique.

The heat capacities of the thiourea - cyclohexane and thiourea - 2, 2 dimethylbutane were also measured in the range, 12-300°K.

Again regions of anomalously high heat absorption were observed and an attempt has been made to explain them by considering the ferroelectric properties of the thiourea lattice and the onset of rotation of the guest molecules. The latter has been represented by an Ising - Weiss model similar to that used for the urea adducts, but considering six possible rotational configurations of the molecules.

In addition during these experimental investigations a new heater has been installed in the calorimeter vessel and the accuracy of the new arrangement checked by measuring the heat capacity of a standard substance.

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Chapter 1. Introduction

Section A. Discovery of Urea and Thiourea Inclusion Compounds.

Urea inclusion compounds were discovered by Bengen (1940) whilst he was involved in the investigation of the possible quantitative determination of milk fat, by separating the fat out from the milk by addition of urea. During these experiments Bengen added a few drops of n-octanol to one of the samples, so as to achieve better separation. At the boundary of the alcohol surface appeared fine crystals, which Bengen analysed and found to contain urea and n-octanol only. He repeated the preparation of these crystals in the absence of milk, and then proceeded to prepare similar crystals with various organic reagents replacing n-octanol. Bengen's choice of organic reagents was not always successful and eventually he deduced the following rules. (1) The molecules must have more than 4 to 6 carbon atoms and (2) the carbon atoms must be linked to form a straight chain.

After the war the knowledge of Bengen's discovery was made freely available (1946, 1951), and much research was done to establish the nature of the compounds.

In 1947 Fetterly (1947) and Angla (1947) reported their independent discoveries of the related thiourea series of compounds.

The information obtained by determining the structure of these compounds led them to be called inclusion compounds. In addition they are referred to as occlusion compounds, complexes or adducts. The last term will frequently be used in this thesis.

Section B. The structure of Urea and Thiourea Inclusion Compounds.

In view of the weak interactions expected between urea and n-hydrocarbon molecules, the existence of stable compounds between them would hardly have been predicted. Their chance discovery set an interesting problem as to their nature, a problem which was solved by deducing the structure of the compounds by X-ray crystallography. These investigations by Smith (1952), Hermann and Lenné (1952), and several other observers, showed that the urea molecules form a hollow channel just large enough to accommodate the hydrocarbon molecule in its planar zigzag configuration.

Smith examined powder patterns of urea adducts with various straight chain compounds from C_{10} - C_{50}, and found that they were essentially identical. He then did a detailed single-crystal study of the n-hexadecane adduct from which he deduced that the unit cell consists of six urea molecules in the hexagonal space group $P6_12$ or $P6_52$ with $a = 8.230 \pm 0.004$ Å, and $c = 11.005 \pm 0.005$ Å. The urea molecules are linked by hydrogen bonds between the oxygen and nitrogen atoms (see Fig. 1) in such a way as to form a continuous helix of urea molecules, which form the walls of a hexagonal shaped cavity or channel. The channels are surrounded by six identical parallel channels with the result that the complete structure is rather like a honeycomb. Each urea molecule helps to make up the walls of three such channels, and in this way the channels are interconnected.

Smith's more complete study of the urea -n-hexadecane and n-bromodecane adducts revealed at room temperature that the hydrocarbon is in its extended planar configuration and is randonly orientated about its long c axis. X-ray analysis is unable to distinguish between rotation and random distribution amongst the energetically favourable sites. In addition Smith assumed that the packing distances between terminal methyl groups in the channel is 4·0Å, which is the same as the pure hydrocarbon, but in a more recent paper (Laves, Nicolaides and Peng (1965), give a value of 3·74Å, which is consistent with the potential energy calculations of Parsonage and Pemberton. The opportunity for increased interaction with the urea lattice (per unit length of the urea lattice) has the effect of drawing the terminal methyl groups closertogether than their van der Waals packing radii.

Hermann and Lenne's (1952) preliminary report of the structure of thiourea inclusion compounds was followed by an extensive report by Lenné (1954). Lenné reported that the ground structure of the thiourea in the adducts belongs to the rhombohedral space group $R\overline{32}/C$ with a = 15·8Å and c =12·5Å. Six thiourea molecules make up the unit cell, which is hexagonal shaped and rather similar in many ways to the urea cell. The positions of the nitrogen atoms, however, are slightly dependent on the guest molecules. The main differences between the urea and thiourea cages are: -

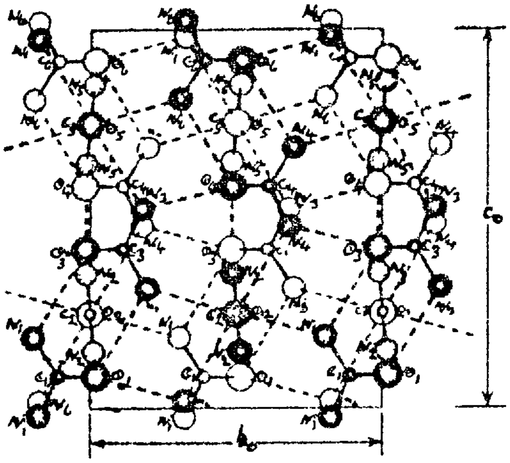
(1) The greater size of the sulphur atoms compared with the oxygen atoms results in a channel of larger dimensions. The edge length of the hexagonal channel is 5·37Å in thiourea and 4·8Å in urea. How this effects the nature of the guest molecule will be discussed in the next section.

(2) The absence of any strong hydrogen bonds in the thiourea lattice. This will be discussed in the next section when considering stability.

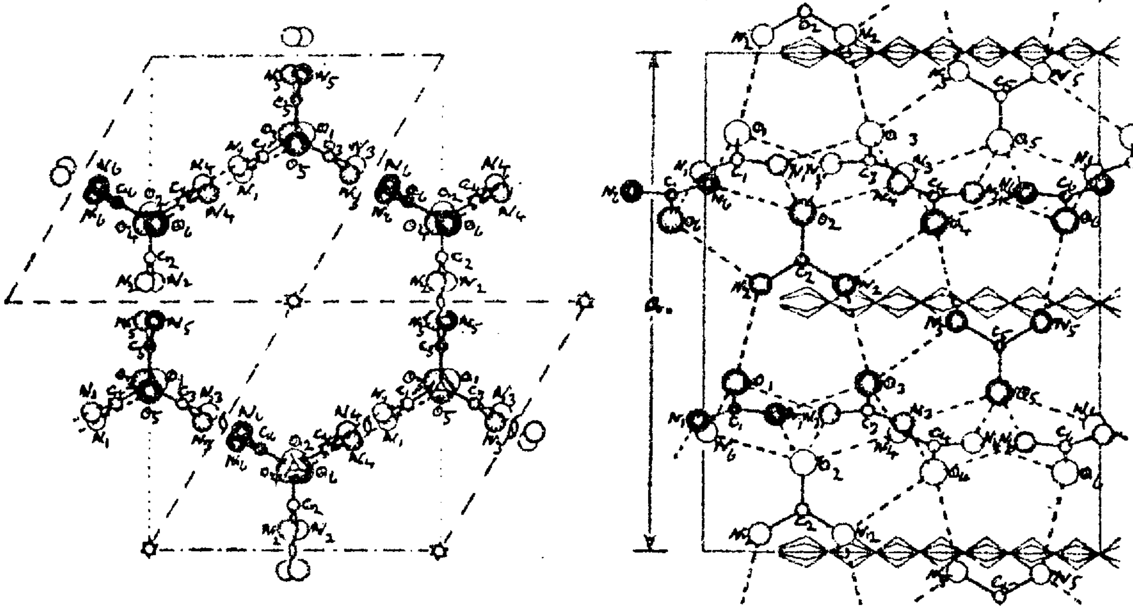
(3) In the urea adducts it has been mentioned that the guest molecule is orientated about it's longitudinal axis in order to achieve maximum interaction with the oxygen

atoms. In the thiourea adducts the even larger sulphur atoms not only influence the orientation of the guest molecules, but also affect the position of the guest along the axis of the channel.

FIG. 1. The n-hexadecane - hexagonal urea structure.
(After Smith 1952).



(a). Projection along the "a" axis.

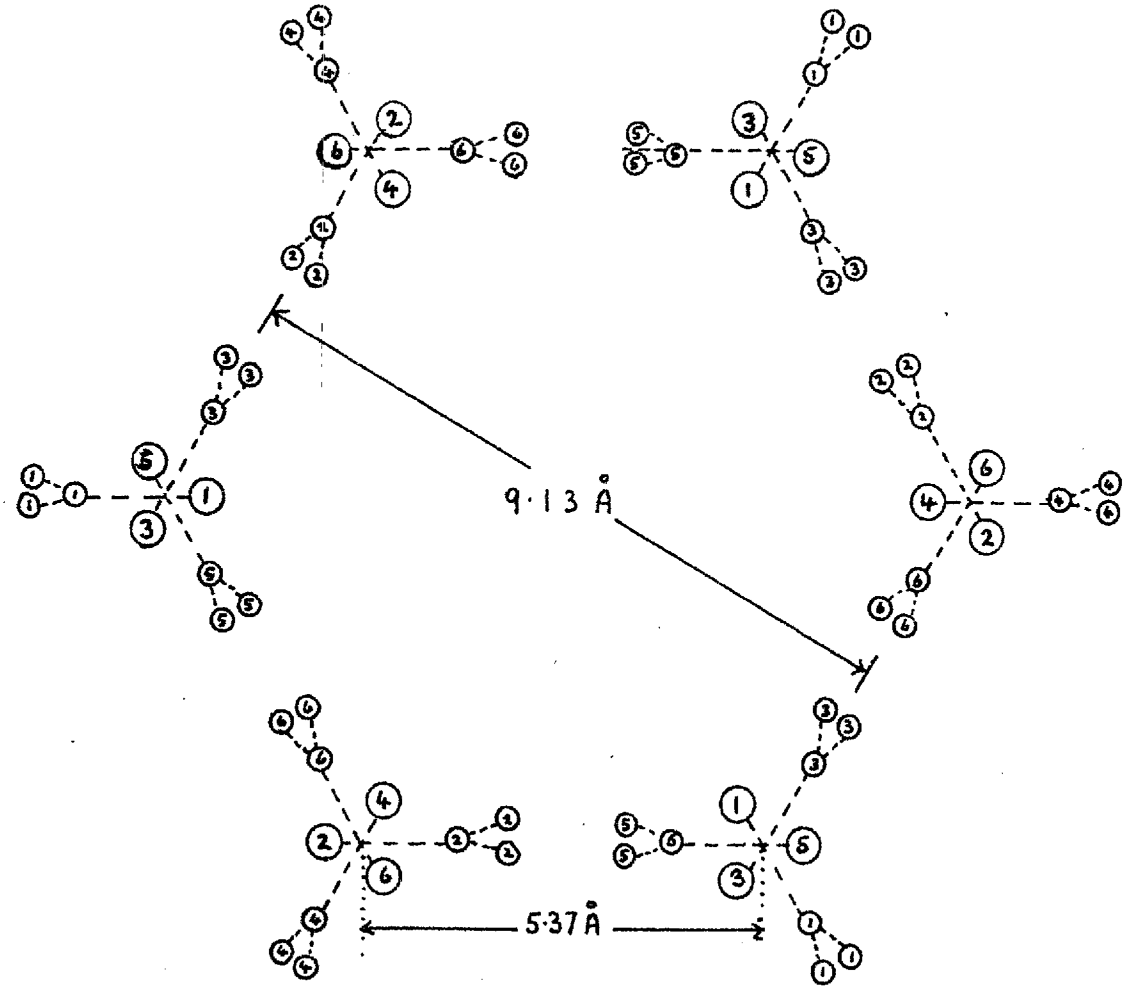


(b). Projection along the "c" axis.

(c). Projection along the "b" axis.

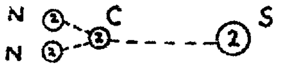
Fig. 2. The Rhombohedral Thiourea Structure.

(in the thiourea-cyclohexane adduct)



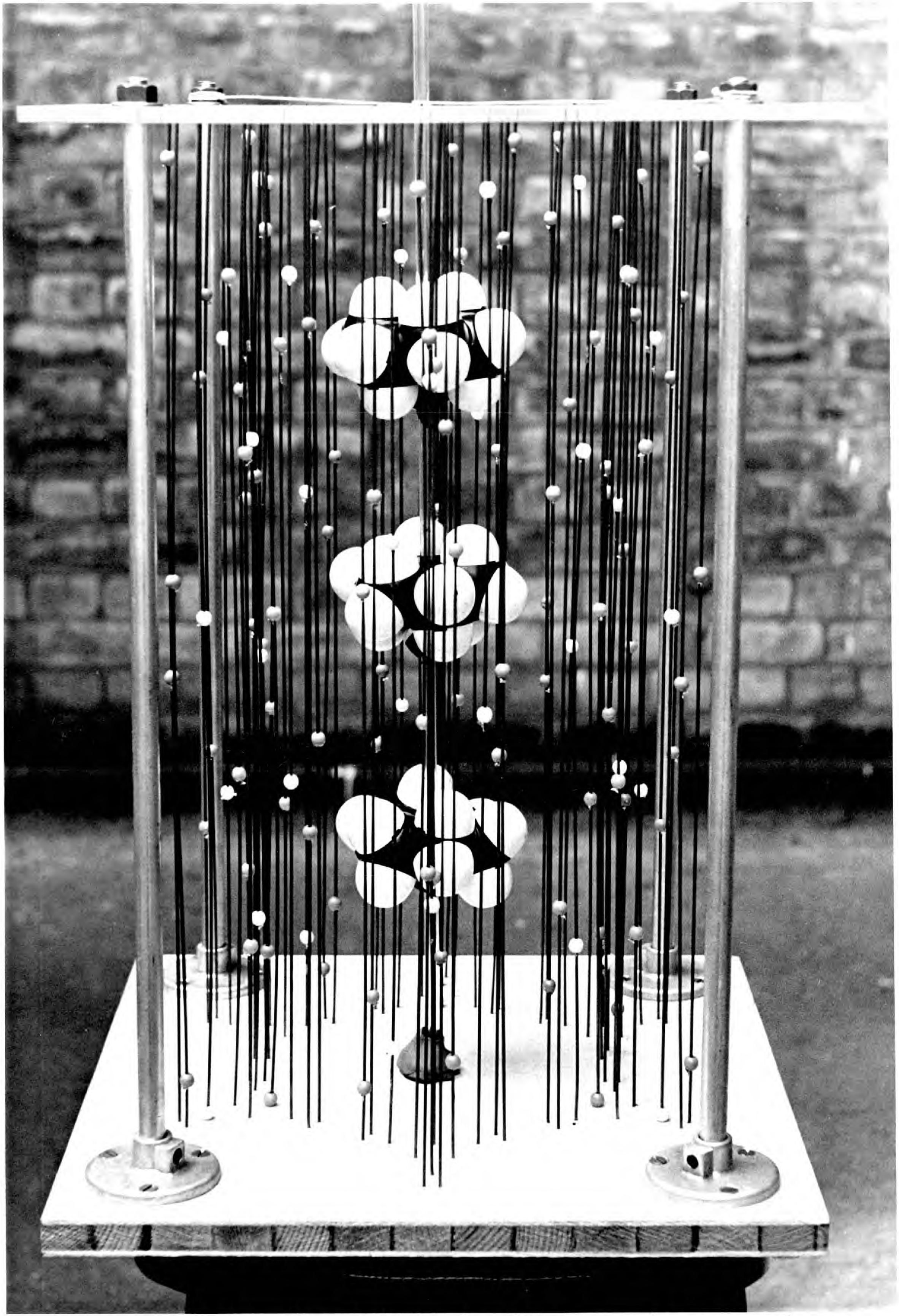
Projection along the "c" axis.

Thiourea molecule



The number indicates the plane of the molecule

Fig. 3



A Model of the Rhombohedral Thiourea Lattice showing included Cyclohexane Molecules.

Section C. Stability and Composition.

The principal requirement for hydrocarbon adduction with urea is a long unbranched chain. Alkanes with less than six carbon atoms will form adducts, but they are unstable at room temperature. Organic substances which will form adducts with urea include n-alkanes, n-alkenes, n-carboxylic acids, esters and ketones (Schlenk, 1949). Branching and bulky substituents can be tolerated provided the hydrocarbon chain is sufficiently long for the interaction with the urea lattice to offset any unfavourable interaction due to the side groups. Such a side group can be tolerated more successfully at the end of the chain rather than in the middle, where the chain has less room to manoeuvre.

In contrast n-hydrocarbons with less than sixteen carbon atoms in the chain will not form adducts with thiourea, as the n-hydrocarbon molecules are incapable of sufficient interaction with the wide thiourea cage. n-Hydrocarbons with more than 16 atoms can form stable adducts, presumably by coiling around the walls of the thiourea cage. Evidence of the existence of this coiling is given by Laves, Nicolaides, and Peng (1965), e.g., the length of 2, 6, 11, 15 - tetramethylhexadecane in the thiourea adduct is 21.35Å as opposed to 22.64Å in the planar configuration.

The most welcome guest of the thiourea cage is one of larger cross section such as a branched chain or a cyclic molecule. Schliesser and Flitter (1952) have studied Fisher-Hirschfelder molecular models to deduce the dimensional requirements of molecules adducting with thiourea and they found that the cross section of the guest molecule should be 5.8 ± 0.5Å by 6.8 ± 0.3Å. Some examples of molecules adducting and non-adducting with urea or thiourea are given in TABLE 1. The values quoted are based mainly on the values of Redlich, Gable, Dunlop and Millar (1950) and Redlich, Gable, Beason and Millar.(1950).

TABLE 1. The adducting properties of various molecules.

Reactant (guest)	Adducting with urea at 25°C.		Adducting with thiourea at 25°C.	
	urea/guest mole ratio	ΔHf K cal/mole	thiourea/guest mole ratio	ΔHf K cal/mole
n-hexane	5•6	-	-	-
2,2-dimethyl butane	-	-	2•6	4•4
benzene	-	-	-	-
cyclohexane	-	-	3•0	3•6
n-heptane	6•1	7•3	-	-
2,2,3-trimethy butane	-	-	2•9	3•7
Toluene	-	-	-	-
methyl cyclohexane	-	-	2•9	-
n-octane	6•73	9•7	-	-
cycloctane	-	-	3•1	-
n-dodecane	9•3	16•1	-	-
2,6,9,11 tetramethyl dodecane	-	-	7•9	-
2-methyl pentadecane	-	-	-	-

ΔHf is the heat of formation of the adduct).

Lenné (1954) in his study of thiourea cyclohexane found that cyclohexane molecules were located near the planes containing the three sulphur atoms in order to attain maximum interaction with the sulphur atoms. The effect this has on the packing of the cyclohexane molecules in the channel is clearly indicated by the constituent analysis of the adduct, which shows the thiourea to cyclohexane molecule ratio to be three to one. There are several such examples of stoichiometry in these compounds, e.g., cyclohexanol, carbon tetrachloride and perhaps most striking of all the w. w' methylene-bridged dicyclohexyls. (Schlenk W. Jr. 1951). In the latter series of compounds there is a strong tendency for the methylene bridge to coil in order to accommodate the terminal cyclohexyl groups in the plane of the sulphur atoms.

Smith (1952) explained extra discrete spots found in the n-hexadecane adduct X-ray pattern, but absent in the n-bromodecane adduct pattern, by suggesting the n-hexadecane molecule fitted exactly into two unit cells of the lattice (22•02Å). He suggested the terminal methyl groups were displaced slightly to shorten the molecule by the necessary 0•82Å from its planar configuration length, 22•84Å. However, Lenné (1954, 1963), disagrees with Smith's interpretation of the X-ray data and claims that the n-hexadecane molecules are in their extended configuration. This view is supported by Nicolaides, Laves and Peng (1965). The analysis results of Redlich (1950) and Schlenk (1949), although not conclusive, tend to favour Lenné's view.

In recent work Lenné (1963b) reports examples of stoichiometry in urea adducts. However, in these cases the urea lattice is no longer hexagonal, but rhombohedral (or pseudorhombohedral) as in the thiourea lattice. This lattice accommodates much larger molecules and the distribution of the lattice molecules is such that the lattice field in the channel is non-uniform. In consequance, the guest molecules behave in a similar manner to those in thiourea, seeking maximum interaction with, in this case, the oxygen atoms. Guest molecules to this lattice include trioxane (unit cells/guest molar ratio 1 : 2), 6-chloro-undecane (3 : 2), dihydrocitronellyl hexadecane (3 : 1), and hexadecylcyclohexane (5 : 2).

$$\begin{tikzcd}[column sep=small]
\text{Urea}_{(\text{tetragonal})} + \text{Hydrocarbon}_{(\text{liq})} \arrow[rr, dash, "\Delta \text{ Hf}"] \arrow[dr, "\Delta \text{ H vap}"'] & & \text{urea}_{(\text{hex})}\text{-hydrocarbon adduct} \\
& \text{Urea}_{(\text{tetr})} + \text{Hydrocarbon}_{(\text{gas})} \arrow[ur] &
\end{tikzcd}$$

(1.1)

The factors controlling the heat of formation of urea adducts is best shown by an enthalpy cycle (1.1). A similar cycle can be drawn for a thiourea adduct formation. The value of the heat of formation will depend on (1) the comparative strength of the hydrocarbon - hydrocarbon interactions in the liquid and the hydrocarbon - urea interactions in the adduct, and (2) the relative stabilities of the urea tetragonal and hexagonal lattices.

Infra-red studies of urea (Stewart 1957) and urea adducts (Fischer and Mc Dowell 1960) have confirmed that there is strong hydrogen bonding in both urea lattices. The relative strengths of the hydrogen bonds are indicated by the nitrogen oxygen distances, which, together with the bond lengths of tetragonal (Wyckcoff and Corey 1932 (a)) and hexagonal (Smith 1952) urea lattices obtained from X-ray data are listed in TABLE 2.

TABLE 2. Atomic distances in the urea crystal lattices.

	Urea-hydrocarbon complex	Tetragonal urea
C - O	1.28 Å	1.25 Å
C - N	1.33	1.37
N....N	2.30	2.31
N - H....O	2.93	2.98
N - H....O	3.04	3.03

It will be noticed there are two types of hydrogen bond in the hexagonal lattice, one of length 2·93 Å and the other of length 3·04 Å (also see Fig. 1).

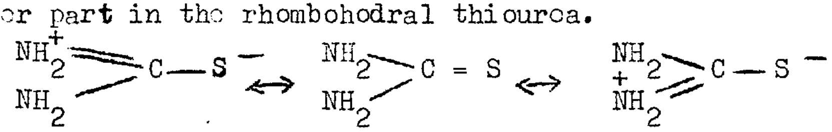
The net shortening of the hydrogen bonds in the hexagonal lattice is confirmed by Fischer and McDowell's report of a corresponding reduction in the N - H stretching frequency. On first reflection it might be considered that the empty hexagonal lattice would be stable at room temperature, but although observers (Kyri[illegible]au 1959) have reported preparing quantities of the empty lattice, it is generally considered to be unstable. The reason is that the hydrogen bonds are directed so that they have a component in towards the centre of the channel and in the absence of guest molecules the structure collapses. This property le~~a~~d Fetterly (1964) to call these bonds 'supported' hydrogen bonds.

The electron arrangement of the sulphur atom inhibits the function of hydrogen bonds with sulphur. N - H....N hydrogen bonds have been found in many compounds, e.g., hydroxylamine, hydrochloride and to a lesser extent ammonia, but the nitrogen - nitrogen distances in orthorhombic thiourea (Wyckoff and Corey 1932b) and in the thiourea adducts (Lenné 1954) are much greater than the limiting N - H....N bond distances (Pimental McClellan 1960) (TABLE 3). Mecke and Kutzelnigg (1959) infra-red studies of thiourea and thiourea adducts showed there was negligible difference between the respective N - H stretohing frequencies. Thus in contrast to the urea adducts, the thiourea adducts are not stabilised by the increase in hydrogen bond strength. The lack of strong directional bonds to link the thiourea lattice molecules would suggest the possibility of deformation of the lattice structure to accommodate molecules in their most favourable position, e.g., the W - W′methylene bridged dicyclohexyls instead of coiling could extend the sulphur atom repeat distance. However, the X-ray evidence of Lenné (1954) and Laves, Nicolaides and Peng, (1965), refute this.

TABLE 3. ATOMIC DISTANCES IN THE THIOUREA CRYSTAL LATTICE

	Thiourea (Orthorhombic)	Thiourea (Rhombohedral)
Intra mol.		
C - N	1.35 Å	1.26 Å
$NH_2 \vdots NH_2$	2.18 Å	2.16 Å
C = S	1.64 Å	1.75 Å
Inter mol.		
$NH_2 \ldots S$	3.45 Å	3.30 Å
$NH_2 \ldots NH_2$	3.85 Å	4.1 Å

The lengthening of C = S bond and the shortening of the C - N bond in going from orthorhombic to rhombohedral thiourea (Table 3) indicate that the charged tautomeric forms play a larger part in the rhombohedral thiourea.



The greater electron density in the region of the sulphur atom could then account for the very strong affinity the guest molecules have for the sulphur atoms.

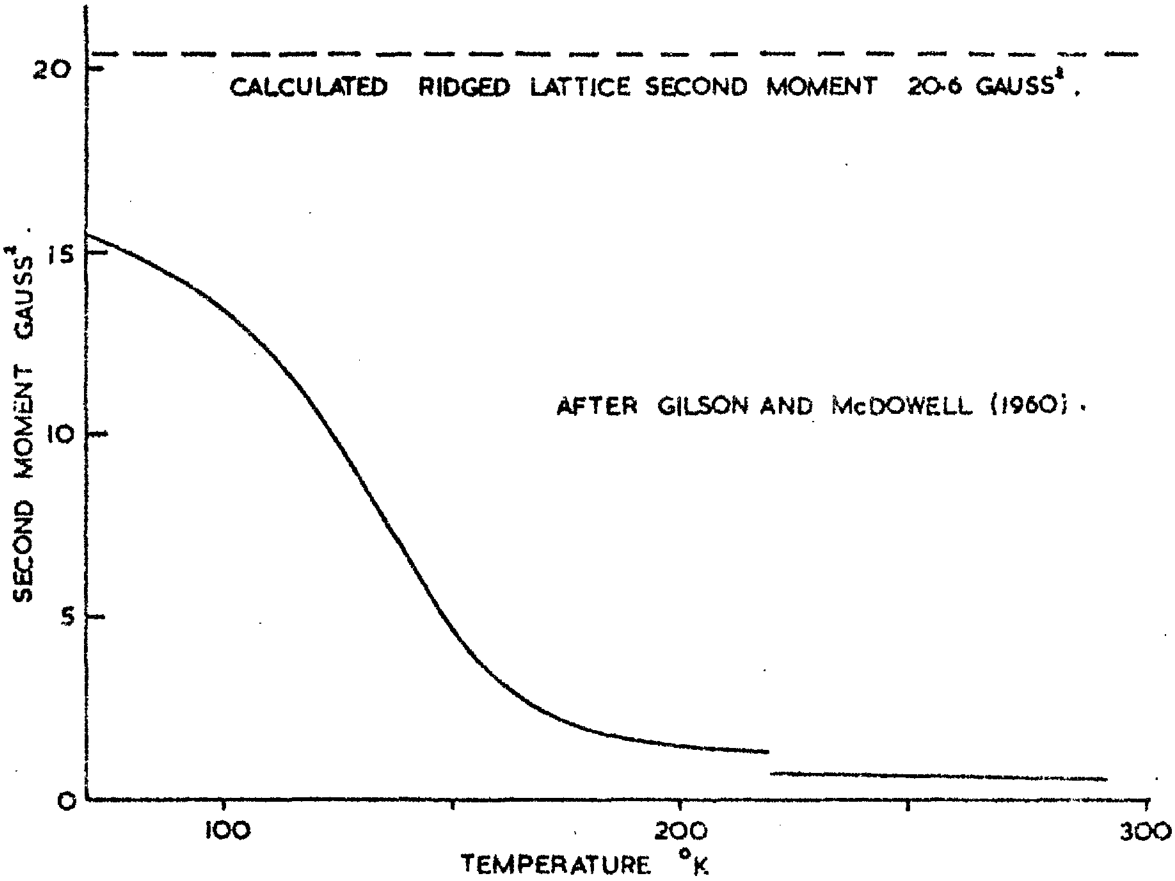
SECTION D THE STUDY OF THE MOVEMENT OF THE GUEST MOLECULES

(i) Nuclear Magnetic Resonance

Gilson and McDowell (1959) have studied the n.m.r. spectra of urea adducts with n-alkanes (C_7-C_{13}, C_{16} and C_{26}) at 25°C. The spectra of the adducts were similar, each having one broad line of width 7·1 - 7·3 gauss due to the relatively rigid urea lattice protons and a narrow line of modulation width attributed to the hydrocarbon, which has a greater freedom of movement. Use of fully deuterated urea resulted in a spectrum consisting of only the narrow band.

Later investigations (Gilson and McDowell 1961) of the urea d_4· n-tridecane and n-hexadecane adducts, using wide line proton magnetic resonance over the temperature range 77-298°K, revealed more information of the nature of the movement of the hydrocarbon molecules. At 77°K the resonance curve of the tridecane adducted consisted of two components, a broad line of width 10·8 gauss and a narrow line of width 3·3 gauss. The two lines gradually converged into a single line at 119°K. At 140°K the separate components re-appeared with line widths of 6·8 and 1·8 gauss. Above this temperature the broad line intensity diminished until it disappeared at 230°K and the narrow line decreased slowly to a width of 1·0 gauss at 270°K, when it too disappeared. The second moment decreased from 12·6 gauss^2 at 77°K to 2·8 gauss^2 at 160°K and then slowly to 2·1 gauss at 225°K, when it fell to 0·7 gauss^2. (See Fig. 4). The behaviour of the n-hexadecane adduct was similar to that of the tridecane adduct.

FIG. 4.



VARIATION OF THE SECOND MOMENT WITH TEMPERATURE FOR THE PROTON MAGNETIC RESONANCE LINE FROM N-HEXADECANE-UREA-D_4 ADDUCT.

Gilson and McDowell considered the most important contributing factors to the second moment of the resonance line to be intra molecular from the hydrocarbon chain and inter molecular from the terminal methyl groups of adjacent molecules in the same channel. They estimated the second moment contribution from the former to be 20.9 $gauss^2$ and 20.6 $gauss^2$ for tridecane and hexadecane respectively, and from the latter to be .1 $gauss^2$, i.e., assuming a 4 Å separation of the terminal carbon atoms. These estimated values exceed those obtained experimentally at 77°K, which would suggest the hydrocarbon chains are not rigid at this temperature. In fact an angular amplitude of oscillation of 45° and 30° would be necessary to account for the reduced observed values of the second moments of the tridecane and hexadecane adducts respectively. The steady decrease in second moments of both adducts in the range 77 - 160°K could be due to an increasing amplitude of rotational oscillation until an amplitude of 60° is achieved, which on account of the nature of the urea cell is effectively free rotation. Gilson and McDowell suggested the sharp change in second moment at 225°K could be due to an expansion of the urea lattice giving the hydrocarbon molecules more freedom.

In addition Gilson and McDowell reported similar studies on the thiourea adducts with four cyclic hydrocarbons. Their study on thiourea d4 - cyclohexane showed the line widths and second moments to diminish from 4.6 gauss and 2.7 $gauss^2$ at 77°K to 1.6 gauss and 0.3 $gauss^2$ at 298°K. The calculated intra molecular second moment for a rigid cyclohexane molecule is 17.3 $gauss^2$ and 3.6 $gauss^2$ for one re-orientating about its triad axis. In pure cyclohexane at 298°K the second moment is zero (Andrew and Eades 1953), indicating the freedom of movement of the cyclohexane molecules. In the thiourea adduct the observed second moment is even lower than the value calculated for cyclohexane with free rotation about the triad axis. This would suggest that the cyclohexane molecules were capable of some motion in the channel. The narrower line found for the thiourea d_4 cyclopentane adduct indicates that the smaller ring has greater freedom along the length of the channel.

(ii) Dielectric Properties

Meakins (1955) studied the dielectric absorption at microwave frequencies of urea adducts with long chain compounds with polar groups. He found that at 20°C there was large dielectric absorption at high frequencies in all cases (~~x~~1 x 10^{9} to 3 x 10^{11} c.p.s). Study of a non-polar chain hydrocarbon revealed no dielectric absorption. Most of the compounds studied give little or no dielectric absorption in their pure state, and so it was concluded that this effect was due to the special situation of the long chain molecules in the urea lattice.

The high frequency of absorption is indicative of the loose nature of the forces between the lattice and the guest molecules. The comparatively low frequency observed of the absorption maximum of 12 - bromotricosane ($C_{23}H_{47}Br$) is a result of the hindrance to re-orientation by the urea lattice encountered by the bromine atom in the centre of the long chain. The maxima of absorption of the 1-bromo-octadecane adducts occurred at a much higher frequency, as bromine atoms in the terminal positions have greater freedom to re-orientate themselves.

The X-ray evidence (Smith 1952) showed that the 1, 10 - dibromodecane molecules in the urea lattice are fully extended. In this case the polar groups would oppose each other and the resultant dipole moment would be zero. The large dielectric absorption of this adduct indicates that in the presence of an electric field, the polar groups orientate themselves independently of the long chain. Further evidence for the orientation of the polar groups independent of the chain is given by the similarity of the dielectric loss factors of several ketones of vastly different chain lengths (C_{17}, C_{31} , C_{35}) studied by Meakins.

The high dielectric absorption of these polar components in the adducts, as opposed to very little in the pure state, would suggest that the molecules in the adduct are not able to rotate freely about their long axis. This is not a contradiction of the findings of the n.m.r. (section D(i))and heat capacities (section D(iii)) investigations, as Meakins studied long chain molecules with bulky substituent groups. Both these factors oppose the free rotation of the guest molecule within the lattice.

By considering the re-orientation of the polar group about the long axis from one position of minimum potential energy in the urea field to another, Lauritsen (1958) was able to deduce the relaxation times of these re-orientations and calculate values for the dielectric properties, which

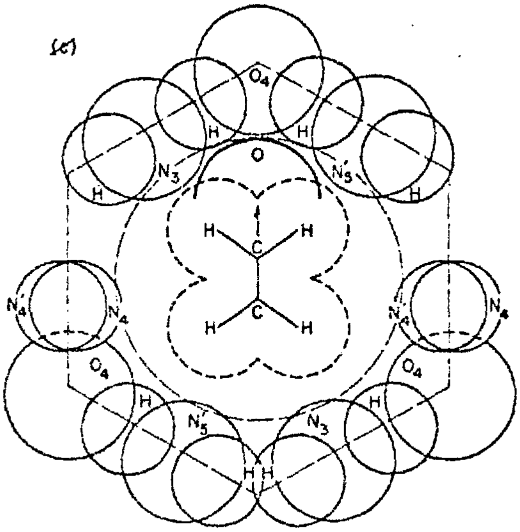


Fig. 5. Intersection of the van der Waals spheres of the host and guest atoms. In this example the guest is a ketone. (Lauritzen 1958)

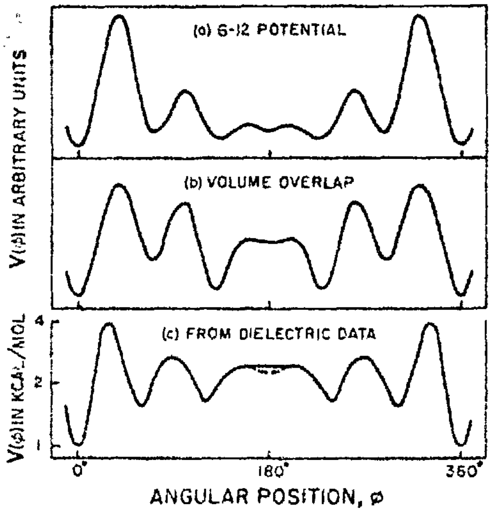


Fig. 6. Potential energy as a function of angular position of the dipolar group for 16-hentriacontane in urea. (Lauritzen 1958). See the text for details of the potentials considered in (a) and (b).

are in good agreement with Meakin's experimental values. Lauritsen deduced these potential energy minima by assessing the contributions to the potential energy using a 6 - 12 potential, (1.2.).

$$V(r) = C \left[\tfrac{1}{2} \left({}^{ro}/_{r} \right)^{12} - \left({}^{ro}/_{r} \right)^{6} \right] \qquad (1.2.)$$

where r is the distance between two atoms and ro the sum of their van der Waals radii, and also by using a simpler potential (1.3).

$$V(r) = C \left[\text{volume of overlapped by van der Waals spheres} \right] \qquad (1.3.)$$

The overlapping of the van der Waals spheres is clearly shown in fig. 5 where the polar group is a ketone. The angular dependence of the potential energy of the guest molecule can be seen by examining fig. 5 and is demonstrated for both above potentials and for deduction from dielectric data at room temperature in fig. 6.

(iii) Heat Capacity

Pemberton and Parsonage (1965, 1966) measured the heat capacities of five urea-n-alkane adducts (C_{10}, C_{12}, C_{15}, C_{16}, C_{20}) and the urea - 2-methylpentadecane adduct. Gradual transitions were observed in the heat capacities of the n-alkane adducts, but not in that of the urea - 2-methylpentadecane adduct. The transition temperature of the 'even' n-alkane adducts increased approximately linearly with increasing chain length. The transition temperature of the only 'odd' adduct (C_{15}) studied was slightly higher than this linear relationship would suggest. The variation of the transition temperature with n-alkane chain length and the absence of a transition in the heat capacity of the 2-methylpentadecane indicated that the transitions were associated with the n-alkane molecules, and probably due to the onset of rotation or re-orientation of these molecules about their long axis in the urea cage. The larger interactions of the 2-methyl group with the urea cage hinders any rotation or re-orientation of the 2-methylpentadecane molecule about its long axis.

Similar transitions are exhibited by many of the pure n-alkanes (Finke, Gross, Waddington and Huffman 1954, Broadhurst 1962) at temperatures approximately twice those of the corresponding n-alkane adducts. The distances separating two adjacent parallel n-alkanes in the adduct is about 8·23 Å as compared with 4·46 Å in the pure state, and since the attractive part of the potential energy between two long parallel chains is approximately proportional to r^{-5} (where r is the distance separating the two long axis) (Salem 1962), the lateral interactions of the n-alkanes are about $(\frac{4\cdot46}{8\cdot23})^5 = 0\cdot047$ times smaller in the adducts than in the pure state. Therefore, it at first seems strange that the transition temperatures of the adducts ~~is~~ are as high as observed.

In order to explain these transitions, Parsonage and Pemberton (1967) first estimated the molecular interactions experienced by the alkane molecules.

(i) the urea alkane interactions. These were estimated for various orientations of the alkane molecules and in various positions along the channels relative to the urea molecules. Several n-alkanes of differing chain lenths were considered. On account of the CH_2 units being in different environments, and consequently having different interactions with the urea molecules, the potential barrier to rotation varied erratically with chain length.

(ii) the alkane lateral interactions. The interactions between alkanes in adjacent channels were estimated. Various orientations of both alkane ~~s~~ molecules and the staggering of the molecules were taken into consideration. As mentioned before, these interactions were very small but nevertheless important, as was shown.

(iii) the longitudinal interactions. The interactions between the terminal methyl groups were estimated for selected relative orientations of the two groups. The distance separating the terminal groups was estimated by comparing the forces of the urea lattice interactions. Having obtained this position the potential energy barrier to rotation was determined. This barrier was of course independent of chain length and of value 293 and 780 cal/mole of hydrocarbon for set I and set II parameters respectively. (See Chapter 7 D (ii)).

The calculations showed that there were six minima in the graph of potential energy versus angle of orientation. The treatment of the system was however simplified by considering the alkane molecules capable of occupying two possible orientational positions with respect to the urea lattice. The orientating effect of the lattice was taken as V cos ϕ where 2V is the difference in potential between the greatest and least minima of the calculated potential energy graphs, and ϕ is the phase angle related to the position of the molecules along the channel. Parsonage and Pemberton then represented the n-alkane adducts in the urea channels by an Ising model. The Ising model potential energy of interaction was then $- J\mu_1\mu_2$, where J is dependent on the nature of the longitudinal interactions and μ_1 and μ_2, are either +1 or -1 depending on which of the two orientational states they are in. A similar treatment of the lateral interactions in the other two directions was not adopted as so far no exact solution has been found for the three dimensional lattice Ising model. Instead the energy of interaction is taken as $J'\mu_i\langle\mu_i\rangle$ where $\langle\mu_i\rangle$ is an average of μ_i over all the alkane molecules. This approximation was first used by Bragg-Williams and Weiss. $\langle\mu_i\rangle$ is therefore a measure of the long range order existing, since if $\langle\mu_i\rangle = 0$ there is no long range order, but if $\langle\mu_i\rangle = 1$, there is complete order in the system. Therefore, a Bragg-Williams or Weiss model was employed for the lateral interactions, whilst an Ising model was chosen for the longitudinal interactions. The role of the urea lattice was analgous to that of an external field in a magnetic system.

The partition function for this model was evaluated using a matrix method (ter Haar 1954). The variation of $\langle\mu_i\rangle$ with temperature was determined by solving iteratively the derived equations relating $\langle\mu_i\rangle$ with the partition function. This was solved for various values of J, J' and V and it was found that the transition temperature, (i.e., temperature when $\langle\mu_i\rangle \simeq 1$ goes to $\langle\mu_i\rangle = 0$) was very dependent on the value chosen for J, but largely unaffected by variation of V. An approximate linear relationship existed between the value of J' and the transition temperature. J' is approximately proportional to the chain length and so the model correctly indicated that the transition temperature is related to chain length. The results also predicted that the transition temperatures of the 'odd' adducts would be relatively higher than those of the even series.

The experimental values of the entropy increase with chain length, which is con~~s~~trary to the Ising model prediction of a constant entropy of R ln 2, or R ln W where W is the no. of possible states of the guest molecule. The shapes of the heat capacity curves are dominated to a large extent by the use of the Bragg-Williams - Weiss approximation for the lateral interactions and are not accurate representations of those observed experimentally[1]

However there is sufficient agreement between experimental results and theoretical predictions for one to conclude that the representation of the system by this Ising - Weiss model gives a good indication of the nature of these transitions.

SECTION E THIS THESIS

The work reported in this thesis is an extension of the study of Parsonage and Pemberton (Section D (iii)).

Their theory predicted that the transition temperature of the 'odd' n-alkane adducts would be relatively higher than those of the 'even' series. Only one 'odd' adduct was studied by them and indeed the transition temperature was observed to be relatively high compared with the transition temperatures of the 'even' adducts studied. In this work, the first task was to study in a similar way a second 'odd' adduct (n-undecane, $C_{11}H_{24}$) and so providing further evidence to assess this prediction.

It was also mentioned that the predicted transition temperature was very sensitive to changes in the hydrocarbon longitudinal interactions (J). The truth of this was tested by studying the heat capacities in the range 12-300°K of three 1-alkene adducts, 1-decene ($C_{10}H_{20}$), 1-hexadecene, ($C_{16}H_{32}$), and 1-eicosene ($C_{20}H_{40}$). The interpretation of the result is complicated by the different possible arrangements of the unsymmetrical alkene molecules in the channels. The values of the interactions between terminal methyl-methyl, methyl-methylene, and methylene-methylene groups were calculated in an attempt to interpret the heat capacity transitions observed experimentally.

Finally the heat capacities of two thiourea adducts (cyclohexane (C_6H_{12}) and 2, 2-dimethylbutane were measured from 12-300°K. An attempt is made in this thesis to understand the diverse transitions found in the heat capacities of these adducts.

During this research the calorimeter heater was re-designed and the calorimeter recalibrated. The accuracy of the apparatus was tested by measuring the heat capacity of a standard substance, benzoic acid. Throughout this work an automatic shield control system has been developed and satisfactory completely automatic control was eventually obtained during the heat capacity measurements on the last adduct to be studied.

CHAPTER 2.

APPARATUS FOR MEASURING HEAT CAPACITIES IN THE RANGE 12 - 300°K - THE ADIABATIC CALORIMETER SYSTEM

A. Introduction.

An adiabatic system is one in which there is no heat interchange with its surroundings. In this experimental work a vessel, the calorimeter, is maintained in adiabatic conditions, while the heat properties of a sample enclosed in the vessel are measured. A perfect adiabatic system is impossible to attain in practice, but all efforts are made to approach this condition as closely as possible. The way this is achieved is discussed in detail later, but essentially it is by surrounding the calorimeter by metal shields, which are maintained at the same temperature as the calorimeter. When there is no temperature difference between the calorimeter and its surroundings, it follows from the second law of thermodynamics, there will be no net heat flow.

The first systematic and reliable low temperature specific heat determinations date from the design of the 'vacuum' calorimeter first used by Eucken (1909) in Nernst's laboratory. Lange's (1926) calorimeter was the first intended to be operated adiabatically, and Southard and Brickwedde's (1933) refinement of the calorimeter is the basis for the design of the calorimeter used in this research. This apparatus was constructed by Kington and Edwards (1962) and has been described in detail (Edwards 1959). Later, Pemberton (1966) used the apparatus to measure the heat capacities of six urea - hydrocarbon adducts. In this research the apparatus used to measure the heat capacities of four further urea adducts was as described by Pemberton, but before continuing with a similar study on thiourea adducts, certain modifications were carried out on the apparatus and the calorimeter was recalibrated.

The most significant development of the apparatus during this research has been the automation of the procedure for controlling the temperature of the surrounding shields. This work has been the responsibility of Stroud, but the features of this control are outlined in Section J.

B. The Cryostat and Refrigerants.

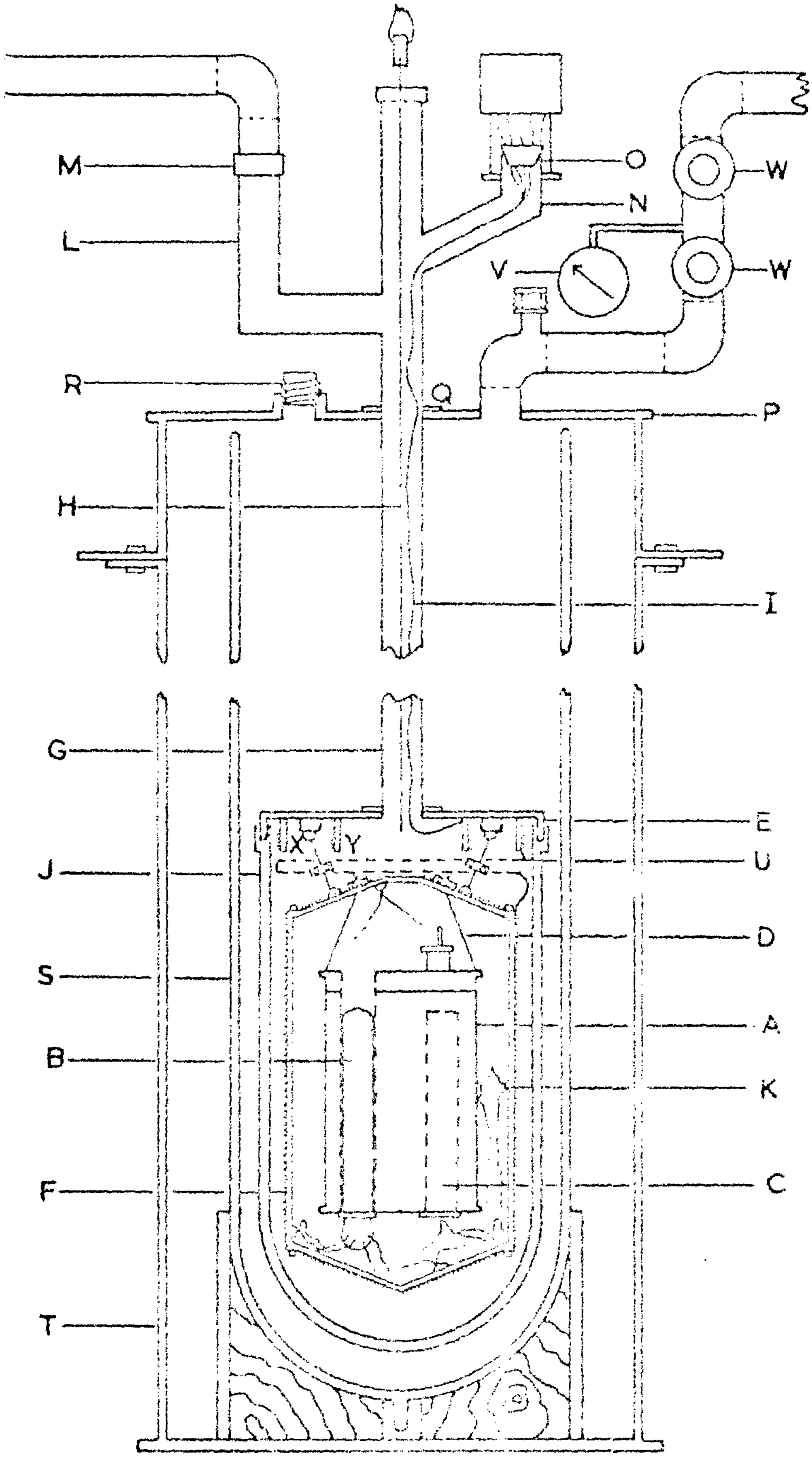
The calorimeter vessel and shields are suspended inside a copper can (J), see Fig. 7, by nylon threads, which hang from a brass plate (E). At the commencement of each series of runs, the copper can is soldered to the brass plate with an indium/tin eutectic solder (Johnson Matthey Ltd). The brass plate was supported to the main frame of the apparatus (P) by a 1 inch diameter monel metal tube (G). The monel metal tube led to a glass line.

The coolant was stored in a large glass Dewar (S), which completely surrounded the copper can. The Dewar was mounted inside an iron can (T), which could be raised on runners and bolted to the main frame, so as to make a vacuum tight seal with the frame. The can could be evacuated using a high capacity Kinney pump situated in a pumphouse at ground level. Alternatively, the can could be vented to the roof of the building by way of a two inch pipe.

Liquid nitrogen is used as a coolant for measurements in the range 78 - 300°K, but in the range 48 - 78°K, it is necessary to reduce the pressure above the liquid nitrogen using the Kinney pump, resulting in the evaporation of the liquid and consequent cooling of the mother liquid. Nitrogen is solid below its triple point, 64°K.

For the range 12 - 48°K hydrogen is used as the coolant. In order to minimise the loss of hydrogen, the system is pre-cooled with liquid nitrogen, which is forced out of the apparatus by nitrogen gas, before transferring the liquid hydrogen from its container to the Dewar by way of an evacuated glass siphon, which fits in the opening (R). The heat capacity of materials falls off rapidly below 80°K and the pre-cooling to 78°K saves a considerable amount of hydrogen, which would have been lost by evaporation. When the system has cooled to 30°K, pumping is commenced on the liquid hydrogen and the system is eventually cooled to about 12°K. The triple point of hydrogen is 14°K.

FIG. 7. THE CALORIMETRIC APPARATUS



C. The calorimeter vessel.

The calorimeter vessel was constructed of a platinum - 10% iridium alloy by Johnson Matthey Ltd., and had a total weight of ~115g. and a capacity of 41 cm^3. The cylindrical body of the calorimeter (3.1 cm. diameter; 6.5 cm. long; and 0.04 cm. wall thickness) was gold soldered to circular top and bottom plates (3.7 cm. diameter). The bottom plate carried two re-entrant tubes (0.8 cm. diameter) to hold the thermometer and the heater. The thermometer tube extended the length of the calorimeter and was joined to the top plate. In addition a short (0.8 cm. diameter; 1 cm. long) German silver tube with brass collar was soldered to the top plate of the calorimeter. The vessel was loaded and eventually sealed by way of this tube.

D. The thermometer.

The thermometer (called "C") was a platinum resistance thermometer of the coiled filament type described by Meyers (1932). The thermometer "C" was constructed by Pemberton (1966) and was calibrated over the range 12 - 300°K by comparison with thermometer "A". Thermometer "A" had previously been calibrated by Edwards against a similar thermometer made available by Dr. J. A. Morrison of the National Research Council of Canada. The calibration of this thermometer was based on the Provisional Temperature Scale of the National Bureau of Standards below 90°K. Above 90°K and below 0°C the temperature was defined as a function of the resistance by the Callendar - Van Dusen equation

$$t = 100\,\frac{Rt - R0}{R100 - R0} + \frac{\delta t}{100}\left[\frac{t}{100} - 1\right] + \beta\left[\frac{t}{100}\right]^3\left[\frac{t}{100} - 1\right] \qquad (2.1)$$

and above 0°C by the Callendar equation

$$t = 100\,\frac{Rt - R0}{R100 - R0} + \frac{\delta t}{100}\left[\frac{t}{100} - 1\right] \qquad (2.2)$$

where t is the temperature in °C, R is the resistance of the thermometer at the appropriate temperature and β and δ are constants characteristics of the thermometer.

The resistances quoted in the calibration of both "A" and Morrison's thermometer were in international ohms, but for the calibration of thermometer "C" the resistances were converted to absolute ohms to coincide with the units in which the standards of the measuring circuit were quoted.

The thermometer was fitted into the calorimeter by way of the re-entrant tube of the base of the calorimeter. To ensure a tight fit and good thermal contact, a piece of aluminium foil was wrapped around the thermometer and the thermometer was coated with Apiezon T grease.

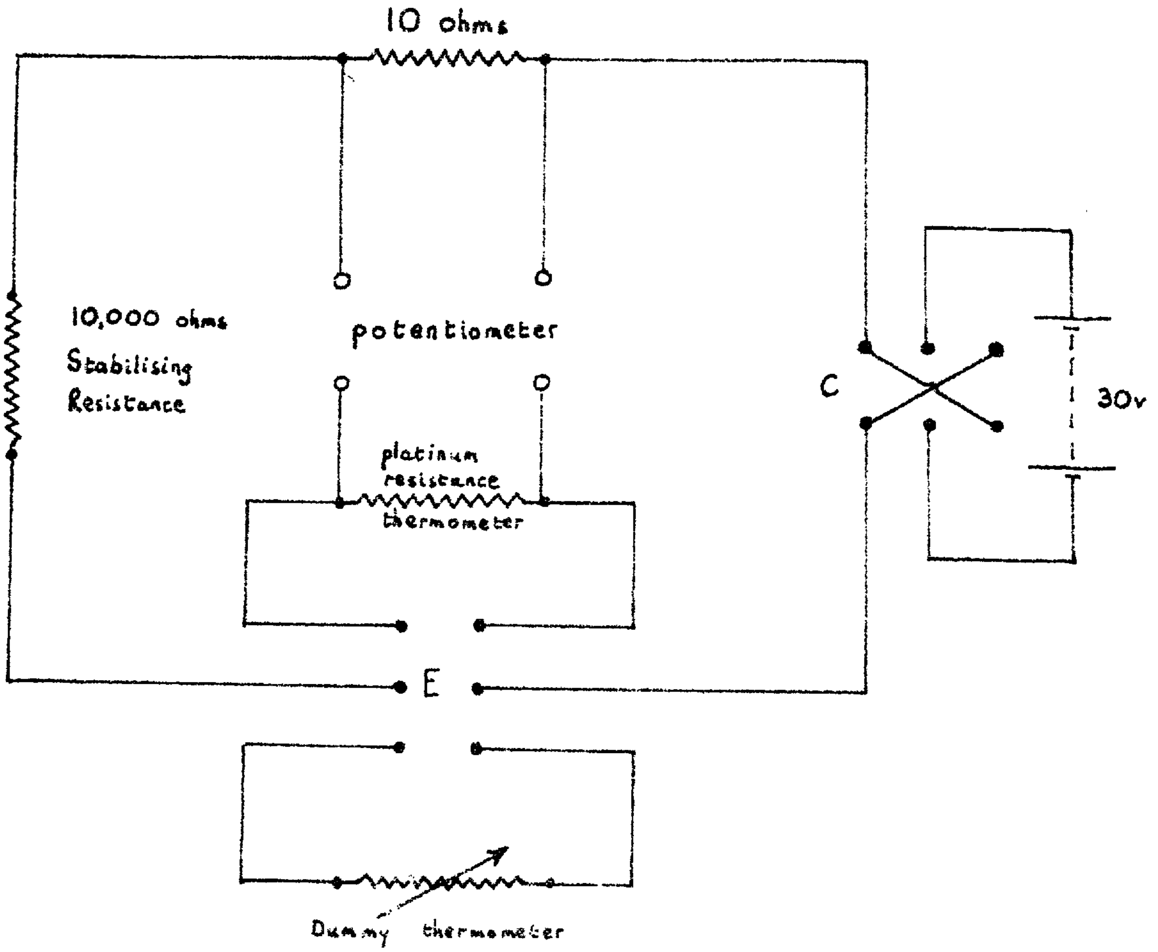
E. The Thermometer Circuit and Measurement.

The resistance of the thermometer was determined by finding the ratio of the potential drops across the thermometer and the standard 10 ohm resistance. The latter potential drop was a measure of the current through the thermometer. The potentials were measured on an H. Tinsley vernier potentiometer (type 4363) in conjunction with an H. Tinsley galvanometer (type 4500L). The potentiometer was calibrated and the corrections were applied to the values obtained. The standard 10 ohm resistance was found by Pemberton in 1963 to be 10.0044 absolute ohm at 20°C. The current through the potentiometer was supplied by a 2 volt accummulator battery. After each measurement the direction of this current and that through the thermometer was reversed and a further reading noted. The mean of the forward and reverse values was then accepted.

The current through the thermometer was supplied by five (or six) six volt 50 amp. hour 'Silver Exide' accummulators. The 10,000 ohm resistance ensured the maintenance of a nearly constant thermometer current (~ 3 milli amps) despite the change of resistance of the thermometer. The current through the thermometer could be reversed by switch C. Switches C and E were

Fig. 8.

Thermometer Circuit



Northrup pinch type switches with copper - beryllium blades.

When runs were not in progress the current was passed through the dummy resistance thermometer which could be set at the appropriate value.

F. The Heater.

The original heater, used by Pemberton and for the measurements on the urea adducts, was constructed of (s.w.g. 38) cotton-covered varnished manganin wire, total resistance ~400 ohms, wound non-inductively in two layers around a brass former over an insulating layer of cigarette paper. In order to promote good thermal flow the layers were separated by a piece of aluminium foil, and a further piece of foil was wrapped around the outer layer to ensure efficient thermal contact with a brass sheath, within which the heater former was soldered. Finally, the brass sheath was soldered with Wood's metal into the second re-entrant well of the calorimeter vessel as shown in diagram 10a.

Finke reported that use of such a heater results in an appreciable temperature gradient along the outside surface of the vessel. In view of this it was decided to aim at a more even heating distribution by winding the heater wires around the outside of the vessel. (See diagram 10b).

This heater was constructed in the following way. Two copper rings of (s.w.g.20) wire were soldered onto the inside of the flanges formed by the overlap of the bottom and top plates. Grade K solder (See footnote i) was used and applied with a small gas iron using Baker's fluid for flux. The outside surface of the vessel was coated with a layer of varnish (See footnote ii) and a coil of (s.w.g.40) cotton-covered, manganin wire of resistance 410 ohms was wound uniformly and non-inductively around the calorimeter and then held in position by more varnish. In order that no hot manganin wires should be exposed to the shields, the manganin wires

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Footnote i: 60% Sn/40% Pb.

ii: Insulating varnish Oxford Cryogenic Ltd).

Fig. 9.

The Calorimeter

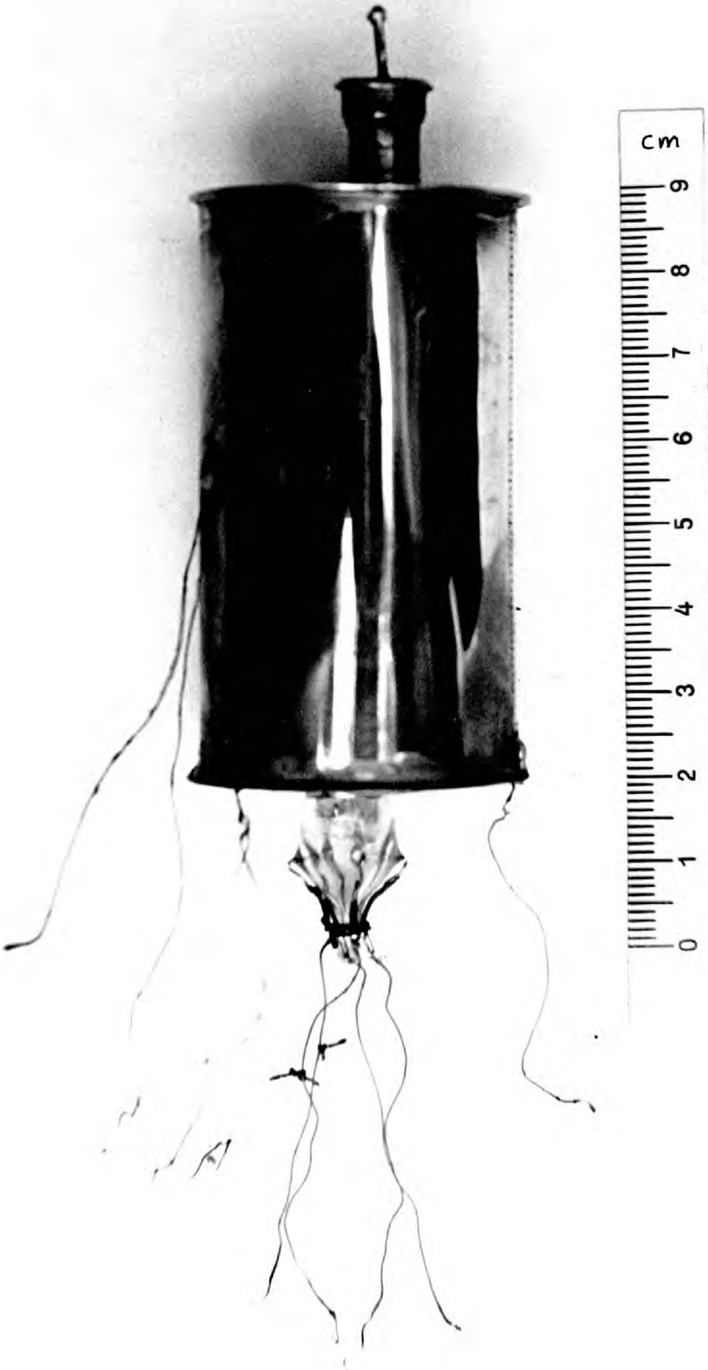
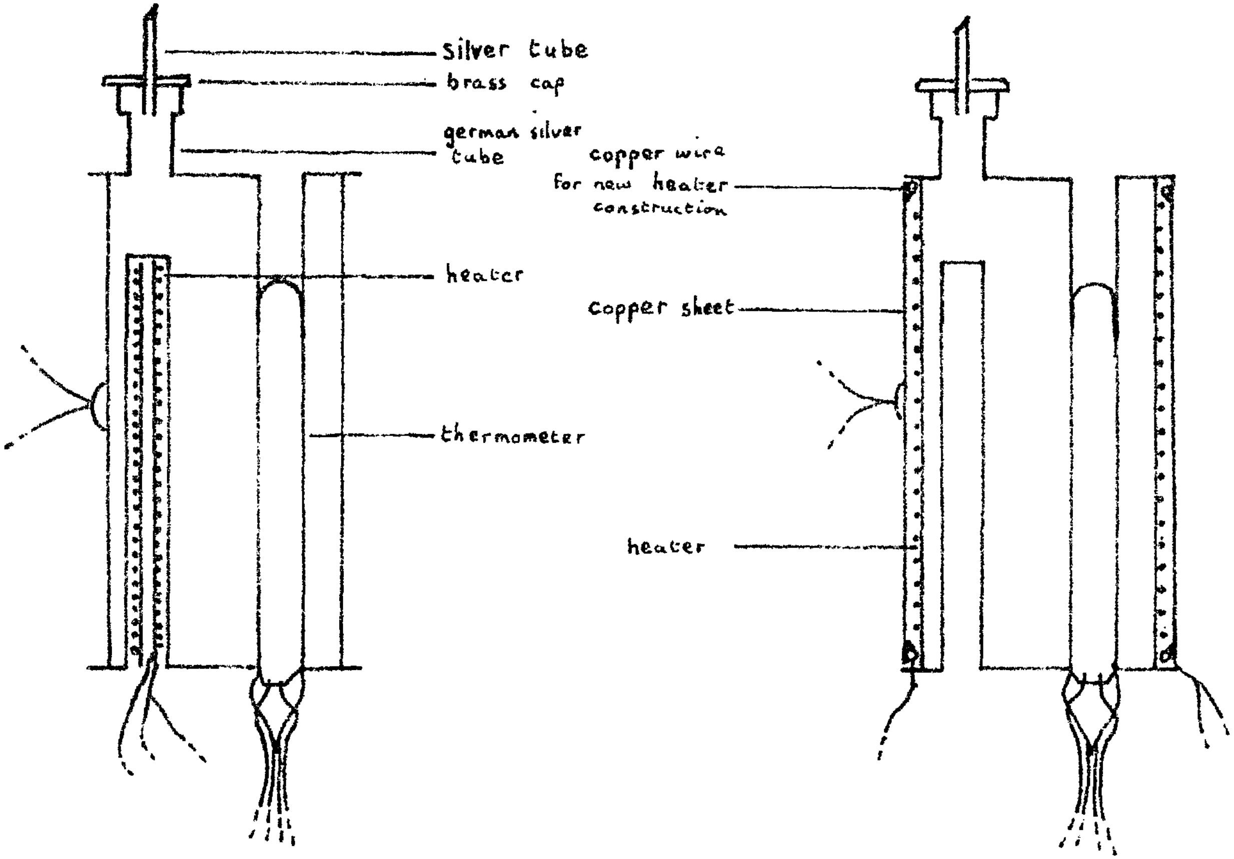


Fig. The Calorimeter Vessel.

Fig. 10.



a) with Inner Heater

b). with Outer Heater

were terminated before the end of the cylinder and(s.w.g. 34) copper wires were soldered to them. The two copper wires were then lead through separate holes drilled in the flange of the bottom plate. These wires were fixed in position in the holes by varnish and then cut shortly after the holes and bent to form hooks. To one of these hooks was joined a single lead of (s.w.g. 38) copper wire, the single junction heater lead, and to the other hook was joined a double lead, the double junction heater lead. The significance of the choice of leads is explained in the notes on the heater circuit.

Finally the wires on the surface of the vessel were covered by a layer of cigarette paper stuck down with varnish, and a thin copper* sheet was soldered to the two copper rings using Grade K solder, so as to completely surround the wires without making contact with them. In this way no heater wire was directly exposed to the surroundings.

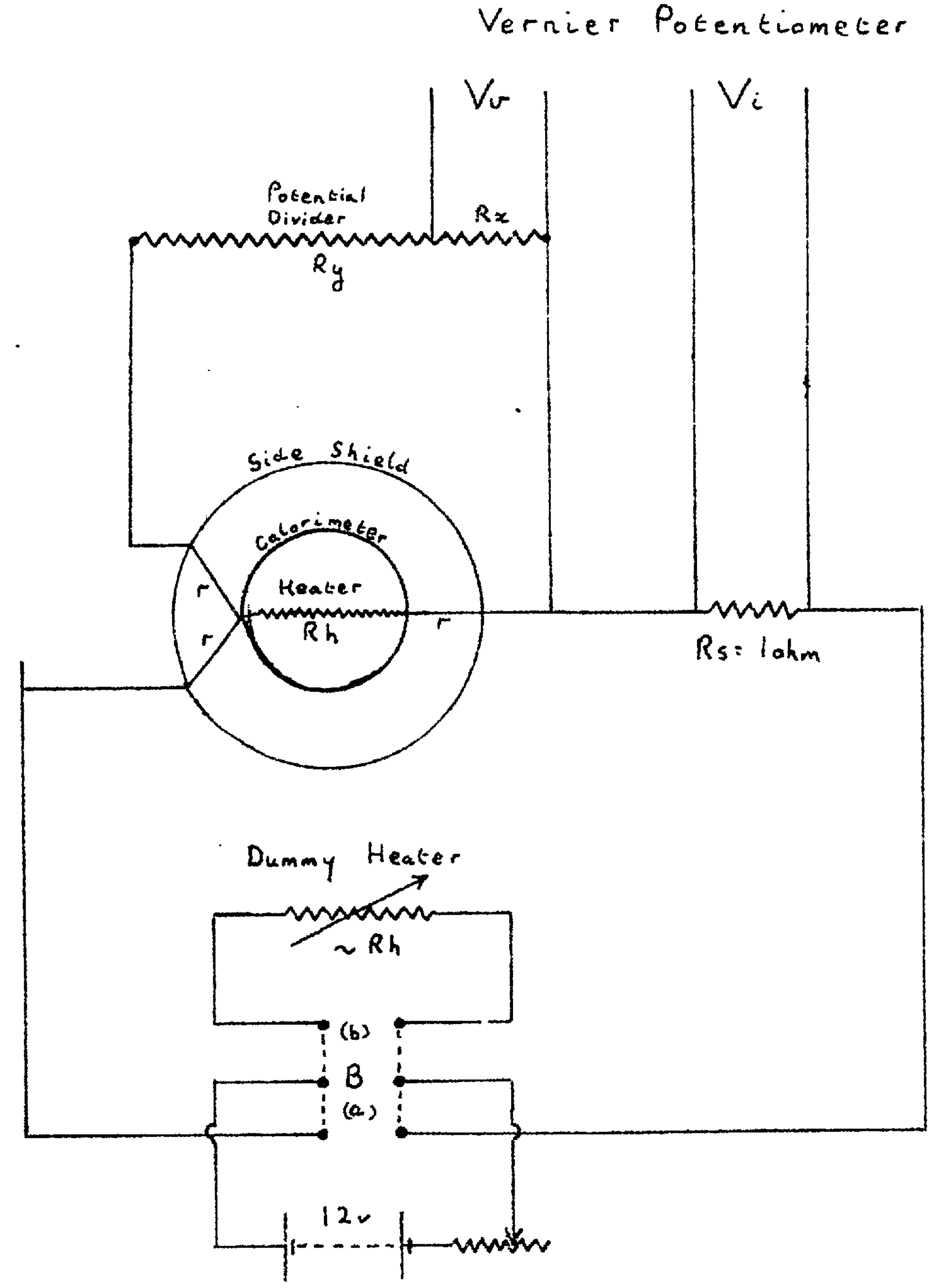
* Thickness 4 thou.

G. The Heater Circuit and Measurements.

The heater current was supplied by two six volt accummulators. When heating was not in progress the current was passed through a dummy heater, the resistance of which was selected to be similar to that of the heater. A switch ganged to switch B, the on-off switch for the heater current, served to activate a "decatron timer" (Labgear type D.4108), which together with a ten second "add on register" (type D.4109) gave an accurate value for the time of heating.

In order to measure the energy supplied to the calorimeter during a run, it was necessary to measure with the vernier potentiometer the potential drops across the standard 1 ohm resistance, Rs, and across Rx, Vi and Vv respectively (See diagram 11). In addition it was required to know the exact value of Rs (1·0001(3) abs. ohms at 20°C), the ratio of the

Fig. 11. Calorimeter Heater Circuit



Switch B(a) is ganged to timing system.

potential divider Ry : Rx (100.015 : 1 at 20°C) and Rx (100.015 abs. ohms. at 20°C).

The energy supplied to the calorimeter may then be calculated in the following way.

Let Rh be the resistance of the heater, Rl the resistance of the leads to the base of the side shield and r the resistance of each lead from the shield to the calorimeter heater.

Let the current passing through Rs be i, and the currents through the potential divider and the calorimeter heater be i_1 and i_2 respectively, (i.e., $i_2 \approx 25\ i_1$).

Then by Kirchhoff's law

$$i = i_1 + i_2$$

and by Ohm's law

$$i = \frac{Vi}{Rs} \quad \text{and } i_1 = \frac{Vv}{Rx}$$

$$\therefore \quad i_2 = \frac{Vi}{Rs} - \frac{Vv}{Rx}$$

The energy supplied in unit time to the heater,

$$Eh = i_2^{\,2}\, Rh$$

$$(Rh + r)i_2 = (Rl + Ry + r)i_1$$

$$Rh = (Rl + Ry + r)\,\frac{i_1}{i_2} - r$$

$$Eh = (Rl + Ry + r)\, i_2\, i_1 - i_2^{\,2} r$$

In addition the calorimeter gains heat through heating in the three copper wires. It is assumed that half this heat goes to the shield and half to the calorimeter.

Energy obtained in unit time by the calorimeter from the wires,

$$Ew = \frac{r}{2}\,(i_2^{\,2} + i_1^{\,2} + i^2)$$

$$= r\,(i_2^{\,2} + i_1^{\,2} + i_1 i_2)$$

$\therefore$ Total energy supplied to calorimeter in unit time,

$$E = Eh + Ew$$

$$= (Rl + Ry) i_1 i_2 + r i_1 i_2 - i_2^{\,2} r + i_2^{\,2} r + i_1^{\,2} r + i_1 i_2 r$$

(The choice of one double and one single heater lead results in the only significant terms of r, $i_2^{\,2} r$, being elimintated, leaving only terms involving i_1).

i.e., $E = (Rl + Ry)\, i_1 i_2 + (2 i_1 i_2 + i_1^{\,2})\, r.$

or very nearly

$$E = (Rl + Ry + r)\, i_1 i_2$$

$$E = (Rl + Ry + r)\left(\frac{Vv}{Rx}\right)\left(\frac{Vi}{Rs} - \frac{Vv}{Rx}\right)$$

$Ry = 10000$ ohms.

$Rl = 4$ ohms.

$r = 0{\cdot}1$ ohm.

Clearly for measurements to 0·1% Rl is just significant, but r can be ignored.

Thus the final value for the heat supplied in unit time to the calorimeter is

$$E = (Ry + Rl)\left(\frac{Vv}{Rx}\right)\left(\frac{Vi}{Rs} - \frac{Vv}{Rx}\right) \qquad (2.1.)$$

$$\text{or} \quad E = \left(Ry/Rx + \frac{Rl}{Rx}\right) Vv \left(\frac{Vi}{Rs} - \frac{Vv}{Rx}\right)$$

H. The Shields and Wiring Systems.

(Letters in brackets refer to fig. 7).

Heat transfer between the calorimeter vessel and its surroundings is minimised by the following methods. The calorimeter vessel (A) is completely surrounded by brass shields (F) which are maintained at the same temperature as the calorimeter. The system is enclosed within a vacuum can (J) and evacuated to a pressure of 10^{-6} m.m. of mercury. The electrical leads between the calorimeter and the shields are chosen to be as thin as practical. In order to prevent a big heat leak along the electrical leads, the leads, which enter by way of the monel metal tube (G), are first wrapped around two rings (X and Y) attached to the brass plate (E) which is in direct contact with the coolant, and then wound around the side shield in order to attain thermal equilibrium with the side shield and consequently the calorimeter. The surface of the calorimeter vessel is polished and the surfaces of the shields are plated with rhodium to reduce their radiative properties. The shields are suspended from the brass plate (E) and the calorimeter suspended from the shields by non-conducting nylon threads (D).

After completing the measurements on the urea adducts the shields were completely rewired, but no major modifications were made. 16 copper wires (S.W.G 40) and 6 constantan wires (S. W.G. 34) were wound individually inside 22 helical grooves in the side shield. The wires were insulated from and fixed to the shield by varnish. The constantan wires were led directly through the holes at the bottom of the side shield, and the holes were filled with insulating varnish. Prior to reaching the holes, the copper wires were soldered to thicker (S.W.G. 26) copper wires.

The thicker wires were chosen as it was found that the thinner copper wires broke easily when subjected to the twisting and bending that is difficult to avoid during the soldering of these wires to the wires from the calorimeter.

The wires around the shield were covered with cigarette papers and a coil of manganin wire (S.W.G. 36 410 ohms) was wound uniformly and non-inductively over the papers to form the side shield heater. The heater was covered with cigarette papers and then stuck down with varnish.

The top and bottom shield heaters were also rewound. Manganin wire (S.W.G. 36) was used and the resistance of the top and bottom shield heaters were 70 and 65 ohms respectively.

The exterior surfaces of all the shields were covered with Al. foil to reduce heat exchange with the can in contact with the refrigerant.

The 22 wires from the side shield were led from the shield as one cable for a distance of about three feet, before being spaced out and individually stuck down by varnish onto two brass rings (X and Y). From the inner ring (Y) the wires were taken as one cable again up the monel metal tube and out of the vacuum space to a tag board, where the wires were connected to screened thick copper wires, which led to the measuring circuits. The wires left the vacuum space individually by way of grooves cut in a brass cone (A), which made a tight fit with a brass socket. In order to obtain a perfect vacuum tight exit for the wires, the wires were bared and the grooves were filled with Apiezon W. wax.

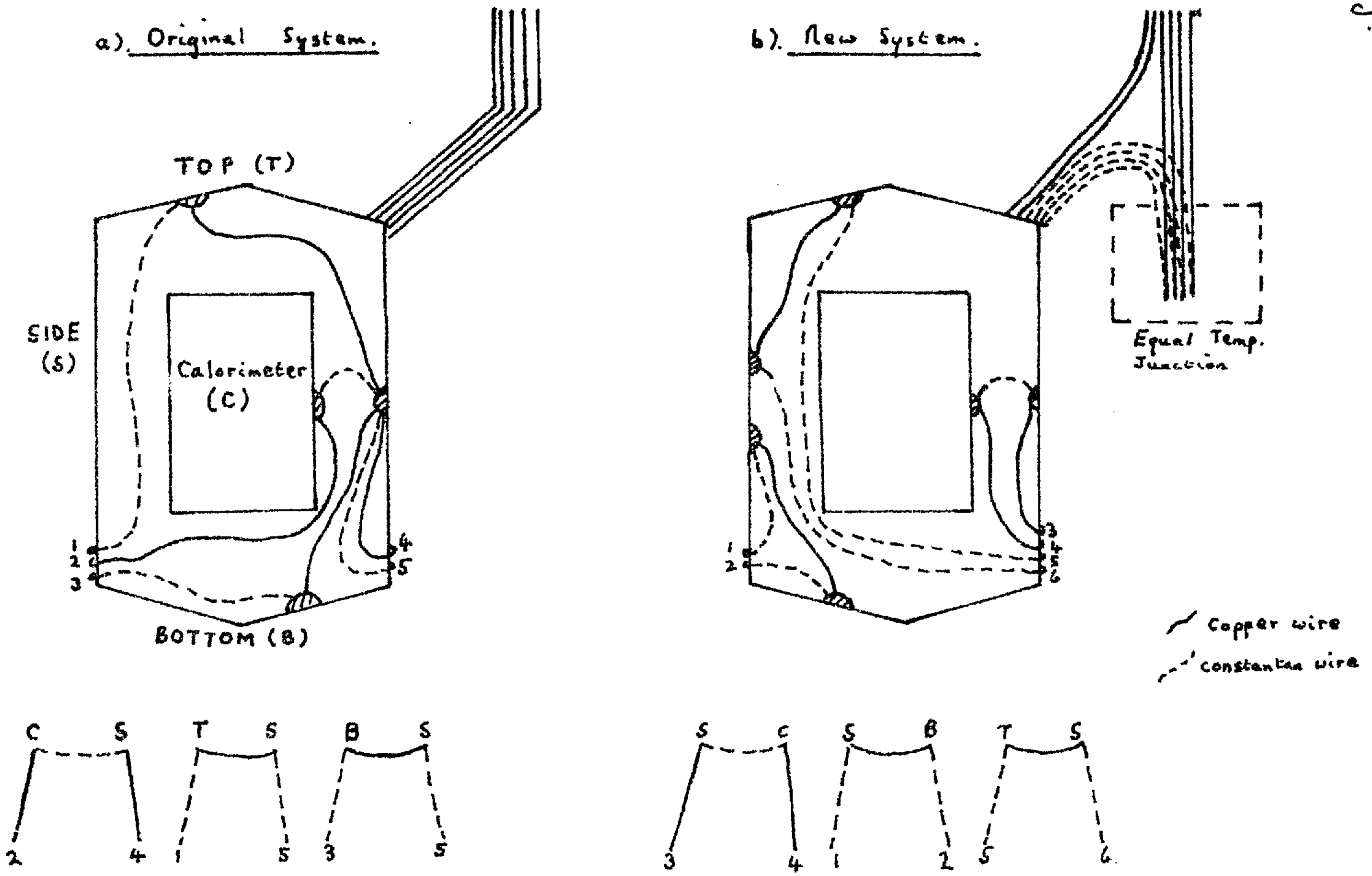
I. The Differential Thermocouple Circuit.

Once again the system reported by Pemberton was retained for the urea series of measurements, but several changes were made on reconstructing the apparatus.

The two arrangements are illustrated in diagrams a and b (11') and it will be seen that they are basically the same in that the temperature of the side shield is compared with that of the calorimeter and the temperature of the bottom and top shields compared with the side shield.

In the arrangement described by Pemberton the constantan thermocouple wires were joined to copper wires at the base of the side shield and held so as to be in thermal contact with the shield and in consequence to each other. This was not very satisfactory as these junctions were close to the side shield heater and there is the danger that thermal gradients are set up in their proximity. In the new arrangement the constantan wires were taken all the way out of the vacuum space and joined to copper wires inside separate holes drilled in a massive brass

Fig. 11' Differential Thermocouple Systems.



a). Original System.

b). New System.

Fig. 11'

block. The wires and the block were electrically insulated from each other by varnish. The copper and constantan wires were wrapped around the outside of the block several times to attain thermal equilibrium with the block, and the block was surrounded by a case of expanded polystyrene as a safeguard against thermal gradients within the block.

It will be observed that in the old arrangement, the constantan lead to the side shield junction was common to both the top and bottom shield comparison circuits. Such a common lead can cause considerable interaction between the thermocouples of the bottom and top shields. It is of no consequence when one of these circuits is open, as is the case with manual control of the shields, but with the automatic control, when all the circuits are maintained complete, the circuits interfere with each other. This interference was eliminated satisfactorily by including a second constantan wire to the side shield as illustrated in the diagram.

It was also feared that the advent of the automatic control would uncover a noticeable inductive effect in the thermocouple wires on changing the currents in the various heaters in view of the proximity of the heater and thermocouple wires down the long unscreened cable leading to the calorimeter. However, it appears that the environment of each pair of thermocouple wires is sufficiently identical for no net current to be induced.

J. The Shield Control.

Progress has been made during this research towards the automation of the shield control. This work has been the responsibility of H.J.F. Stroud, and it will be reported in full elsewhere. However, it is necessary to point out the basic units of the control and their function (See Fig. 12).

The input signal from each thermocouple is amplified by a microvoltmeter (Pye - type 11340/S). The microvoltmeter deflection is displayed on a chart recorder (Leeds and Northrup Speedomax H recorder). The C.A.T. control unit (Leeds and Northrup, current adjust type), which is integrally built with the recorder, responds to a deflection of the recorder needle from zero by producing a control current, which is a function of the displacement of the needle from zero, the time the needle has been displaced from zero and the rate of change of displacement. The relative importance of these factors may be chosen at will by adjustment of the "Proportional", "Automatic Reset" and "Rate" controls respectively. Different settings of these controls are required for measurements in different temperature ranges.

The control current from the C.A.T. unit is then fed into a transistorised unit (See Fig. 14) which gives a process current, which passes through the appropriate shield heater. At present the three shield heaters are powered by one 60 volt. d.c. voltage supply, but it appears separate heating supplies will have to be included. Increased demand by one shield results in a reduction of the voltage and consequent reduction in the current through the other shields. This constant readjusting of the heater currents results in continuous fluctuations and a reduction in the quality of the control.

The zero of the microvoltmeters must still be checked manually. With the C.A.T. unit set in the 'manual' position, the thermocouple is short-circuited by switching to an appropriate position on a rotary thermal e.m.f. free switch (Croydon Instrument Co. Ltd). Coarse zero may be obtained by adjusting the microvoltmeter "zero adjust" control, but fine adjustment is effected by change of the potential drop across the one ohm. resistor by varying R as shown in Fig. 13

The control of single shields were occasionally automated during the heat capacity measurements on the empty calorimeter, benzoic acid and the thiourea - cyclohexane adduct, but the control was exactly as described by Pemberton during measurements on the urea adducts. The thiourea - 2, 2. - dimethylbutane measurements were undertaken with fully automatic shield control, except for the hydrogen run, when the cold sink was too small. In this case if the shields were overheated at any stage, there would be no means to cool them.

Fig. 12. Block diagram of shield control system

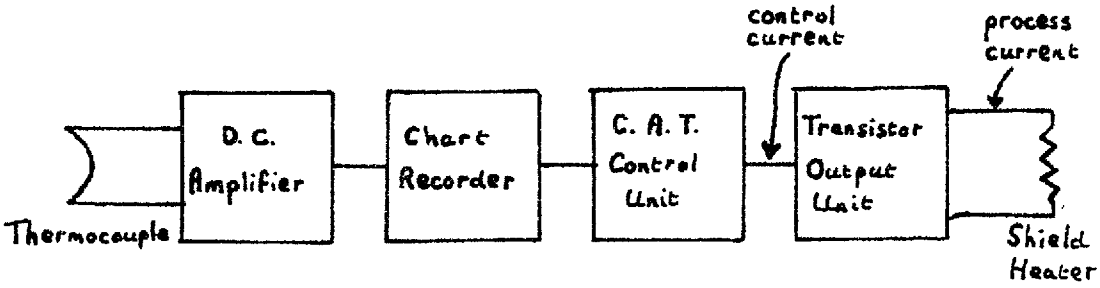
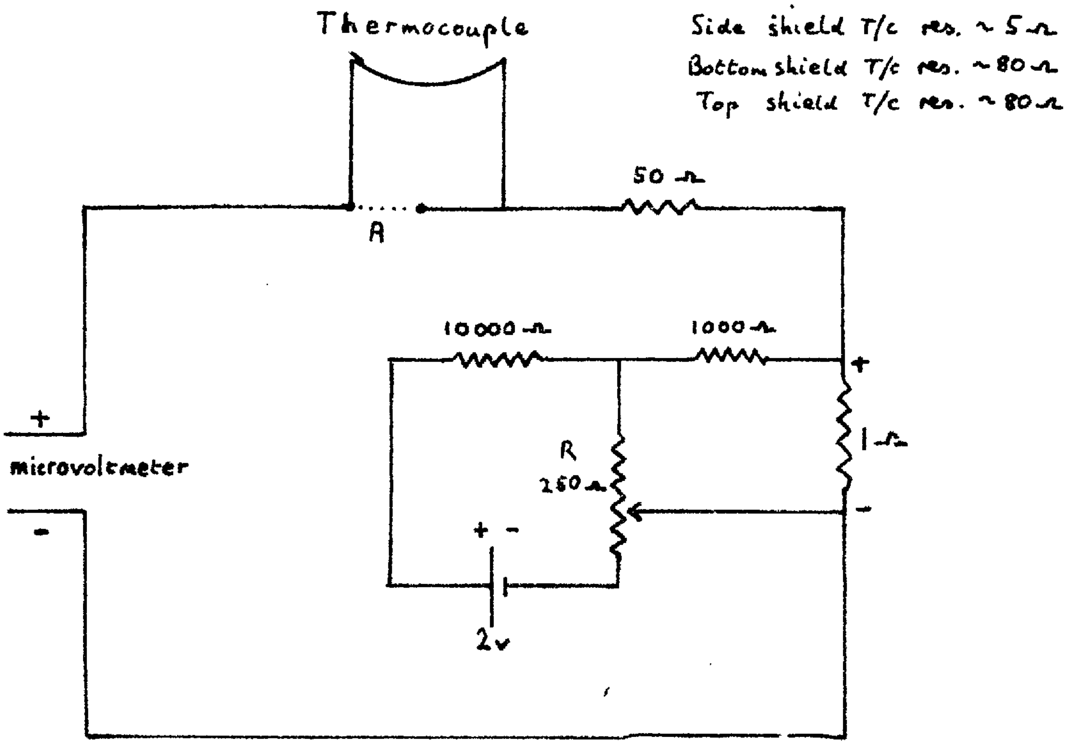


Fig. 13. D.C. amplifier input circuit



Side shield T/c res. ~ 5 Ω
Bottom shield T/c res. ~ 80 Ω
Top shield T/c res. ~ 80 Ω

A is thermal e.m.f free selection switch.

To zero microvoltmeter, A is switched to short-circuit thermocouple.

Fig. 14 Transistorised output unit to heaters

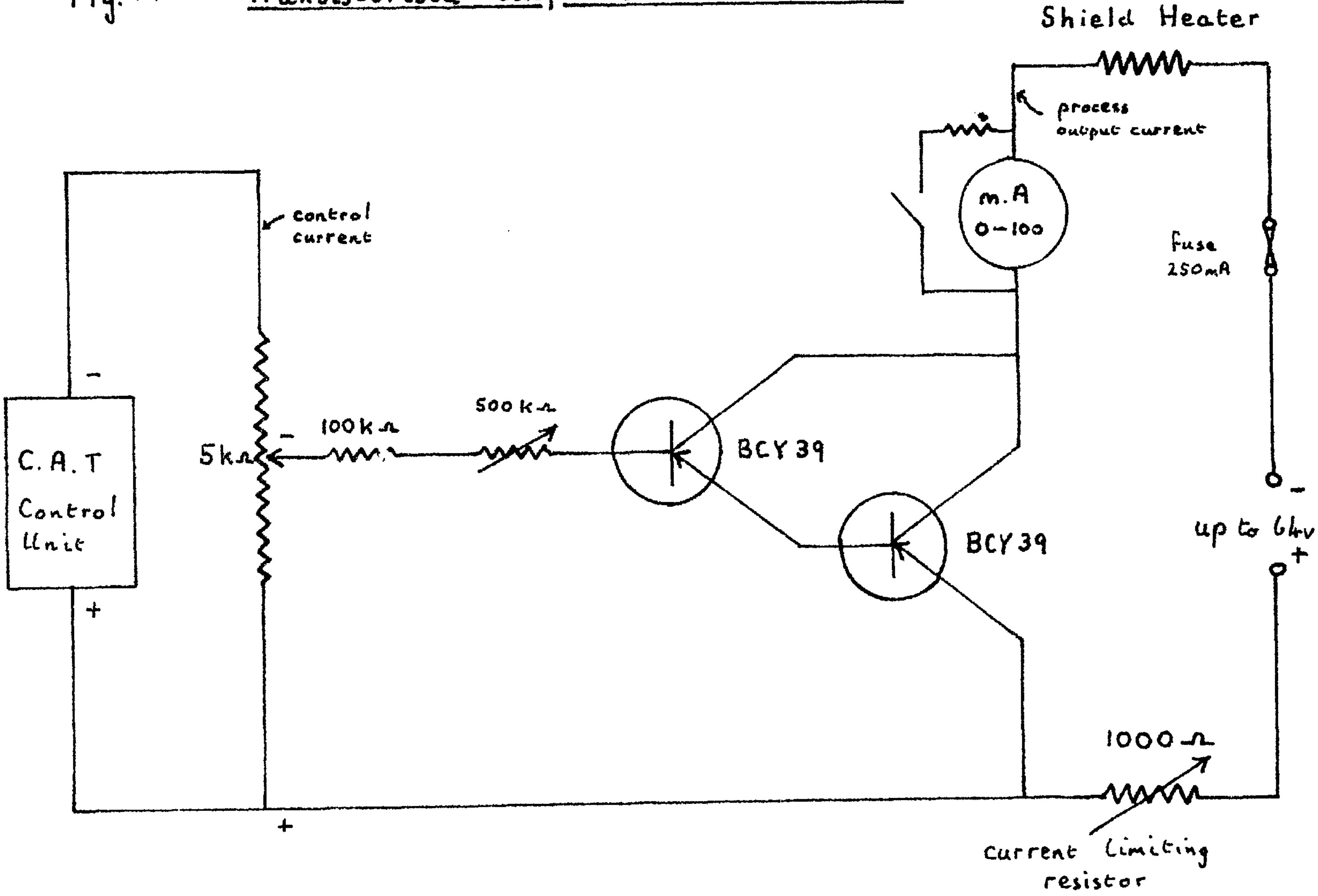


Fig. 14

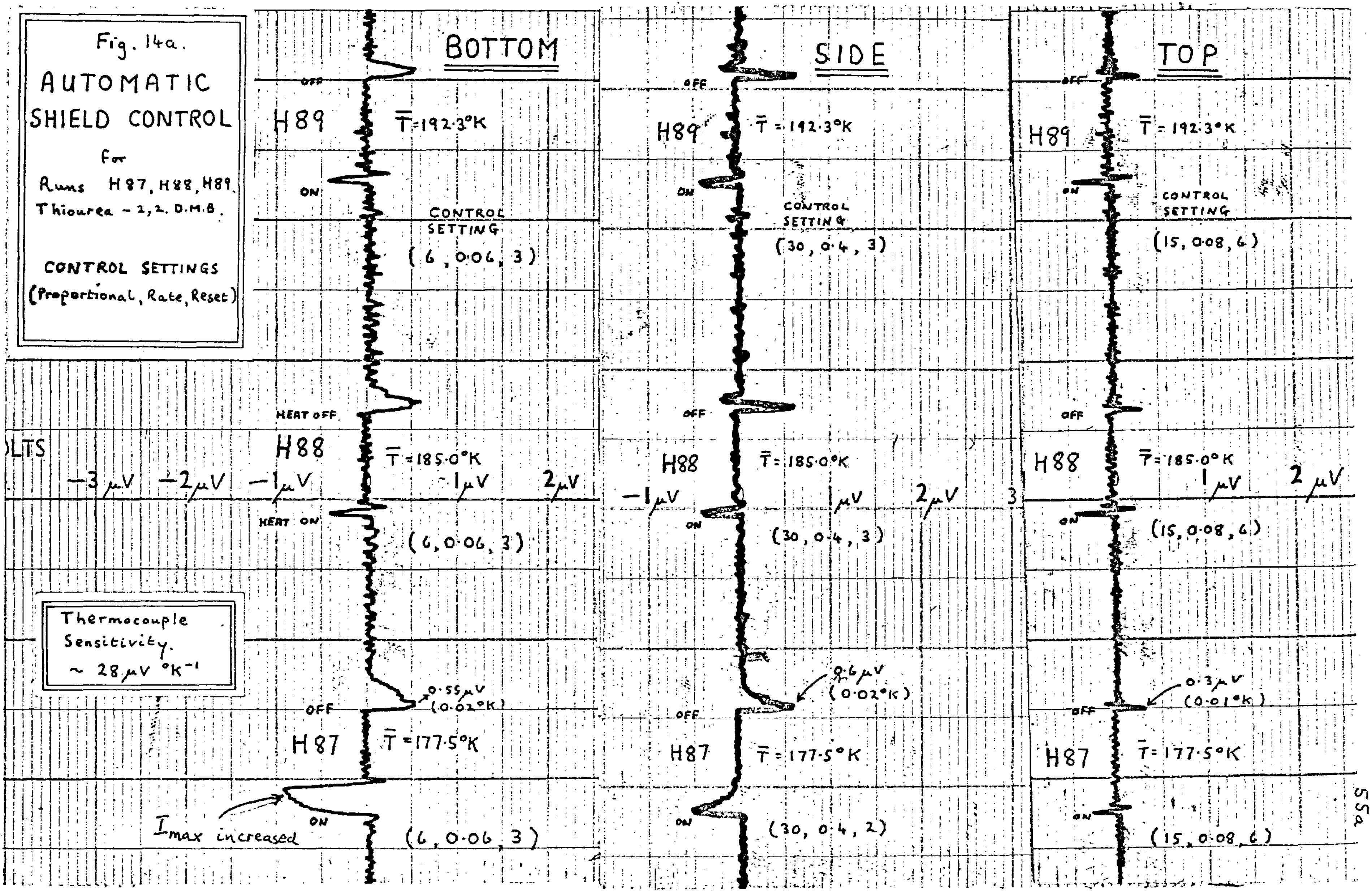


Fig. 14a.
AUTOMATIC SHIELD CONTROL
for
Runs H87, H88, H89
Thiourea - 2,2. D.M.B.

CONTROL SETTINGS
(Proportional, Rate, Reset)

Thermocouple Sensitivity
~ 28 μV °K⁻¹

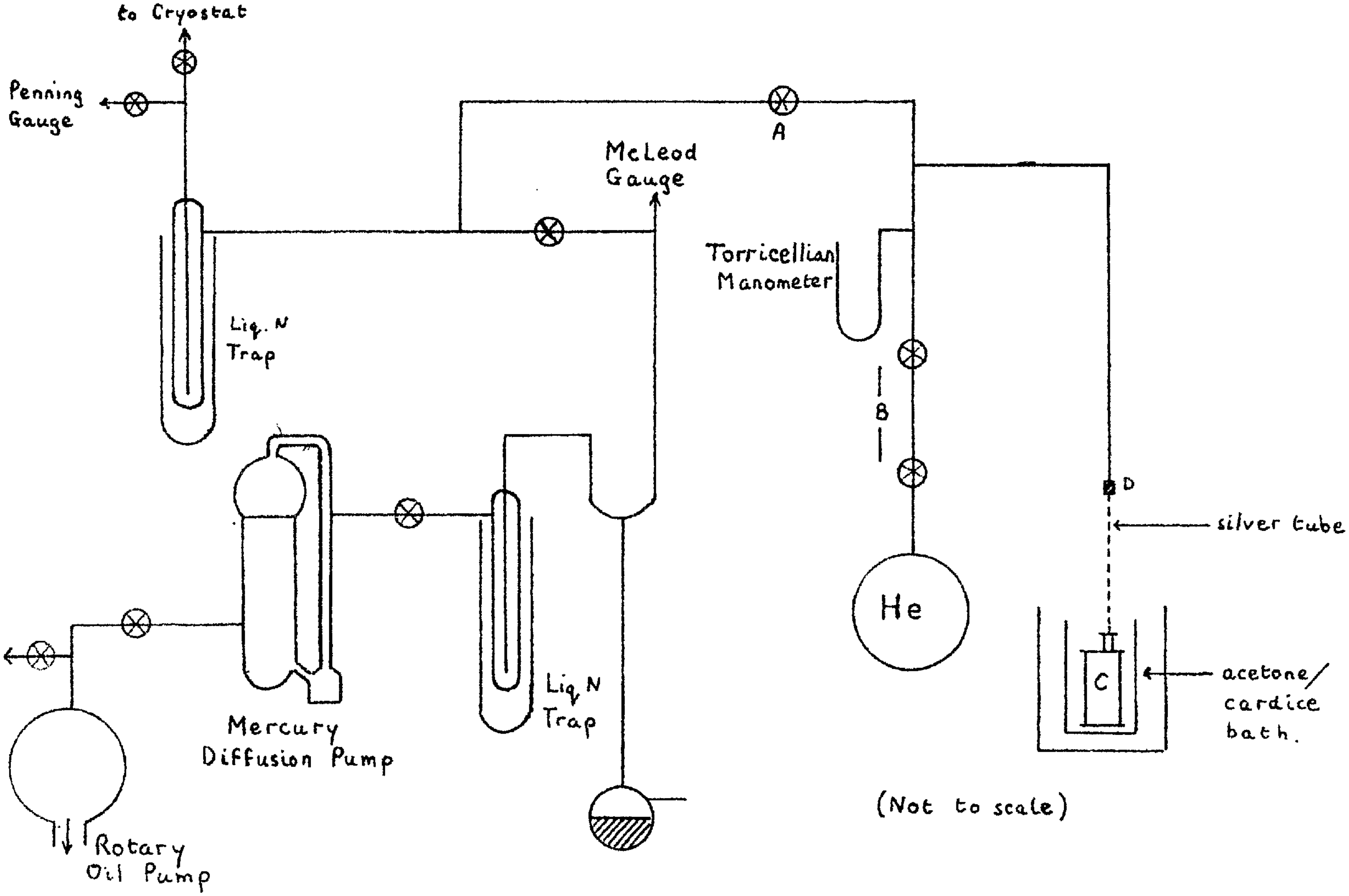
CHAPTER 3 - EXPERIMENTAL PROCEDURE

A) THE ASSEMBLY OF THE CALORIMETER SYSTEM

The sample is loaded into the calorimeter by way of the German silver tube (see Fig. 10). A silver tube (see Fig. 15) of external diameter 1 m.m. was soldered into a hole drilled in a brass disc and then attached to the glass line by picein wax (D). The brass cap is then soldered to the brass rim of this tube using a low melting point solder (40% Pb; 40% Sn; and 20% Bi). In addition to the use of this solder a significant rise in the sample temperature is prevented during this operation by the poor thermal conductivity of the German silver tube. The calorimeter vessel (C) is then evacuated to a pressure of about 5×10^5 m.m. of mercury. In cases when the sample is unstable, the vessel is surrounded by an acetone/cardice bath.

When the vessel is evacuated, the system is isolated from the pumps and a dose of helium (B) admitted into the vessel. The purpose of the helium (pressure about 1 cm. of mercury) is to promote heat exchange between the sample and the vessel. The vessel is sealed by pinching the soft silver tube close to the brass cap with a pair of pliers, cutting the tube at the seal, and applying a small amount of low melting point solder to complete the seal. Finally the thermometer, with its wrapping of aluminium foil and coating of Apiezon T grease is eased into position. During the filling and sealing operations a careful record is kept of the weights of the vessel and components. Apart from the weight of the sample, the weights of the silver tube, low melting point solder and Apiezon T grease are calculated in order to apply the appropriate

Fig. 15 Glass Line for Pumping-out and Dosing.



(Not to scale)

corrections to the calorimeter calibration (Heat Capacity of Apiezon T grease - Westrum, Chien Chou, Osborne, and Flotow - 1967).

The vessel is then mounted in position within the shields. Care is taken to have the vessel in exactly the same position with respect to the shields each time. The various electrical connections are made, and the circuits checked for correct values of resistance and the absence of short circuits. The copper can is soldered into position around the shields using eutectic Sn/In solder. In order to prevent any decomposition of the sample and charring of electrical wiring during this soldering operation, the can was immersed in an ice/water bath. The vacuum can was evacuated by the pumping system (see Fig.15) over a period of several days until a pressure of about 1×10^{-6} m.m. of mercury was achieved.

B) THE HEAT CAPACITY MEASUREMENTS

Basically the heat capacity of the calorimeter and sample is determined by measuring the initial temperature, introduing a known amount of heat, and after equilibration measuring the final temperature. The heat capacity is then equal to the "heat in" divided by the temperature rise.

In practice corrections must be made for heat exchange with the surroundings and for internal heating by the thermometer current. Instead of one initial and one final temperature reading, two series of values of the temperature are required over a period of about ten minutes before the heating period and after equilibration. The 'fore' and 'after' temperature drifts with time, so obtained, are then extrapolated to the mid-time of the heating period, and the values of the temperatures at this time taken as the initial and final temperatures. In practice the drifts of the thermometer current and voltage are measured, their ratio giving the resistance of the thermometer and hence the temperature. The difference of these two temperatures is the temperature rise, and their average is the temperature assigned to the heat capacity. This is only true if the temperature rise is chosen such that the heat capacity effectively varies linearly with temperature over the temperature range. Temperature intervals are chosen of about 2 °K below 20 °K, 4 - 5 °K at about 80 °K and about 7 °K at 300 °K. In the regions of anomalous heat capacity smaller temperature intervals are chosen to expose the shape of the curve.

The heat supplied to the calorimeter is determined by taking several measurements of Vi and Vv (see Fig.11) during the heating period, and inserting their average values of the product Vi, Vv in equation(2.1)derived in section G chapter 2.

A programme has been written for the University of London Atlas computer, which evaluates the heat capacities in abs. Joule $^{\circ}K^{-1}$ from the temperature drift and heating data and the thermometer and potentiometer calibrations.

The heat capacity of the sample is obtained by subtraction of the corrected heat capacity of the calorimeter from the bulk heat capacity.

CHAPTER 4 THE CALIBRATION OF THE EMPTY CALORIMETER

A. CALIBRATION

The calorimeter used for the heat capacity measurements on urea adducts was calibrated by Pemberton (1966). After the modifications were made (Chapter 2, F), the calorimeter was recalibrated, and in view of the significant change to the heating arrangement the calorimeter was checked by measuring the heat capacity of a standard thermodynamic substance, benzoic acid.

The heat capacity of the empty calorimeter was measured from 12 °K - 305 °K at similar temperature intervals and adopting similar heating rates in deg.$^{-1}$ min.$^{-1}$ to those to be used during the heat capacity measurements on samples. The value (TABLE 4) of the heat capacity was plotted against temperature and a smooth curve drawn through the points. The temperature intervals had been chosen such that the correction for curvature was negligible. The heat capacity of the empty calorimeter at intervals of 1 °K was estimated from the curve (TABLE 5). These values are suitable for linear interpolation.

The heat capacity of a sample of benzoic acid was then measured over a similar temperature range. The sample was obtained from the National Bureau of Standards (N.B.S.), Washington. The heat capacity of samples of the same batch of benzoic acid has been measured by several observers (Ginnings and Furukawa at the N.B.S. 1953; Cole, Hutchens, Robie and Stout 1960; and Osborne, Westrum and Lohr 1955). The values of the heat capacity were compared with those of the N.B.S. and other observers. (TABLE 7). (See Fig. 17).

TABLE 4. EXPERIMENTAL VALUES OF THE EMPTY CALORIMETER HEAT CAPACITY IN ABS. J. DEG^{-1}

Run No.	Temp. °K	ΔT°	Cp
1	95·91	4·32	15·276
2	100·40	4·71	15·708
3	104·98	4·51	16·131
4	109·53	4·62	16·512
5	114·19	4·73	16·858
6	119·06	5·08	17·254
7	124·55	5·21	17·612
8	129·87	5·43	17·936
9	135·40	5·65	18·210
10	141·15	5·86	18·499
11	147·10	6·06	18·797
12	153·26	6·28	19·044
13	159·61	6·47	19·311
14	166·19	6·69	19·514
15	172·39	5·74	19·726
16	178·23	5·98	19·876
17	184·30	6·17	20·151
18	190·45	6·12	20·303
19	196·67	6·34	20·459
20	202·98	6·30	20·544
21	209·62	6·72	20·718
22	216·28	6·60	20·918
23	222·83	6·54	20·956
24	229·30	6·46	21·090
25	235·85	6·71	21·269
26	242·48	6·63	21·408
27	249·02	6·55	21·547
28	255·65	6·81	21·705
29	262·55	7·05	21·912
30	269·35	6·65	22·049

TABLE 4. (Continued)

Run No.	Temp. °K	Δ T°	Cp
31	275·89	6·55	22·294
32	282·42	6·60	22·040
33	288·91	6·49	22·338
34	295·37	6·44	22·488
35	301·77	6·39	22·604
P36	50·79	4·72	8·173
P37	55·21	4·23	9·071
P38	59·36	4·17	9·869
P39	63·29	3·83	10·275
P40	67·10	3·84	11·419
H41	12·41	1·20	0·525
H42	14·30	2·57	0·551
H43	16·82	2·93	0·845
H44	19·52	3·38	1·150
H45	22·49	3·00	1·651
H46	25·24	2·79	2·186
H47	27·95	3·03	2·744
H48	30·98	3·15	3·423
H49	34·16	3·23	4·118
H50	37·38	3·33	4·989
H51	40·90	3·71	5·783
H52	44·48	3·53	6·675
H53	47·98	3·44	7·477
H54	70·46	4·27	11·987
P55	74·72	4·28	12·664
P56	78·98	4·28	13·351
P57	83·26	4·32	13·880
P58	87·58	4·37	14·408

H indicates refrigerant used was hydrogen. (i.e., solid N).

P indicates refrigerant used was nitrogen at reduced pressure. Otherwise liquid nitrogen at atmospheric pressure was used.

TABLE 5 SMOOTHED VALUES OF THE HEAT CAPACITY OF THE EMPTY CALORIMETER FROM 12- 305°K IN ABS. J. DEG^{-1} AT ONE DEGREE INTERVALS

Temp. °K	Cp	Temp. °K	Cp	Temp. °K	Cp
12	0·401	41	5·819	70	11·893
13	0·480	42	6·071	71	12·063
14	0·566	43	6·317	72	12·232
15	0·652	44	6·556	73	12·394
16	0·746	45	6·800	74	12·558
17	0·847	46	7·023	75	12·708
18	0·954	47	7·253	76	12·866
19	1·075	48	7·487	77	13·019
20	1·221	49	7·719	78	13·175
21	1·372	50	7·949	79	13·322
22	1·554	51	8·179	80	13·468
23	1·744	52	8·398	81	13·607
24	1·937	53	8·602	82	13·733
25	2·129	54	8·807	83	13·857
26	2·334	55	9·016	84	13·984
27	2·559	56	9·223	85	14·107
28	2·777	57	9·442	86	14·225
29	2·998	58	9·656	87	14·337
30	3·216	59	9·863	88	14·448
31	3·436	60	10·064	89	14·559
32	3·667	61	10·259	90	14·670
33	3·893	62	10·450	91	14·780
34	4·128	63	10·642	92	14·886
35	4·357	64	10·841	93	14·988
36	4·602	65	11·031	94	15·092
37	4·851	66	11·213	95	15·193
38	5·093	67	11·389	96	15·290
39	5·334	68	11·568	97	15·387
40	5·573	69	11·736	98	15·485

TABLE 5. (Continued).

Temp. °K	Cp	Temp. °K	Cp	Temp. °K	Cp
99	15·582	129	17·874	159	19·277
100	15·676	130	17·931	160	19·315
101	15·768	131	17·986	161	19·352
102	15·858	132	18·038	162	19·388
103	15·949	133	18·091	163	19·421
104	16·039	134	18·144	164	19·455
105	16·130	135	18·200	165	19·489
106	16·217	136	18·252	166	19·526
107	16·301	137	18·302	167	19·562
108	16·385	138	18·352	168	19·598
109	16·468	139	18·401	169	19·632
110	16·549	140	18·448	170	19·666
111	16·628	141	18·495	171	19·700
112	16·708	142	18·544	172	19·733
113	16·786	143	18·593	173	19·766
114	16·864	144	18·642	174	19·799
115	16·943	145	18·689	175	19·833
116	17·019	146	18·736	176	19·867
117	17·092	147	18·779	177	19·898
118	17·165	148	18·823	178	19·928
119	17·237	149	18·866	179	19·958
120	17·307	150	18·908	180	19·988
121	17·374	151	18·950	181	20·017
122	17·441	152	18·992	182	20·046
123	17·508	153	19·033	183	20·074
124	17·573	154	19·073	184	20·102
125	17·636	155	19·114	185	20·130
126	17·701	156	19·155	186	20·158
127	17·758	157	19·197	187	20·182
128	17·817	158	19·237	188	20·207

TABLE 5. (Continued).

Temp.°K	Cp	Temp.°K	Cp.	Temp.°K	Cp
189	20·232	219	20·901	249	21·546
190	20·257	220	20·922	250	21·569
191	20·283	221	20·943	251	21·593
192	20·309	222	20·963	252	21·617
193	20·336	223	20·986	253	21·639
194	20·361	224	21·010	254	21·662
195	20·385	225	21·032	255	21·686
196	20·409	226	21·054	256	21·711
197	20·432	227	21·077	257	21·735
198	20·454	228	21·100	258	21·760
199	20·478	229	21·122	259	21·784
200	20·500	230	21·143	260	21·808
201	20·523	231	21·164	261	21·831
202	20·547	232	21·186	262	21·852
203	20·571	233	21·209	263	21·875
204	20·594	234	21·231	264	21·900
205	20·617	235	21·252	265	21·923
206	20·639	236	21·273	266	21·947
207	20·662	237	21·293	267	21·971
208	20·683	238	21·312	268	21·992
209	20·704	239	21·332	269	22·011
210	20·725	240	21·352	270	22·030
211	20·746	241	21·373	271	22·050
212	20·765	242	21·395	272	22·070
213	20·783	243	21·418	273	22·090
214	20·802	244	21·440	274	22·109
215	20·822	245	21·461	275	22·129
216	20·842	246	21·481	276	22·147
217	20·862	247	21·502	277	22·164
218	20·881	248	21·524	278	22·180

TABLE 5. (Continued).

Temp. °K	Cp	Temp. °K	Cp	Temp. °K	Cp
279	22.197	289	22.378	299	22.544
280	22.217	290	22.396	300	22.562
281	22.236	291	22.413	301	22.581
282	22.256	292	22.430	302	22.599
283	22.274	293	22.447	303	22.615
284	22.292	294	22.463	304	22.632
285	22.310	295	22.479	305	22.649
286	22.327	296	22.494		
287	22.343	297	22.510		
288	22.360	298	22.527		

Fig. 16. Empty Calorimeter Calibration — Deviations of Experimental Points from the smooth curve.

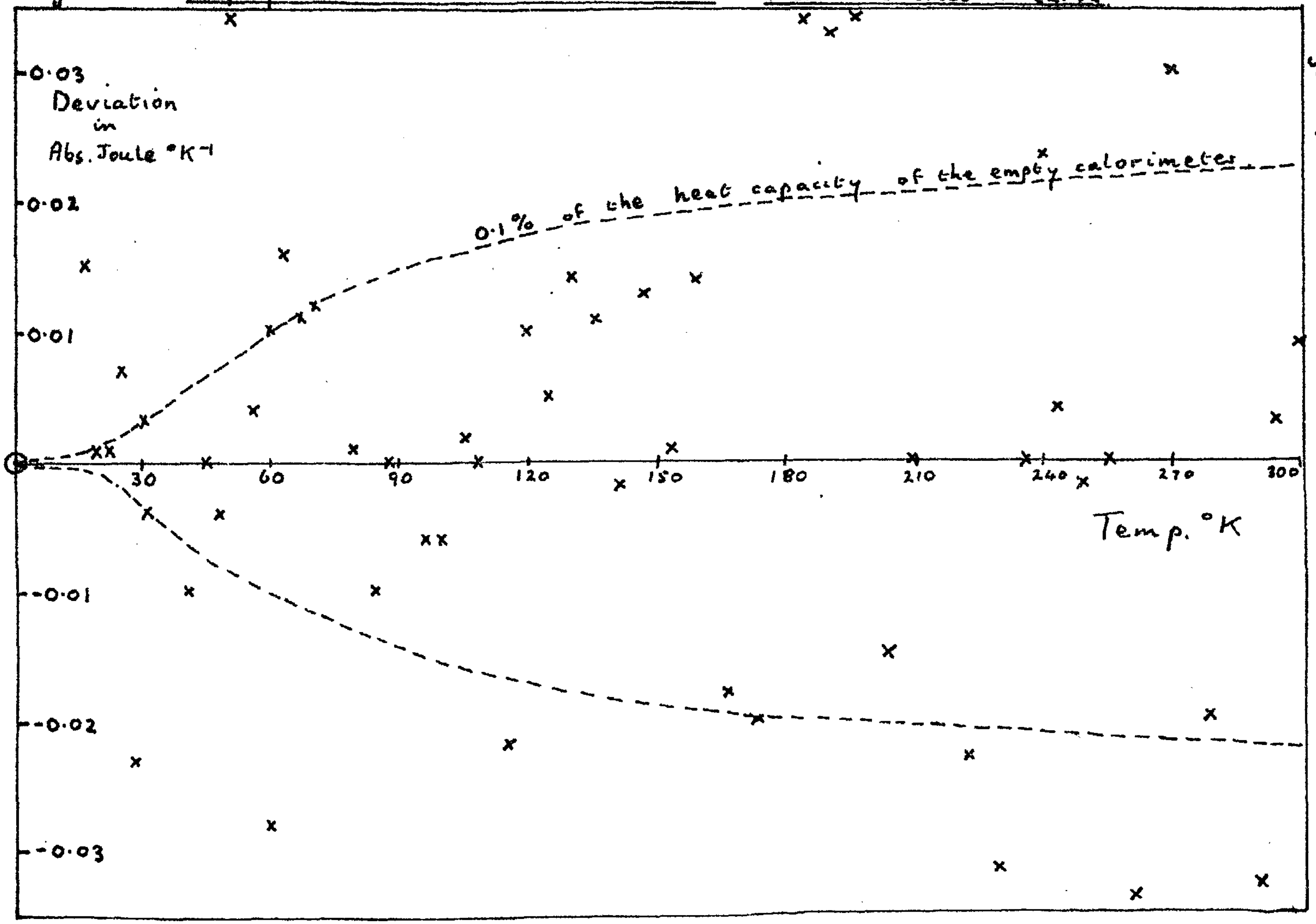


Fig. 16.

TABLE 6. EXPERIMENTAL VALUES OF THE HEAT CAPACITY OF BENZOIC ACID

Wt. of Benzoic Acid in calorimeter = 28·2167g. (in vacuo)

Molecular wt. of Benzoic Acid = 122·18g.

No. of moles of Benzoic Acid in calorimeter = 0·23106g.

Heat Capacity, Cp, in Abs. Joules $^{\circ}K^{-1}$.

Run No.	Temp. °K	Δ T	Cp	Cp/mole
1	79·84	4·13	12·864	55·674
2	84·01	4·21	13·373	57·838
3	88·30	4·30	13·754	59·525
4	92·64	4·40	14·166	61·308
5	97·18	4·70	14·607	63·217
6	101·98	4·83	15·003	64·931
7	106·86	4·91	15·407	66·680
8	111·81	4·99	15·814	68·441
9	116·92	5·23	16·236	70·267
10	122·15	5·29	16·640	72·016
11	127·37	5·16	17·094	73·981
12	132·37	4·85	17·529	75·863
13	137·45	5·35	17·977	77·802
14	142·91	5·60	18·535	80·217
15	146·53	5·65	18·787	81·308
16	152·13	5·67	19·395	83·939
17	157·87	5·80	19·889	86·077
18	163·87	6·21	20·282	87·778
19	169·99	6·07	20·862	90·288
20	176·23	6·42	21·489	93·002
21	182·70	6·53	22·109	95·685
22	189·27	6·63	22·720	98·329
23	195·95	6·72	23·385	101·21
24	202·61	6·60	23·969	103·74

TABLE 6. (Continued).

Run No.	Temp. °K	Δ T	Cp	Cp/mole
25	209·25	6·71	24·593	106·44
26	215·88	6·56	25·328	109·62
27	222·48	6·66	26·043	112·71
28	229·07	6·54	26·593	115·09
29	235·47	6·44	27·269	118·02
30	241·95	6·52	27·914	120·81
31	248·39	6·41	28·500	123·35
32	254·84	6·50	29·109	125·98
33	261·38	6·60	29·657	128·35
34	267·98	6·68	30·306	131·16
35	274·56	6·56	31·029	134·29
36	281·14	6·59	31·862	137·89
37	287·79	6·69	32·643	141·27
38	294·51	6·79	33·198	143·68
P39	56·12	4·58	10·137	43·872
P40	60·66	4·50	10·737	46·468
P41	65·36	4·94	11·239	48·643
P42	70·04	4·45	11·841	51·246
P43	74·45	4·48	12·214	52·861
H44	13·69	1·22	1·322	5·721
H45	15·18	2·18	1·368	5·921
H46	17·91	3·92	1·983	8·582
H47	21·34	3·44	2·95	12·616
H48	24·79	3·54	3·781	16·364
H49	28·33	3·65	4·595	19·887
H50	31·92	3·62	5·522	23·899
H51	35·54	3·63	6·382	27·621
H52	40·10	5·51	7·292	31·559
H53	45·18	4·28	8·330	36·053
H54	49·43	3·84	9·042	39·133
H55	53·27	3·85	9·644	41·738

TABLE 6. (Continued).

Run No.	Temp. °K	Δ T	Cp	Cp/mole
I56	276•86	7•15	31•559	136•58
I57	284•08	7•25	32•188	139•31
I58	291•36	7•33	32•837	142•11
I59	298•67	7•38	33•823	146•38

I Indicates refrigerant used is ice-water

TABLE 7. SMOOTHED VALUES OF THE HEAT CAPACITY OF BENZOIC ACID IN ABS. JOULES. $^{\circ}K^{-1}$ MOLE $^{-1}$.

Temp.°K.	Cp	Cp(N.B.S).	Temp.°K.	Cp	Cp(N.B.S).
0	0·0	0·0	110	67·81	67·69
5		0·243	120	71·33	71·51
10	1·93	1·923	130	75·02	75·27
15	5·79	5·856	140	78·85	79·09
20	10·99	11·00	150	82·80	82·90
25	16·55	16·54	160	86·58	86·75
30	21·90	21·92	170	90·50	90·70
35	27·02	27·08	180	94·57	94·70
40	31·58	31·68	190	98·72	98·75
45	35·77	35·77	200	102·78	102·89
50	39·50	39·50	210	107·02	107·11
55	42·81	42·81	220	111·31	111·40
60	45·88	45·88	230	115·61	115·78
65	48·65	48·65	240	119·71	120·22
70	51·24	51·24	250	123·88	124·71
75	53·52	53·52	260	128·00	129·24
80	55·85	55.85	270	132·40	133·81
85	58·13	58.13	280	137·07	138·40
90	60·22	60·14	290	141·90	143·03
95	62·25	62·04	300	146·72	147·66
100	64·17	63·93			

Fig. 17. Deviations from N.B.S. values of the Heat Capacity of Benzoic Acid.

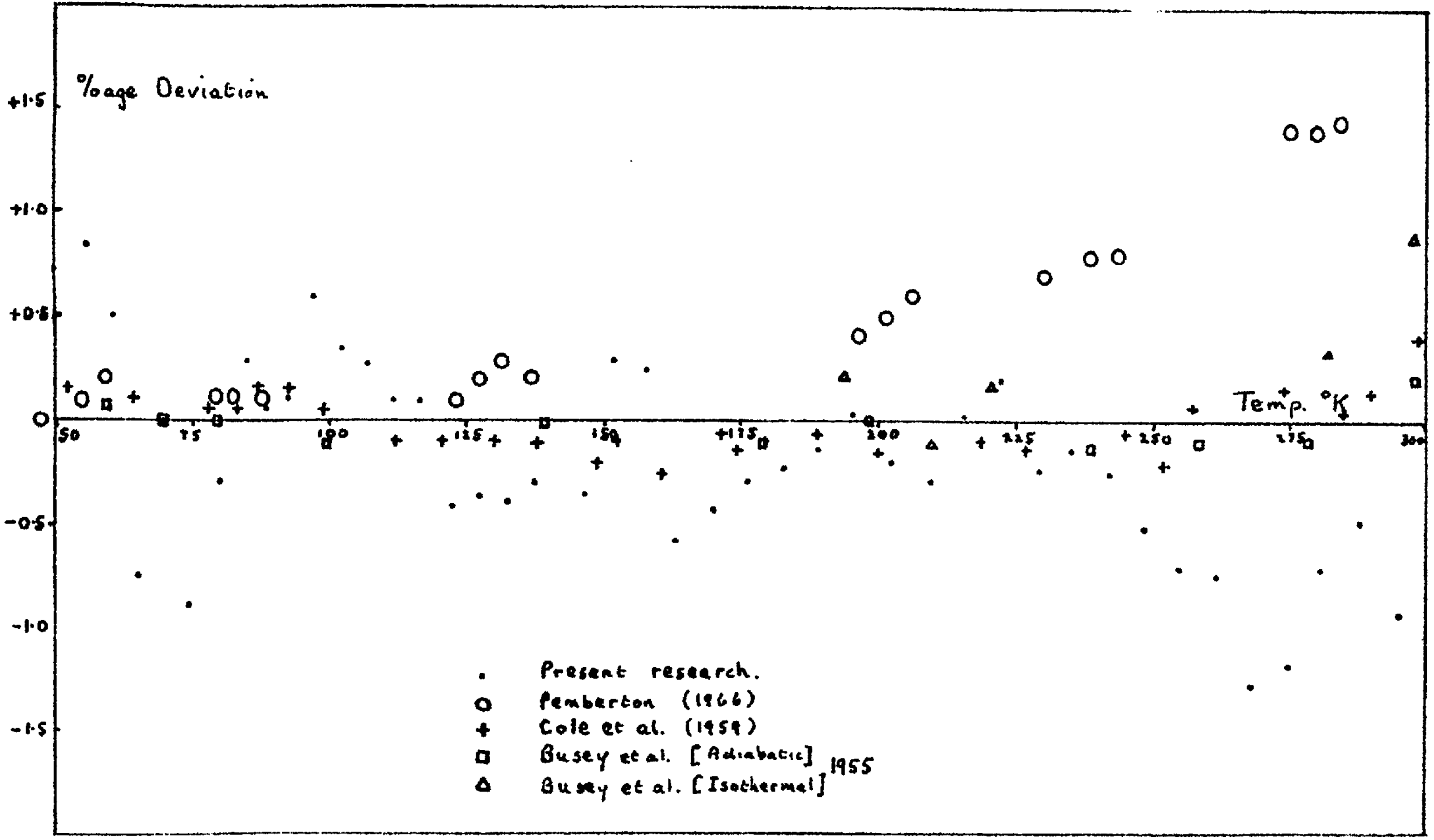


Fig. 17.

B. DISCUSSION OF THE ACCURACY OF THE CALORIMETER

The root mean square percentage deviations from the smooth curve were determined for the measurement on both the empty calorimeter and the benzoic acid sample.

TABLE 8 Root mean square percentage deviations of heat capacity values from a smooth curve

	12-25 °K	25-70 °K	70-300 °K
Empty calorimeter	0·90	0·49	0·11
Benzoic acid	0·86	0·52	0·17

The significant decrease in accuracy at the very low temperature is due to the decrease in both the sensitivity of the thermometer and the heat capacity of the calorimeter. The values shown above are slightly higher than reported elsewhere, but the deviation of the measured benzoic acid smooth curve from that reported by N.B.S. (Ginnings and Furukawa 1953) is within ~~the~~ our ~~accepted~~ required limits. (Fig. 17).

A major source of error in the absolute accuracy of measurements such as these is due to the existence of non-isothermal surfaces. Temperature gradients on the surface of the calorimeter can be appreciable both before and after the attainment of the steady state of the heating period. Those before are often dependent on the heating rate but usually result in negligibly small errors. Those during the steady state can result in significant errors and are independent of the heating rate. A larger heating rate sets up larger temperature gradients, but the time of the heating period is correspondingly shorter.

The old heating arrangement was particularly suspect of having a large steady state temperature gradient. Most of the heat from the heater flowed into the bottom plate and around to the main body of the vessel. In consequence a large quantity of heat is directed through a narrow section of metal, resulting in the setting up of large temperature gradients. The bottom shield was controlled to be at the same temperature as the side shield, which in turn was kept at the temperature of the calorimeter at the thermocouple junction, i.e., at a temperature colder than the bottom plate. The result was a net heat flow from the bottom plate to the shields. The heat flow in the opposite direction from the relatively cold top plate was insufficient to compensate for this. This effect would result in an increase in the values of the heat capacity and would be more pronounced at the higher temperatures on account of the radiation from a surface being proportional to the fourth power of its temperature. The wiring of the heater around the main body of the vessel allows the main part of the calorimeter to be heated directly and in so doing eliminates any such large thermal gradients at the outlet. Wiring in this way has also brought all parts of the wire in close thermal contact with the body of the calorimeter, and the danger of overheating of the wire and consequent heat flow down the connecting wire to the side shield is avoided. Such a danger existed in the old heating system as the heater was so constructed that the wires lay in layers and the heat generated in the middle layer had to pass through other layers in order to reach the outer metallic surface.

In view of the changes made in the thermocouple system before these experiments it is necessary to consider the error caused by the possible offset of the temperature of the control shields. West (1963) has said that the error due to offsetting is negligible providing the value offset is constant and reasonably small. Offsetting of the controls to attain zero heat drift is practised by some observers, particularly for measurements at high temperatures, when large temperature drifts can make any accurate determination of the temperature rise very difficult.

The large root mean square deviation of the points from a smooth line is a matter of some concern. There are two main ways in which this type of error may be introduced - in the evaluation of the temperature rise and in the control of the shields.

By virtue of the temperature intervals chosen and the sensitivity of the potentiometer employed, the accuracy of the measurement of the temperature rise should approach ±0·1% (this error is much larger at the low temperatures). A small error in the estimation of the drifts, from which the initial and final temperatures are calculated by extrapolation, can lead to a large error in the value of the temperature rise and in consequence the heat capacity. With this in mind it has been decided to return the vernier potentiometer to the manufacturers to be serviced, as during the measurements occasional inconsistencies were noticed, which could not be eliminated by cleaning of the contacts.

The shields were controlled manually during the experiments on the empty calorimeter and benzoic acid. The very rapid response of the calorimeter to the heating made control of the shields very difficult at the beginning and the end of the heating periods. Extra heat is required by the shields within fifteen seconds of starting the calorimeter heater current. The use of the automatic control improves this situation, but even this has its limitation in that increase in the response of the control results in fluctuations during the steady state of the heating period. In view of this it may be necessary to reduce this effect by decreasing the heating rate, or by slightly increasing the thermal lag by rewiring the heater with a layer of cigarette paper inserted between the wire and the vessel. The increase of the transient period is to be avoided, but it would in this case have the advantage of reducing the danger of electrical short-circuiting between the wire and the vessel.

Any error in the shield control is greatly exaggerated by any increase in the radiative properties of the surfaces, e.g., by the tarnishing of the copper foil shield. For this reason it would be advisable to gold plate the outside surface of this copper shield.

CHAPTER 5. THE PREPARATION AND ANALYSIS OF THE UREA AND THIOUREA ADDUCTS.

A. Urea Adducts

(i) Preparation

Bengen's original accidental preparation of the urea--octanol adduct demonstrated the ease of the preparation of the adducts. Although a solid phase preparation has been reported (Hermann 1962), the preparations are most successfully accomplished in solution. The hydrocarbon is added directly, or in a suitable solvent, e.g., decalin (Zimmerschied, 1950), to a solution of urea in methanol. Schlenk (1951) used a different method, dissolving the hydrocarbon in benzene and adding finely powdered urea.

The calorimeter samples of the adducts (not eicosene) were prepared by adding the hydrocarbon dropwise from a burette to a saturated solution of urea in methanol, until the hydrocarbon was seen to be in excess. The quality of the hexadecene adduct crystals was improved by addition of isopropanol at 60°C until the mixture was homogeneous. The urea-eicosene adduct was prepared by adding solid eicosene to a saturated solution of urea in methanol. This solution was warmed to about 60°C and isopropanol added from a burette until all the eicosene had dissolved. (McAdie, 1962). The crystals of the adducts were left in solution overnight and then filtered at the pump, washing the filtrate with a little n-pentane. The crystals were left to dry on an open dish for several hours. The time of drying was limited by the instability of the adducts;

in particular the decene and undecane adducts were not left exposed in this manner for more than two or three hours.

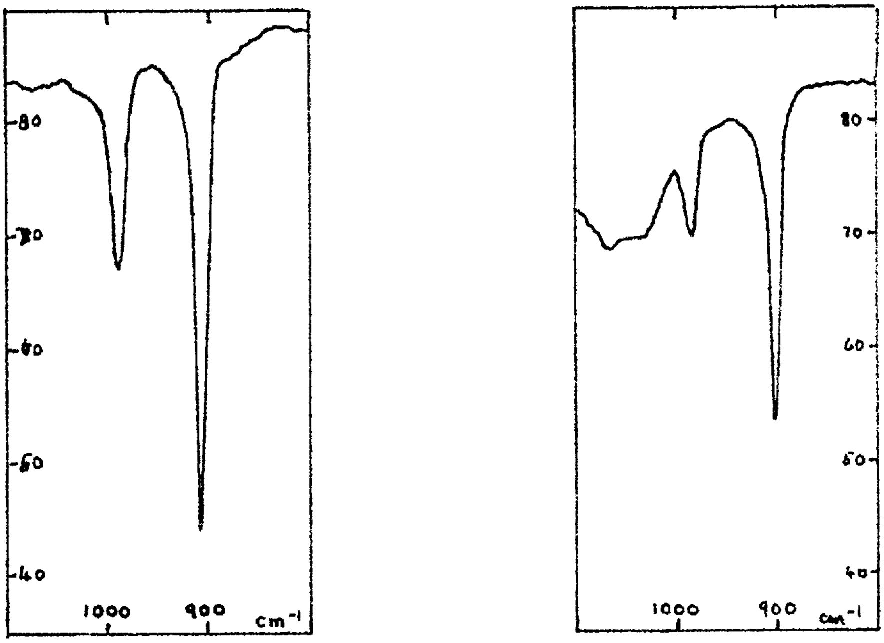
The reagents used for these preparations were

Compound	Source	Purity
Urea	B.D.H.	Analar
Methanol	B.D.H.	Analar
Isopropanol	B.D.H.	Analar
n-Pentane	B.D.H.	G.P.R.
n-Undecane	B.P. Research Sample	S 32.2
1-Decene		S162.2
1-Hexadecene		S231.3
1-Eicosene		S227.0

The purity of the hydrocarbons was checked by gas chromatography and found to be better than 99% pure in every case.

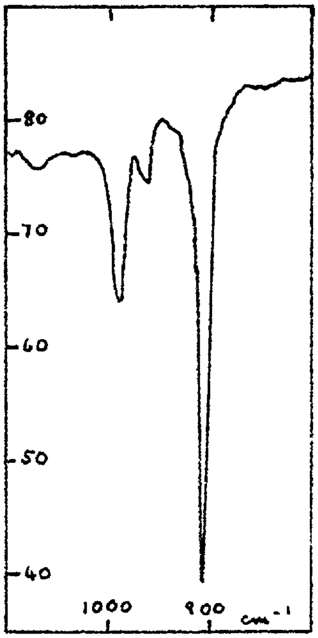
In addition, infra-red spectra of the hydrocarbons using sodium chloride plates were investigated. All the characteristic absorptions of the hydrocarbon were observed. The 1-decene and to a lesser extent 1-eicosene samples had an additional absorption with a double peak at about 1700 cm^{-1}. This was considered to be the result of trace quantities of aldehydes or ketones formed by the atmospheric oxidation of the 1-alkene group. The absorption coincides with the reported range of the very strong C = O stretching frequency absorption. The intensity of these absorptions

Fig. 18 Infrared Spectra of 1-Alkenes



a). 1- Decene

b). 1- Hexadecene



c). 1 - Eicosene

Absorption at 968 cm⁻¹

a). Pure 1-ene

b). Pure 1-ene

c). 99% Pure 1-ene.

cf. Showell, Russell and Swern
J. Org. Chem. 27, 2853, 1962.

at 1700 cm^{-1} was indicative of only very small amounts of the carbonyl group being present. A mass spectrograph on the decene sample showed no sign of molecules having a greater mass than the decene molecule. Any molecules of shorter chain length or containing carbonyl groups would not be preferentially adducted with urea, and consequently it was considered safe to continue with this sample without further treatment.

The infra-red absorption in the region 900 - 1000 cm^{-1} is indicative of the purity of the 1- ene isomer in the alkenes (Showell, Russell and Swern, 1962). An additional absorption at 968 cm^{-1} shows the presence of a trans internal isomer. The hexadecene and decene samples were free of this absorption, but the eicosene sample showed an absorption, which indicated about a 1% impurity (See Fig.18).

(ii) Analysis

The urea : hydrocarbon weight and molar ratios were calculated by determining the weight of urea in a known weight of adduct. The urea was estimated by hydrolysing it to ammonium carbonate with the enzyme urease, and then determining the ammonium carbonate by titration with standard hydrochloric acid. In order to test the complete action of the urease and the accuracy of the method, several trial analyses were made on pure urea. In each case the weight of urea found by analysis was within ± 0.3% of the actual value.

The analysis procedure was as follows: -

Reagents:

Urea solution (0.6g of adduct /250 ml. of aqueous solution).
0.5% $HgCl_2$ solution.
Urease suspension (5B.D.H. tablets in 50 ml. of water).
10% NH_4Cl solution.
0.1 N HCl (B.D.H. standard ampoule).
Screened methyl orange.

Ao	A_1 A_2 A_3
25 ml. of urea sol$^{\underline{n}}$.	25 ml. of urea sol$^{\underline{n}}$.
2 ml. of $HgCl_2$ sol$^{\underline{n}}$.	-
Shake mixture	-

Add 10 ml. of enzyme suspension.
Leave the mixtures overnight (or for at least 3 hours) in stoppered vessels.

1 ml. of NH_4Cl sol$^{\underline{n}}$.	2 ml. of $HgCl_2$ sol$^{\underline{n}}$.

Add a few drops of screened methyl orange indicator

Add 0.1 N HCl until end point.	Add 0.1 N HCl until end point is reached. Bubble nitrogen gas through solution for 5 minutes. Add acid once more until end point is restored.

A_o was a control solution. The volume used in the calculation was $A_1, A_2, A_3, - A_o$.

The mercuric chloride solution inhibited the action of the enzyme. Nitrogen gas was bubbled through to displace any carbon dioxide in solution.

The results of the analyses were slightly higher than the values reported by Schlenk (1949) and Redlich (1950). However, these reported analyses were done in solution, whilst the anaylses in this work were of the dry adduct samples. The samples were analysed before and after the heat capacity measurements.

TABLE 9. ANALYSIS RESULTS OF UREA ADDUCTS

Guest	% of urea	Urea / guest Wt. ratio	Urea / guest Molar ratio
n-Undecane	77.7 (77.4)	3.48	9.06
1-Decene	75.8 (76.1)	3.13	7.31
1-Hexadecene	75.7 (75.1)	3.12	11.63
1-Eicosene	75.2 (76.3)	3.03	14.2

The density of the adducts, which was required for the buoyancy correction in the weighings, was calculated from these analysis results and assuming the unit cell composition and dimensions as reported by Smith (1952).

The absence of unadducted tetragonal urea was checked by comparing the X-ray powder patterns of pure urea and the urea adducts (Fig. 19).

Fig. 19. X-ray powder patterns of Urea (tetragonal) and the Urea Adducts.

Fig. 19

B. Thiourea Adducts

(i) Preparation

The thiourea adducts are prepared in a similar way to urea adducts. However, their instability out of solutions leads to difficulty in preparing a calorimeter sample. The cyclopentane adduct decomposed as it was dried and the dimethylbutanes, cyclohexane and carbon tetrachloride adducts were only a little more stable. Decomposition is evident by the appearance of white powder on the surface of the initially translucent crystals. The reagents used were: -

Thiourea	B.D.H. Lab. reagent.
Methanol	B.D.H. Analar.
Cyclohexane	B.D.H. Spectroscopy Grade.
2, 2- Dimethylbutane	National Chemical Laboratory (99.99% pure).

The purity of the cyclohexane was checked by gas chromatography and was found to be better than 99% pure. The 2, 2- Dimethylbutane was used directly from the National Chemical Laboratory ampoule and in consequence no check was made on its purity.

The thiourea - cyclohexane adduct was the first adduct to be prepared for the heat capacity measurements. The filtration and drying was performed in a cold room at 3 °C. The procedure was the same for the preparation of the urea adducts. The concentration of the thiourea in the methanol solution was such that the solution was saturated at 3 °C. In order to enable the optimum time of drying to be assessed several trial preparations were made before the actual calorimeter sample was prepared. Too short a drying period resulted in a wet sample, while too long a period led to the loss of cyclohexane from the adduct. The trial samples were checked by estimating the thiourea content in the manner described in the next section. The actual calorimeter sample was dried, a few grams at a time, on an open filter paper for about twenty minutes, and then loaded into the calorimeter. The calorimeter was stoppered and stored in a chamber inside an ice bath in between the loading operations. A sample of the crystals was taken at this stage and a determination of the thiourea content was made.

While the necessary weighings were made, the calorimeter was left stoppered and eventually the sealing operation was done in the shortest possible time. During the sealing and pumping out operations the calorimeter was stored inside a vessel immersed in an acetone/cardice bath at about - 80°C. The glass line of the pumping system was arranged so that the volume between the calorimeter and trap A (see Fig. 15) was a minimum, in order to avoid any large condensation of water in the cold calorimeter.

The attempt to prepare a cyclopentane thiourea adduct calorimeter sample was unsuccessful. At 3°C the cyclopentane adduct was extremely unstable and even at - 17°C there were clear signs of the crystals decomposing as the calorimeter was being filled. During these attempted preparations it was found advisable to wash the crystals with cyclopentane rather than with n-pentane.

The 2, 2- dimethylbutane thiourea adduct calorimeter sample was prepared at + 3°C in the same way as the cyclohexane adduct, except that 2, 2-dimethylbutane was used for the washing.

(ii) Analysis

Many methods for the estimation of thiourea have been reported (Prakash Chandra Gupta 1963). Volumetric methods are based on the oxidation of thiourea to urea. The choice of oxidising agent is very important as many only **partially** convert thiourea to urea. In the method employed, the oxidising agent is iodine in alkaline solution (Cuthill and Atkins 1937). The method is as follows: -

Reagents.

0.1 N iodine solution
0.1 N sodium thiosulphate sol^n. (B.D.H. ampoule).
2 N sodium hydroxide sol^n.
4 N sulphuric acid.
Starch solution (indicator).

(a) Standardisation of iodine solution.

The standard sodium thiosulphate solution was titrated against 25 ml. of the iodine solution in 10 ml. of 4 N H_2SO_4. The end point was indicated by the disappearance of the blue starch-iodine complex.

(b) Oxidation of thiourea by iodine solution.

An aqueous solution of the thiourea adduct was prepared with a known concentration of about 0.2 grams of thiourea / 250 ml. of solution. 25 **ml.** of this solution was pipetted into a conical flask and 10 ml. of 2 N Na OH solution added. Finally 50 ml. of the iodine solution was added and the solution stored for 10 - 20 minutes in the dark. It was essential to add the Na OH solution and then to shake the solution well, before adding the iodine solution, otherwise turbidity resulted due to sulphur formed by a side reaction of iodine on thiourea. It was also extremely important to ensure the iodine solution was in a large excess of the amount required to oxidise the thiourea to urea, otherwise incomplete conversion resulted.

(c) Back titration of iodine against sodium thiosulphate solution.

2o ml. of 4 N H_2SO_4 were added to the stored solutions and then the standard sodium thiosulphate solution was titrated against the excess iodine.

The weight of thiourea per gram of adduct was then calculated.

$$2\,NaOH + I_2 \rightarrow NaIO + NaI + H_2O$$

$$4\,NaIO + CS(NH_2)_2 \rightarrow CO(NH_2)_2 + 4\,NaI + H_2SO_4$$

Therefore 4 moles of $I_2 \equiv$ 1 mole of $CS(NH_2)_2$.

Several trial analyses were made on pure thiourea, which showed the error in the analysis to be about ± 1%.

The calorimeter samples were analysed before and after the heat capacity measurements. The X-ray powder patterns of the thiourea adducts were not taken, as the long exposures required resulted in their decomposition. Suitable low temperature X-ray equipment was not available.

TABLE 10 Analyses results of the thiourea adduct

Guest	% thiourea	thiourea/guest Wt. ratio	thiourea/guest molar ratio
cyclohexane	73.5 (74.6)	2.8	3.1
2,2.dimethylbutane	72.2 (72.0)	2.6	2.9

Figures in brackets are results of analysis of samples after the heat capacity measurements.

CHAPTER 6. THE EXPERIMENTAL DETERMINATION OF THE HEAT CAPACITIES OF SOME UREA-HYDROCARBON ADDUCTS

The heat capacities were measured in the manner described in chapter 4. The experimental results of the studies on the urea -n- undecane, 1- decene, 1- hexadecene and 1- eicosene adducts are listed in chronological order in Tables 12, 13, 14 and 15. These tables include the temperature interval (ΔT) of each determination and the heat capacity of the adduct expressed as per mole of urea (Cp mole $^{-1}$). 1 mole of urea = 60.06g; 1 cal. = 4.1840 abs. Joules; 0°C = 273.15°K.

For each of the adducts, a large scale graph was drawn of the heat capacity (Cp) against temperature (T). (Small scale graphs are shown, figs. 20, 22 and 23. From these curves the smoothed heat capacity data were determined (Tables 16 and 17).

The root mean square percentage deviation of the points from the smooth curves was calculated (Table 11).

TABLE: 11 The root mean square percentage deviations of the experimental heat capacity determinations from a smooth curve.

		Temperature Range	
Adduct	12-25°K	25-80°K	80-300°K
urea -n- undecane	0.73	0.19	0.21
urea -1- decene	0.23	0.16	0.11
urea -1- hexadecene	0.60	0.26	0.14
urea -1- eicosene	0.34	0.19	0.13

TABLE 12. EXPERIMENTAL VALUES OF THE HEAT CAPACITY OF UREA — n - UNDECANE

Wt. of adduct sample in calorimeter = 11·3888g. (8·8491g. of urea + 2·5397g. of n - undecane).

Heat capacity of sample, Cp, in Abs. Joules Deg. $^{-1}$.

Heat capacity per mole of urea, Cp/mole in Cals. mole $^{-1}$ Deg. $^{-1}$.

Run No.	Temp. °K	ΔT	Cp	Cp/mole
1	118·64	6·75	10·419	16·902
2	123·77	3·52	11·453	18·579
3	128·03	4·94	9·808	15·911
4	133·17	5·31	9·768	15·846
5	138·56	5·48	10·123	16·422
6	144·04	5·67	10·396	16·865
7	149·67	5·77	10·614	17·218
8	155·79	5·30	10·969	17·794
9	161·28	5·69	11·228	18·214
10	167·04	5·83	11·477	18·618
11	172·96	5·99	11·741	19·046
12	179·01	6·12	11·945	19·377
13	185·02	5·99	12·384	20·090
14	191·05	6·11	12·722	20·638
15	197·09	6·01	13·068	21·199
16	202·94	5·68	13·460	21·835
17	208·58	5·69	13·663	22·172
18	214·15	5·52	13·890	22·532
19	219·01	6·58	14·149	22·953
20	225·45	6·45	14·525	23·563
21	231·95	6·63	15·021	24·367
22	238·50	6·53	15·383	24·955

TABLE 12. (Continued).

Run No.	Temp. °K.	△ T	Cp	Cp/mole
23	245.08	6.74	15.681	25.438
24	251.71	6.65	16.037	26.014
25	258.35	6.83	16.429	26.651
26	265.04	6.72	16.884	27.389
27	271.62	6.65	17.216	27.928
28	278.18	6.82	17.631	28.601
29	284.77	6.72	18.078	29.326
30	291.43	6.87	18.483	29.984
31	298.13	6.80	18.935	30.716
32	79.56	3.57	6.999	11.354
33	83.70	4.69	7.281	11.811
34	88.41	4.73	7.580	12.296
35	93.16	4.77	7.881	12.784
36	97.95	4.82	8.213	13.323
37	102.80	4.87	8.494	13.779
38	107.58	4.71	8.873	14.394
39	112.32	4.75	9.322	15.122
40	117.08	4.75	9.957	16.152
41	121.73	4.54	11.939	19.368
42	126.53	5.01	9.909	16.075
P43	57.66	5.28	5.125	8.314
P44	62.82	5.18	5.619	9.115
P45	67.85	4.98	6.017	9.761
P46	72.23	3.81	6.354	10.308
P47	75.94	3.63	6.687	10.868
H48	12.31	1.52	0.377	0.612
H49	14.27	1.91	0.526	0.853
H50	17.34	2.88	0.965	1.565
H51	21.39	4.11	1.189	1.929

TABLE 12. (Continued).

Run No.	Temp. °K	△ T	Cp	Cp/mole
H52	25•47	2•89	1•662	2•696
H53	29•28	3•73	2•068	3•353
H54	32•95	3•61	2•500	4•056
H55	36•53	3•52	2•929	4•751
H56	40•04	3•46	3•352	5•438
H57	43•65	3•70	3•728	6•048
H58	47•12	3•22	4•095	6•643
H59	50•37	3•27	4•426	7•180
H60	53•70	3•40	4•758	7•719
T61	114•42	3•08	9•403	15•254
T62	117•01	3•10	9•746	15•810
T63	119•07	2•03	10•434	16•926
T64	120•51	0•85	11•423	18•531
T65	121•26	0•67	12•529	20•325
T66	121•91	0•60	13•257	21•506
T67	122•47	0•53	14•042	22•779
T68	123•06	0•63	11•782	19•113
T69	123•72	0•67	10•106	16•394
T70	124•39	0•68	9•673	15•692
T71	125•07	0•68	9•616	15•599
T72	125•75	0•68	9•527	15•455
T73	126•64	1•10	9•860	15•995

TABLE 13. EXPERIMENTAL VALUES OF THE HEAT CAPACITY OF UREA — 1- DECENE

Wt. of adduct sample in calorimeter = 14•4713g.
(10•9692g. of urea + 3•5021g. of 1- Decene).
Heat capacity of adduct sample, Cp, in Abs. Joules $^{o}K^{-1}$.
Heat capacity of adduct per mole of urea, Cp/mole in Cals. $^{o}K^{-1}$ mole^{-1}.

Run No.	Temp. ^{o}K	Δ T	Cp	Cp/mole
1	81•56	4•38	9•109	11•920
2	85•96	4•42	9•507	12•441
3	90•70	5•06	9•843	12•881
4	95•99	5•56	10•221	13•376
5	101•28	5•04	10•672	13•966
6	106•53	5•45	11•120	14•552
7	111•42	4•37	11•460	14•997
8	116•29	5•40	11•867	15•530
9	121•74	5•51	12•261	16•045
10	127•31	5•64	12•572	16•452
11	132•93	5•66	12•946	16•942
12	139•04	4•96	13•238	17•324
13	144•08	5•13	13•508	17•677
14	149•31	5•32	13•697	17•924
15	155•28	6•69	14•042	18•376
16	161•92	6•73	14•532	19•017
17	168•69	6•86	15•064	19•713
18	175•61	7•02	15•480	20•258
19	182•28	6•32	15•815	20•696
20	188•71	6•51	16•110	21•082
21	195•16	6•39	16•542	21•647
22	201•47	6•27	17•063	22•329
23	207•78	6•42	17•551	22•968
24	210•38	6•64	17•642	23•087

TABLE 13. (Continued).

Run No.	Temp.°K	△ T	Cp	Cp/mole
25	217·03	6·78	18·106	23·695
26	223·82	6·93	18·637	24·389
27	230·73	7·05	19·187	25·109
28	237·66	7·01	19·603	25·653
29	244·63	7·06	20·112	26·319
30	251·60	7·10	20·691	27·078
31	258·68	7·28	21·378	27·976
32	266·92	7·31	21·999	28·789
33	274·18	7·49	22·588	29·560
34	281·48	7·42	23·011	30·113
35	288·76	7·51	23·547	30·814
36	296·16	7·63	24·150	31·603
H37	12·83	2·01	0·519	0·679
H38	15·13	2·55	0·766	1·002
H39	18·09	3·36	1·081	1·415
H40	22·34	5.10	1·651	2·161
H41	26·81	3.79	2·294	3·002
H42	30·45	3·44	2·837	3·713
H43	33·80	3·34	3·337	4·367
H44	37·14	3·34	3·845	5·032
H45	40·72	3·71	4·341	5·681
H46	44·81	4·47	4·921	6·440
H47	49·14	4·18	5·523	7·276
P48	50·74	4·63	5·760	7·538
P49	55·40	4·69	6·404	8·381
P50	60·06	4·67	7·134	9·338
P51	65·16	5·56	7·646	10·006
P52	70·76	5·67	8·043	10·525
P53	76·57	5·95	8·668	11·343

TABLE 14. EXPERIMENTAL VALUES OF THE HEAT CAPACITY OF UREA — 1 - HEXADECENE ADDUCT

Wt. of adduct sample in calorimeter = 21•2297g.
(16•0709g. of urea + 5•1588g. of 1-Hexadecene).

Heat capacity of adduct sample, Cp, in Abs. Joules $^{\circ}K^{-1}$.
Heat capacity of adduct per mole of urea, Cp/mole, in Cals. mole^{-1} $^{\circ}K^{-1}$.

Run No.	Temp. °K	Δ T	Cp	Cp/mole
1	246•43	6•09	28•886	25•800
2	252•53	6•28	29•486	26•336
3	258•79	6•43	30•154	26•933
4	265•07	6•36	30•776	27•489
5	271•37	6•50	31•552	28•182
6	277•79	6•65	32•316	28•864
7	284•40	6•83	32•809	29•304
8	291•12	6•95	33•745	30•140
9	297•99	7•11	34•359	30•689
T10	131•09	3•09	18•392	16•427
T11	134•24	3•22	18•869	16•853
T12	136•91	2•12	19•769	17•657
T13	138•46	1•01	20•903	18•670
T14	139•47	1•03	22•004	19•654
T15	140•49	1•01	23•147	20•674
T16	141•45	0•91	29•628	26•463
T17	142•43	1•07	23•440	20•936
T18	143•57	1•23	19•267	17•209
T19	144•82	1•27	19•196	17•145
T20	146•52	2•12	19•381	17•311
T21	149•40	3•64	19•722	17•615
P22	54•67	4•55	8•785	7•847
P23	59•15	4•40	9•626	8•598
P24	63•62	4•56	10•337	9•233

TABLE 14. (Continued).

Run No.	Temp. °K	ΔT	Cp	Cp/mole
P25	68·14	4·51	11·012	9·836
P26	72·77	4·79	11·650	10·406
P27	77·46	4·73	12·291	10·978
H28	36·68	3·21	5·281	4·717
H29	39·54	2·50	5·868	5·241
H30	42·02	2·45	6·302	5·629
H31	45·03	3·58	6·932	6·192
H32	48·62	3·63	7·590	6·779
H33	52·26	3·66	8·305	7·418
H34	11·65	1·26	0·515	0·460
H35	13·20	1·57	0·722	0·645
H36	15·30	2·80	1·073	0·958
H37	18·70	3·62	1·543	1·378
H38	22·26	3·44	2·225	1·987
H39	25·71	3·38	2·907	2·596
H40	29·18	3·52	3·628	3·240
H41	32·71	3·53	4·405	3·934
42	80·10	4·96	12·755	11·393
43	85·07	4·98	13·359	11·932
44	90·10	4·95	13·899	12·414
45	95·18	5·11	14·464	12·919
46	100·36	5·20	15·009	13·406
47	105·58	5·27	15·573	13·909
48	110·90	5·39	16·130	14·407
49	116·41	5·64	16·676	14·895
50	120·71	5·56	17·095	15·269
51	125·78	5·70	17·752	15·856
52	131·83	6·42	18·507	16·530
53	137·87	5·69	20·683	18·474
54	143·55	5·70	22·041	19·687
55	149·57	6·31	19·662	17·562

TABLE 14. (Continued).

Run No.	Temp. °K	Δ T	Cp	Cp/mole
56	155·93	6·44	20·180	18·024
57	162·42	6·56	20·772	18·553
58	169·10	6·10	21·536	19·236
59	175·33	6·34	21·987	19·638
60	181·80	6·58	22·481	20·080
61	188·48	6·79	23·176	20·700
62	195·39	7·02	23·818	21·274
63	202·50	7·22	24·464	21·851
64	209·79	7·40	25·240	22·544
65	217·09	7·25	25·966	23·192
66	224·39	7·43	26·725	23·870
67	231·65	7·23	27·759	24·794
68	238·80	7·11	28·384	25·352

TABLE 15. EXPERIMENTAL VALUES OF THE HEAT CAPACITY OF UREA – 1 – EICOSENE

Wt. of adduct sample in calorimeter = 21·9119g.
(16·4777g. of urea + 5·4341g. of 1 – eicosene).

Heat capacity of adduct sample, Cp, in Abs. Joules ^{o}K $^{-1}$.
Heat capacity of adduct per mole of urea, Cp/mole, Cals.mole^{-1} ^{o}K^{-1}

Run No.	Temp. ^{o}K	Δ T	Cp	Cp/mole
1	81·91	3·98	13·201	11·437
2	86·38	4·98	13·760	11·921
3	91·36	5·01	14·317	12·403
4	96·18	4·66	14·896	12·905
5	100·93	4·85	15·428	13·366
6	106·05	5·40	15·950	13·818
7	111·50	5·56	16·527	14·318
8	117·05	5·59	17·139	14·848
9	122·78	5·87	17·704	15·388
10	128·88	6·36	18·301	15·855
11	135·28	6·47	18·982	16·445
12	141·79	6·56	19·686	17·055
13	145·24	5·68	20·181	17·484
14	151·05	5·62	22·216	19·247
15	156·77	5·86	22·069	19·119
16	162·80	6·19	21·315	18·466
17	169·03	6·32	21·976	19·039
18	175·41	6·45	22·527	19·516
19	181·90	6·57	23·088	20·002
20	188·55	6·77	23·751	20·576
21	196·31	6·22	24·449	21·181
22	202·60	6·43	25·147	21·786

TABLE 15. (Continued).

Run No.	Temp. °K	ΔT	Cp	Cp/mole
23	208·79	6·00	25·729	22·290
24	214·87	6·22	26·272	22·761
25	221·15	6·42	26·812	23·228
26	227·60	6·59	27·592	23·904
27	234·23	6·77	28·295	24·513
28	240·85	6·65	28·917	25·052
29	247·33	6·53	29·917	25·745
30	252·34	6·69	30·300	26·250
31	259·02	6·83	30·938	26·803
32	265·80	6·98	31·725	27·485
33	272·75	7·13	32·439	28·103
34	280·08	7·80	33·124	28·697
35	287·40	7·13	34·109	29·550
36	294·34	7·04	34·768	30·121
37	301·12	6·90	35·781	30·999
P38	50·37	5·18	8·210	7·113
P39	55·38	4·84	9·167	7·942
P40	60·35	5·11	10·065	8·806
P41	65·23	4·64	10·878	9·424
P42	69·86	4·59	11·574	10·027
P43	74·43	4·57	12·187	10·558
P44	78·99	4·54	12·858	11·139
P45	83·79	5·04	13·431	11·636
P46	88·82	5·05	14·068	12·188
47	93·88	5·06	14·607	12·655
48	99·41	6·01	15·253	13·214
49	105·40	5·98	15·879	13·757
T50	144·58	2·71	19·926	17·263
T51	146·78	1·71	20·260	17·552

TABLE 15. (Continued).

Run No.	Temp. °K	Δ T	Cp	Cp/mole
T52	148·54	1·80	20.635	17.877
T53	150·06	1·22	20.989	18·184
T54	151·30	1·23	21·425	18·561
T55	152·44	1·06	22·688	19·656
T56	153·45	0·97	22·795	22·795
T57	154·46	1·05	22·427	21·626
T58	155·59	1·22	22·427	19·429
T59	156·88	1·46	21·025	18·215
T60	158·57	1·94	21·127	18·303
T61	160·64	2·15	21·173	18·343
T62	163·39	3·45	21·538	18·659
T63	11·03	1·02	0·421	0·365
H64	12·39	1·75	0·613	0·531
H65	14·76	2·95	0·993	0·860
H66	17·90	3·19	1·441	1·248
H67	20·97	2·92	2·015	1·746
H68	23·76	2·57	2·535	2·196
H69	26·35	2·59	3·076	2·665
H70	29·06	2·77	3·665	3·175
H71	32·05	3·82	4·311	3·735
H72	35·44	3·58	5·073	4·395
H73	39·04	3·60	5·840	5·059
H74	42·76	3·85	6·636	5·749
H75	46·69	4·01	7·463	6·406

TABLE 16. SMOOTHED VALUES OF THE HEAT CAPACITY OF UREA - N - UNDECANE

Heat capacity, Cp, per mole of urea in cals. mole^{-1} ^{o}K^{-1}.

Temp. ^{o}K	Cp	Temp. ^{o}K	Cp
0	0·000	95	12·97
5	0·170	100	13·52
10	0·413	105	14·06
11	0·489	110	14·64
12	0·583	115	15·35
13	0·692	120	17·79
14	0·817	125	15·52
15	0·950	130	15·66
16	1·086	135	16·08
17	1·229	140	16·48
18	1·382	145	16·88
19	1·547	150	17·27
20	1·714	155	17·66
25	2·572	160	18·06
30	3·494	165	18·46
35	4·463	170	18·85
40	5·404	175	19·26
45	6·289	180	19·68
50	7·127	185	20·11
55	7·922	190	20·53
60	8·696	195	20·97
65	9·403	200	21·42
70	10·05	205	21·84
75	10·61	210	22·25
80	11·33	215	22·68
85	11·90	220	23·07
90	12·46	225	23·53

TABLE 16. (Continued).

Temp. °K	Cp	Temp. °K	Cp
230	24·12	273·15	28·12
235	24·67	275	28·31
240	25·08	280	28·81
245	25·43	285	29·33
250	25·86	290	29·85
255	26·34	295	30·37
260	26·81	298·15	30·71
265	27·29	300	30·88
270	27·80		

TABLE 17. SMOOTHED VALUES OF THE HEAT CAPACITIES OF UREA — 1 - ALKENES

HEAT CAPACITIES, Cp, PER MOLE OF UREA IN CALS. MOLE^{-1} ^{o}K^{-1}

T^{o}K	1 - Decene	1 - Hexadecene	1 - Eicosene
0	0·000	0·000	0·000
5	0·114	0·079	0·075
10	0·383	0·321	0·271
11	0·470	0·402	0·361
12	0·575	0·502	0·486
13	0·699	0·619	0·607
14	0·838	0·748	0·747
15	0·981	0·893	0·881
16	1·117	1·033	1·008
17	1·254	1·161	1·132
18	1·400	1·289	1·269
19	1·557	1·434	1·414
20	1·726	1·595	1·583
25	2·649	2·472	2·417
30	3·624	3·400	3·342
35	4·599	4·378	4·302
40	5·532	5·306	5·237
45	6·482	6·183	6·152
50	7·404	7·038	7·033
55	8·336	7·899	7·899
60	9·314	8·723	8·723
65	9·991	9·121	9·144
70	10·45	10·08	10·04
75	11·11	10·72	10·64
80	11·74	11·33	11·24

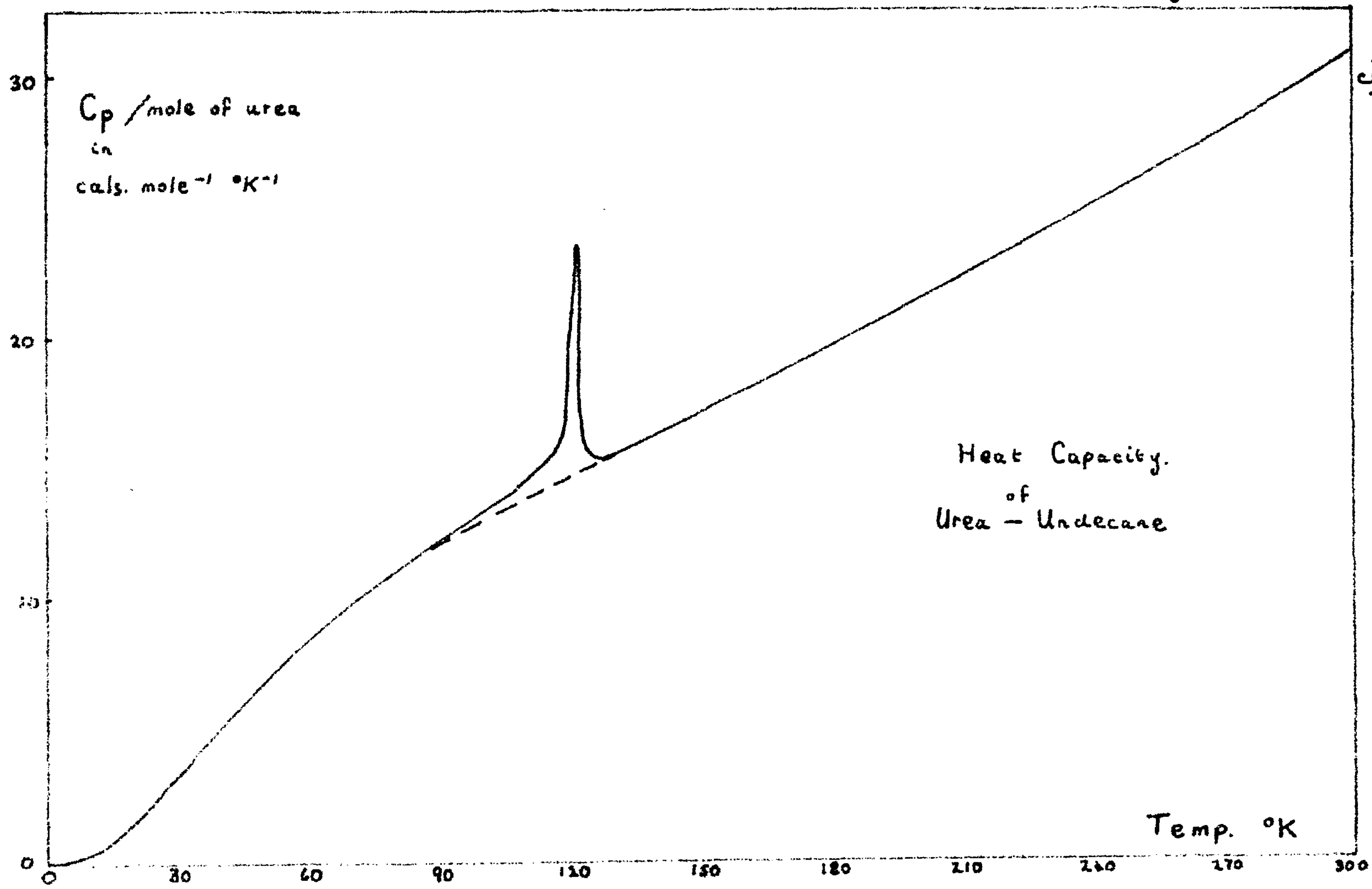
TABLE 17. (Continued).

T°K	1 - Decene	1 - Hexadecene	1 - Eicosene
85	12·32	11·89	11·77
90	12·82	12·40	12·29
95	13·28	12·90	12·79
100	13·82	13·37	13·27
105	14·36	13·85	13·74
110	14·89	14·32	14·20
115	15·38	14·79	14·64
120	15·88	15·35	15·08
125	16·30	15·76	15·52
130	16·70	16·29	15·96
135	17·08	17·09	16·39
140	17·42	20·18	16·82
145	17·72	17·18	17·32
150	17·99	17·57	18·19
155	18·35	17·98	19·84
160	18·81	18·40	18·36
165	19·35	18·82	18·69
170	19·83	19·24	19·07
175	20·22	19·62	19·46
180	20·55	20·00	19·85
185	20·87	20·41	20·25
190	21·27	20·82	20·67
195	21·70	21·24	21·10
200	22·14	21·67	21·53
205	22·60	22·12	21·96
210	23·05	22·55	22·38
215	23·50	23·00	22·78
220	23·99	23·44	23·22
225	24·51	23·94	23·67

TABLE 17. (Continued).

T°K	1 - Decene	1 - Hexadecene	1 - Eicosene
230	25·03	24·60	24·12
235	25·44	25·10	24·59
240	25·87	25·42	25·03
245	26·35	25·71	25·51
250	26·89	26·11	25·98
255	27·51	26·58	26·45
260	28·12	27·05	26·91
265	28·63	27·53	27·38
270	29·14	28·01	27·85
273·15	29·45	28·33	28·13
275	29·62	28·51	28·31
280	30·00	28·98	28·77
285	30·42	29·47	29·25
290	30·94	29·96	29·74
295	31·47	30·07	30·25
298·15	31·80	30·78	30·67
300	31·95	30·98	30·87

Fig. 20



Heat Capacity of Urea – Undecane

Fig. 20

Comparison of Experimental and Estimated Heat Capacity of 1-Decene. (Fig. 21)

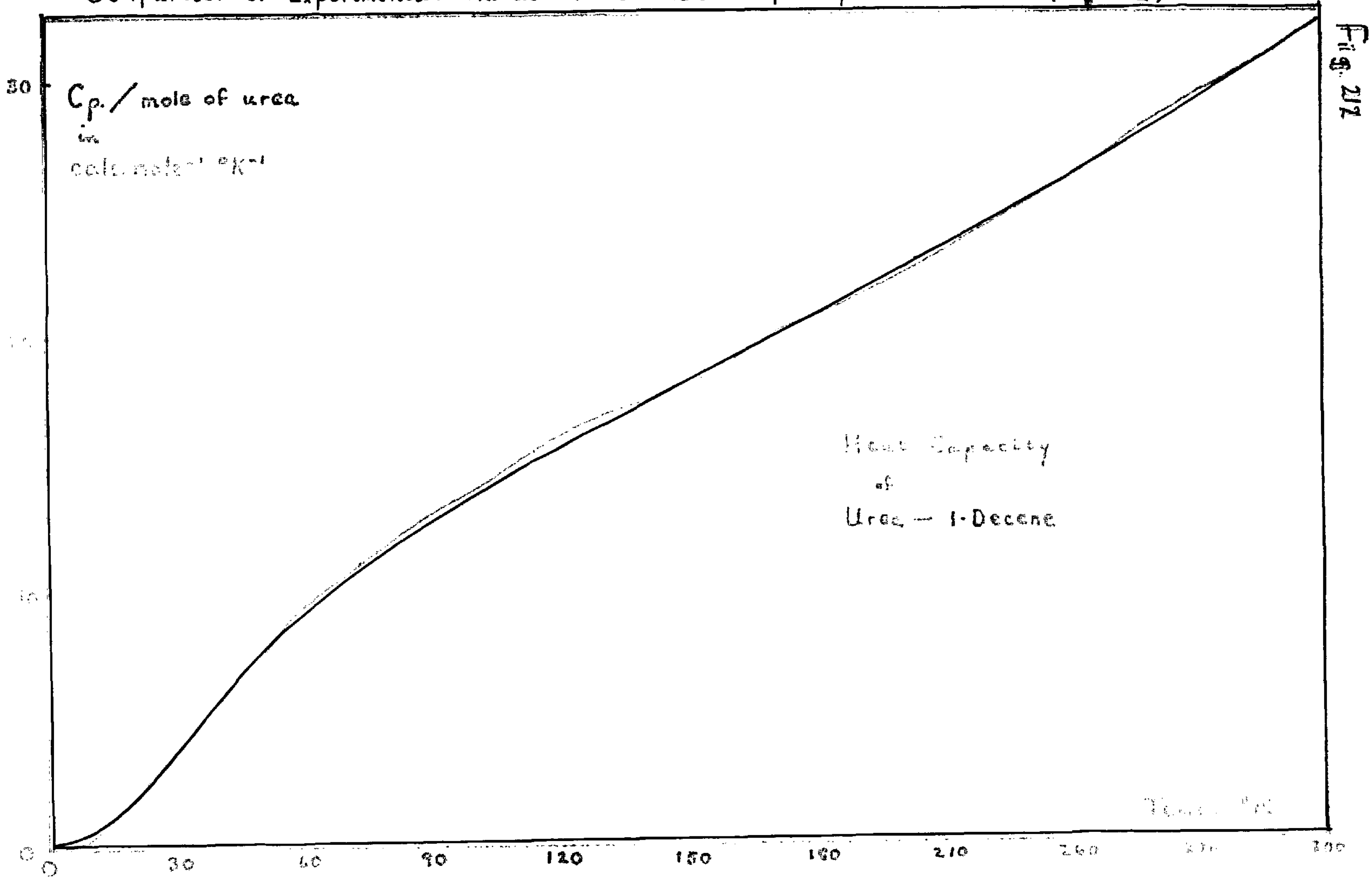


Fig. 21

Fig. 22

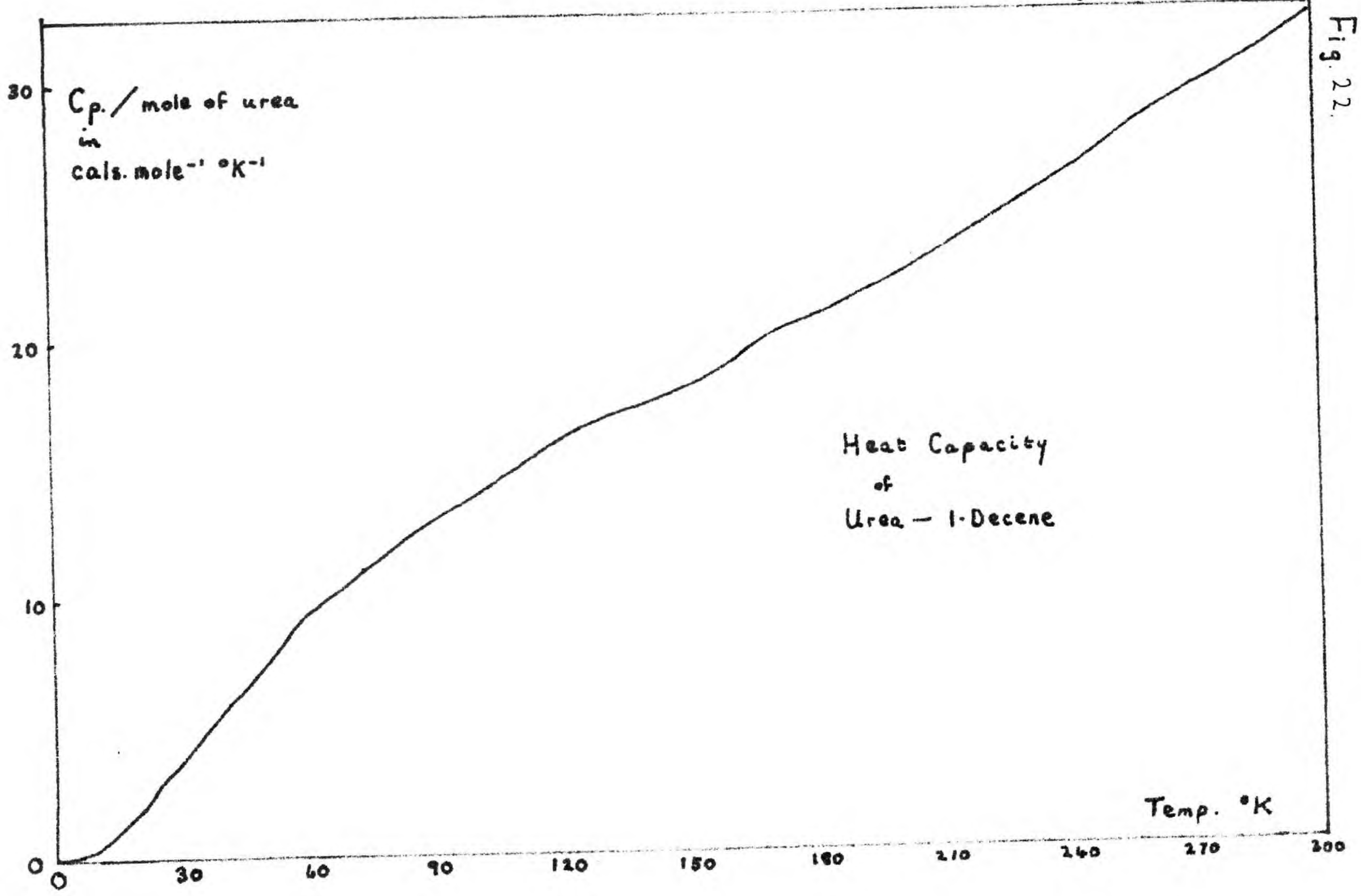

Cp./mole of urea
in
cals. mole⁻¹ °K⁻¹
Heat Capacity
of
Urea — 1-Decene
Temp. °K
0
10
20
30
0
30
60
90
120
150
180
210
240
270
300

Fig. 22.

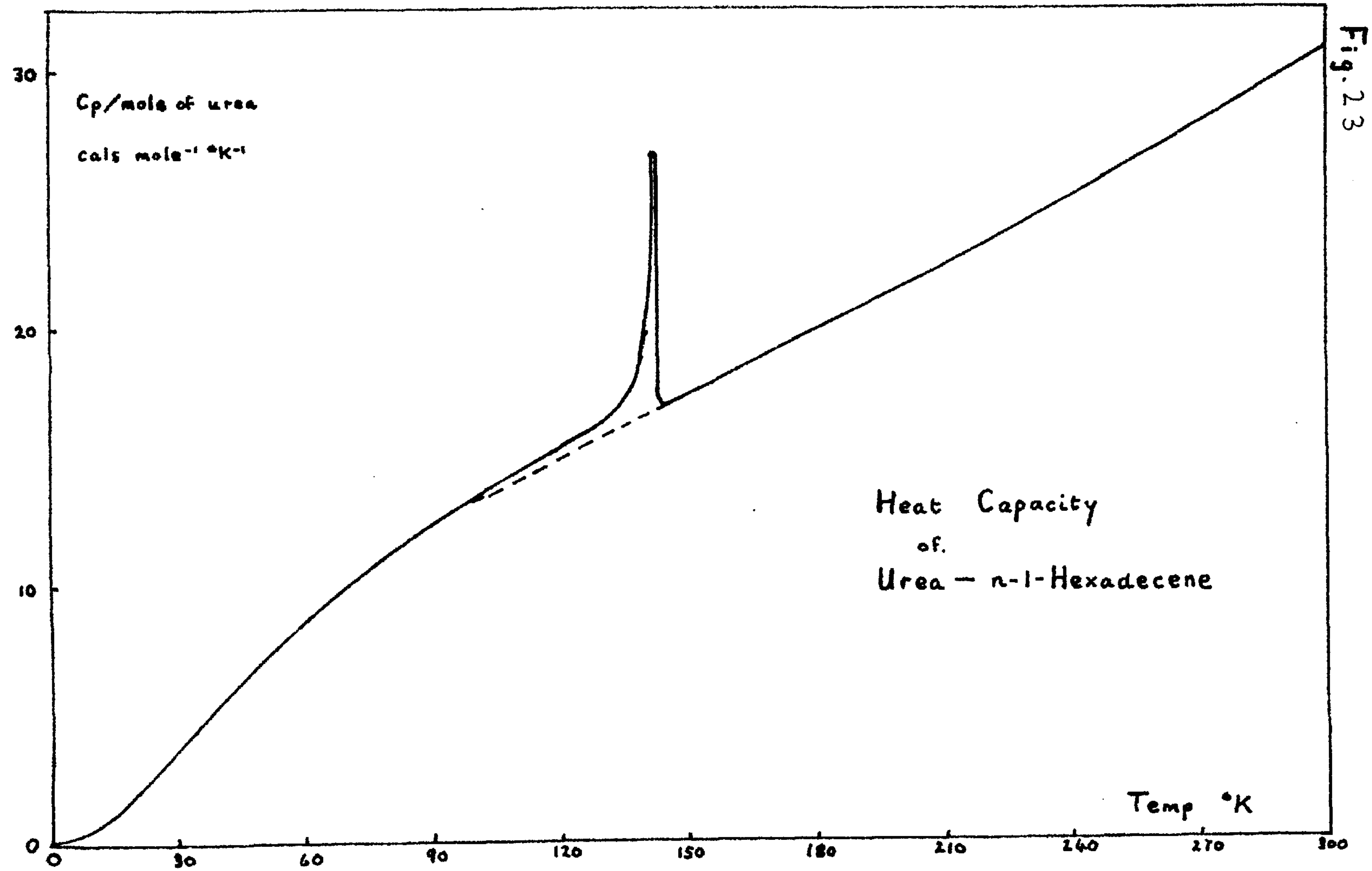
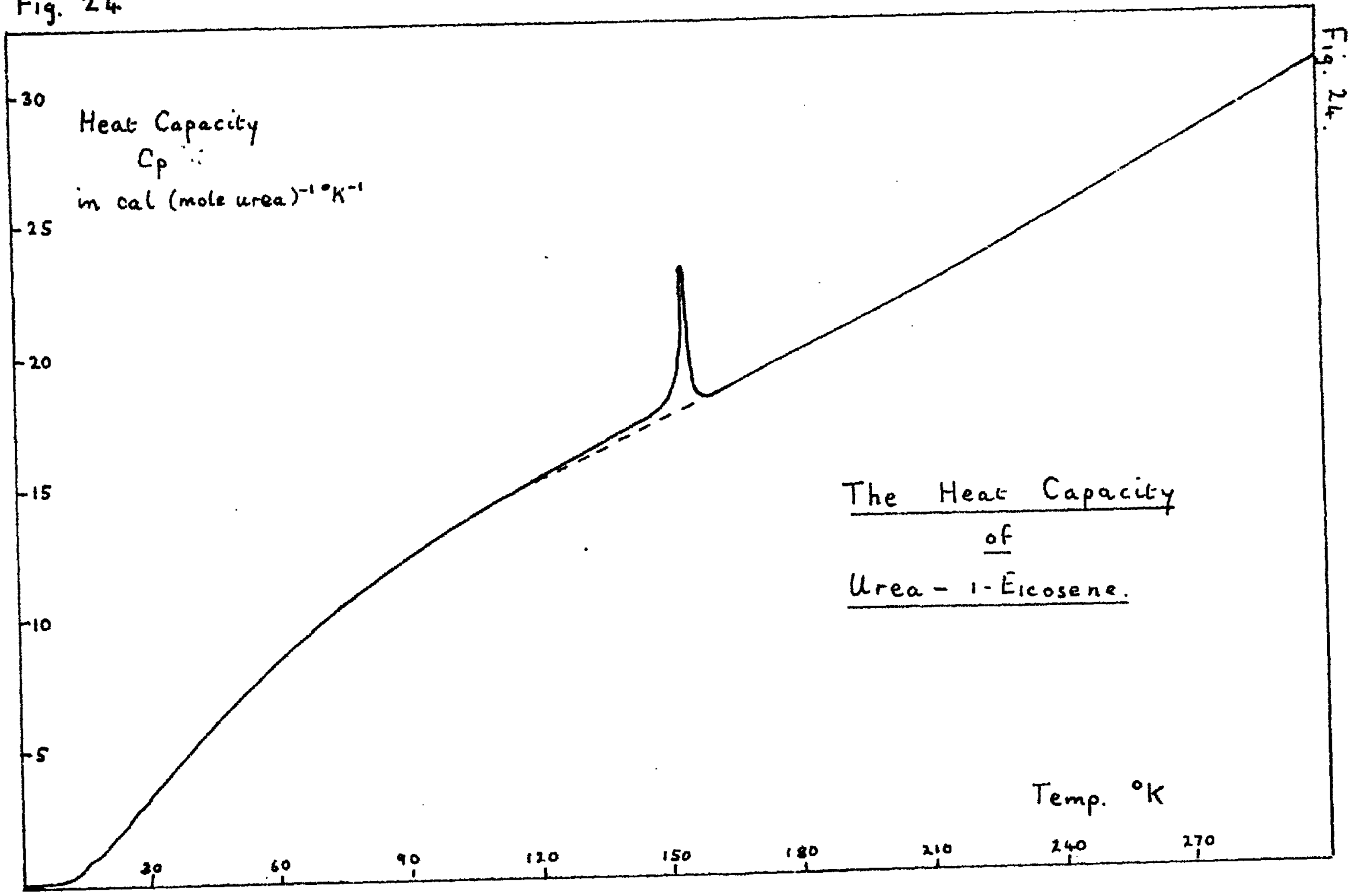

Cp/mole of urea
cals mole⁻¹ °K⁻¹
30
20
10
0
Heat Capacity
of.
Urea — n-1-Hexadecene
Temp °K
0
30
60
90
120
150
180
210
240
270
300

Fig. 23

Fig. 24



The Heat Capacity of Urea - 1-Eicosene.

A region of very high anomalous heat absorption was clearly evident in the heat capacities of all the adducts except that of 1- decene. The heat capacities in these anomalous regions were investigated further adopting smaller temperature intervals to expose the shape of the curve. The excess heat (ΔH) in these regions was determined graphically by estimating the area between the experimental curve, $Cp : T$, and a smooth curve $Cp_o : T$, where Cp_o is the heat capacity excluding the irregular contribution.

$$\Delta H = \int (Cp - Cp_o)\, dT \quad .... \quad (6.1)$$

The excess entropy (ΔS) was determined in a similar fashion by plotting $^{Cp}/_{T} : T$.

$$\Delta S = \int \frac{(Cp - Cp_o)}{T}\, dT \quad .... \quad (6.2)$$

TABLE 18. THE PROPERTIES OF THE MAJOR ANOMALIES IN THE HEAT CAPACITIES OF THE UREA ADDUCTS

Adduct	n-undecane	1-hexadecene	1-eicosene
* Transition Temp. °K.	122.4	141.7	153.9
Heat, ΔH (cal (mole urea)$^{-1}$)	36.6	35.5	23.4
(cal (mole hydrocarbon)$^{-1}$)	332	390	339
Entropy, ΔS (cal (mole urea)$^{-1}$ $^{o}K^{-1}$)	0.284	0.240	0.153
(cal (mole hydrocarbon)$^{-1}$ $^{o}K^{-1}$)	2.57	2.79	2.22

* The transition temperature is defined as the temperature at which the maximum value of the heat capacity occurs.

Although such a strongly co-operative anomaly was clearly absent from the heat capacity of the urea -1- decene adduct, there existed several anomalous regions, which appeared as smooth humps in the heat capacity. A preliminary drawing of a smooth curve (Cp_o : T) under these 'humps' and a calculation of the excess heat involved revealed that the excess heat was indeed comparable to those of the co-operative anomalies found in the other adducts.

Pemberton (1966) showed that the heat capacity of a urea - alkane adduct can be estimated to about 1% by adding the separate heat capacities of the components. In view of this and the similarity of the heat capacities of alkanes and 1- alkenes, an estimate, excluding irregular contributions, was made of the heat capacity of the urea - 1- decene adduct by combining the heat capacities of the urea n-undecane adduct (0.1162 mole of decane, 1 mole of urea) from Pemberton's data with 0.0208 moles of 1- decene (Finke, Gross, Waddington and Huffmann 1954). This was then compared with the experimental heat capacity of the urea - 1- decene adduct (0.1370 moles of 1- decene, 1 mole of urea). The lines outside the anomalous regions were very nearly co-incident. The regions of excess heat absorption occurred over several temperature ranges (figs. 21, 22, and 25). The excess heat and entropy were estimated as before and are given in Table 19.

Fig. 25 The Anomalies in the Heat Capacity of the Urea-1-Decene.

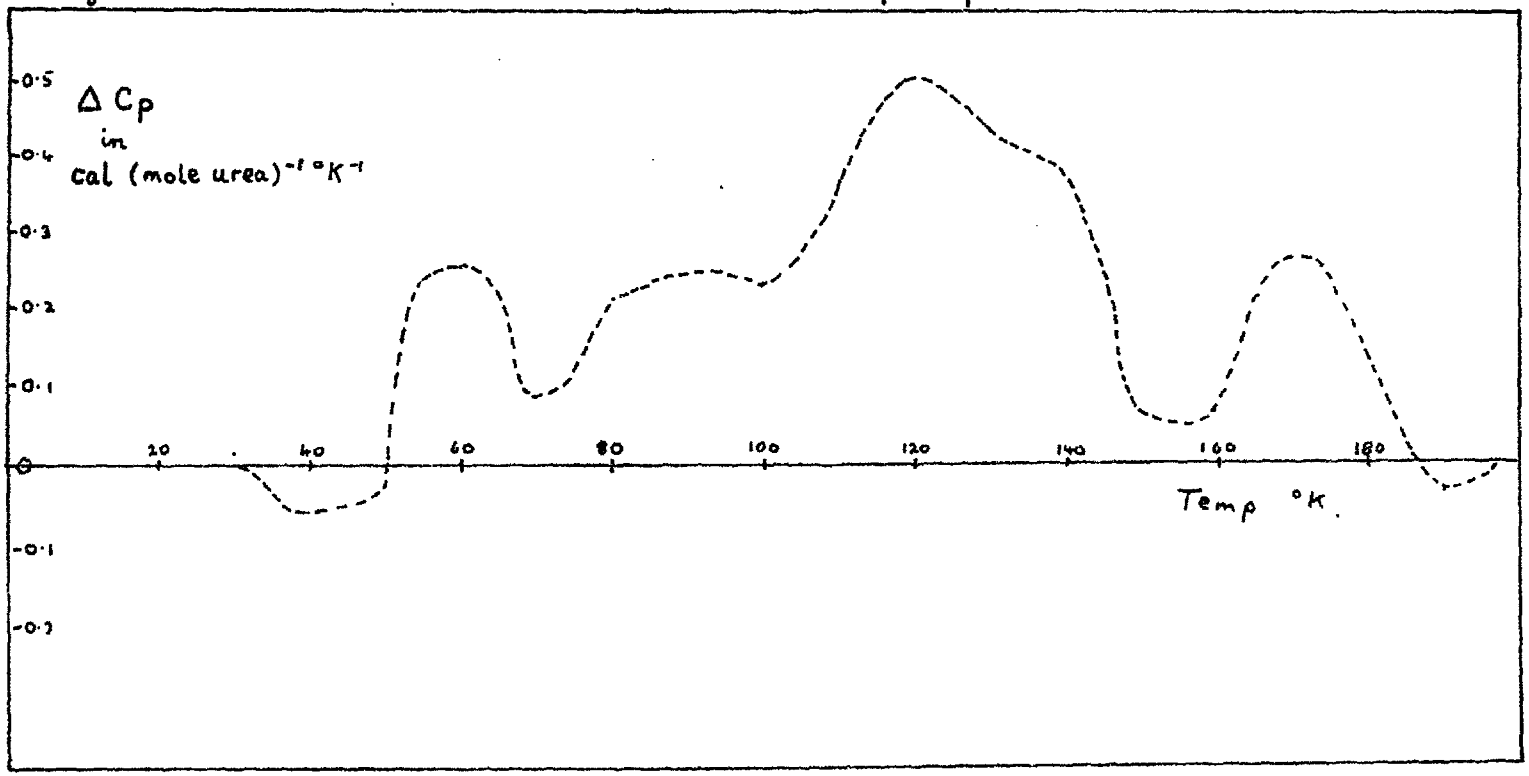


Fig. 25.

TABLE 19. THE PROPERTIES OF THE ANOMALIES IN THE HEAT CAPACITY OF UREA – 1- DECENE.

Temp. Range	50-75°K	75-155°K	165-190°K	250-285°K
Excess heat (ΔH)				
in cal (mole urea)$^{-1}$	4.2	21.4	4.1	5.9
in cal (mole decene)$^{-1}$	31	156	30	43
Excess Entropy (ΔS)				
in cal (mole urea)$^{-1}$ °K^{-1}	0.073	0.181	0.029	0.023
in cal (mole decene)$^{-1}$ °K^{-1}	.53	1.32	0.21	0.17

Total ΔH = 35.6 ± 24 cal (mole urea)$^{-1}$
= 260 ± 190 cal (mole decene)$^{-1}$

Total ΔS = 0.306 ± 0.14 cal (mole urea)$^{-1}$ °K^{-1}
= 2.24 ± 1.0 cal (mole decene)$^{-1}$ °K^{-1}

The errors quoted arise largely from the chemical analysis results. Similar comparisons were made between the urea – 1- hexadecene and 1- eicosene adducts and the corresponding n- alkane adducts. In these cases the excess heat and entropy were insignificant compared with the error involved (see below).

1- hexadecene $\Delta S = +\,0.86 \;\; \pm\, 1.5$ cal (mole hexadecene)$^{-1}$ $^{\circ}K^{-1}$
$-\,0.12$

1-eicosene $\Delta S = +\,1.80 \;\; \pm\, 1.8$ cal (mole eicosene)$^{-1}$ $^{\circ}K^{-1}$
$-\,0.15$

The positive and negative signs indicate that the experimental line ($^{Cp}/_{T}$: T) is respectively above or below the control line.

Two further anomalies previously reported by Pemberton (1966) were observed in the heat capacity data of all the adducts studied.

(i) The low temperature anomaly - a slight excess heat ($\sim$7 cal (mole urea) $^{-1}$) was absorbed at around 16°K. The inaccuracy of the measurements in this region and the small quantities of heat involved make any closer study difficult. No such irregularity was observed in the data on the calorimeter and benzoic acid, and so it must be concluded this effect is due to the adducts.

(ii) The high temperature anomaly - a smooth hump in the heat capacity was observed in the temperature region 225 - 235°K. The deviation of the experimental points from a smooth curve is a little larger in this region than the quoted values for the root mean square deviation, but even so the error is sufficiently small not to throw any doubt on the existence of this anomaly. The properties of this anomaly are summarised for each adduct in Table 20.

TABLE 20. THE THERMODYNAMIC PROPERTIES OF THE HIGH TEMPERATURE (225 - 235°K) ANOMALIES IN THE HEAT CAPACITIES OF THE UREA ADDUCTS.

Adduct	Undecane	Decene	Hexadecene	Eicosene
Δ H in cal mole $^{-1}$				
(mole of urea)	3.33	2.46	5.54	0.14
(mole of hydrocarbon)	30.2	18.0	64.4	2.0
Δ S in cal mole $^{-1}$ $^{o}K^{-1}$				
(mole of urea)	0.0145	0.0107	0.0241	0.006
(mole of hydrocarbon)	0.131	0.078	0.280	0.085

Error in Δ H = ± 0.57 cal (mole urea) $^{-1}$.

Δ S = ± 0.0025 cal (mole urea) $^{-1}$ $^{o}K^{-1}$.

The entropy of each adduct was calculated at intervals of 10°K by assessing the area beneath the $^{Cp}/_{T}$: T curve (Tables 22 and 23).

The heat capacity below 12°K was estimated using the modified Debye relationship of Lord, Ahlberg and Andrews (1937).

$$Cv = 6 \; R \; D(x) \qquad .....(6.3.)$$

where Cv is the heat capacity at constant volume, which approximates to Cp, the heat capacity at constant pressure, R is the gas constant and D(x) is the Debye function.

Hence the values of the modified Debye characteristic temperature, Θ , were calculated from the tables and are listed for each adduct in Table 21. The presence of the low temperature anomaly complicated this procedure and the calculations were based on the experimental values below 15°K. The non-rigorous relationship used to assess the heat capacity in this region, no doubt, gives a subsequntly poor estimation of the entropy in this region. However, the contribution to the total entropy at room temperature from the region below 10°K is about 0.5%, and consequently even an error of 20% in the Debye extrapolation would introduce a negligible error in the entropy at room temperature.

TABLE 21. THE MODIFIED DEBYE CHARACTERISTIC TEMPERATURE, Θ , FOR THE ADDUCT STUDIES.

Adduct	Θ
urea -n- undecane	140
urea -1- decene	140
urea -1- hexadecene	147
urea -1- eicosene	150

TABLE 22. ENTROPY ($S_T - S_0$) OF UREA - N-UNDECANE IN CAL. MOLE $^{-1}$ (UREA) $^{\circ}K^{-1}$.

1 cal. = 4·1840 Joules. 0 °C = 273·15 °K

Temp. °K	$S_T - S_0$	Temp. °K	$S_T - S_0$
0	0.000	170	19.52
10	0.112	180	20.62
20	0.796	190	21.70
30	1.098	200	22.78
40	2.370	210	23.84
50	3.763	220	24.90
60	5.203	230	25.95
70	6.450	240	26.99
80	8.077	250	28.03
90	9.476	260	29.07
100	10.83	270	30.10
110	12.17	273.15	30.42
120	13.53	280	31.12
130	14.90	290	32.15
140	16.09	298.15	32.99
150	17.26	300	33.18
160	18.40		

TABLE 23. ENTROPY ($S_T - S_0$) OF UREA - 1-ALKENE ADDUCTS IN CAL. MOLE $^{-1}$ (UREA) $^{\circ}K^{-1}$.

1 Cal. = 4·1840 Joules. 0 °C = 273·15 °K

T °K	Decene	Hexadecene	Eicosene
0	0·000	0·000	0·000
10	0·112	0·096	0·092
20	0·729	0·668	0·646
30	1·754	1·637	1·612
40	3·064	2·874	2·838
50	4·500	4·247	4·203
60	6·017	5·618	5·637
70	7·549	7·130	7·082
80	9·029	8·558	8·500
90	10·48	9·956	9·875
100	11·88	11·31	11·22
110	13·25	12·63	12·53
120	14·58	13·92	13·80
130	15·89	15·18	15·04
140	17·15	16·47	16·25
150	18·37	17·81	17·45
160	19·56	18·97	18·70
170	20·73	20·11	19·83
180	21·88	21·23	20·94
190	23·01	22·33	22·04
200	24·12	23·42	23·12

TABLE23. (Continued).

T °K	Decene	Hexadecene	Eicosene
210	24•12	24•50	24•19
220	26•32	25•57	25•25
230	27•41	26•63	26•30
240	28•49	27•70	27•35
250	29•56	28•75	28•39
260	30•64	29•79	29•42
270	31•72	30•83	30•46
273•15	32•06	31•15	30•78
280	32•80	31•86	31•50
290	33•87	32•90	32•52
298•15	34•74	33•74	33•36
300	34•93	33•92	33•55

CHAPTER 7. DISCUSSION OF THE ANOMALIES FOUND IN THE HEAT CAPACITIES OF THE UREA ADDUCTS STUDIED

(A) THE LOW TEMPERATURE ANOMALY

A typical example of this anomaly is illustrated in Fig. 26. The anomaly is in the form of a discontinuity ~~in~~ of the slope of the heat capacity against temperature curve.

The inadequacy of the measurements in this temperature region (~ 16°K) inhibits any conclusions as to the source of the anomaly. The apparent independence of the guest molecules would suggest that the origin of the anomaly lay with the host lattice. Any major change in the crystal structure of the lattice would be unlikely.

Pemberton (1966) postulated as a possible mechanism the onset of low frequency librational twisting of the urea molecules parallel to the lattice channels through flexing of the hydrogen bonds. In view of the scanty evidence available any further comment would perhaps be unwise.

B. THE HIGH TEMPERATURE ANOMALY

Pemberton (1966) put forward two suggestions as to the origin of the high temperature anomaly, 225 - 235 $^{\circ}$K,

(a) that it was due to the fusion of an aqueous solution of urea.

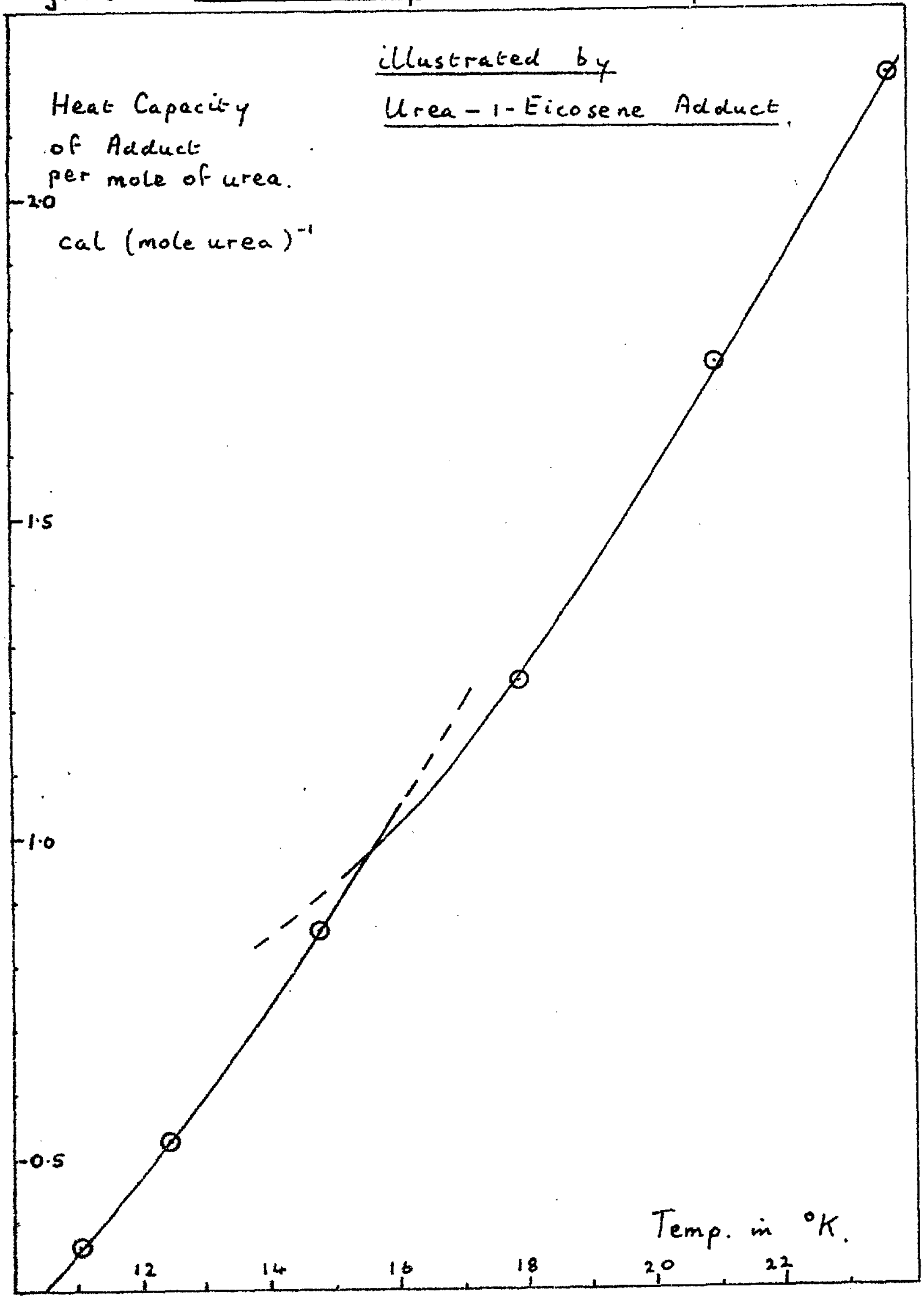
(b) that it was due to a slight expansion of the lattice permitting the guest molecules to rotate with greater freedom.

The first suggestion is based on the evidence of the heat capacity of pure urea (Ruehrwein and Huffman 1946). A similar region of excess heat absorption was observed in the heat capacity of pure urea at about 255 - 265 °K. Further evacuation failed to remove this anomaly, but on doubling the estimated weight of water in the calorimeter, the size of the irregularity was doubled. However, in the present study the excess heat was found at a much lower temperature, and in fact well below the eutectic point (-11.5 °C, ~ 262 °K) of the aqueous urea solution, (Chadwell and Politi 1938). It seems unlikely that the conditions in the calorimeter would cause such a significant modification to the properties of the aqueous urea solution.

The second suggestion was first put forward by Gilson and McDowell (1961) to explain the sudden drop in the second moment of the urea-d_4 - alkane adducts (Fig. 4). Such a change in the lattice and the consequent greater freedom of the guest molecules would not necessarily be associated with a large entropy change, as it is thought that the guest molecules already have considerable rotational freedom at these temperatures (Chapter 1. D.).

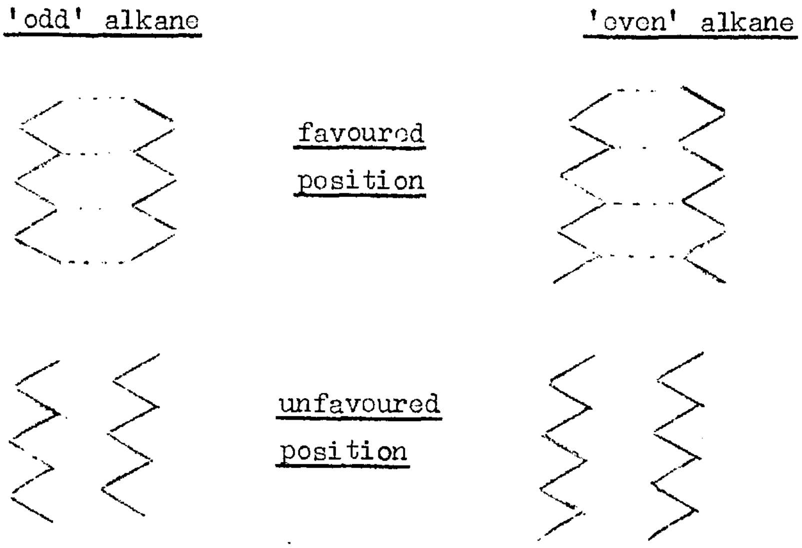
The comparatively low value for the heat of transition of the urea - 1-eicosene adduct is consistent with Gilson and McDowell's explanation in the light of a suggestion that will be made later in this chapter concerning greater restriction of the 1-eicosene guest molecules.

Fig. 26 The Low Temperature Anomaly.



C. THE MAJOR ANOMALY IN THE HEAT CAPACITY OF THE UREA - N- UNDECANE

In view of the anomalies observed in the heat capacities of the urea -n- alkane adducts (Chapter 1, D (ii)), the presence of a similar anomaly in the urea -n- undecane adduct was to be expected. It would also be expected that the properties of this adduct would be similar to those of the other 'odd' alkane adduct studied, n-pentadecane. Here 'odd' refers to the number of carbon atoms in the chain. Indeed the transition temperatures of both these 'odd' alkane adducts are relatively higher than those of the 'even' alkane adducts (Fig. 27). This arises from the relatively larger barrier to rotation experienced by an 'odd' alkane guest molecule due to its interaction with its neighbours in adjacent channels. This is demonstrated in the illustrations below, remembering that the alkane molecules are sufficiently far apart for the attractive forces to dominate.



The interactions in the unfavoured position are similar, whilst in the favoured position there are $^{n+1}/_2$ large carbon-carbon interactions with the 'odd' alkane, as opposed to $^{n}/_2$ with the 'even' alkane system. n refers to the number of carbon atoms in the chain. The greater difference between the favoured and the unfavoured positions of the 'odd' alkanes leads to a larger lateral potential barrier, i.e., a greater lateral interaction. The theory of Parsonage and Pemberton (1967) predicts an approximately linear relationship between the transition temperature, Tt, and the lateral interaction parameter J'.

The size of the heat of transition is largely controlled by the stronger longitudinal interactions, which are not expected to differ between 'even' and 'odd' alkanes in the channels. However, other factors are obviously involved as the heat of transition varies with the alkane chain length (Fig. 27). In view of the slightly greater rotational barriers of the 'odd' alkanes, it would be expected that the heats of transition would be correspondingly higher than those of the 'even' alkane adducts. This is true for the urea -n- undecane adduct, but not so for the urea -n- pentadecane adduct.

The anomalous contribution to the heat capacity, i.e. the configurational heat capacity, is plotted against temperature (Fig. 29). In addition the theoretically obtained values from the data of Parsonage and Pemberton (1967) are also presented (Fig. 28). The solution of the two-dimensional Ising lattice gives a heat capacity which exhibits a logarithmic relationship with $|T - Tc|$, where T is the temperature and Tc the critical or transition temperature.

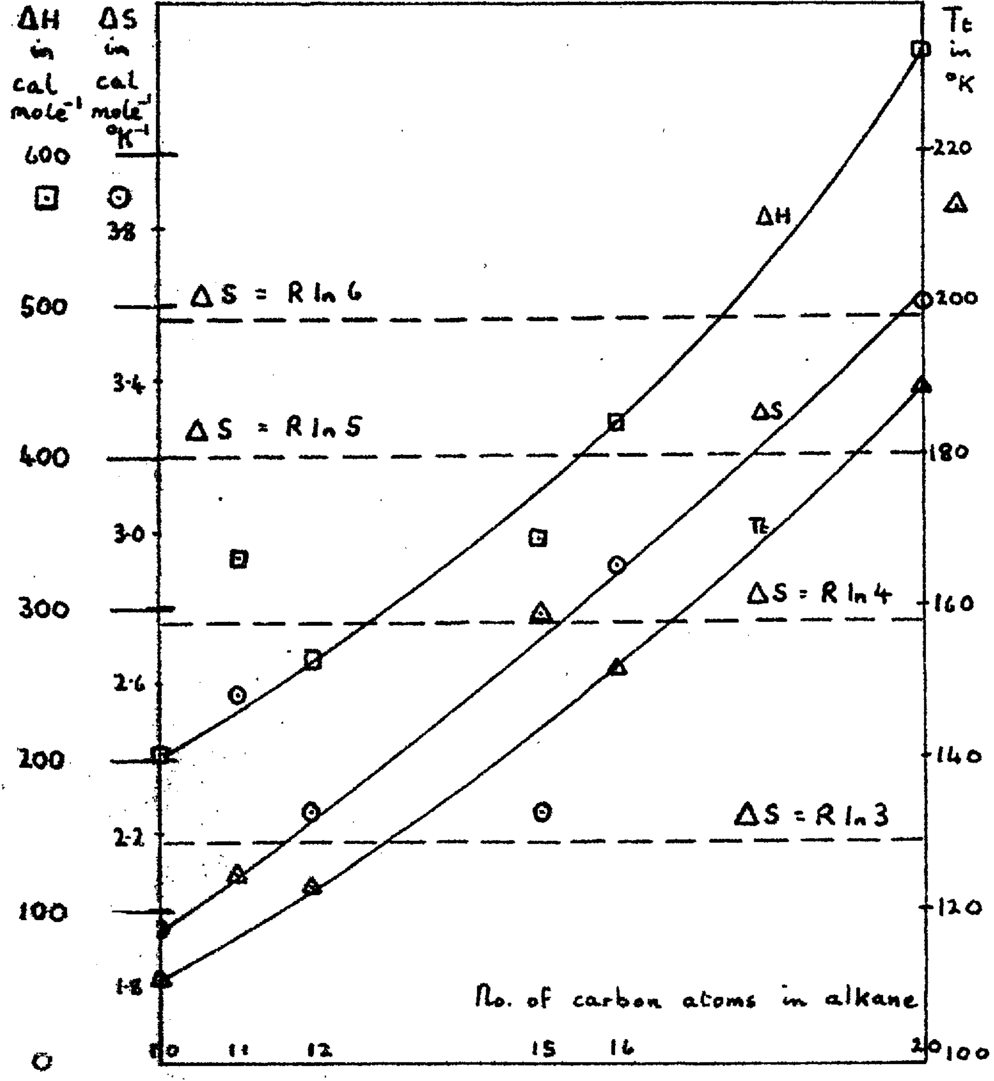
$$C \approx A \log(T - Tc) \qquad T > Tc \quad \ldots.7(1)$$

$$C \approx B \log(Tc - T) \qquad Tc > T \quad \ldots.7(2)$$

The plot of the configurational heat capacity, C, (or $\Delta Cp = Cp - Cp_0$, where Cp_0 is the smooth curve drawn to exclude the anomalous contribution) against $\log |T - Tc|$ (Fig. 30), shows that this relationship does not strictly apply in this case. Similar curves are drawn for the urea - alkene transitions (Figs. 31, 32, 33, 34).

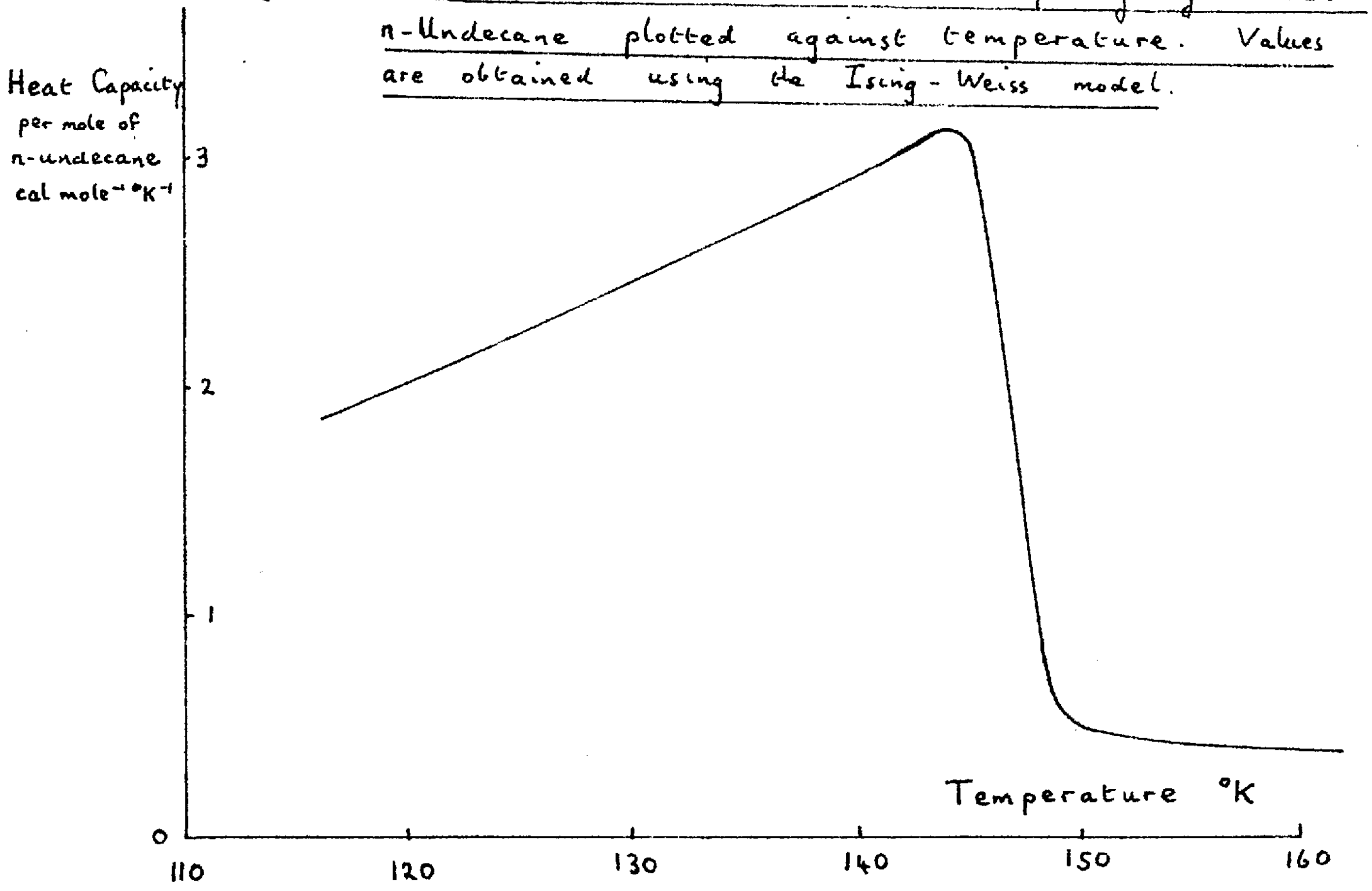
The Ising - Weiss model chosen by Parsonage and Pemberton (1967) to represent these urea - alkane systems, and the urea - n-undecane system in particular, predicts a major change in the order parameter and a maximum in the configurational heat capacity at a somewhat higher temperature than that observed experimentally. This can however be explained by appreciating that the actual nature of the lattice makes it impossible for all the molecules to be in their most favoured or unfavoured state simultaneously. In consequence, an exact calculation, bearing in mind the hexagonal nature of the lattice, would present a smaller lateral interaction and as a result the theoretically predicted transition temperature would be lower.

Fig. 27 The Transition Temperatures, and the Heats and Entropies (per mole of alkane) of Transition of the Urea-n-Alkane adducts.



Full lines are drawn through the 'even' alkane adduct points only.

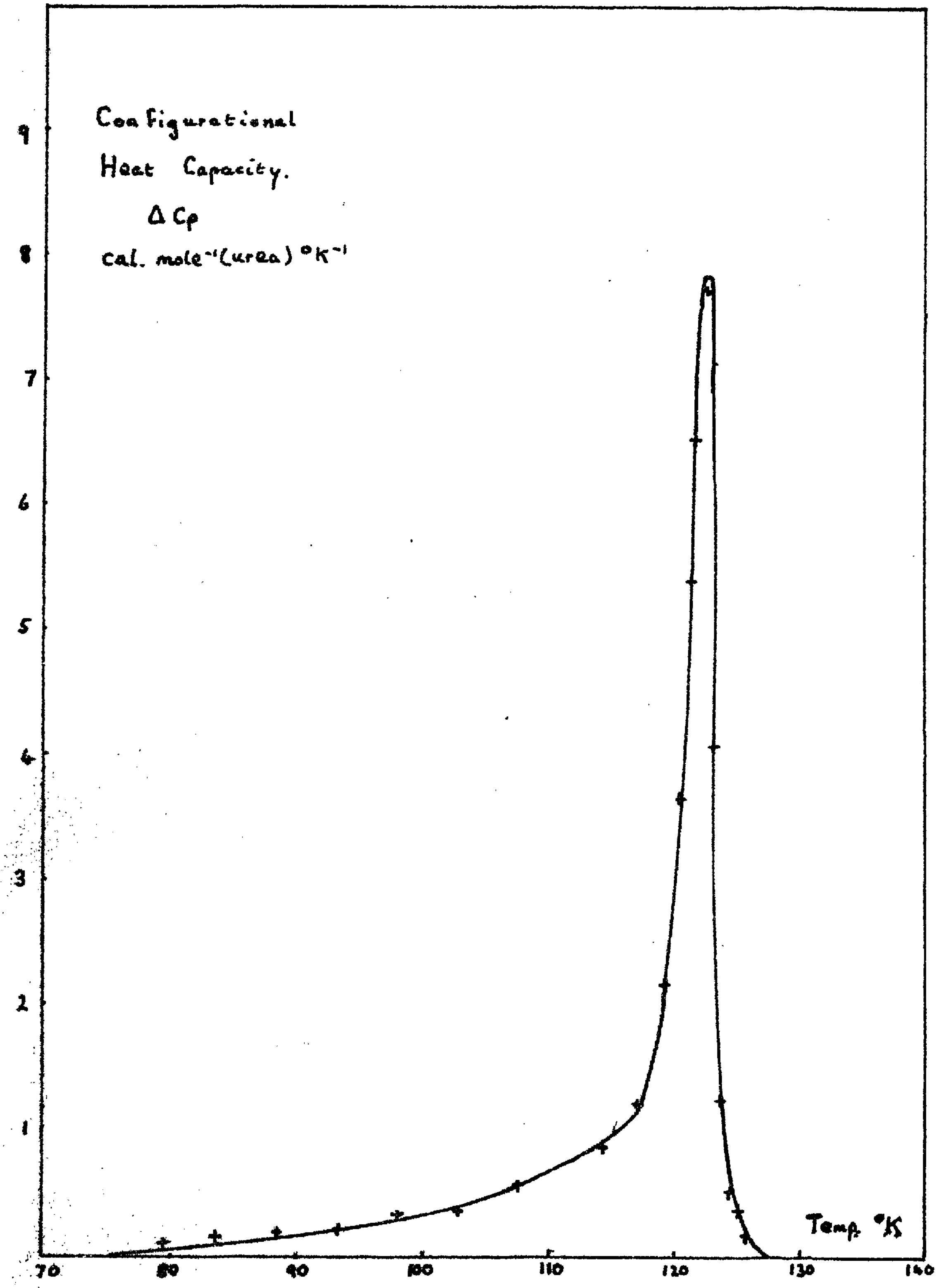
Fig. 28 Calculated values of the Heat Capacity of Urea-n-Undecane plotted against temperature. Values are obtained using the Ising-Weiss model.



NB. The shape of the curve is largely determined by the Weiss approximation employed.

Fig 28

Fig. 29 Urea - n-Undecane Adduct.



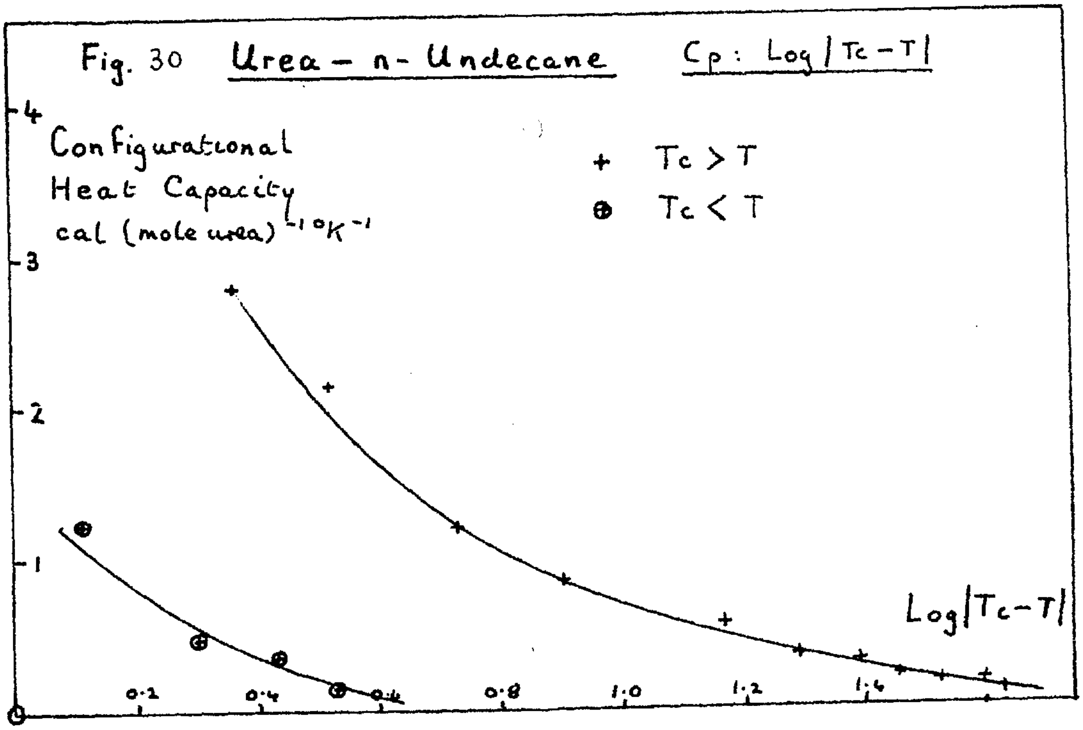


Fig. 30 Urea – n-Undecane Cp : Log|Tc − T|

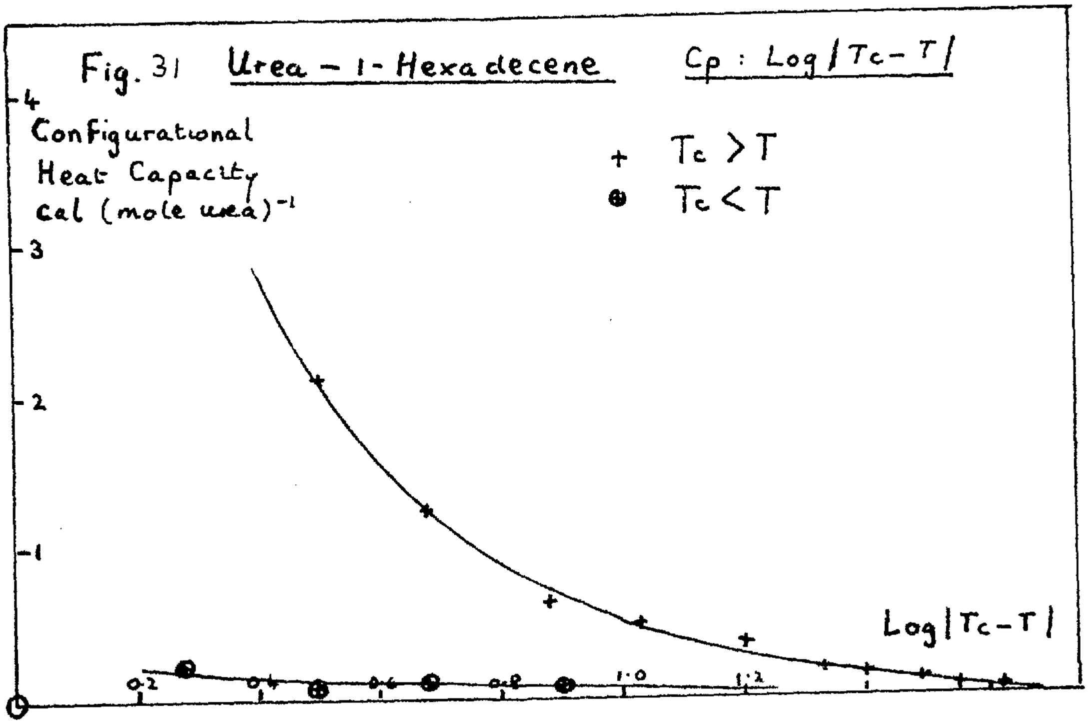


Fig. 31 Urea – 1-Hexadecene Cp : Log|Tc − T|

Fig. 32 Urea - 1-Hexadecene Adduct.

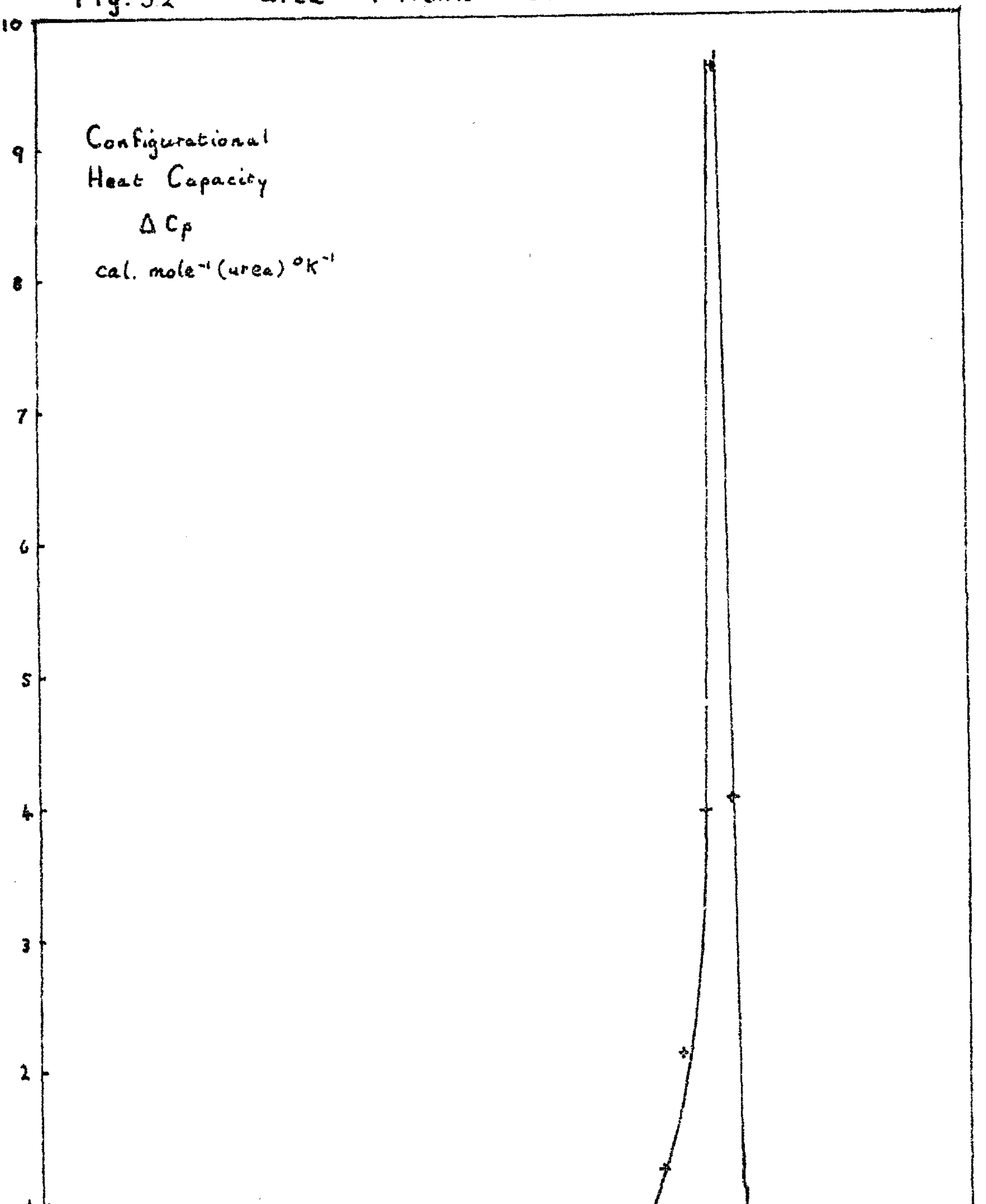


Fig. 33 Urea – n-1-Eicosene Configurational Heat Capacity (ΔC_p)

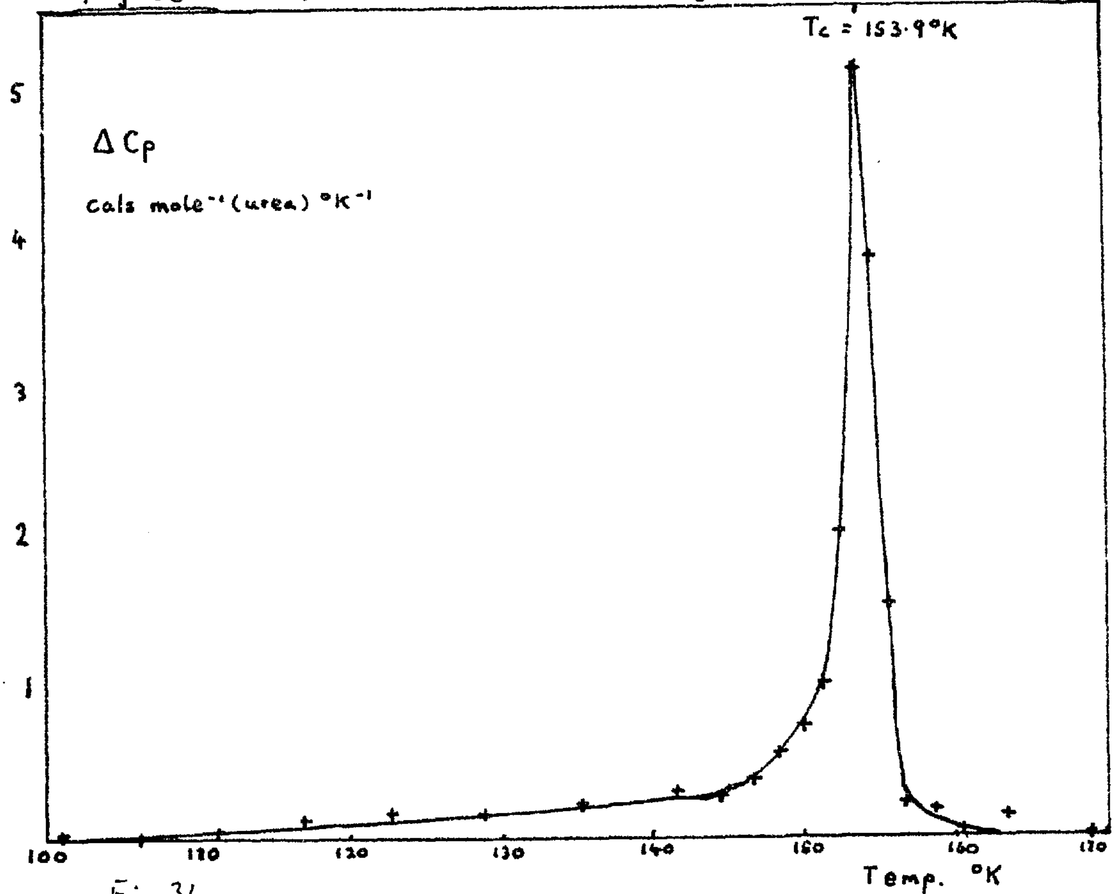
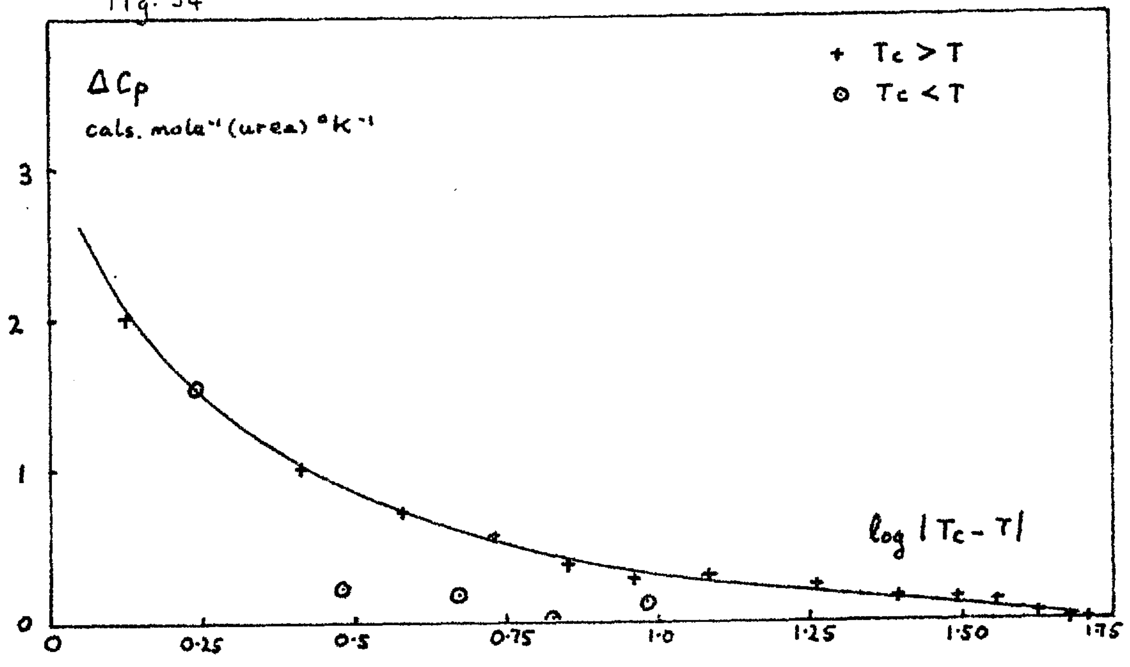


Fig. 34



D. THE MAJOR ANOMALIES IN THE HEAT CAPACITIES OF THE UREA - 1 - ALKENE ADDUCTS

(i) INTRODUCTION

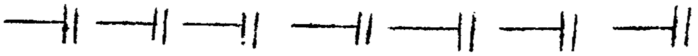
Following the studies of the urea -n- alkane adducts, similar investigations were undertaken on some urea -1- alkene adducts with a view to studying the effect of the different longitudinal interactions. Preliminary calculations suggested that the alkene molecules would have greater interactions with their neighbours in the same channel, with the result the rotational transitions would be expected to occur at somewhat higher temperatures than in the alkane adducts.

Experiment proved this to be wrong. The transition temperatures of the urea -1- hexadecene and 1- eicosene adducts were found to be respectively 11 °K and 35 °K lower than those of the corresponding urea - alkane adducts. No co-operative anomaly was found in the heat capacity of the urea - 1-decene adduct. A further complication arose in that the entropy of the anomaly in the urea -1- eicosene heat capacity was approximately half the value measured in the eicosane adduct, whereas the entropies of transition of the urea hexadecane and hexadecene adducts were similar.

A more searching treatment of the terminal interactions revealed that the presence of the one terminal group not only affected the longitudinal interactions, but also significantly modified the lateral interactions.

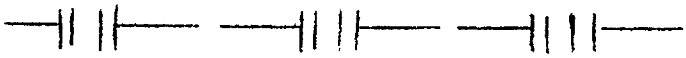
The effect of the possible arrangements of the alkene molecules in the channels was also considered. There are three possible arrangements.

(a) complete order (head - tail, head - tail).

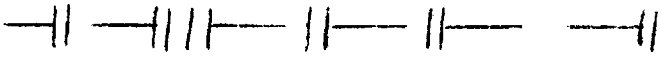


(– indicates terminal group is single bond, end;
⊣∥ indicates terminal group is double bond, end).

(b) complete order (- head, head - tail, tail -).



(c) complete disorder.



Later in this section, an attempt will be made to explain the different natures of these anomalies in the light of the effect of the terminal group interactions and the various arrangements of the molecules in the channels. The system will be represented by an Ising model, similar in many respects to that used for the urea alkane adducts, but with a few simplifications. Application of the Monte Carlo technique enables the order and the configurational heat capacity of the system to be calculated for different arrangements of the molecules in the channels.

(ii). TERMINAL GROUP INTERACTIONS

In the pure crystalline state of the alkanes and alkenes, the molecules are arranged with their chains parallel. This is also so in the urea hydrocarbon adducts, but in this case the lateral spacing of the hydrocarbon molecules is much greater, as it is controlled by the dimensions of the urea lattice.

In the solid pure hydrocarbon the terminal groups are spaced apart by the sum of their van der Waal's radii, i.e., ~4.0 Å in the case of ane, ane. The longitudinal spacing of the hydrocarbon molecules in the adducts is determined by both its strong lattice interactions and the interaction of the terminal groups. The closer approach of two terminal groups of hydrocarbon molecules in the urea lattice results in repulsion interaction of the hydrocarbon with the urea lattice, i.e., increased interaction per length of urea lattice. The terminal groups will therefore approach until their net repulsive force is balanced by the attraction of the urea lattice. By equating these forces the distance separating neighbouring hydrocarbon molecules may be calculated, and in addition the longitudinal rotational barriers may then be estimated.

The urea - hydrocarbon and hydrocarbon - hydrocarbon interactions were calculated using the Lennard - Jones 6 - 12 potential, summing the interactions from all pairs of atoms.

$$\varepsilon = 4\varepsilon^{*} \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \quad \ldots . \; 7(3)$$

or $$\varepsilon = -A r^{-6} + B r^{-12} \quad \ldots . \; 7(4)$$

where ε is the potential energy when the atoms are r apart, and σ and ε^{*} are parameters depending on the atoms involved.

The parameters used in this work are the same as those used by Parsonage and Pemberton (1967) and are listed in Table 24.

TABLE 24. INTERMOLECULAR FORCE PARAMETERS FOR THE INTERACTION OF VARIOUS PAIRS OF ATOMS. THE PARAMETERS REFER TO EQUATION 7(j)

	Set I		Set II	
	A	B	A	B
C—C	3.73×10^5	1.36×10^8	3.73×10^5	4.08×10^8
C—H	1.33×10^5	2.05×10^7	1.33×10^5	5.89×10^7
H—H	5.15×10^4	4.93×10^6	5.15×10^4	1.35×10^7
$N^{+0.2}$—C	3.63×10^5	1.61×10^8	3.63×10^5	4.83×10^8
$N^{+0.2}$—H	1.31×10^5	2.54×10^7	1.31×10^5	7.31×10^8
$O^{-0.4}$—C	3.79×10^5	2.03×10^8	3.79×10^5	6.07×10^8
$O^{-0.4}$—H	1.37×10^5	3.30×10^7	1.37×10^5	9.51×10^7
N—N	3.54×10^5	1.29×10^8	3.54×10^5	3.87×10^8
O—O	3.58×10^5	8.64×10^7	3.58×10^5	2.59×10^8

In the Set I the values of σ are $2^{-1/6}$ x (sum of the van der Waals radii of the atoms), and the values of ε^* were chosen so that the attractive part of the potential ($- 4\varepsilon^*\sigma^6/r^6$) conformed to the Slater – Kirkwood expression for the disperson interaction.

Parsonage and Pemberton compared the CH_4 – CH_4 potential energy of interaction curves obtained in this way, with those obtained by experimental second virial coefficient data, and in view of the poor agreement of the repulsive part of the potential, they adjusted the value of the repulsive parameter B., whilst retaining the same attractive parameter, A, so as to obtain reasonable agreement with the experimental data. This new set of parameters was called set II.

The urea–hydrocarbon interaction was investigated in this way, and it was found that the potential energy of interaction per Å of the urea channel was 3.40 and 2.60 Kcal mole $^{-1}$ using the parameters of set I and set II respectively.

In the consideration of the terminal interactions, z was taken as the distance along the central axis separating the terminal carbon atoms. In the calculations, z was varied by intervals of 0.05 Å between 3.50 and 4.20 Å. Orientations of the two terminal groups with respect to each other were considered from 0 to 360° at intervals of 15°. The phase of the orientation was considered zero when the main chains of the hydrocar~~ebs~~bons were coplanar and the terminal carbon atoms were on the same side of the central axis. Interactions were considered between the terminal methyl or methylene groups only.

The bond lengths were chosen as in the "Tables of Interatomic distances and configurations in molecules and ions", (special publication of the Chem. Soc. 1958), and are listed in Table 25. 109° 54' was taken as the angle between bonds at an sp^3 carbon atom, and 120° at an sp^2 carbon atom.

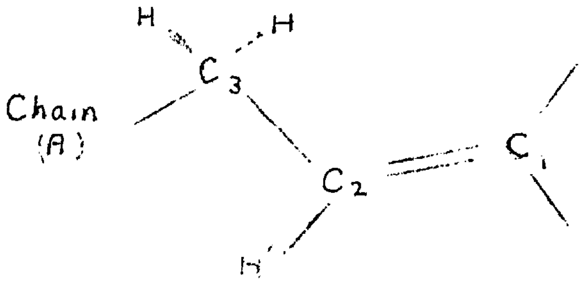
TABLE 25. INTERATOMIC DISTANCES USED IN CALCULATION OF THE POTENTIAL ENERGY OF TERMINAL INTERACTIONS.

Bond	Distance (Å)
$\overset{\diagdown}{\underset{\diagup}{-}}$ C – H	1.09
$=$ C – H	1.07
C $=$ C	1.34
$=$ C – C	1.53
– C – C	1.54

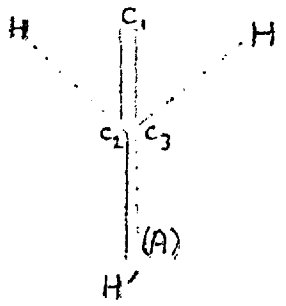
The nature of the hydrocarbon chain is such that the carbon atoms in the alkane molecule are coplanar, and the C — H bonds of each - CH_2 - group are at 54° 57' to this plane. The additional hydrogen atom at the terminal carbon atom is in the same plane as the main chain.

In the alkene molecule a difficulty arises in the nature of the arrangement of the double bond with respect to the main chain. **Far** infra-red spectroscopic investigations have led Radcliffe and Wood (1966) to report that in the allyl halides there exists two rotationally isomeric forms, but with the predominant form non- planar, i.e., the halide group is positioned so as to eclipse the double bond, c.f. (**b**). The proportion of the planar form varies from one halide to another, from 'small' in the chloride to 'virtually nil' in the iodide.

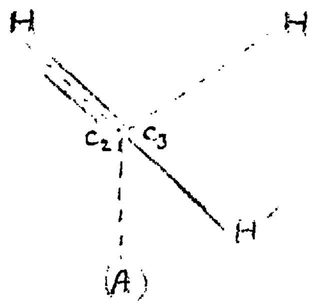
These two possible arrangements about the C_2 — C_3 bond are shown below (a) and (b).



(a)

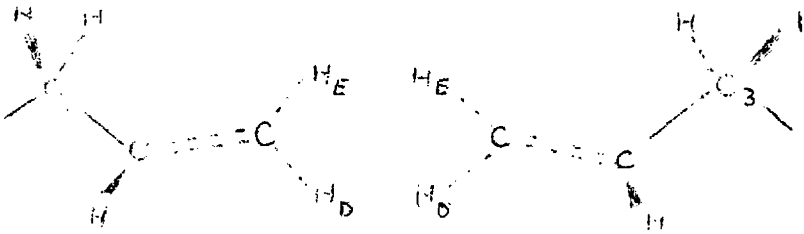


(b)

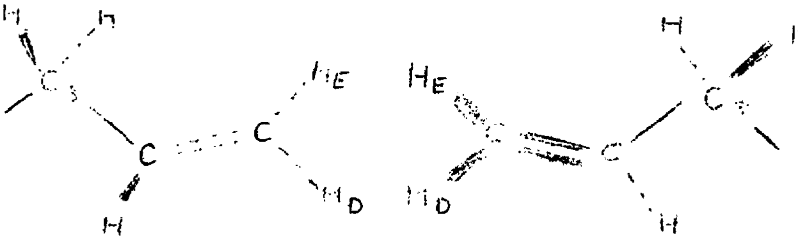


It is considered (Bright-Wilson, 1959, and Wood, 1967), that in the case of the 1-alkenes, i.e., when the halide is replaced by the hydrocarbon chain, the double bond is eclipsed by one of the bonds from the C_3 atom. A large distortion of the urea lattice would be necessary if the double bond was eclipsed by the main chain, and in consequence it is eclipsed by either of the C_3 – H bonds (b). The choice of which C_3 – H bond is eclipsed is unimportant when considering the ene – ane interactions, but leads to two possible types of ene – ene interactions.

(i) mirror image ene – ene interaction



(ii) non mirror image ene – ene interaction



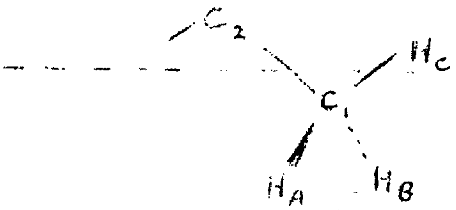
Dotted lines indicate double bond is eclipsed by C_3....H.
Bold lines indicate double bond is eclipsed by C_3 – H.

The barrier to internal rotation in propylene has been shown to be of the order of 2 Kcal mole $^{-1}$ (Calorimetric – 1950 cal mole $^{-1}$ – Kilpatrick and Pitzer, 1946; Spectroscopic – 1978 ± 17 cal mole $^{-1}$ – Lide and Mann 1957) and consequently the arrangements are not easily interconverted.

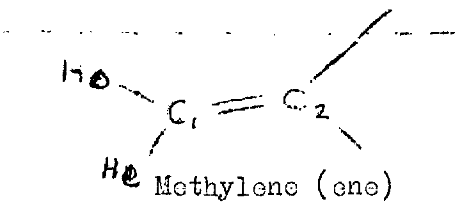
The hydrogen atom, He, bonded to the terminal carbon atom is ~1.8 Å from the central axis of the molecule as opposed to 1.4 Å, which is the distance from the axis of the hydrogen atoms of the main chain. A large repulsive interaction with the urea lattice, however, is not forthcoming, as in contrast with the hydrogens of the main chain, this hydrogen atom is directed near the oxygen atoms instead of the carbon and nitrogen atoms (see Fig. 5) on account of the non-planar nature of the molecule. Thus this hydrogen atom and the main chain may occupy their more favourable positions with respect to the urea lattice without any further distortions of the molecules. In addition there is no significant increase in the barrier opposing the rotation of the hydrocarbon molecules due to the urea lattice.

The interaction potential energy was assessed in this way for the terminal ane - ane interaction. This is displayed in Figs. 35, 36, for two important values of the phase angle. The slopes of the curves (the force of repulsion or attraction) were compared with the attractive force of the urea lattice. That spacing, z, where these two forces were equal and opposite was considered the equilibrium spacing. The value obtained was ~3.78 Å using the Set I parameters (the potential relating to the Set I parameter is referred to as Pot I on the graphs) and ~4.0 Å using the Set II parameters. Laves, Nicolaides, and Peng (1965) have reported a value of 3.74 Å from X-ray data. Clearly the Set II have given a far too repulsive potential. The interaction energy varies with the phase of the terminal groups. It is a maximum when the phase is zero and a minimum when the phase is 180° (Fig. 41).

The ane - ene and the ene - ene interactions exhibit different features on account of the terminal atoms in the ene group being located further away from the central axis. The calculation of the equilibrium spacings in the one - ene and ene - ane systems revealed a much closer spacing of the terminal groups (Figs. 37, 38, 39, 40). In consequence, the barriers to rotation at these equilibrium spacings are large compared with those of the ane - ane system. This is particularly so in the case of ene - ene. In ene - ane the barrier is reduced on account of the locus of the two hydrogens, which are the major contributors to the terminal interaction, H_c and H_d, describing circles of different radii centred at the longitudinal axis.



Methyl (ane)



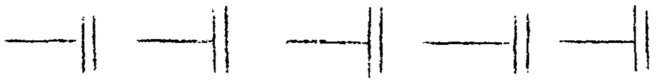
Methylene (ene)

The barriers to rotation at the calculated equilibrium spacing of ene - ane groups are > 500 cal and > 1000 cal using Set I and Set II parameters respectively (Figs. 45, 46), as compared with ~140 and ~100 cal mole $^{-1}$ (here per mole really refers to per Avagadro's number of interaction) in the ane - ane interactions. Clearly if this were the case the rotational transition temperatures would be much larger in the alkene adducts than the alkane adducts. Experiment has shown that this is not so and it must be concluded that these terminal interaction calculations do not give a complete understanding of the problem. The apparent discrepancy in the assessment of the spacings probably arises from the fact that the hydrocarbon molecules are packed in the channels at room temperature, which is far above the temperature of the transitions. The packing of rotating molecules will clearly be less close than those of stationary molecules. Until X-ray data on the lengths of the alkene molecules in the urea channels becomes available, no conclusion can be drawn as to the spacing of these groups. In subsequent calculations the spacing of the terminal carbon atoms for all three types of interactions is chosen to be 3.70 Å. Hence the longitudinal interaction parameter, J, is chosen as half the rotational energy barrier at this spacing using the Set I parameter in the potential energy equation. The values for J are 146, 125, and 433 cal mole $^{-1}$ for the ane - ane, ene - ane, and ene - ene interactions respectively.

The high value for the ene - ene parameter is probably an underestimate in reality on account of the close packing of these groups in the actual crystals. The size of the rotational barrier is shown in Figs. 43, 44. If the molecules ordered in the channel head - head, tail - tail

it is feasible that they would commence rotation in pairs, the ene - ene interactions locking the two molecules together. Such a rotational transition would have an entropy value of half that which would be expected if the molecules were rotating freely with respect to each other. Such a low value for the entropy was found to be so in the rotational transition of the urea - 1- eicosene adduct and it is therefore considered that the eicosene molecules are arranged in this way. If this were so the eicosene molecule would behave as a C_{40} molecule, i.e., the lateral interactions and in consequence the transition temperature would be approximately doubled. However, Figs. 43, 44, show that the two molecules would not necessarily be locked so as to be coplanar, in fact the most energetically favourable arrangements would be for the pair or molecules to be locked so that the planes of their main chains were at angles to each other of 60° or 20° depending whether the ene - ene interaction was of the mirror image or non-mirror image type respectively. Such an arrangement would result in a greatly reduced lateral interaction and hence a much lower transition temperature.

The nature of the rotational transition in the Hexadecene and 1-decene adducts can also be explained by the arrangement of the molecules in the channels. The broad unco-operative nature of the decene anomaly would perhaps indicate that the decene molecules have a variety of possible environments, i.e., they are in a disordered arrangement in the channels. The co-operative anomaly of the urea - 1-hexadecene adduct would similarly suggest that the arrangement of the molecules was ordered, this time with all ene - ane longitudinal interactions, i.e.,



The temperature of the transition is less than in the urea - hexadecane adduct, but this probably stems from either a smaller longitudinal interaction between neighbouring molecules in the channels or from a reduced lateral interaction arising in a similar way to that suggested for the eicosene molecule

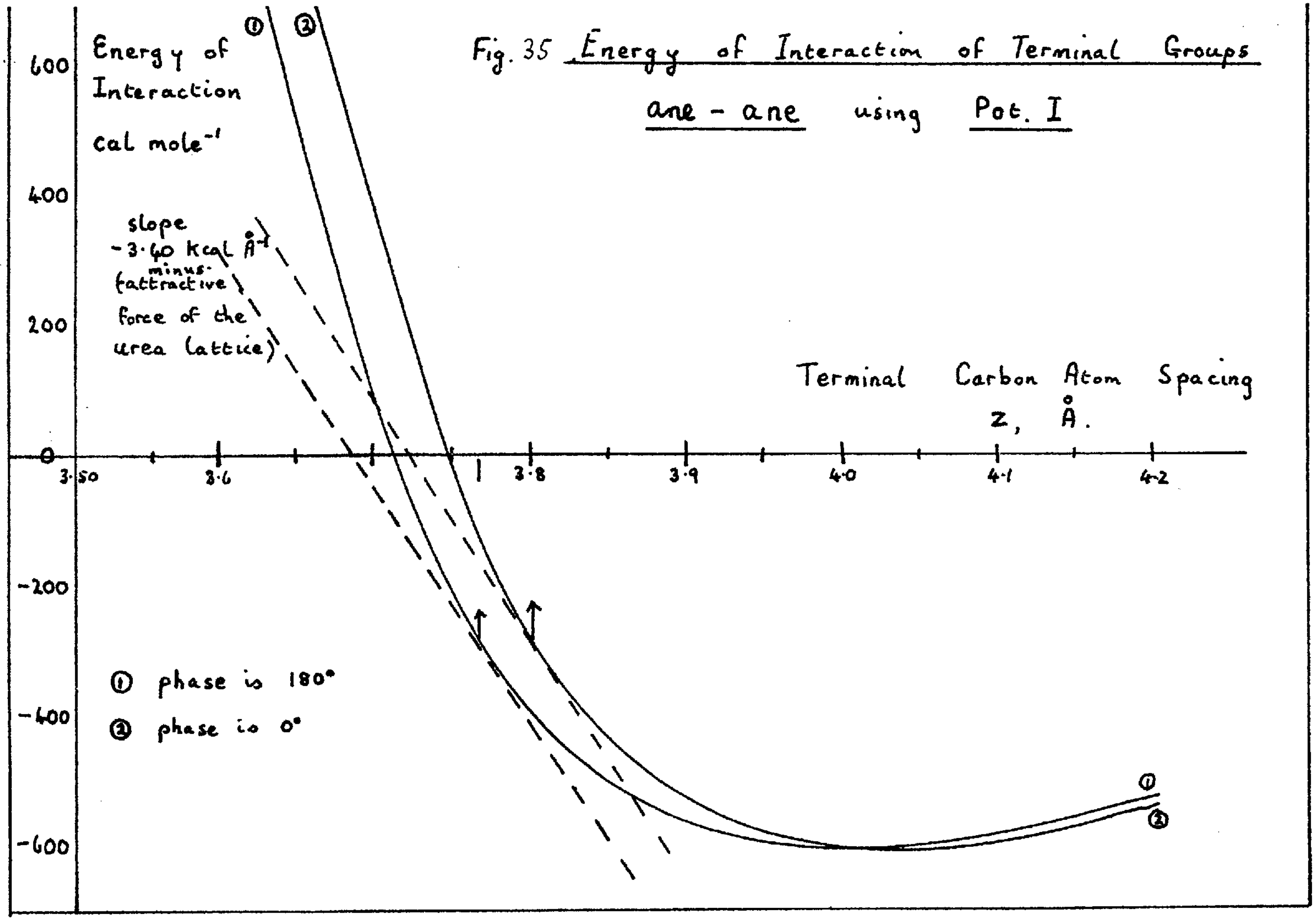


Fig. 35 Energy of Interaction of Terminal Groups ane - ane using Pot. I

Fig. 35

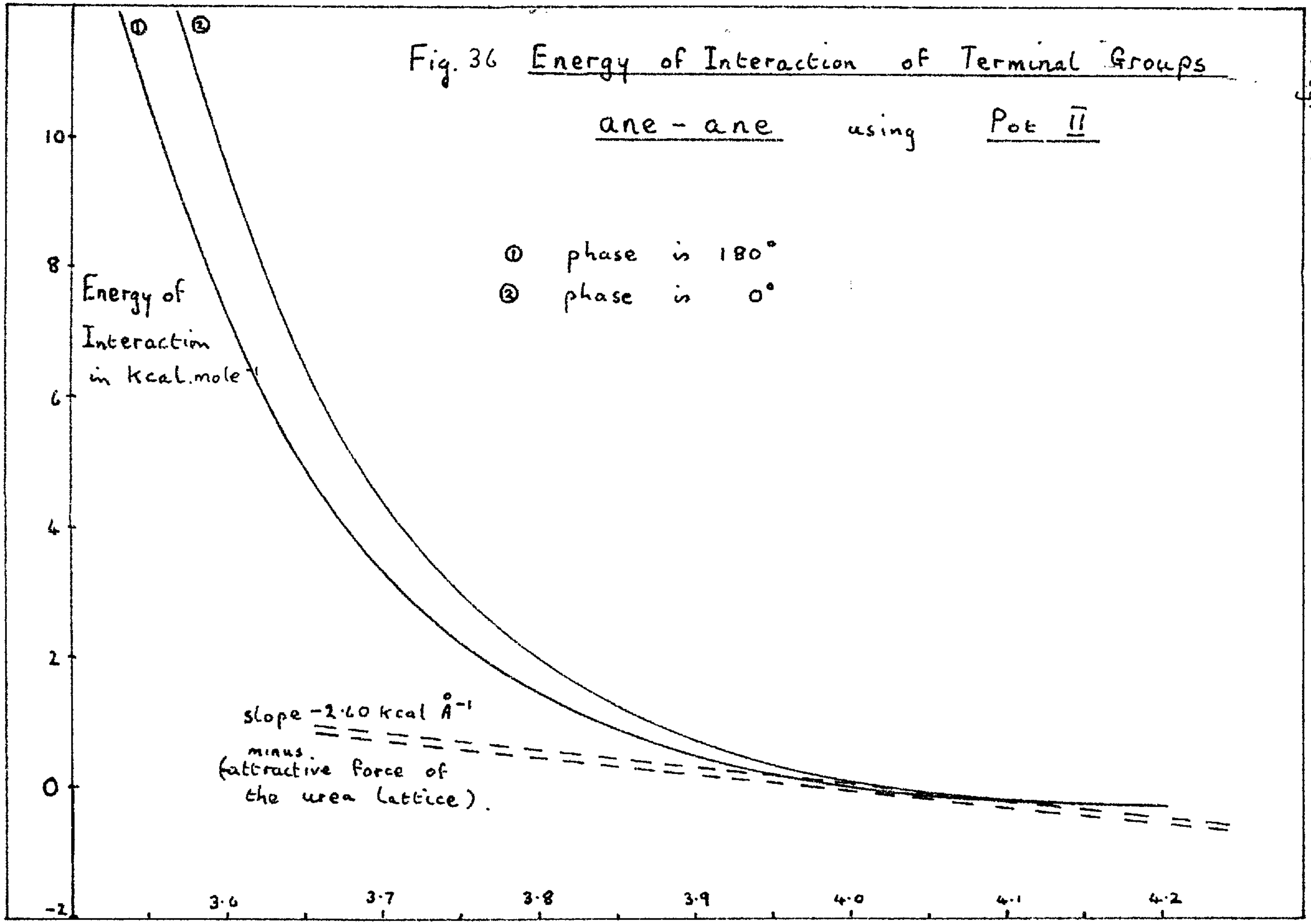


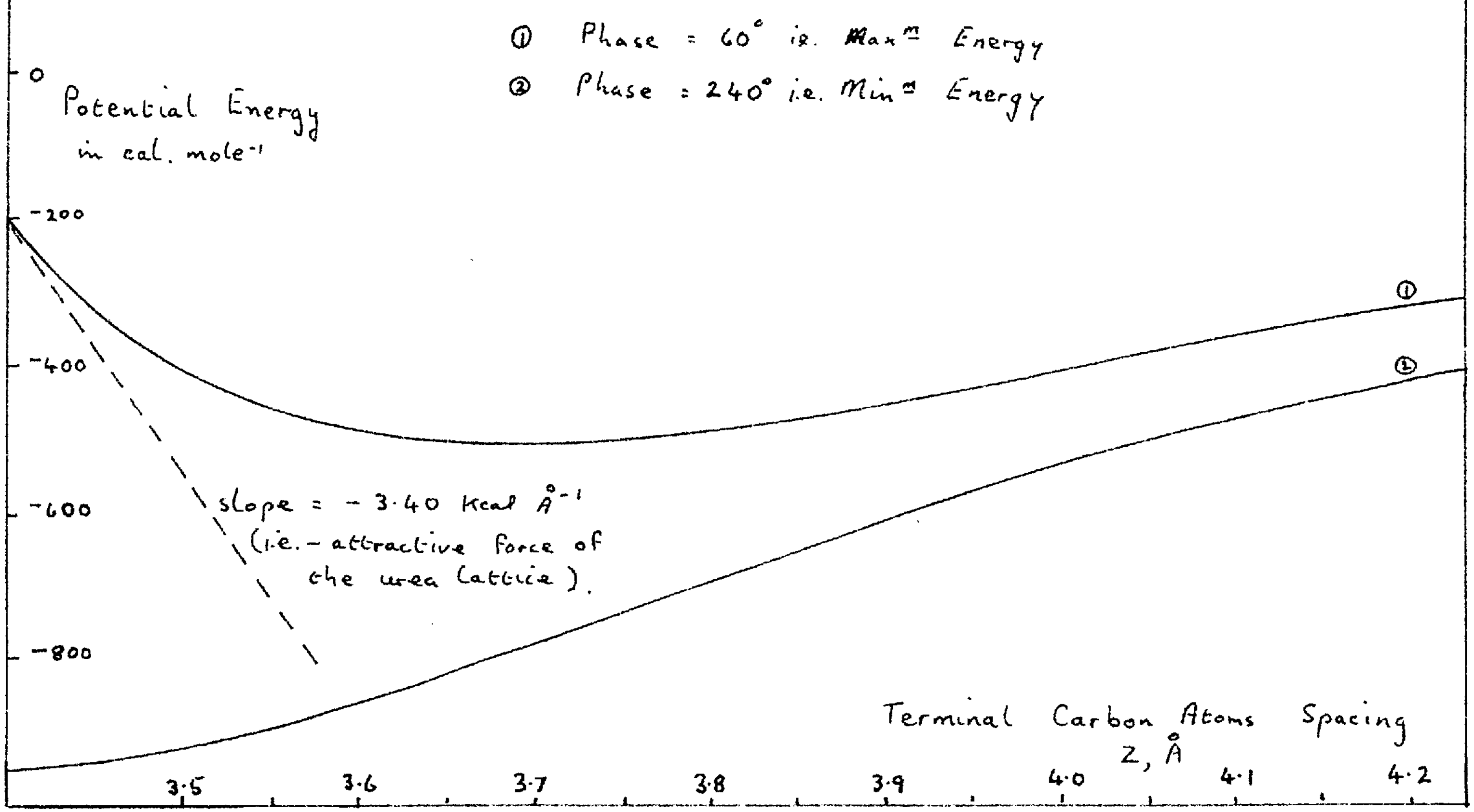
Fig. 36 Energy of Interaction of Terminal Groups ane - ane using Pot II

Fig. 36.

Fig. 37.

Fig. 37 Potential Energy of Terminal Group Interaction

ene - ane using Pot I



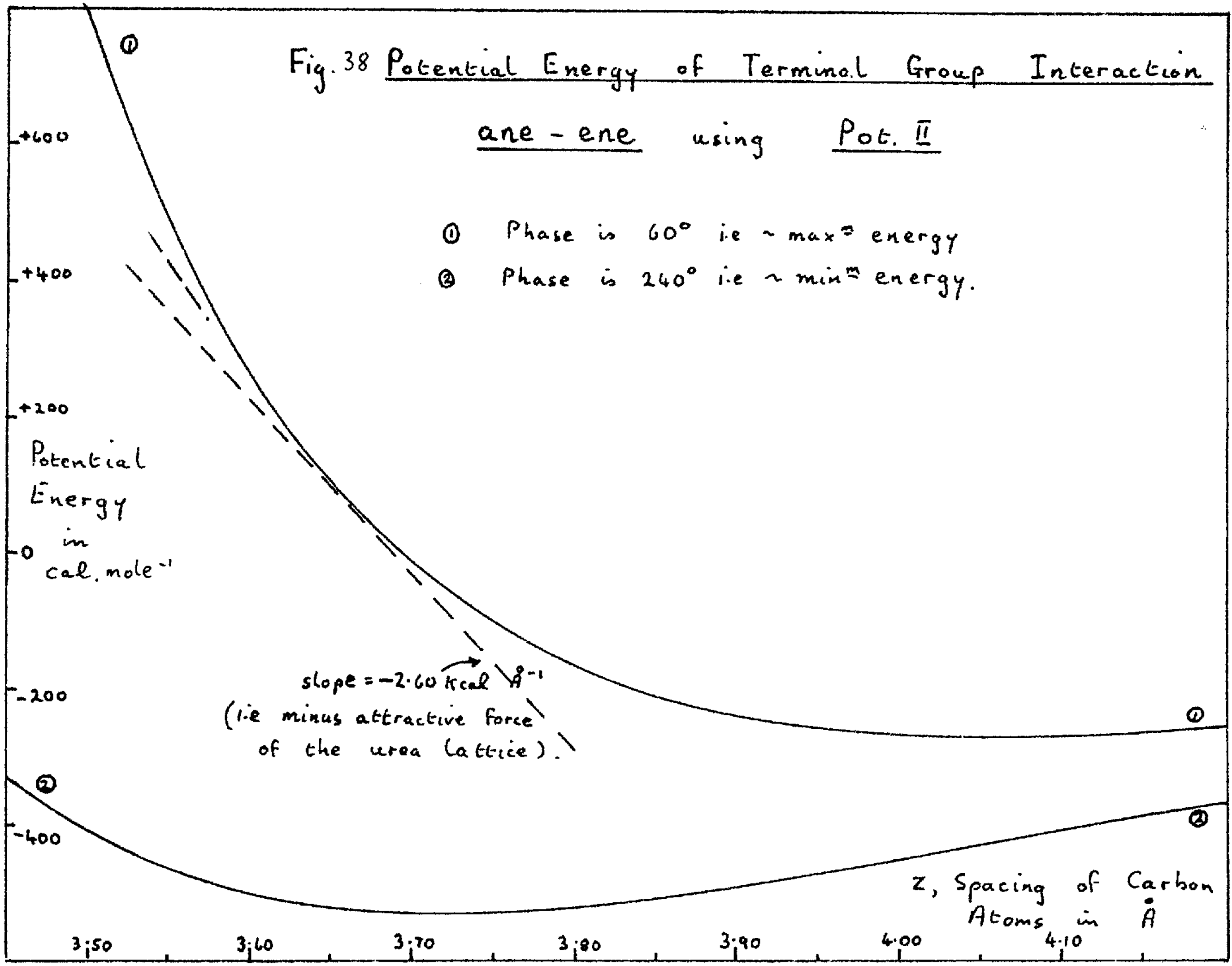


Fig. 38 Potential Energy of Terminal Group Interaction ane - ene using Pot. II

Fig. 38.

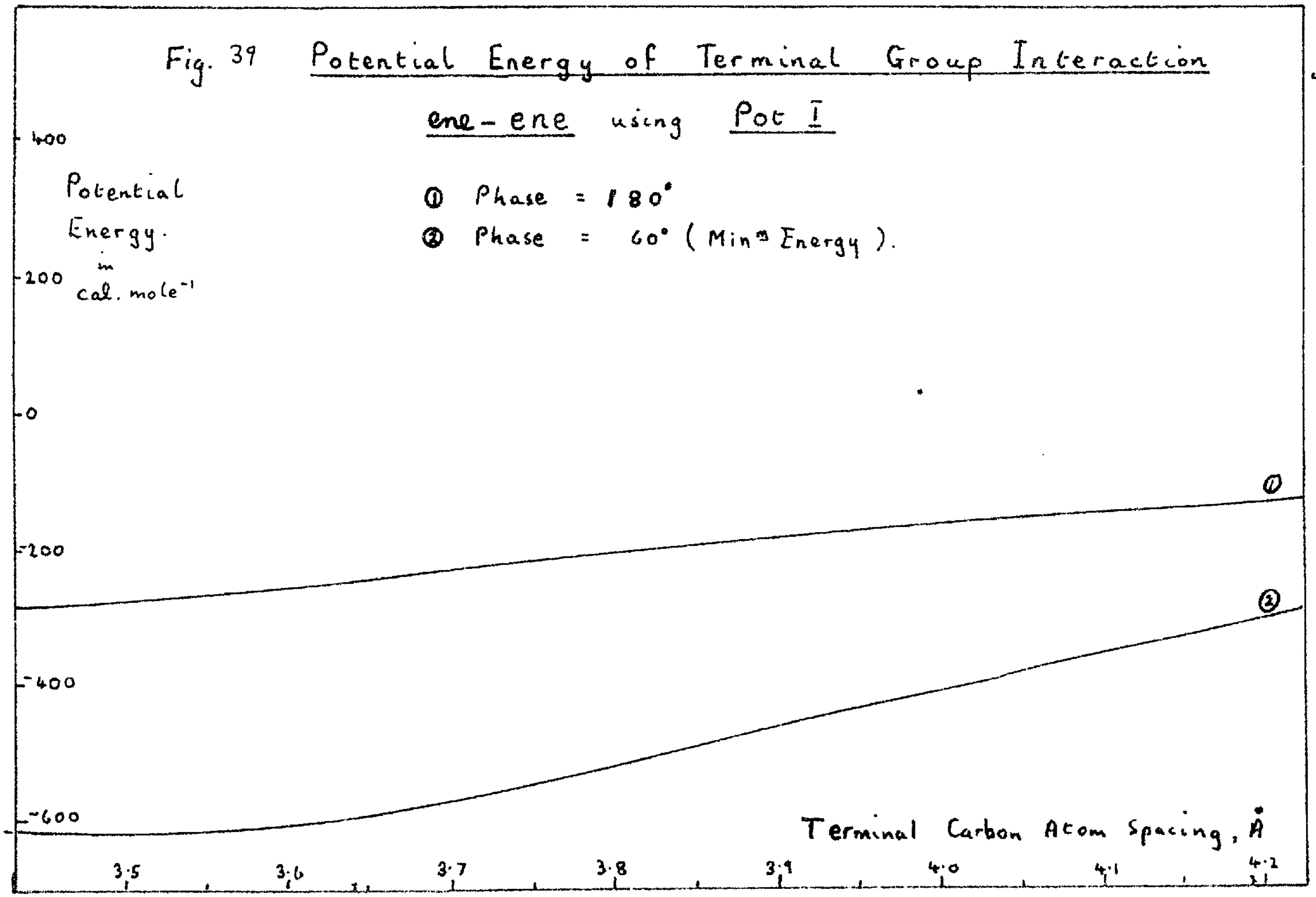


Fig. 39 Potential Energy of Terminal Group Interaction ene-ene using Pot I

Fig. 39.

Fig. 40 Potential Energy of Terminal Group Interaction

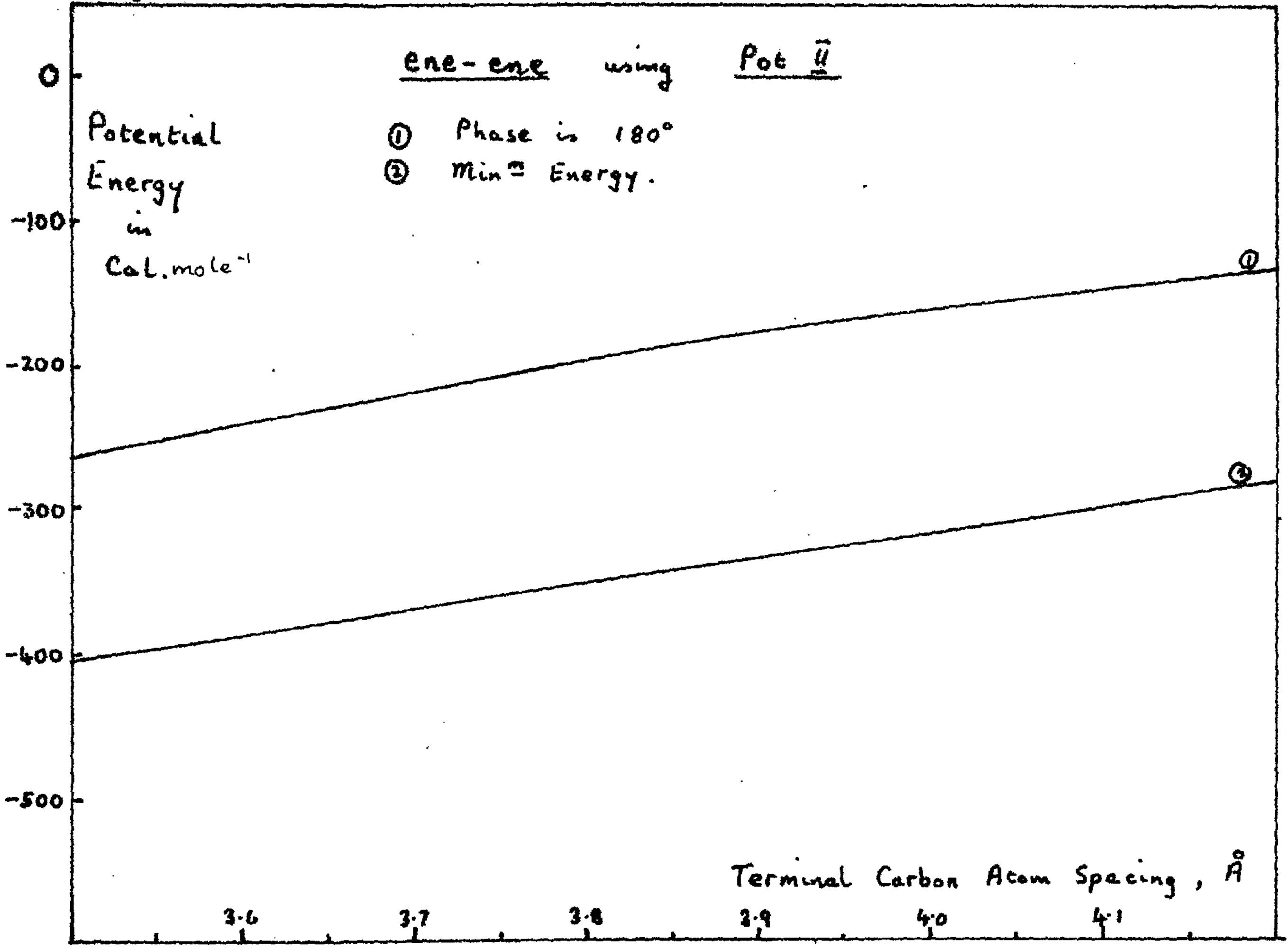


Fig. 40

Fig

Fig. 41 Potential Energy of Interaction of Terminal Groups for different orientations

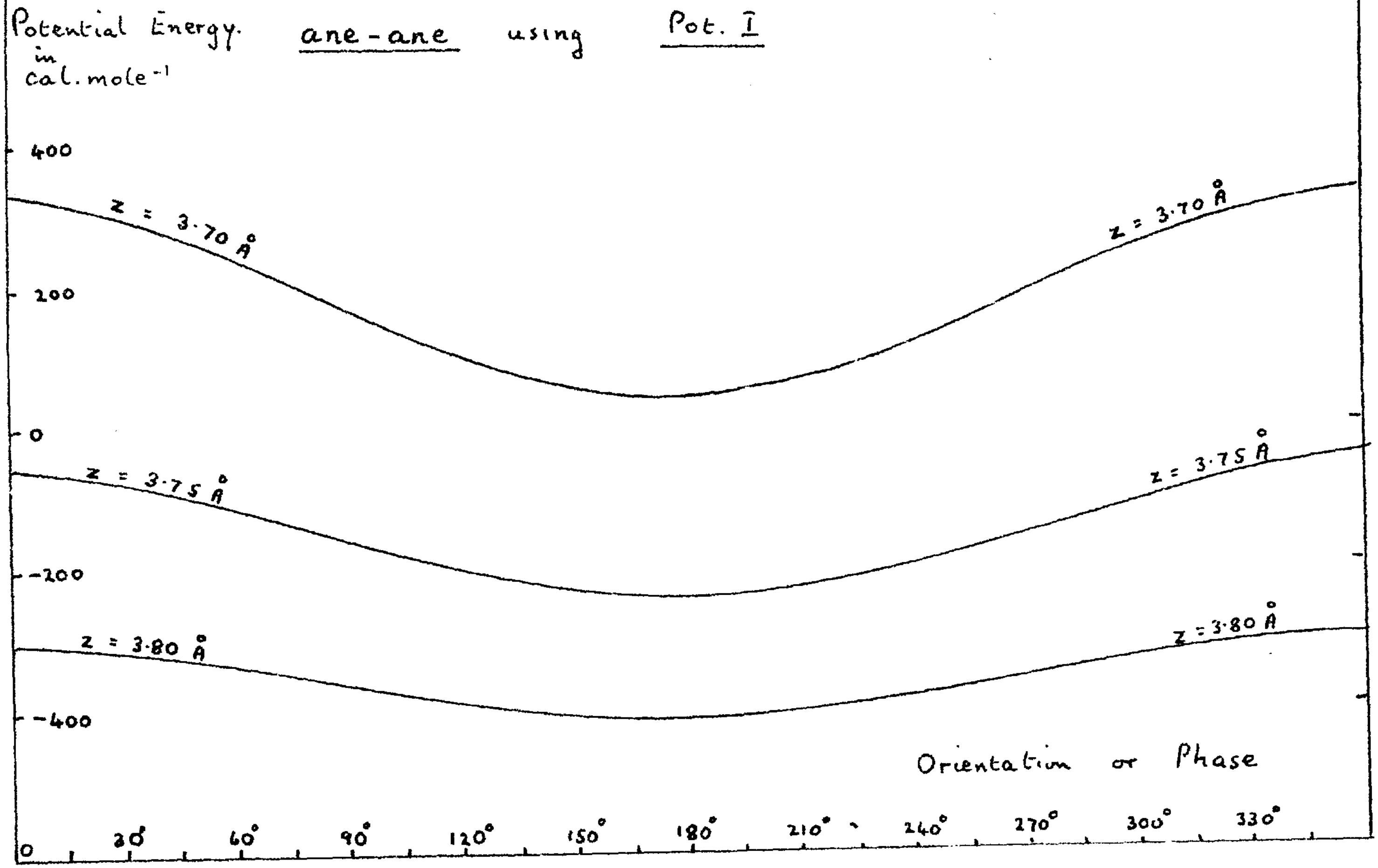


Fig. 41

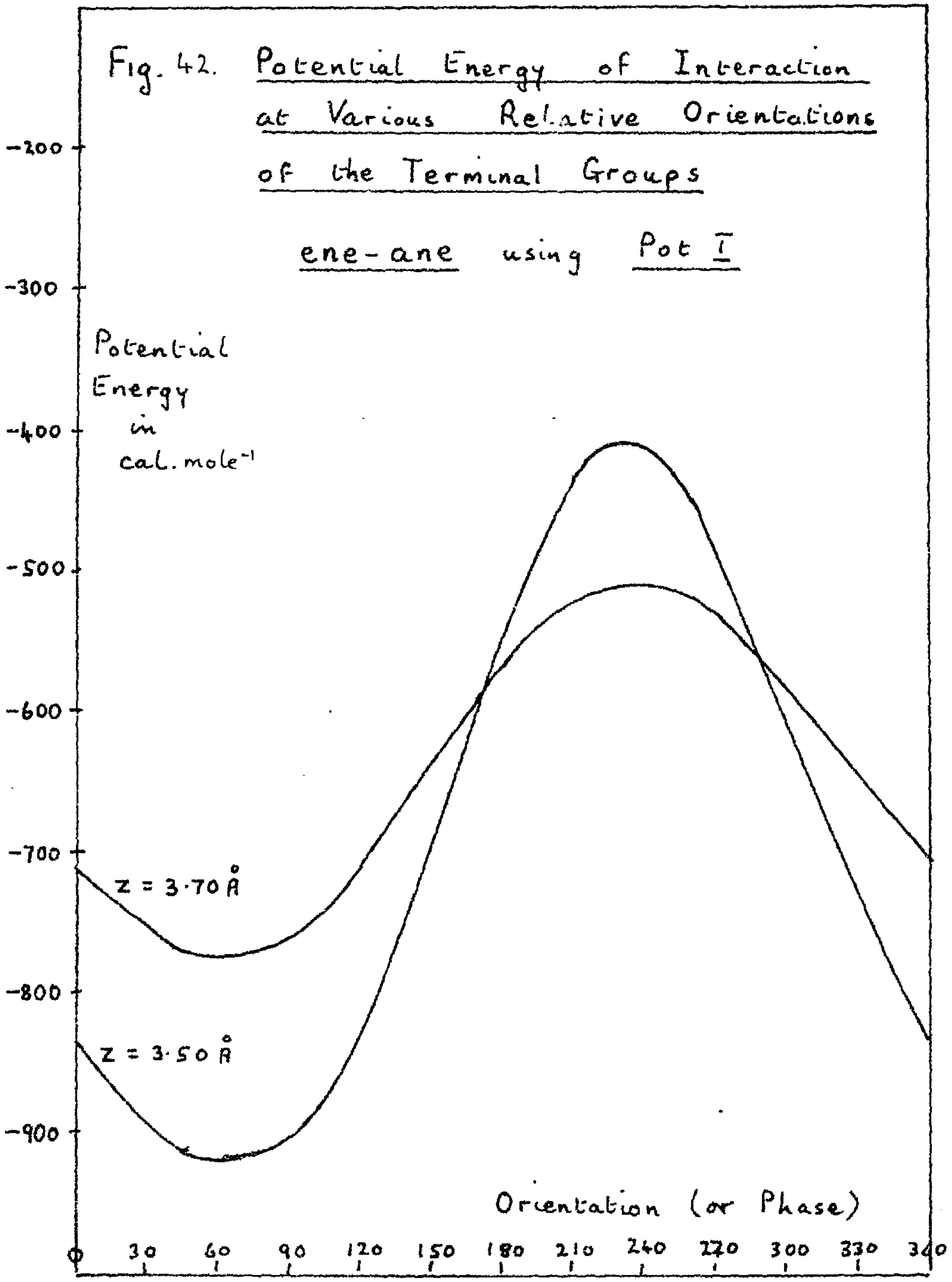


Fig. 42. Potential Energy of Interaction at Various Relative Orientations of the Terminal Groups

ene-ane using Pot I

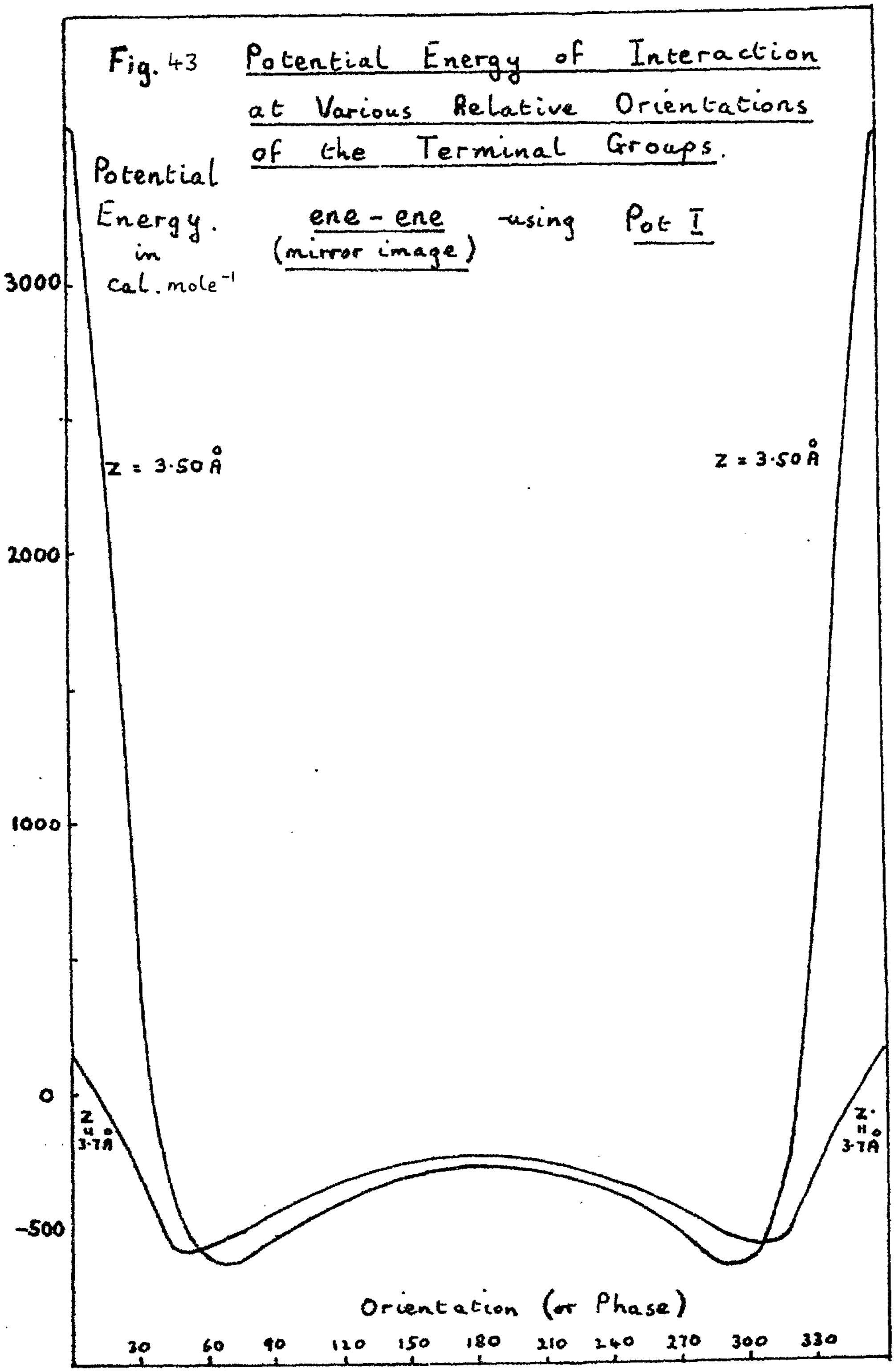


Fig. 43 Potential Energy of Interaction at Various Relative Orientations of the Terminal Groups.

ene - ene (mirror image) using Pot I

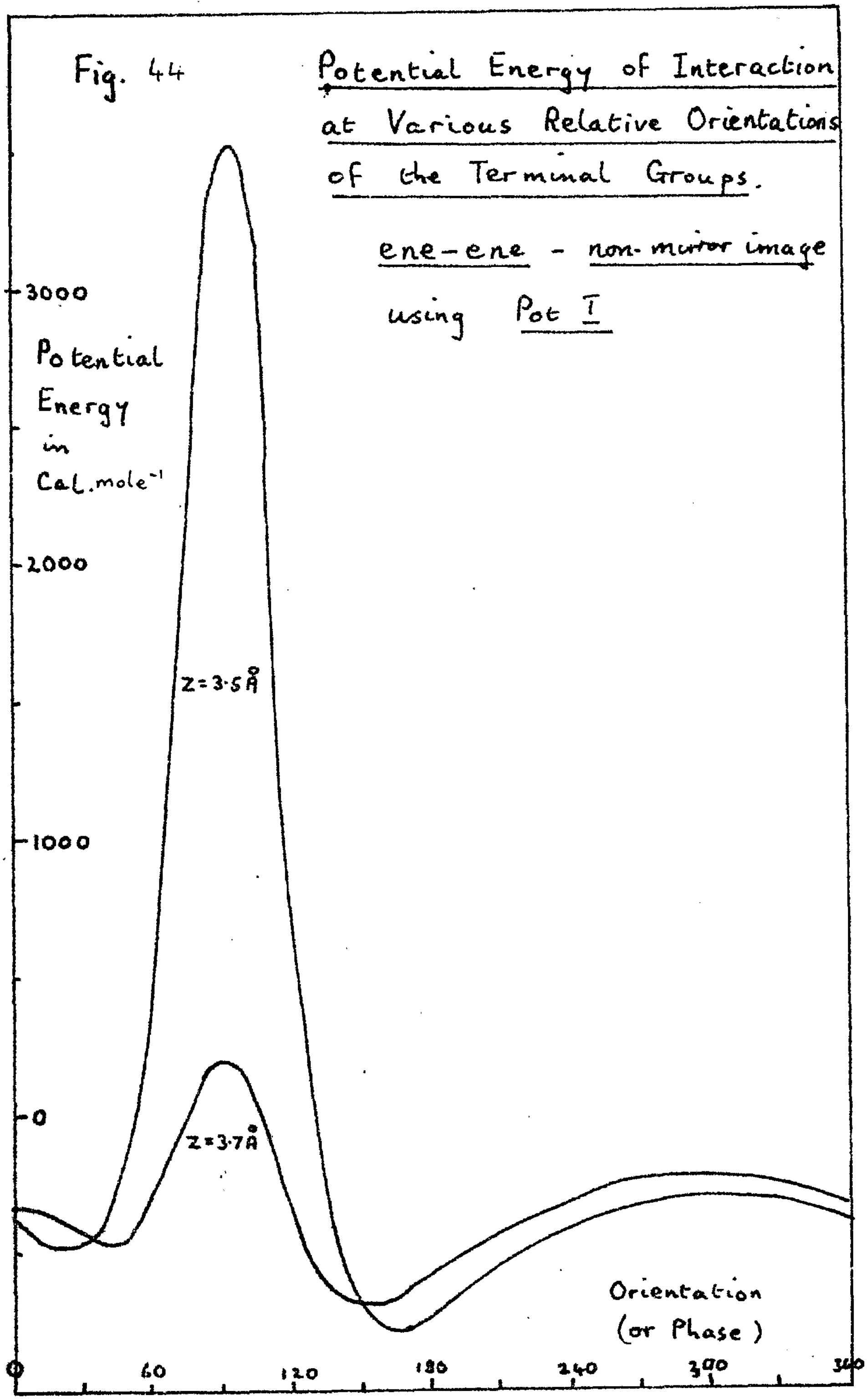
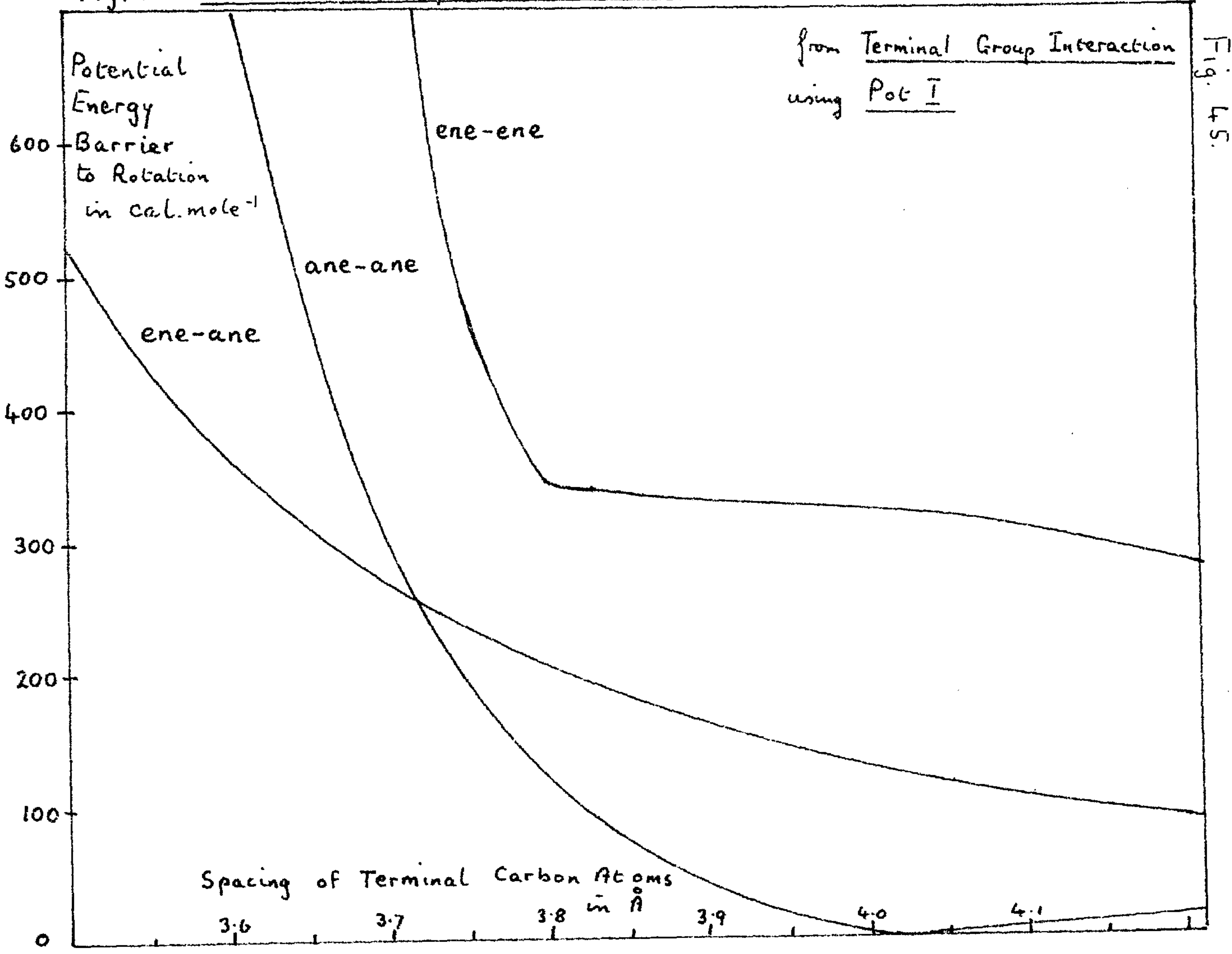


Fig. 44 Potential Energy of Interaction at Various Relative Orientations of the Terminal Groups.

ene-ene - non-mirror image

using Pot I

Fig. 45. Potential Energy Barriers to Rotation



from Terminal Group Interaction using Pot I

Fig. 45.

Fig. 46.. Potential Energy Barriers to Rotation

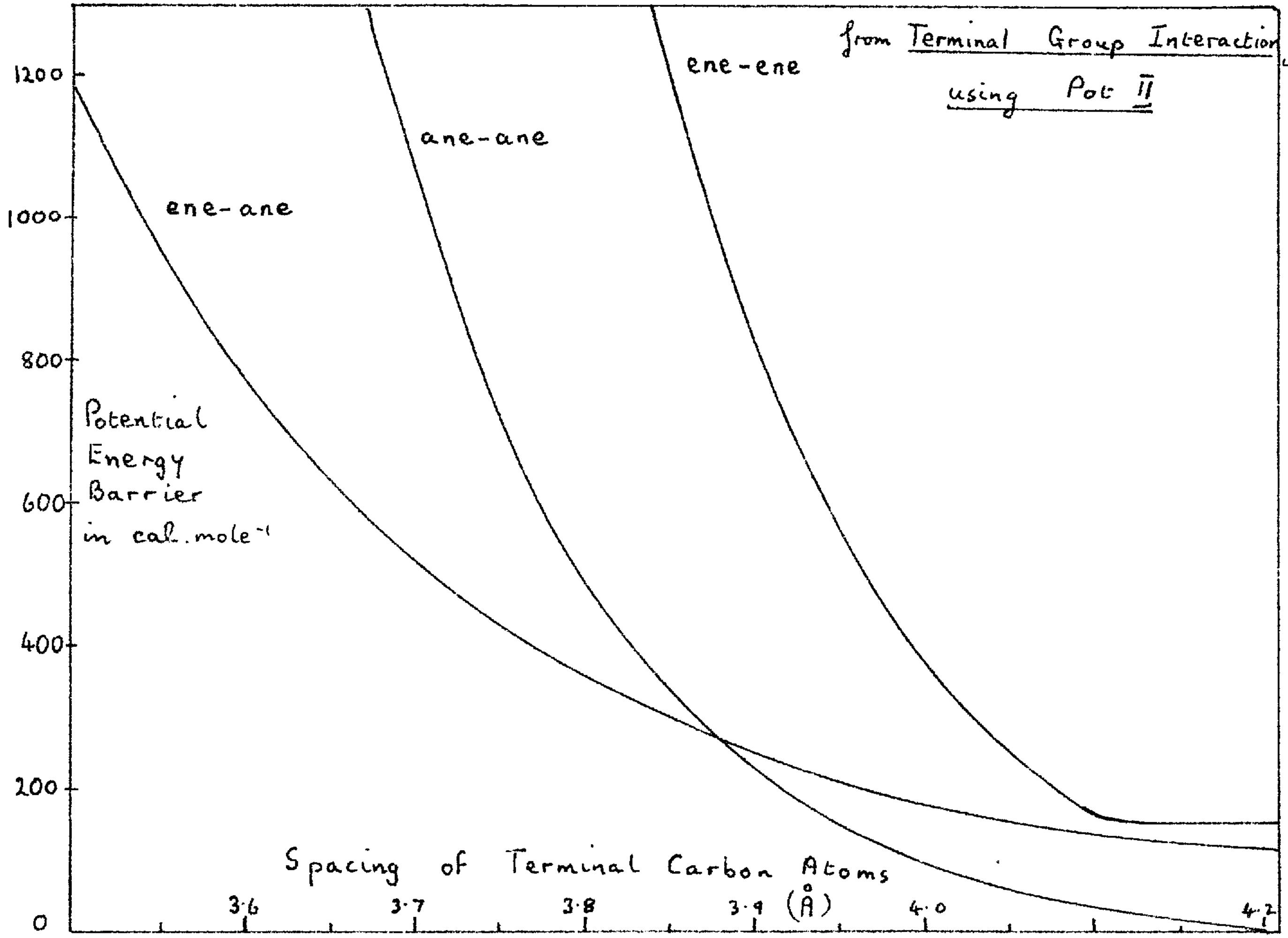


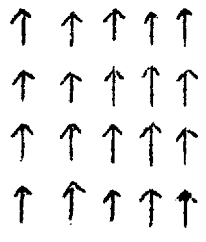
Fig. 46.

(iii) ISING - MONTE CARLO METHOD

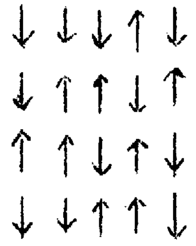
The Ising - Weiss model used by Parsonage and Pemberton (1967) to describe the behaviour of the alkanes within the urea lattice has been discussed in Chapter 1. D(iii). The adaptation of this theory to explain the behaviour of the head-tail ordered alkenes in the urea lattice is simple, as it requires only the changing of the value of the longitudinal coupling parameter. The case of the head-tail disordered alkene arrangement is complicated by the non-uniformity of the longitudinal parameters. Indeed this system cannot be treated in this way.

This problem has been tackled by considering the alkene molecules as occupying the sites of a simple cubic lattice. Domb (1960) has shown that in general the nature of the transition depends much more on dimensionability than on details of the crystal structure. A set of 512 molecules is chosen forming a cube of side 8 molecules. The longitudinal interaction can be arranged to be the same throughout the system, corresponding to an ordered ene-ane arrangement in the channels, or it can vary throughout the system, corresponding to a head-tail disordered arrangement in the channels.

The lateral interaction chosen is dependent on the length of the molecule. In addition an allowance is made for the fact that in the crystal each hydrocarbon has at least six neighbours, while in this theoretical lattice it has only four.



a) A rotationally ordered lattice



b) A rotationally disordered lattice

Each molecule is considered to have two possible rotational positions, corresponding to configurations μ, such that $\mu = +1$ or $\mu = -1$. The interaction between nearest neighbours only is considered. The total energy of the system is of the form

$$E = -B \sum_{kk'} \mu_k \mu_{k'}$$

where E is the energy, B is the relevant interaction parameter and μ_k and $\mu_{k'}$ are the configurations of two neighbouring molecules k and k'.

Two sets of molecules are considered. One is arranged, initially (a), so that all the molecules are in the same configuration, i.e., $\sum_k \mu_k = \pm N$, where N is the number of molecules, and the other set is arranged to be completely disordered, (b), i.e., $\sum_k \mu_k = 0$. The properties of these systems ~~is~~ are now investigated using the Monte Carlo method (Fosdick 1963). In this method each molecule is examined in turn. If by changing its configuration, there is an energy, ΔE, decrease, then the new configuration is accepted. If the new configuration leads to an arrangement of higher energy, the move is given a "Boltzmann - chance" of being accepted. By this is meant that the Boltzmann factor, $e^{-\Delta E/kT}$ is compared with a random number between 0 and 1, and if the factor is the greater, the move is accepted, if it is the smaller, the molecule is retained in its original configuration. It is necessary to make some assumption about the potential energy of the molecules at the surface of the cube. In these investigations periodic boundary conditions are maintained throughout the investigation, i.e., the system is surrounded by ghost systems composed of molecules with configurations which match the central system at all times.

This procedure is continued for both sets of molecules until the properties of the sets converge. This convergence is tested by examining the relationships (7.5) (7.6) over the previous 25 cycles, where one cycle is a set of 512 ~~times~~ tries, one for each molecule.

$$\frac{\left[\langle U\rangle - \langle U'\rangle\right]^2}{\left[\langle U\rangle + \langle U'\rangle\right]^2} < 0.005 \quad \ldots\ldots \quad (7.5)$$

$$\frac{\left[\langle U^2\rangle - \langle U'^2\rangle\right]^2}{\left[\langle U^2\rangle + \langle U'^2\rangle\right]^2} < 0.01 \quad \ldots\ldots \quad (7.6)$$

where U and U' are the energies of the molecules in the first and second **sets** and $\langle\ \rangle$ indicates that the average value is taken.

When this convergency test has been satisfied a further 27 cycles of both sets of molecules are undertaken. The two sets of the molecules are combined after each third cycle and the average energy of the molecules, $\langle U\rangle$, and the average of the square of the energy of each molecule $\langle U^2\rangle$ is determined. A running average is maintained of these two values and the final values after 27 cycles, are used to calculate the heat capacity, C, employing the relationship between the heat capacity and the fluctuation of the molecular energies about the mean.

$$\frac{C}{R} = \frac{\langle U^2\rangle - \langle U\rangle^2}{(RT)^2\ N}$$

where R is the gas constant, T is the temperature, and N is the number of molecules considered. The value of the long range order parameter ($\frac{1}{N}\left|\sum_k \mu_k\right|$) is also calculated after each third cycle.

These calculations were done for various values of temperature on the University of London Atlas computer using a programme written by Dr. N.G. Parsonage.

For those situations where the system is supposed to be "frozen" into a head - tail disordered configuration, the programme begins by making an allocation of head - tail orientations using pseudo-random numbers.

The following arrangements of the molecules were studied in this way.

a) 1-Hexadecene, ene - ane ordered; i.e., longitudinal and lateral coupling parameters are 125 and 67 respectively.

b) n-Hexadecane; i.e., longitudinal and lateral parameters were 146 and 67.

c) 1-Hexadecene, disordered; i.e., longitudinal coupling parameters were 146, 125 and 433 corresponding to ane - ane, ane - ene, and ene - ene interactions respectively and the lateral parameter was 67.

d) 1-Decene, disordered; i.e., as for (c) except lateral parameter was reduced to 47.

The values for $C/_R$ and the long range order parameter obtained for these arrangements were plotted against temperature (Figs.47, 48, 49, 50, 51). It was hoped that this method would demonstrate both the co-operative nature of the transition in the heat capacity of the head - tail ordered arrangement of molecules, and the non-co-operative nature of the transition in a head - tail disordered arrangemnt. The $C/_R$: T curves certainly confirm the co-operative nature of the ordered arrangement, but they also predict very similar behaviour for the disordered arrangement of molecules. There is however broadening to a certain extent in the head - tail disordered systems studied. In considering the actual values of $^{C}/_{R}$ it must be remembered that in the head - tail disordered arrangement, with interactions of 433, 125 and 146, the total heat of transition will be greater than in the ordered arrangement, with interactions of either 146 or 125. A plot of the reduced heat capacity (allowing for this extra heat) against temperature would show a smaller maximum in the heat capacity of the disordered arrangement, but is not given here owing to the difficulty in estimating the reduction factor in the disordered system. The plot of the long range order parameters against temperature indicates that there is a significant amount of rotational order left in the head - tail disordered arrangement, even at 300°K. This order is probably associated with the configurations of the molecules involved in one - one interaction. Thus this method does indicate that after the bulk of the transition in the disordered arrangement, there is still a significant amount of rotational order left.

No attempt has been made to reproduce the proposed eicosene arrangement. The molecules could be effectively locked together by choosing an infinite one - one coupling parameter, but this would lead to no change of configuration being accepted. A simpler solution would be to assume that two eicosene molecules behaved as one new molecule, and to establish a new lattice with 512 of these new molecules. The longitudinal coupling parameter would be then 146 (all ane - ane) and a suitable lateral parameter corresponding to the longer molecule would have to be chosen, bearing in mind that not all of the carbon atoms of the new molecule would lie in the same plane.

The presence of a fairly sharp transition in the heat capacities of the head - tail disordered systems and the existence of a certain amount of rotational order after the transition suggests the possibility that the low experimentally deduced entropy value of the 1-eicosene anomaly could be indicative of a lack of head - tail order in the 1-eicosene adduct. If this is so it is hard to understand the non-co-operative anomalies observed in the heat capacity of the 1-decene adduct,

Fig. 47 Variation of the Long Range Order Parameter with Temperature in the Monte Carlo - Ising Model

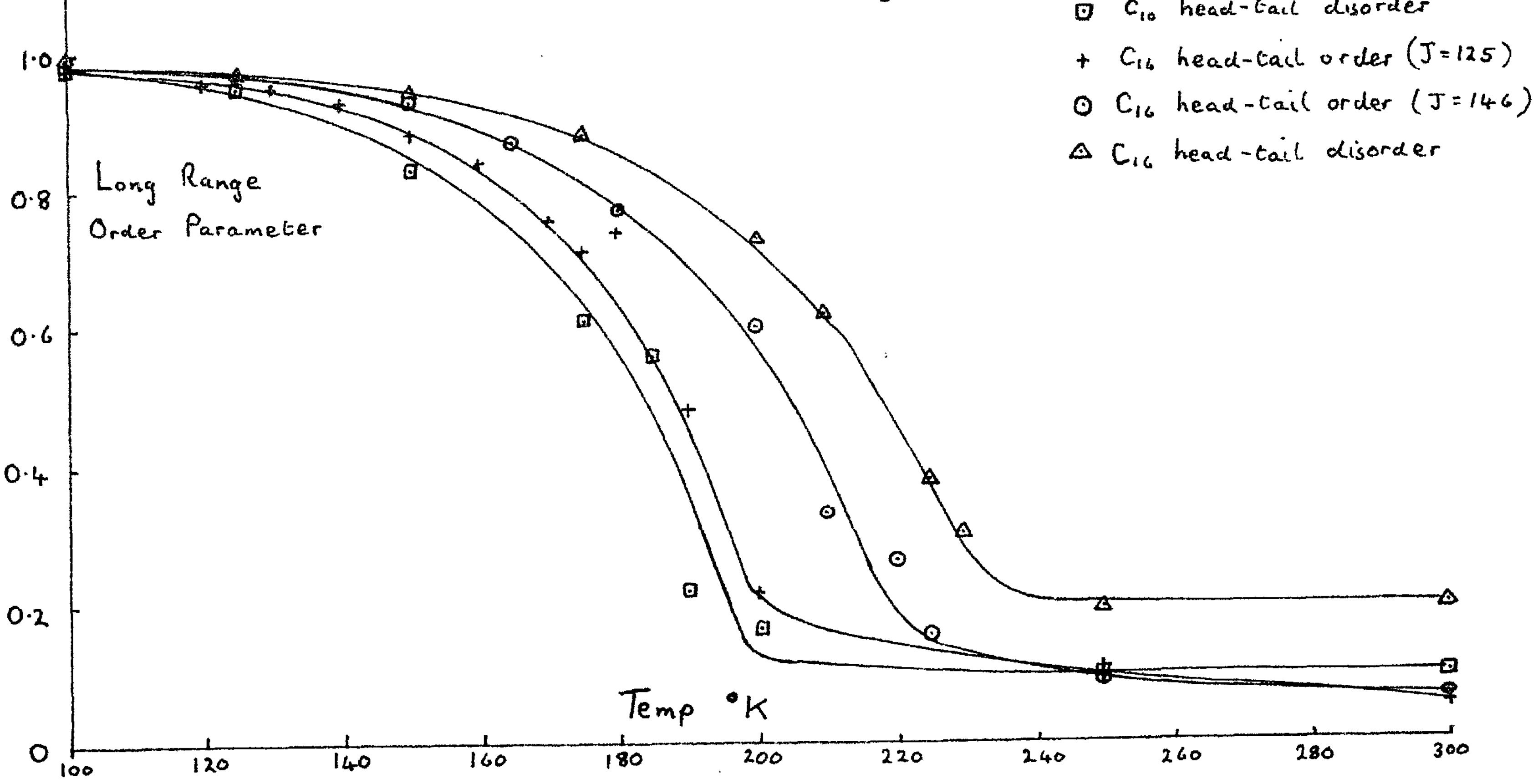


Fig. 47.

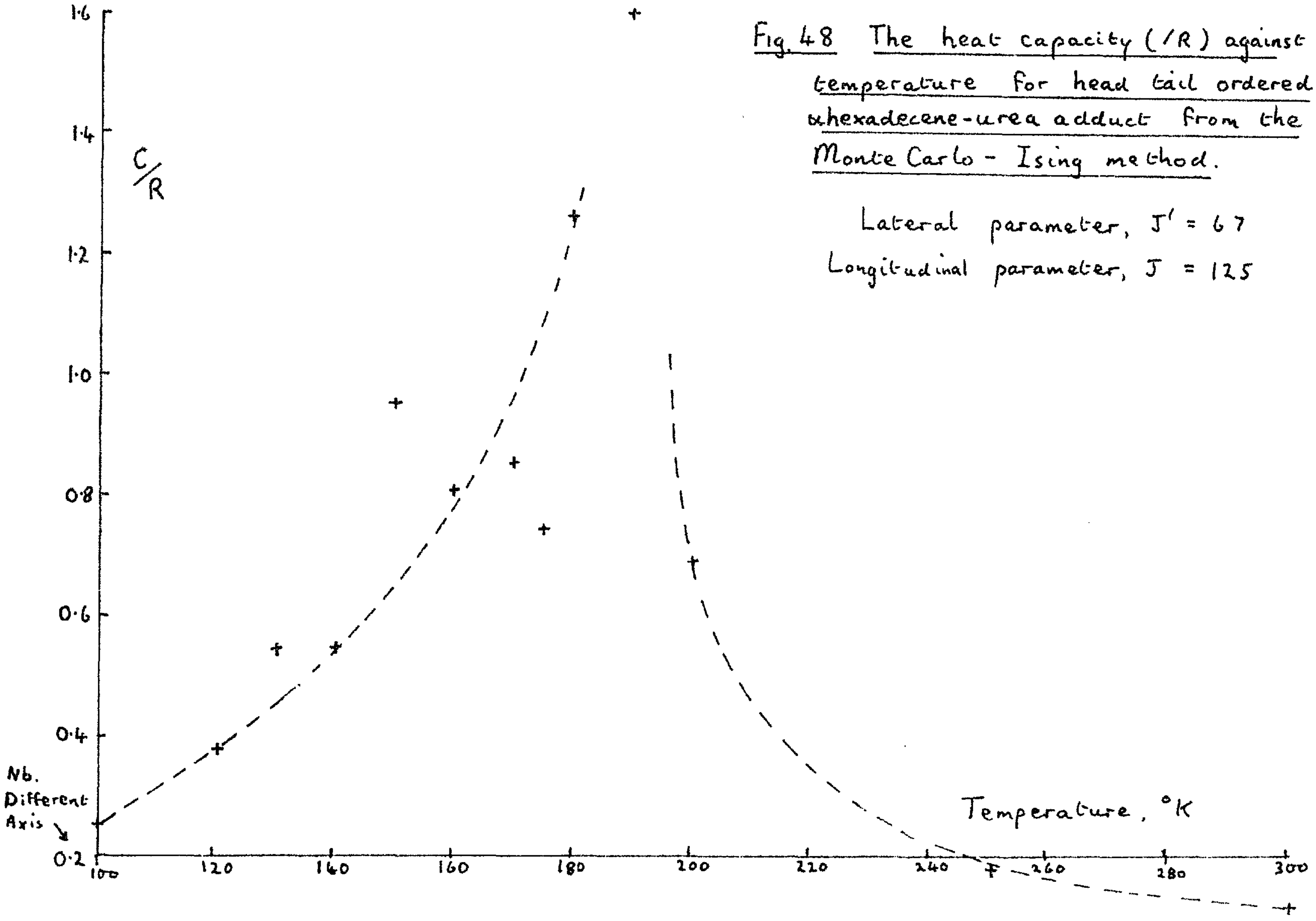


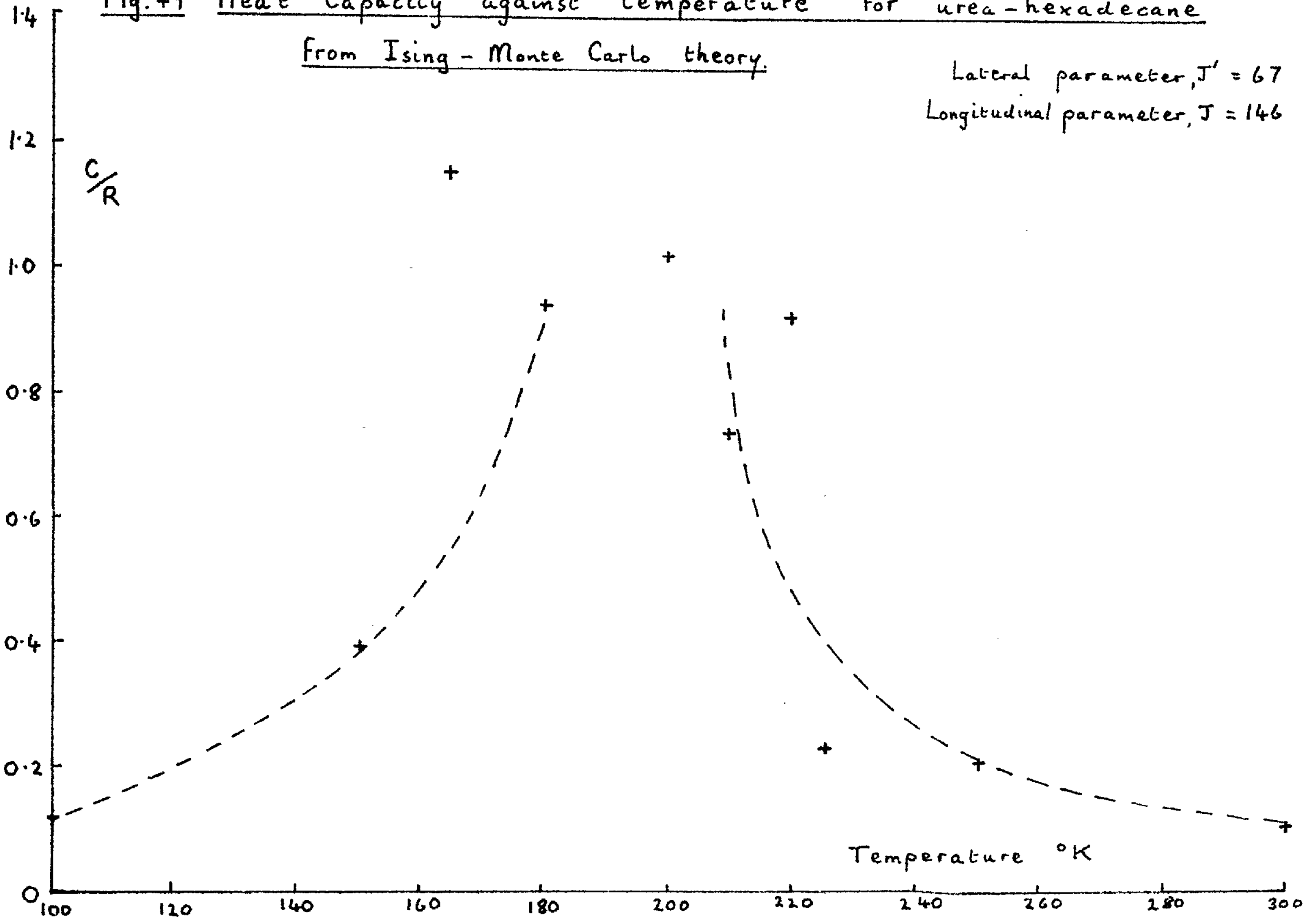
Fig. 48 The heat capacity (/R) against temperature for head tail ordered αhexadecene-urea adduct from the Monte Carlo - Ising method.

Lateral parameter, J′ = 67

Longitudinal parameter, J = 125

Fig. 48

Fig. 49 Heat Capacity against temperature for urea-hexadecane from Ising-Monte Carlo theory.



Lateral parameter, J' = 67
Longitudinal parameter, J = 146

Fig. 49

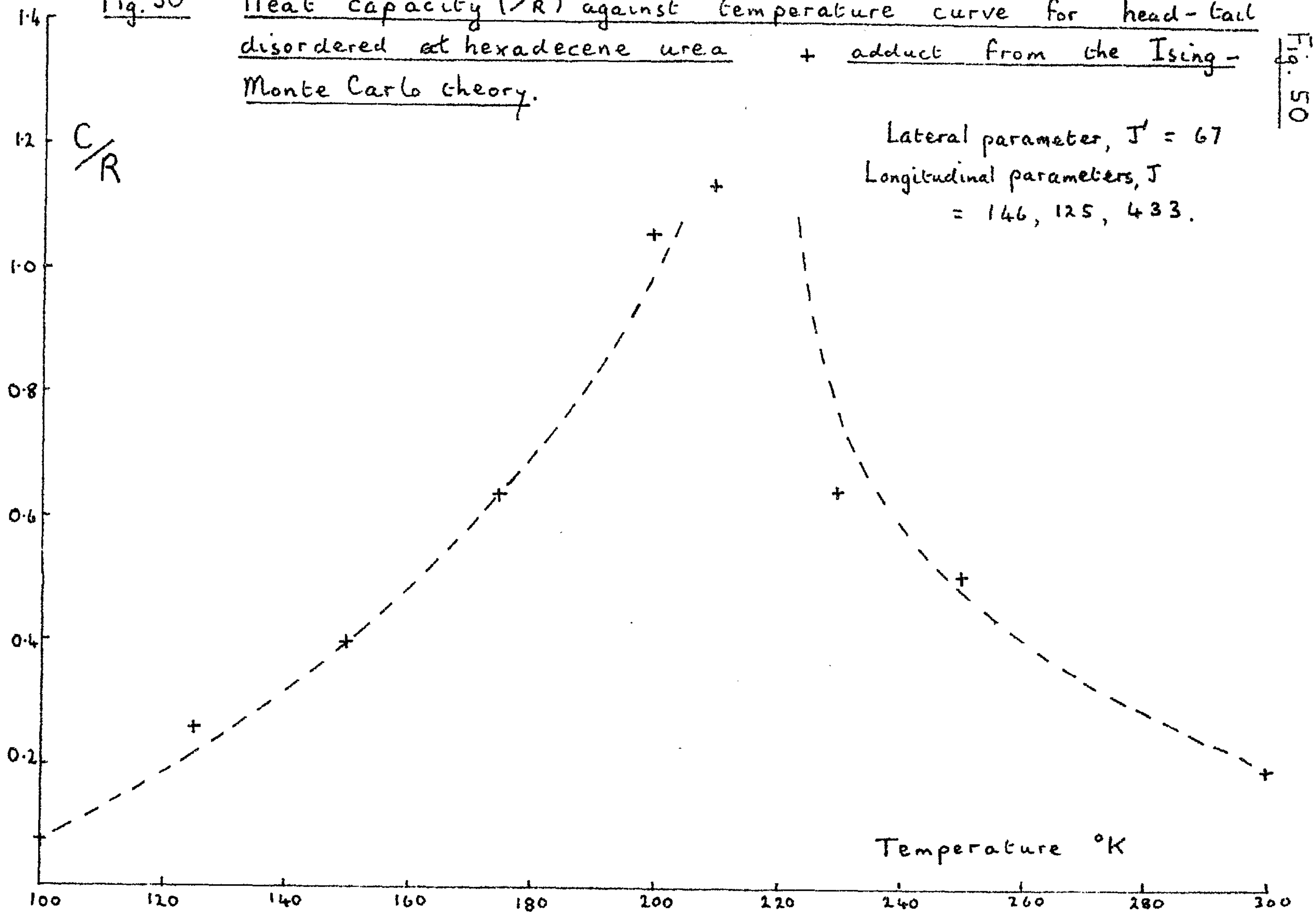


Fig. 50 Heat capacity (/R) against temperature curve for head-tail disordered at hexadecene urea adduct from the Ising-Monte Carlo theory.

Fig. 51 Heat capacity (/R) against temperature for head-tail disordered decene urea adduct from Ising-Monte Carlo method.

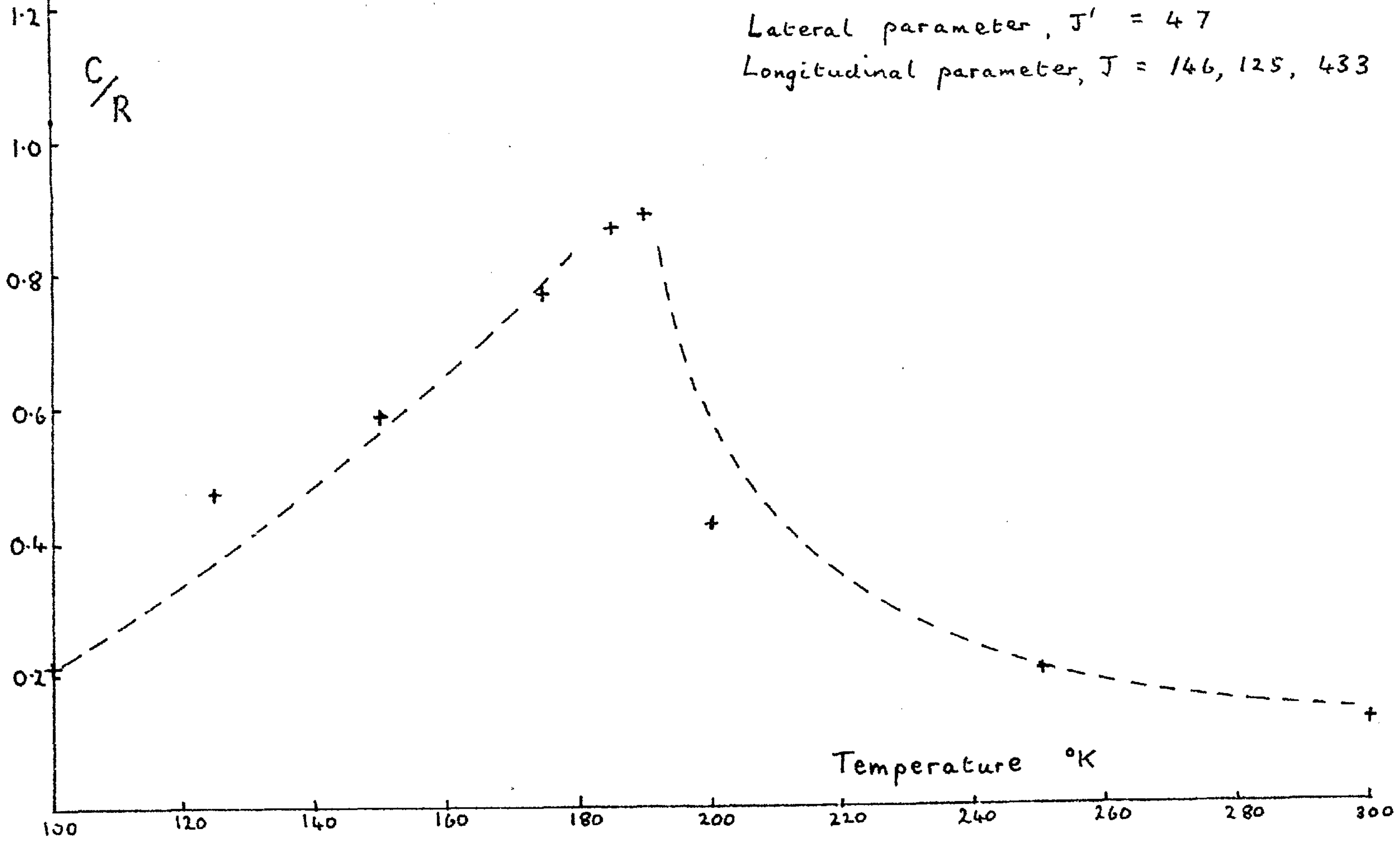


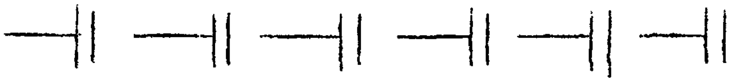
Fig. 51

(iv) COMMENTS AND PROPOSALS FOR FURTHER WORK

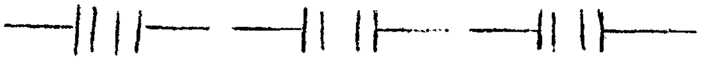
The indication is that the alkene molecules are arranged in the channels in the manner described in the previous sections and illustrated again below.

1-Decene (disordered head - tail)

1-Hexadecene (ordered head - tail)



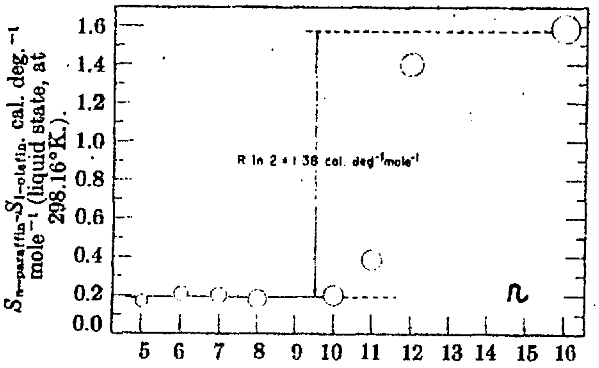
1-Eicosene (ordered head - head, tail - tail)



However the arguments put forward are by no means conclusive and further investigations are necessary. X-ray data on the alkene adducts similar to that described by Laves, Nicolaides and Peng (1965) would certainly throw some light as to the head - tail arrangement of the molecules. Perhaps better would be neutron diffaction studies, as in this case the positions of the hydrogen atoms would be located.

The alkene molecules in their pure state exhibit a similar phenomenon. Up to C_{10} the alkenes are apparently head - tail ordered in the crystalline form, whilst from C_{16} upwards there is complete head - tail disorder. (McCullough, Finke, Gross, Messerly and Waddington, 1957). The consequent residual entropy at 0°K of R ln 2 of the hexadecene, etc., is demonstrated by comparing the entropies at 298°K of the alkane and alkene homologous series (Fig. 52).

Fig 52.—The entropy difference between liquid *n*-paraffins and 1-olefins at 298.16°K. as a function of number of carbon atoms. The diameters of the circles represent 0.1% of the observed entropy values for each pair of hydrocarbons.



Such an entropy difference is not exposed in these measurements on the urea alkane and alkene adducts, as the molecules are confined to the channels and are therefore unable to change the order in which they are packed.

Comparison of the vapour pressures of the alkene molecules in the adducts (P_1) and in their pure form (P_2) would enable the entropy difference between the two states to be evaluated.

However the vapour pressure of the alkene in the adduct is so low, and the contribution to the entropy from the packing order so small, that the method would be insensitive in detecting this residual entropy.

Another thermodynamic method which may be a little more successful in revealing this head-tail order or disorder is the measurement of the enthalpies of solution of the adducts. Choice of an efficient solvent giving a low heat of solution, and a direct comparison of corresponding alkene and alkane adducts (c.f. the study of the heat of transformation of α to β - quinol -

Richards and Evans, 1952) would enable the small enthalpy differences due to the different degrees of head-tail order to be revealed. If the alkene molecules were rotating in pairs, as is suggested for 1-eicosene, there might be a further, observable increment in the enthalpy difference between the 1-alkene and n-alkane adduct systems.

A major difference between the relative behaviours of the 1-decene and 1-hexadecene molecules is that whereas in the pure crystalline state the 1-decene molecules are ordered and the hexadecene disordered, in the urea lattice the opposite is thought to be the case. In the pure state the packing is done at the crystallisation temperature, and presumably at these temperatures, in contrast to decene, the larger molecules have insufficient freedom to rearrange themselves in the ordered fashion. Packing inside the urea lattice is done at room temperature and in solution, when it is expected that the molecules are randomly arranged. The ordering of the C_{16} and C_{20} alkenes in the urea lattice can be explained in terms of packing in exact unit cells. The lengths of the 1-hexadecene and 1-eicosene molecules are very nearly simple multiples, 2 and $2\frac{1}{2}$ respectively, of the length of the urea lattice unit cell, but no such simple relationship exists for the length of the 1-decene molecule. The choice of head - head, tail - tail or head - tail ordering may be controlled by the most efficient way of packing into the unit cells or on the other hand it may stem from the quest of the ene group for a particular environment. A specific location of the ene group would also go a long way to justifying the postulation of unit cell packing, whereas previously (Chapter 1, (B)), arguments were laid out against the packing of n-hexadecane in two unit cells.

The possibility of the guest molecules moving along the length of the channel has not been considered so far. If ene groups were preferentially located in a specific position in the channel, the presence of a neighbouring, and similarly restricted, ene group could well restrict any motion along the channel severely. The absence of any significant high temperature anomaly, 225 - 235 °K, (see Table 20) in 1-eicosene could possibly be explained by this lack of translational freedom.

So far three alkene adducts have been studied and all three have been found to behave differently. Study of further urea-alkene adducts in this way would probably reveal what indeed controls the packing of the molecules, the size of the molecule or its ability to fit inside an integral number of unit cells.

Clearly much interesting work has yet to be done in this field.

CHAPTER 8. THE EXPERIMENTAL DETERMINATION OF THE HEAT CAPACITIES OF THIOUREA - CYCLOHEXANE AND THIOUREA 2, 2 DIMETHYLBUTANE ADDUCTS.

The preparation of the calorimeter sample was complicated in both cases by the instability of the adduct (see Chapter 5 B(i)). The heat capacities were determined between .12 and 300°K in the manner described previously. Partial and fully automatic control of the shields was maintained in the measurements on the cyclohexane and the 2, 2 - dimethylbutane adducts, respectively. The experimental values of the heat capacities are listed in Tables 30, 31, and the heat capacities at various temperatures corresponding to smooth curves drawn through the experimental points are presented in Table 32. The root mean square deviations of the experimental points from the smooth curves are shown in Table 26.

TABLE 26. THE ROOT MEAN SQUARE DEVIATIONS OF THE EXPERIMENTAL POINTS FROM A SMOOTH CURVE FOR THE HEAT CAPACITIES OF THE CYCLOHEXANE AND 2, 2 DIMETHYLBUTANE THIOUREA ADDUCTS.

	Temperature range		
	12-25°K	25-80°K	80-300°K
cyclohexane (13gm)	0.76	0.16	0.13
2,2 dimethylbutane (10gm)	0.37	0.29	0.15

As explained in Chapter 6, the Debye characteristic temperatures, Θ, were calculated and found to be 109 and 117 for the the cyclohexane and 2, 2 dimethylbutane adducts respectively. The entropies $S_T - S_0$ were evaluated for both adducts for various values of temperature, T, up to T = 300°K. The error introduced by the Debye approximation for the low temperature region was again insignificant.

A number of anomalous regions were observed in the heat capacities of both adducts studied. These regions were studied in greater detail and the shapes, enthalpies and entropies involved in the transitions were assessed. Tables 27, 28.

TABLE 27. THE PROPERTIES OF THE ANOMALIES IN THE HEAT CAPACITY OF THE THIOUREA CYCLOHEXANE ADDUCT.

	ΔH cal mole^{-1}		ΔS cal mole^{-1} °K^{-1}		
Temp. °K	mole of thiourea	mole of hydrocarbon	mole of thiourea	mole of hydrocarbon	Nature
128.8	89	273	0.69	2.12	Very sharp
130-150	26	79	0.19	0.56	Broad
153-161	2.8	8.7	0.02	0.06	Broad
170.8	11	34	0.065	0.20	Sharp
210-240	6.5	20	0.03	0.09	Broad

TABLE 28. THE PROPERTIES OF THE ANOMALIES IN THE HEAT CAPACITY OF THE 2, 2 DIMETHYLBUTANE ADDUCT.

	ΔH cal mole^{-1}		ΔS cal mole^{-1} °K^{-1}		
Temp. °K	mole of thiourea	mole of hydrocarbon	mole of thiourea	mole of hydrocarbon	Nature
69.9	25	73	0.36	1.04	Sharp
89.5	94	277	1.05	3.09	Very Sharp
169.6	19.5	57	0.115	0.34	Sharp

In addition there was a discontinuity in the heat capacity of the 2, 2 dimethylbutane at ~16°K adduct comparable with the low temperature anomaly reported in the heat capacites of the urea adducts. Owing to the extra large scatter of the points in this region in the study of the cyclohexane adduct, it is not possible to say whether such an anomaly is present in the heat capacity of this adduct.

The transition at 69.9°K in the thiourea - 2, 2 dimethyl-butane adduct heat capacity displayed a characteristic novel to this present study. The transition had a long relaxation time and in consequence a long period was required after the heating run (~3 hours in the case of run no. H 75) before equilibrium was reached. On the first occasion the sample was cooled below the temperature of this transition, the post transition state was "frozen in". This was revealed by large warming drifts between the heating periods below the transition temperature, as the crystals slowly changed to their more ordered form. A cooling rate through the transition region of about 1°K per 50 minutes was required to avoid the 'super cooling'. This feature introduced added complications to the hydrogen run as the rapid evaporation of the refrigerant necessitates that the sample should be cooled as rapidly as it is expedient to do so. In this case the sample was again cooled through the transition region at a rate of 1°K in 50 minutes. A slight anomalously high region of heat absorption (~1 cal mole $^{-1}$) was then observed in the region 45 - 55°K. There is insufficient evidence to conclude whether there is an increase in the heat capacity in this region or whether the anomaly is as a consequence of the sample being cooled too rapidly through the transition at 69.9°K. The curve (Table32) has been drawn ignoring these points, but a second curve passing through these points is indicated in brackets. The entropy involved is insignificant when estimating the total entropy of the sample.

In view of the difficulties experienced in preparing the calorimeter samples, it is possible that one or more of the anomalies ~~adducts~~ were due to the solvents used or to unadducted thiourea. The properties of the anomalies in the heat capacities of the pure compounds involved are listed in Table 29. However, any impurity would be present in very small quantities and in such circumstances the properties of the anomalies would not necessarily resemble those of the pure compound.

It should be noted that the anomalies in the heat capacity of the cyclohexane adduct at ~155°K and 170°K correspond approximately to those in pure methanol. The heats of the anomalies are in the right proportions and if due to an impurity of methanol would indicate the presence of 0.002 moles (0.064g). The error introduced to the smooth heath capacity and the total entropy of the adduct is insignificant compared with the component anaylsis error.

TABLE 29. THE ANOMALIES IN THE HEAT CAPACITIES OF THE SOLVENTS, ETC. USED.

Compound	Properties	References
Methanol	1) Solid I → Solid II. Temp. 145 160. H = 154 cal $mole^{-1}$. 2) Solid II → Liquid, 175.22°K. H = 757 cal $mole^{-1}$.	Ahlberg, Blanchard & Lundberg. (1937). Kelley. (1929).
n-Pentane	1) Solid → Liquid. 143.47°K. H = 2011 cal $mole^{-1}$.	Messerley & Kennedy, (1940). Parks and Huffman, (1930).
Thiourea	See Chapter 9.	
Cyclohexane	1) Solid I → Solid II. 186.09°K. H = 1600 cal $mole^{-1}$. 2) Solid II → liquid. 279.84°K. H = 624 cal $mole^{-1}$.	Aston et al. (1943). Parks, Huffman and Thomas. (1930).
2, 2 dimethylbutane	1) Solid I → Solid II, 126.81°K. H 1293 cal $mole^{-1}$. 2) Solid II → Solid III, 140.79°K. H = 68 cal $mole^{-1}$. 3) Solid III → Liquid, 174.28°K. H = 138 cal $mole^{-1}$.	Kilpatrick and Pitzer. (1946). Douslin and Huffman. (1946).

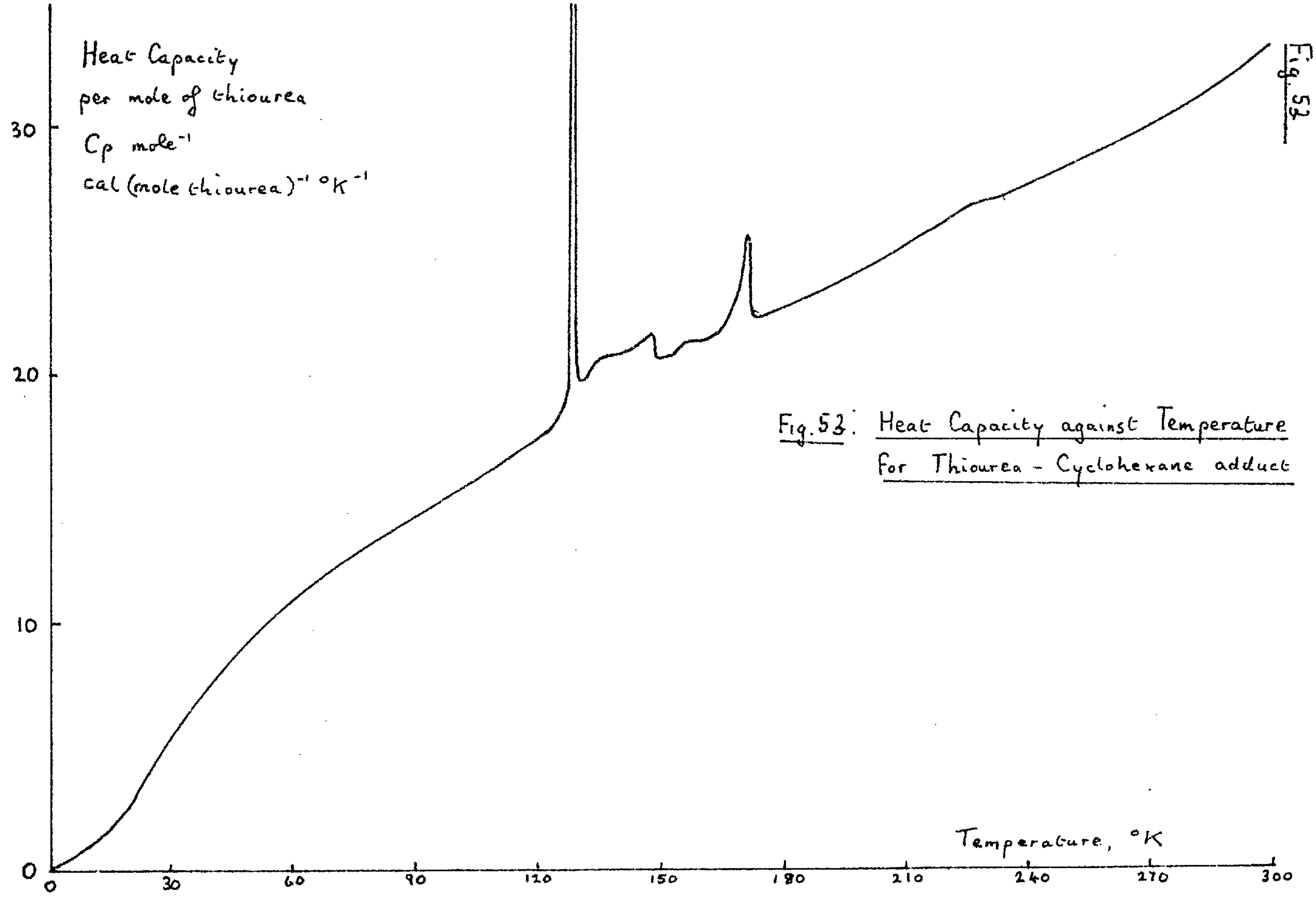


Fig. 53. Heat Capacity against Temperature for Thiourea - Cyclohexane adduct

Fig. 53

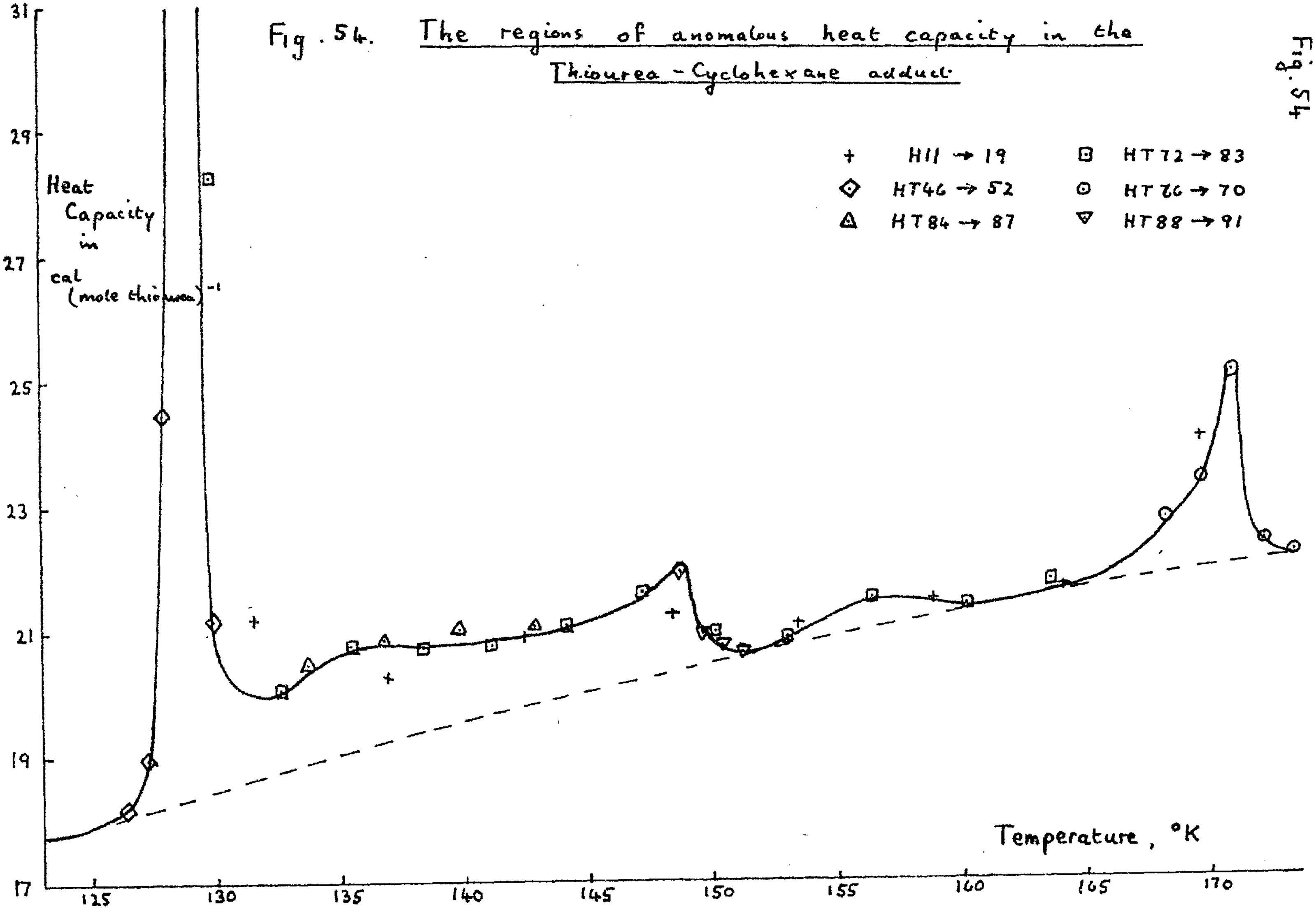


Fig. 54. The regions of anomalous heat capacity in the Thiourea - Cyclohexane adduct

Fig. 54

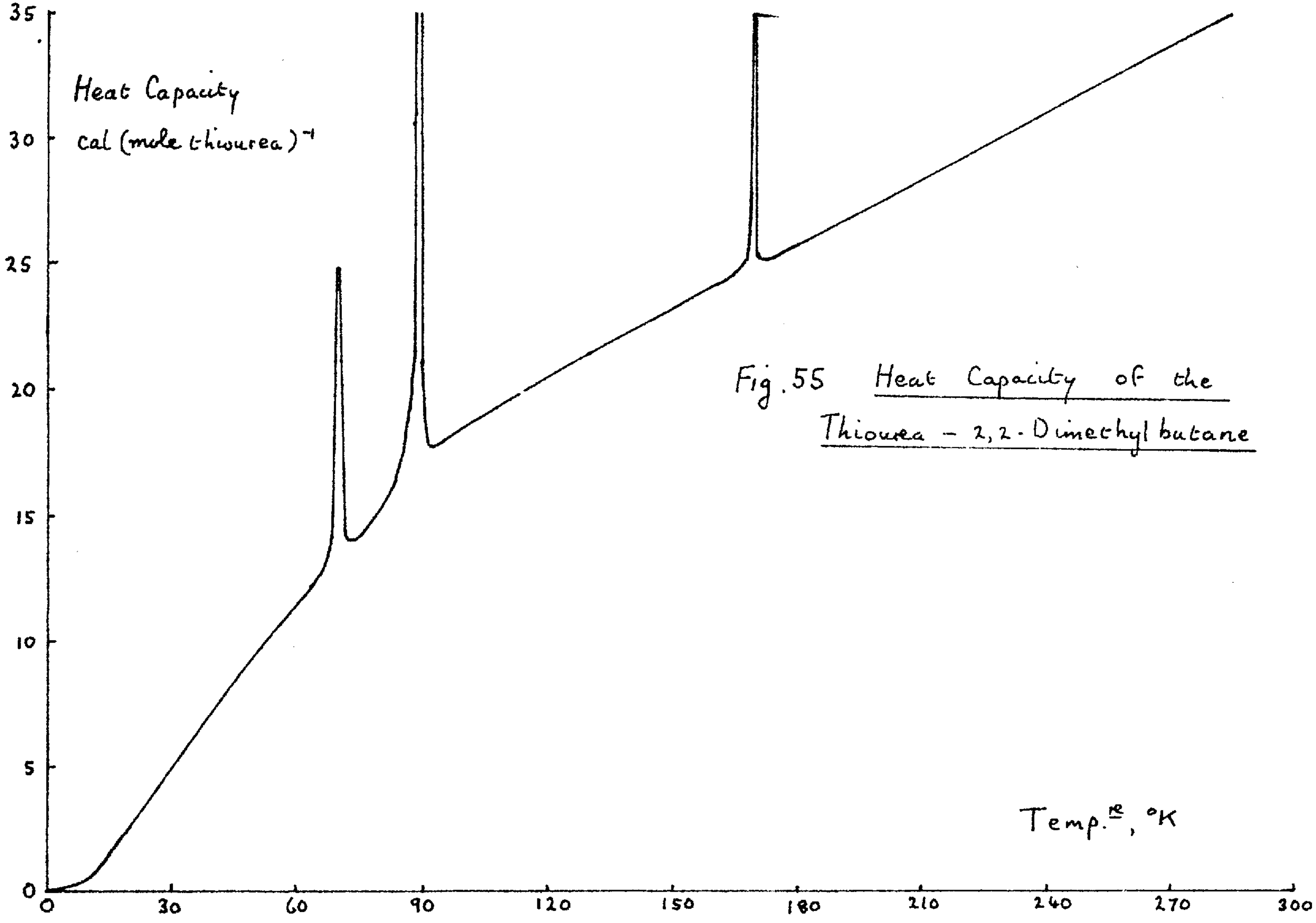


Fig. 55 Heat Capacity of the Thiourea - 2,2-Dimethylbutane

Fig. 55

Thiourea - 2,2 - Dimethylbutane.

Fig. 57. The Anomalous Regions in the Heat Capacity

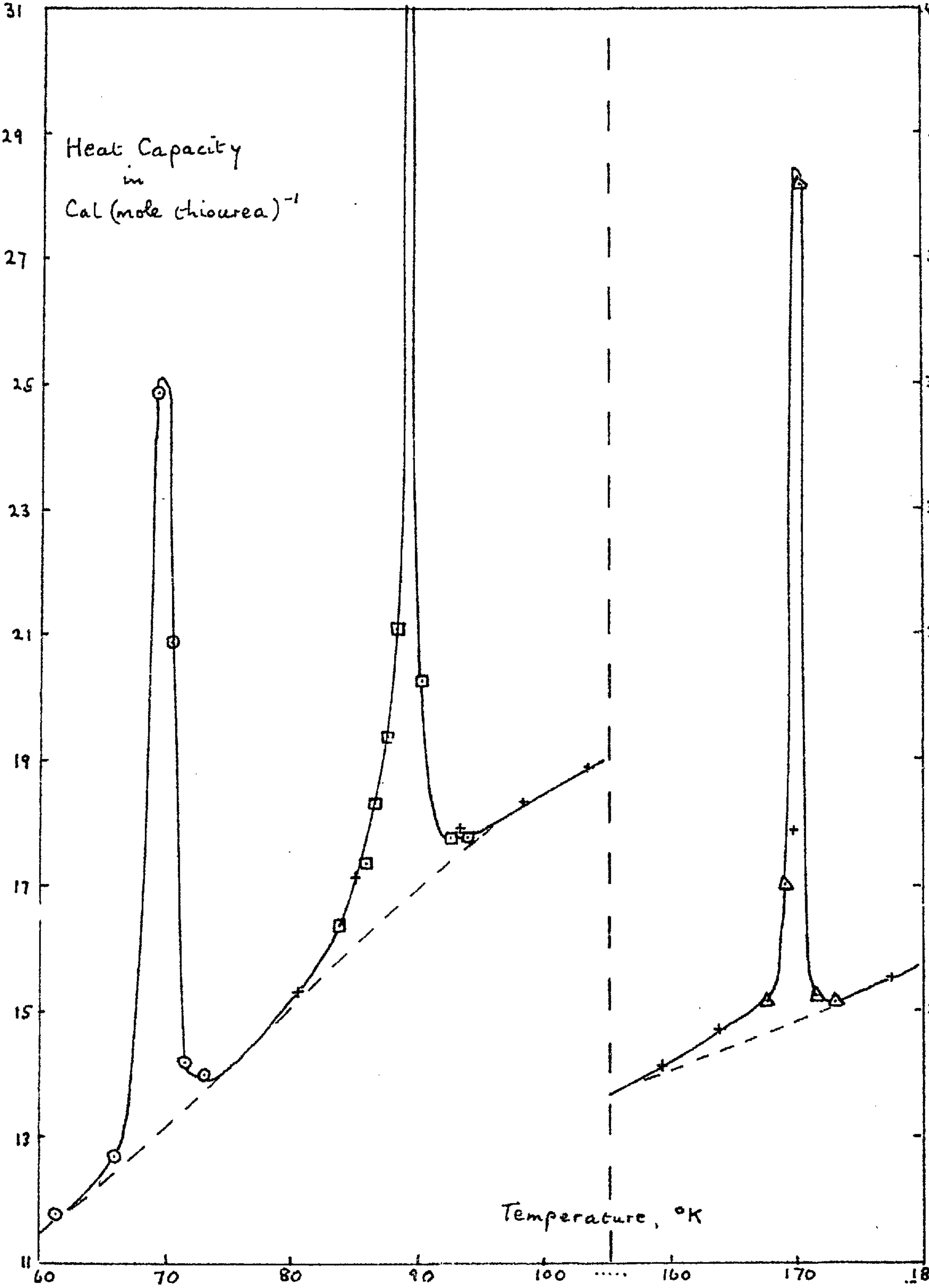


TABLE 30 EXPERIMENTAL VALUES OF THE HEAT CAPACITY OF THE THIORUREA - CYCLOHEXANE ADDUCT

Wt. of adduct in calorimeter = 13·4719 g.
(9·9018g. of thiourea + 3·5701g. of cyclohexane)

Heat capacity of sample, Cp, in abs. Joules $^{o}K^{-1}$.
Heat capacity of adduct, Cp/mole, in cal. mole^{-1} $^{o}K^{-1}$ (thiourea)

Run No.	Temp. ^{o}K	ΔT ^{o}K	Cp	Cp/mole
1	80·21	4·48	7·292	13·398
2	84·74	4·55	7·589	13·944
3	89·33	4·63	7·859	14·440
4	93·99	4·64	8·070	14·828
5	98·62	4·65	8·359	15·359
6	103·33	4·74	8·578	15·761
7	108·10	4·76	8·856	16·272
8	112·90	4·85	9·128	17·319
9	117·78	4·93	9·426	17·319
10	122·77	5·01	9·746	17·907
11	127·15	3·73	21·757	39·976
12	131·61	5·18	11·534	21·192
13	136·93	5·40	11·015	20·239
14	142·52	5·74	11·353	20·860
15	148·35	5·90	11·549	21·220
16	153·43	5·33	11·462	21·060
17	158·79	5·37	11·657	21·418
18	164·23	5·52	11·758	21·604

Table 30 (Cont'd).

Run No.	Temp. °K	ΔT °K	Cp	Cp/mole
19	169·79	5·58	13·050	23·978
20	175·59	6·00	12·265	22·535
21	181·66	6·13	12·457	22·888
22	187·55	5·63	12·659	23·258
23	193·55	6·38	13·013	23·911
24	200·00	6·49	13·316	24·467
25	206·46	6·41	13·562	24·919
26	212·87	6·41	13·922	25·580
27	219·29	6·41	14·287	26·251
28	225·76	6·50	14·660	26·936
30	232·81	6·80	14·961	27·490
31	239·68	6·93	15·086	27·719
32	246·65	7·02	15·390	28·277
33	253·68	7·02	15·649	28·753
34	260·66	6·91	15·963	29·330
35	267·53	6·80	16·273	29·900
36	274·47	7·03	16·644	30·581
37	281·59	7·17	17·055	31·337
38	288·85	7·34	17·436	32·037
39	296·29	7·48	17·953	32·986
P40	53·03	4·37	5·466	10·043
P41	57·56	4·55	5·817	10·688
P42	62·07	4·45	6·180	11·355
P43	66·61	4·61	6·472	11·892
P44	71·21	4·56	6·756	12·413
P45	75·77	4·54	7·016	12·891
T46	126·43	0·81	9·888	18·168
T47	127·26	0·86	10·323	18·967
T48	128·08	0·78	13·288	24·415

Table 30 (Cont'd).

Run No.	Temp. °K	Δ T °K	Cp	Cp/mole
T49	128·62	0·28	67·740	124·464
T50	128·86	0·20	103·291	189·785
T51	129·23	0·55	26·089	47·935
T52	129·92	0·82	11·493	21·117
H54	14·41	1·25	0·887	1·630
H55	16·48	2·34	1·144	2·102
H56	19·23	2·92	1·463	2·688
H57	24·11	4·42	2·282	4·193
H59	28·93	2·99	2·780	5·108
H60	32·44	2·91	3·246	5·964
H61	35·52	3·11	3·690	6·781
H62	38·76	3·26	4·100	7·533
H63	42·13	3·38	4·437	8·152
H64	45·79	3·90	4·759	8·744
H65	49·52	3·54	5·112	9·393
T66	168·25	1·62	12·337	22·668
T67	169·69	1·25	12·689	23·315
T68	170·93	1·24	13·666	25·110
T69	172·20	1·29	12·133	22·293
T70	173·51	1·30	12·041	22·124
T71	127·97	1·66	31·647	58·148
T72	130·03	2·47	15·364	28·230
T73	132·69	2·82	10·903	20·033
T74	135·51	2·78	11·283	20·731
T75	138·31	2·67	11·278	20·722
T76	141·21	2·99	11·310	20·781
T77	144·20	2·96	11·454	21·045
T78	147·16	2·91	11·746	21·582
T79	150·11	2·93	11·388	20·924

Table 30 (Cont'd)..

Run No.	Temp. °K	ΔT °K	Cp	Cp/mole
T80	153·05	2·92	11·350	20·854
T81	156·45	3·83	11·664	21·431
T82	160·29	3·72	11·620	21·350
T83	164·10	3·77	11·822	21·722
T84	133·73	3·11	11·122	20·435
T85	136·82	3·07	11·344	20·843
T86	139·87	3·04	11·439	21·018
T87	142·90	3·02	11·467	21·069
T88	148·62	3·10	11·924	21·909
T89	149·62	0·83	11·365	20·882
T90	150·44	0·75	11·300	20·762
T91	151·26	0·93	11·216	20·608

TABLE 31. EXPERIMENTAL VALUES OF THE HEAT CAPACITY OF THIOUREA - 2,2 DIMETHYLBUTANE

Wt. of calorimeter sample = 10.2328 g.
(7.3881 g. of thiourea, 2.8447 g. of 2,2 dimethylbutane).

Heat capacity of sample, cp, in abs. Joule $^{\circ}K^{-1}$.
Heat capacity of adduct per mole of thiourea, Cp/mole, in cal mole $^{-1}$ $^{\circ}K^{-1}$.

Run No.	Temp. °K.	Δ T	Cp	Cp/mole
1	80.24	4.84	6.210	15.296
2	85.06	4.89	6.965	17.155
3	89.09	3.27	18.093	44.564
4	93.25	5.04	7.260	17.882
5	98.32	5.12	7.480	18.424
6	103.49	5.22	6.694	18.951
7	108.74	5.30	7.947	19.574
8	114.08	5.38	8.164	20.108
9	119.51	5.48	8.347	20.559
10	125.03	5.57	8.543	21.042
11	130.66	5.68	8.735	21.515
12	136.39	5.78	8.936	22.010
13	142.21	5.87	9.132	22.493
14	148.16	5.98	9.350	23.030
15	154.21	6.08	9.568	23.517
16	159.14	4.73	9.698	23.887
17	163.92	5.82	9.992	24.611
18	169.71	5.74	11.279	27.781

Table 31 (Cont'd)..

Run No.	Temp. ^{o}K.	Δ T	Cp	Cp/mole
22	193.90	6.28	10.963	27.002
23	200.23	6.40	11.222	27.640
24	206.65	6.44	11.378	28.025
25	213.08	6.46	11.652	28.699
26	219.64	6.69	11.927	29.377
27	226.23	6.51	12.148	29.921
28	232.75	6.53	12.354	30.429
29	239.27	6.54	12.616	31.074
30	244.77	6.66	12.861	31.677
31	251.48	6.78	13.108	32.286
32	258.26	6.78	13.318	32.803
33	265.29	7.28	13.601	33.500
34	272.67	7.48	13.796	33.980
35	280.24	7.68	14.055	34.618
36	287.98	7.84	14.446	35.581
37	295.90	8.01	14.820	36.502
38	304.42	8.12	15.335	37.771
P39	53.97	5.22	4.289	10.564
P40	59.02	4.63	4.872	12.000
P41.	63.72	4.38	4.766	11.739
P42	53.21	4.45	5.122	12.616
P43	58.19	4.36	5.165	12.722
P44	63.00	4.38	4.942	12.172
P45	67.35	4.31	5.261	12.958
P46	71.33	3.56	8.579	21.131
P47	75.50	4.68	5.811	14.313
H48	12.50	1.64	0.432	1.064
H49	14.54	2.00	0.614	1.512
H50	17.08	2.85	0.865	2.131

Tablo 31 (Cont'd).

Run No.	Temp. $^{\circ}$K.	Δ T	Cp	Cp/mole
H51	20.37	3.80	1.160	2.857
H52	24.35	3.97	1.495	3.672
H53	28.03	3.25	1.849	4.544
H54	31.36	3.25	2.179	5.367
H55	34.73	3.42	2.499	6.155
H56	38.34	3.68	2.899	7.140
H57	42.20	3.99	3.260	8.030
H58	46.22	3.99	3.709	9.135
H59	50.19	3.90	3.979	9.800
H60	54.47	4.59	4.301	10.594
H61	59.06	4.46	4.616	11.369
T62	83.72	3.24	6.653	16.387
T63	85.73	0.79	7.060	17.390
T64	86.58	0.69	7.436	18.315
T65	87.50	0.92	7.873	19.392
T66	88.43	0.94	8.568	21.103
T67	89.20	0.59	24.929	61.401
T68	89.55	0.12	183.34	451.57
T69	90.17	1.12	8.223	20.254
T70	91.67	1.83	7.222	17.788
T71	93.88	2.57	7.229	17.805
P72	56.75	4.63	4.436	10.926
P73	61.31	4.50	4.779	11.771
PT74	66.01	4.87	5.151	12.687
PT75	69.18	1.43	10.076	24.818
PT76	70.38	0.98	8.467	20.855
PT77	71.46	1.18	5.765	14.199
PT78	73.03	1.94	5.684	14.000
T79	167.74	1.21	10.231	25.199
T80	168.98	1.27	10.979	27.042

Table 31 (Cont'd).

Run No.	Temp. °K.	Δ T	Cp	Cp/mole
T81	170.19	1.16	15.760	38.818
T82	171.49	1.46	10.240	25.222
T83	173.08	1.72	10.208	25.143
84	135.93	5.77	8.938	22.015
85	141.78	5.88	9.142	22.517
86	147.64	4.77	9.324	22.965
87	177.49	7.56	10.367	25.534
88	184.98	7.42	10.621	26.160
89	192.34	7.30	10.916	26.887

TABLE 32

SMOOTH VALUES OF THE HEAT CAPACITY OF THIOUREA - CYCLOHEXANE AND THIOUREA - 2, 2-DIMETHYLBUTANE

Heat Capacity in cal (mole thiourea)$^{-1}$

Temp. °K	Cyclohexane	2, 2-Dimethylbutane
0	0.000	0.000
12	1.172	0.962
15	1.756	1.622
20	2.902	2.764
25	4.114	3.844
30	5.362	5.018
35	6.644	6.264
40	7.760	7.492
45	8.640	8.648 (8.800) *
50	9.480	9.664 (9.768) *
55	10.29	10.62 (10.66) *
60	11.04	11.53
65	11.70	12.49
70	12.29	24.60
75	12.83	14.22
80	13.40	15.22
85	13.94	17.05
90	14.46	21.15
95	14.96	18.05
100	15.44	18.61
105	15.95	19.14
110	16.46	19.66

TABLE 32 (Continued).

Temp. °K	Cyclohexane	2, 2-Dimethylbutane
115	17.01	20.17
120	17.56	20.60
125	18.17	21.04
130	20.75	21.48
135	20.68	21.91
140	20.75	22.34
145	21.13	22.76
150	20.77	23.17
155	21.23	23.64
160	21.37	24.00
165	21.69	24.75
170	23.95	25.00
175	22.39	25.30
180	22.75	25.76
185	23.12	26.20
190	23.54	26.64
195	23.97	27.09
200	24.41	27.54
205	24.85	28.00
210	25.30	28.41
215	25.78	28.86
220	26.31	29.33
225	26.85	29.79
230	27.31	30.25
235	27.57	30.69
240	27.74	31.15
245	28.10	31.62

TABLE 32 (Continued).

Temp. °K	Cyclohexane	2, 2-Dimethylbutane
250	28.50	32.07
255	28.87	32.52
260	29.26	32.96
265	29.69	33.39
270	30.14	33.81
273.15	30.42	34.07
275	30.61	34.23
280	31.13	34.68
285	31.66	35.18
290	32.20	35.74
295	32.81	36.37
298.15	33.25	36.80
300	33.50	37.06

* see text.

TABLE 33. ENTROPY ($S_T - S_0$) OF THIOUREA CYCLOHEXANE AND 2, 2 DIMETHYLBUTANE ADDUCTS IN CAL. (MOLE THIOUREA) $^{-1}$ $^{o}K^{-1}$.

1 Cal = 4.1840 abs. Joules. 0 °C = 273.15 °K.

	Cyclohexane	2,2 - Dimethylbutane
Temp. T °K.	$S_T - S_0$	$S_T - S_0$
0	0	0
10	0.271	0.192
20	1.441	1.236
30	3.073	2.773
40	4.952	4.554
50	6.882	6.468
60	8.753	8.389
70	10.55	10.46
80	12.26	12.56
90	13.90	15.47
100	15.48	17.40
110	17.00	19.22
120	18.48	20.98
130	20.60	22.66
140	22.11	24.28
150	23.58	25.85
160	24.93	27.38
170	26.25	28.88
180	27.57	30.32
190	28.82	31.74
200	30.05	33.13

TABLE 33 (Continued).

Temp. T °K.	$S_T - S_0$	$S_T - S_0$
210	31.26	34.49
220	32.46	35.84
230	33.65	37.10
240	34.82	38.47
250	35.97	39.76
260	37.10	41.03
270	38.22	42.27
273.15	38.57	42.66
280	39.34	43.52
290	40.45	44.75
298.15	41.35	45.75
300	41.56	45.99

CHAPTER 9. DISCUSSION OF THE ANOMALIES OF THE THIOUREA - HYDROCARBON ADDUCTS.

(A) Host Lattice contributions.

The heat capacity of pure thiourea has been measured by Chang and Westrum (1961) and has been discussed by Westrum and McCullough (1963). (Fig. 58). Anomalous high values of the heat capacity were recorded in the temperature range 150 - 200°K, and three distinct heat capacity anomalies were observed.

a) at $169.33^{\circ}K$ $\Delta S \sim 0.04$ cal $^{\circ}K^{-1}$ mole $^{-1}$

b) at $171.20^{\circ}K$ $\Delta S < 0.01$ cal $^{\circ}K^{-1}$ mole $^{-1}$

c) at $\sim 200^{\circ}K$ $\Delta S \sim 0.17$ cal $^{\circ}K^{-1}$ mole $^{-1}$

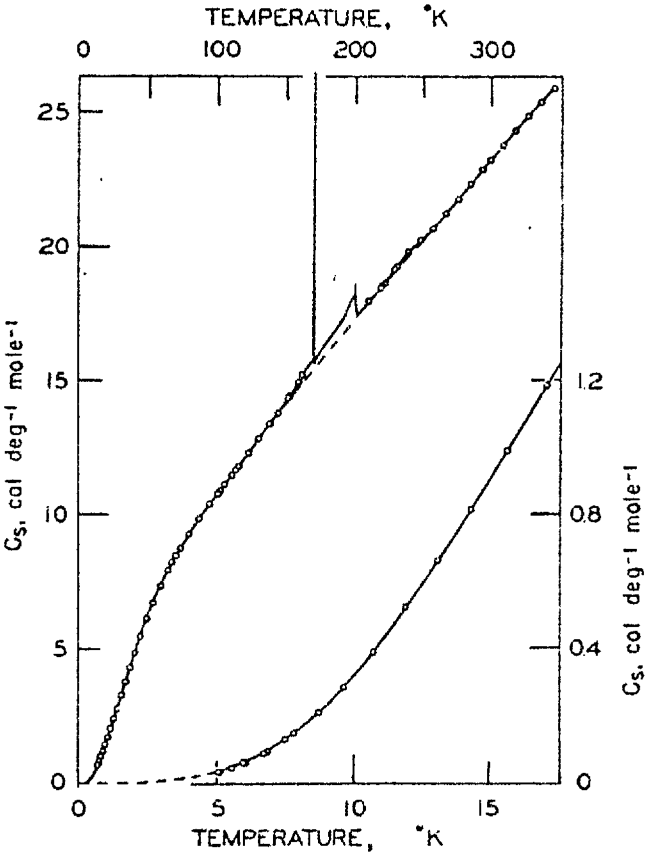
In addition a slight hump in the heat capacity was observed between 210 and 260°K.

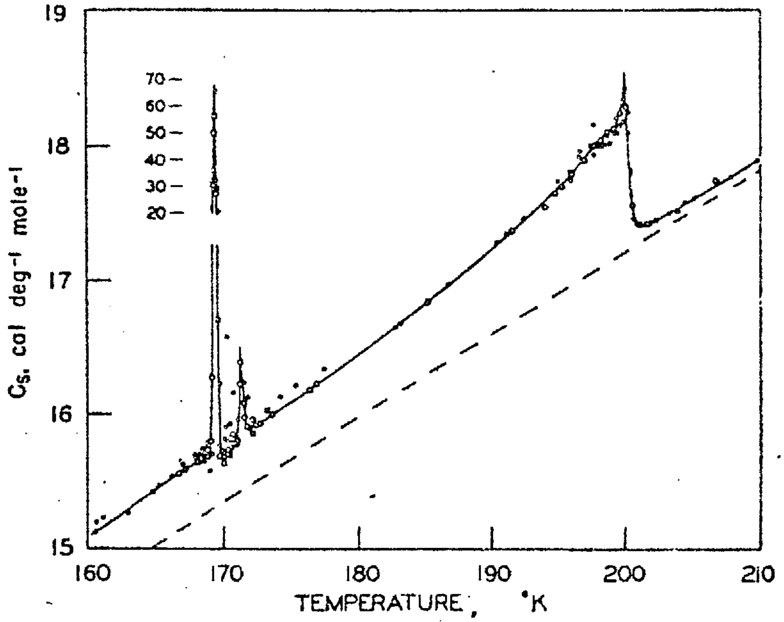
These anomalies are associated with the ferroelectric properties of thiourea, which were discovered by Solomon (1956) and further investigated by Goldsmith and White (1959) and Calvo (1960). Goldsmith and White have reported that thiourea is unique among known ferroelectrics in that it forms molecular instead of ionic crystals. The ferroelectric behaviour is associated with the relative displacements of entire molecules rather than with the motion of ions within the crystal. It is possible that the thiourea molecules in the rhombohedral lattice of the adducts may be capable of similar movements. Therefore, in attempting to explain the origin of the anomalies in the heat capacity of the thiourea adducts, the very real possibility of contributions from the thiourea lattice must be considered.

In pure thiourea and in the thiourea adducts, similar transitions in both shape and size have been found at about 170°K and therefore it seems likely that the transitions have a common origin. The fact that the enthalpies of the transitions in the two adducts do differ to a certain extent, when it would be expected that the molecules would have rather similar environments, is not unduly worrying, as Lenné (1954) has reported that the positions of the nitrogen atoms vary from adduct to adduct. The broad anomaly between 130 to 150°K in the heat capacity of thiourea - cyclohexane is similar in both shape and entropy change involved to the broad anomaly in the heat capacity of pure thiourea. No corresponding anomaly has been observed in the thiourea - 2, 2 dimethylbutane adduct.

A study of the dielectric properties of the thiourea adducts in the temperature region would no doubt be helpful in establishing if the transitions were due to the thiourea lattice. Valuable information might also be obtained by measuring the heat capacity of a deuterated thiourea adduct, as ferroelectric properties are well known to be often sensitive to deuteration.

Fig. 58. The Heat Capacity of Thiourea





Heat capacity of thiourea in the region of the dielectric anomalies

(B) Guest molecule contributions.

The major co-operative transitions in the heat capacities of the thiourea adducts are almost certainly due to the included hydrocarbon. Whereas in the urea adducts the position of the guest molecules relative to the lattice was fairly straightforward, the greater dimensions of the thiourea lattice leads to many more possible positions of locating the guest molecules. X-ray and analytical evidence indicate that the cyclohexane molecules are located near the plane of the sulphur atoms. Lenne (1954) has also suggested that the cyclohexane molecules are inclined at 35° to this plane. The position of the 2,2 dimethylbutane in the channels is not so clear on account of the shape of the molecule and the absence of any symmetrical packing, as indicated by the component analysis results of Redlich, Gable, Beason, and Millar. (1950).

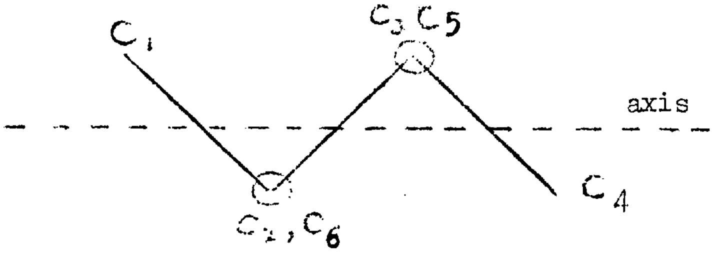
Thus, it is evident, that as far as presenting a theoretical model to explain these transitions, the thiourea - cyclohexane adduct is the simpler system.

Dr. N.G. Parsonage has developed a similar model to that used to explain the transitions in the urea adducts.

As in the urea adduct study, the inter molecular forces were assessed, in an attempt to find the most favourable positions of the molecules relative to each other and to the thiourea lattice. As suggested by other data, calculations were made with the cyclohexane molecules at various angles to the plane of the sulphur atoms and at various relative orientations with respect to the thiourea lattice and to their lateral and longitudinal neighbours. The sulphur atoms plane referred to is the plane perpendicular to the axis of the channel in which there are three sulphur atoms (see Fig. 2.).

There are six such planes in each unit cell. The cyclohexane molecules were considered to be in their chair form. The plane of the molecule is taken as that plane which includes the axis shown in Fig. 59 , and is perpendicular to the paper.

Fig. 59.



It was found that for a given angle to the plane of the sulphur atoms, in general there were three favoured positions.

This study led Dr. Parsonage to assign each cyclohexane molecule six possible configurations, three at 30° and three at 0° to the sulphur atom plane.

The energy of any particular state was then given by

$$\mathcal{E} = AV_2 + BV_3 + CV_4 \quad \ldots . \; 9\ (1)$$

where V_2, V_3, V_4, are interaction parameters determined from the intermolecular potential calculations and A, B, and C, are variables which depend on the configurations of the molecules.

The first term, AV_2, in 9 (1) is dependent on the position of the molecule with respect fo the lattice. V_2 is the lattice interaction parameter and

$$A = \left[1 + (- 1)^{\mu} \right] \quad \ldots . \; 9\ (2)$$

where μ = 1, 2, 3, 4, 5, or 6, according to the configuration of the molecule. If the molecule is in a sloping position with respect to the sulphur atoms, μ is even (i.e., 2, 4, or 6), and if it is in the plane of the sulphur atoms, μ is odd (1, 3 or 5), i.e., $A = 2$ if the molecule is sloping and $A = 0$ if molecule is in the same plane.

The second term, BV_3, refers to the interaction of the molecule with its longitudinal neighbours. V_3 is thus the longitudinal interaction parameter and

$$B = {}^1\!/_4 \left\{ 1 + (-1)^{\mu_1} \right\} \left\{ 1 + (-1)^{\mu_2} \right\} \left| \frac{\mu_1 - \mu_2}{6} \right|_{\text{mod } \frac{1}{2}} \qquad \text{.... 9 (3)}$$

$\mu_1 = 1(1)\,6$ refers to the configuration of the molecule as before and $\mu_2 = 1(1)\,6$ refers to the configuration of one of its longitudinal neighbours. If either one of these molecules is coplanar with the sulphur atoms $(-1)^{\mu} = -1$, and then $B = 0$. If both are sloping

$$B = \left| \frac{\mu_1 - \mu_2}{6} \right|_{\text{mod } \frac{1}{2}}$$

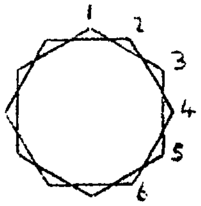
If in this case the molecules have the same values of μ, i.e., they are sloping but parallel, B again equals zero, but otherwise, $B = {}^2\!/_6$. The "mod $\frac{1}{2}$" restricts the number to the range 0 and $\frac{1}{2}$. If the number is greater or less than this range, it is either subtracted from six, or multiplied by minus one, or both.

The third term, V_4C, refers to the lateral interaction of the molecule. V_4 is the lateral interaction parameter and C is given by

$$C = \left(1 - \tfrac{1}{2}\left[1 + (-1)^{\mu_1} \right] - \tfrac{1}{2}\left[1 + \left\langle (-1)^{\mu_2} \right\rangle \right] \right) \left| \frac{1 - 2}{6} \right|_{\text{mod } \frac{1}{2}} \qquad \text{.... 9 (4)}$$

$\mu_1 = 1(1)\ 6$ is the configuration of the molecule as before and $\langle \mu_2 \rangle$ is the mean configuration of all the molecules. In the variables A and B it only mattered whether μ was an odd or even number, but in C the actual value from 1 to 6 is important. This arises as the three sites considered in each of the sloping and horizontal positions are not directly above each other (Fig. 60).

Fig. 60.



Looking down the axis of the thiourea channel.

$\langle \mu_2 \rangle$ has a value between 1 and 6. $\langle (-1)^{\mu_2} \rangle$ has a value between -1 and +1 and is a measure of the relative occupation of the sloping and non-sloping positions. The adoption of an approximation of the lateral interaction in this way is made so as to avoid an exact three dimensional Ising model, for which at present there is no solution. In this way the exact Ising model is retained for the longitudinal interactions, but a Weiss approximation is made for the lateral interactions. This procedure is similar to that developed for the urea adducts.

If μ_1 is even

$$C = 1 - \tfrac{1}{2}\left[1 + \langle (-1)^{\mu_2} \rangle \right] \left| \frac{\mu_1 - \langle \mu_2 \rangle}{6} \right|_{\mathrm{mod}\ \frac{1}{2}} \qquad \text{.... } 9\ (5)$$

and if μ_1 is odd

$$C = -\tfrac{1}{2}\left[1 + \langle (-1)^{\mu_2} \rangle \right] \left| \frac{\mu_1 - \langle \mu_2 \rangle}{6} \right|_{\mathrm{mod}\ \frac{1}{2}} \qquad \text{.... } 9\ (6)$$

The configurational partition function is then determined using the matrix method explained by ter Haar (1954). As there are six possible configurations of each molecule, the matrix is a 6 x 6 square matrix made up of elements of the form 9 (1). The partition function is then the largest eigenvalue, λ, of the matrix. On account of two roots being zero the eigenvalue equation reduces to a quartic equation of the form.

$$\lambda^4 - a_1 \lambda^3 + a_2 \lambda^2 - a_3 \lambda + a_4 = 0 \qquad \ldots .9\ (7)$$

$$\begin{aligned} &\lambda^4 - \lambda^3 \sum_{i=1}^{6} H_i + \lambda^2 \left[1 - \exp\left(-\frac{4/6\, V_3}{kT}\right)\right](H_2 H_4 + H_4 H_6 + H_2) \\ &- \lambda \left\{ \left[1 - 3 \exp\left(-\frac{4/6\, V_3}{kT}\right)\right] + 2 \exp\left(-\frac{2/6\, V_3}{kT}\right) H_2 H_4 H_6 \right. \\ &\left. - \left[1 - \exp\left(-\frac{2/6\, V_3}{kT}\right)\right]^2 (H_1 + H_3 + H_5)(H_2 H_4 + H_4 H_6 + H_6 H_2) \right\} \\ &+ 2 \left[\exp\left(-\frac{2/6\, V_3}{kT}\right)\right]^3 H_2 H_4 H_6 (H_1 + H_3 + H_5) = 0 \end{aligned}$$

$$\ldots .\ 9\ (8)$$

where $H_i = \exp\left[-\frac{1}{kT}\left\{-\frac{V_4}{2}\left(-1 + \langle(-1)^{\mu}\rangle\right)\right\} \left|\frac{i - \langle\mu\rangle}{6}\right|_{\text{mod } \frac{1}{2}}\right]$

for i = 1, 3 and 5

and $H_i = \exp\left[-\frac{1}{kT}\left\{2V_2 - \frac{V_4}{2}\left(1 + \langle(-1)^{\mu}\rangle\right)\right\} \left|\frac{i - \langle\mu\rangle}{6}\right|_{\text{mod } \frac{1}{2}}\right]$

for i = 2, 4 and 6

Equation 9 (7) includes the two unknowns $\langle(-1)^{\mu 2}\rangle$ and $\langle\mu_2\rangle$. In order to solve for the partition function, equation 9 (7) is differentiated with respect to V_2 to give 9 (8) and then equated with equations 9 (10) and 9 (11) which are obtained by differentiating the partition function, λ , by V_2 and V_4 respectively.

$$\lambda = \sum_{\mu} \exp - \frac{1}{kT} \sum_{i} \left(AV_2 + BV_3 + CV_4\right)_i \qquad \ldots .\ 9\ (9)$$

$$\frac{1}{\lambda}\left(\frac{d\lambda}{dV_2}\right)_{V_3\,V_4} = -\frac{(1 + \langle(-1)^{\mu}\rangle)}{kT} \qquad \ldots .\ 9(10)$$

$$\frac{1}{\lambda}\left(\frac{\partial\lambda}{\partial V_{41}}\right)_{\substack{V_2\,V_3\\ V_{42}\ldots V_{46}}} = + \frac{\{(-1)^1 + \langle(-1)^{\mu}\rangle\}\{\sum_i iP(i) - 1\}}{2.6\ kT}\ P(1)$$

$n = 2, 3, 4.$

$$\frac{1}{\lambda}\left(\frac{\partial\lambda}{\partial V_{4n}}\right)_{\substack{V_2\,V_3\\ V_{41}\,V_{45}\,V_{46}}} = + \frac{[(-1)^n + \langle(-1)^{\mu}\rangle][n - \sum_i iP(i)]}{2.6\ kT}\ P(n)$$

$n = 5, 6.$

$$\frac{1}{\lambda}\left(\frac{\partial\lambda}{\partial V_{4n}}\right)_{\substack{V_2\,V_3\\ V_{41}\ldots V_{44}}} = + \frac{[(-1)^n + \langle(-1)^{\mu}\rangle][6 - n + \sum_i iP(i)]}{2.6\ kT}\ P(n)$$

$$\ldots\ 9(11)$$

Similar, somewhat more complicated treatment, leads the to the following expressions for P(1) ..... **P**(6), the probabilities of the included molecules being in states 1 to 6 respectively.

$$P(i)= \frac{\lambda^3 H_i - \lambda\left\{\exp\left(-\frac{\frac{2}{6}V_3}{kT}\right)-1\right\}^2 H_i(H_2H_4+H_4H_6+H_6H_2)-2\left\{\exp\left(-\frac{\frac{2}{6}V_3}{kT}\right)-1\right\}^3 H_2H_4H_6H_i}{4\lambda^4-3\lambda^3 a_1+2\lambda^2 a_2-\lambda a_3}$$

for $i = 1, 3, 5$. 9 (12)

and

$$P(i)= \frac{1}{4\lambda^4-3\lambda^3 a_1+2\lambda^2 a_2-\lambda a_3}\left\{\lambda^3 H_i-\lambda^2\left[1-\exp\left(-\frac{\frac{4}{6}V_3}{kT}\right)\right]\cdots\right.$$

$$\cdots H_i\,(H_{i+2}+H_{i+4})+\lambda\left[1-3\exp\left(-\frac{\frac{4}{6}V_3}{kT}\right)+2\exp\left(-\frac{V_3}{kT}\right)\right]\cdots$$

$$\cdots -\lambda\left[\exp\left(-\frac{\frac{2}{6}V_3}{kT}\right)-1\right]^2 H_i(H_1+H_3+H_5)(H_{i+2}+H_{i+4})\quad\cdots$$

$$\left.\cdots +2\left[\exp\left(-\frac{\frac{2}{6}V_3}{kT}\right)-1\right]^3 H_2H_4H_6(H_1+H_3+H_5)\right\}$$

.... 9 (13)

For $i = 2, 4, 6$ where $H_8 = H_2$ and $H_{10} = H_4$

The coupling parameters chosen from the intermolecular potential energy data were as follows, $V_2 = -400$; $V_2 = 1640$; and $V_4 = -17$. (In cal. per Avagadro's number of interactions). Using these parameters the Ising – Weiss model predicted a major order change between 50 and 90°K (Fig. 61). The probabilities, P(i) (Fig. 62) indicated that below 50°K the molecules were mainly located at the configuration, ~~i.e~~ $\mu = 4$, that is a sloping configuration. Above 90°K the sloping sites were occupied in approximately equal proportions. The population of the horizontal sites gradually increased the temperature (Fig. 62).

The predicted order change occurred at a lower temperature and was far less sharp than the major transition found at ~ 130°K in the heat capacity of thiourea cyclohexane. In view of this it was decided to increase the lateral interaction perameter, V_4, to – 85 and then to – 170. Although the temperature of the order change became more compatible with the experimental observation, the sharpness of the predicted transition was still not improved.

The two thiourea adducts studied in this work have been shown to have anomalous regions in their heat capacities, which differ quite considerably from each other. In the urea adducts much information was gained by studying a series of related guest molecules, that is, the homologous series of n-alkanes and 1-alkenes, but the understanding of the anomalies in the thiourea adducts is often complicated by the difficulty of determining the location of the guest molecules in the channel. However similar studies on guest molecules which are included in an integral molar ratio, as is cyclohexane, could lead to a greater understanding of the problem. The knowledge of the system, and indeed the knowledge of intermolecular forces involved, would then probably be still insufficient to successfuly predict the anomalies in the adducts studied, but their subsequent successful interpretation may be possible.

Fig. 61. Thiourea - Cyclohexane . Ising - Weiss Model.

Variation of RT loge Partitition Function with Temperature

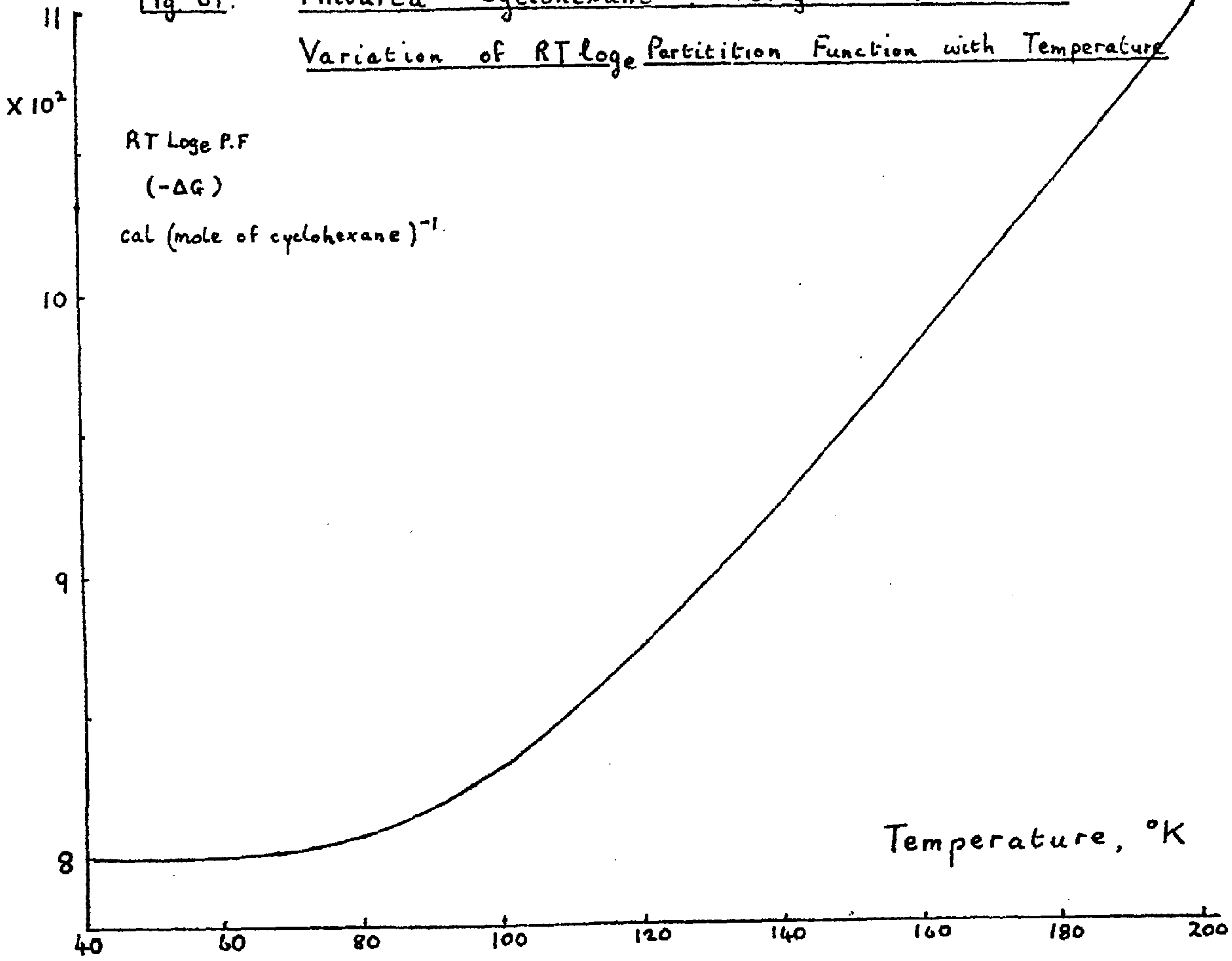
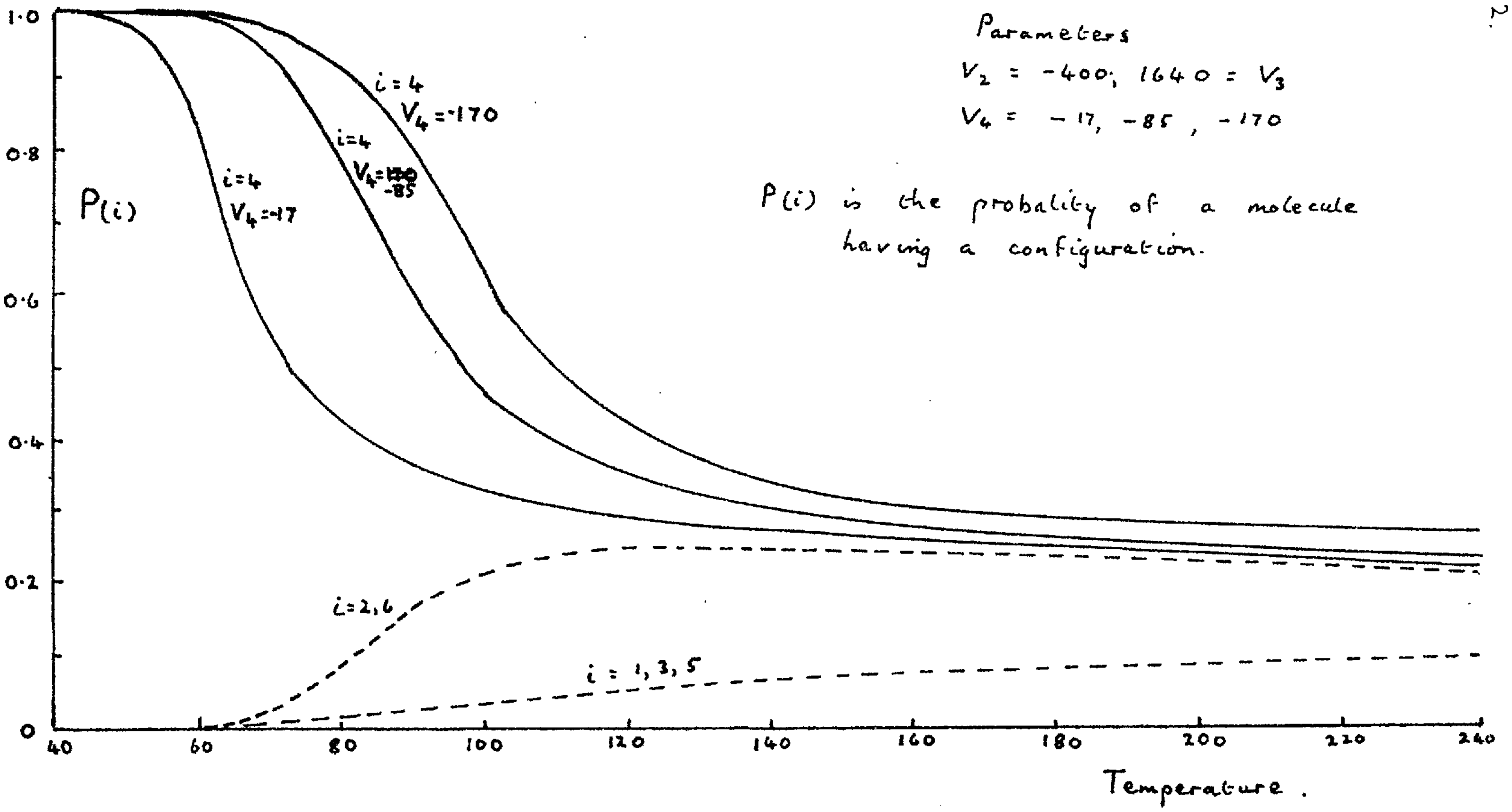


Fig. 61.

Fig. 62. Thiourea Cyclohexane Ising-Weiss Model

Variation of P(i) with Temperature.



Parameters

V_2 = -400; 1640 = V_3

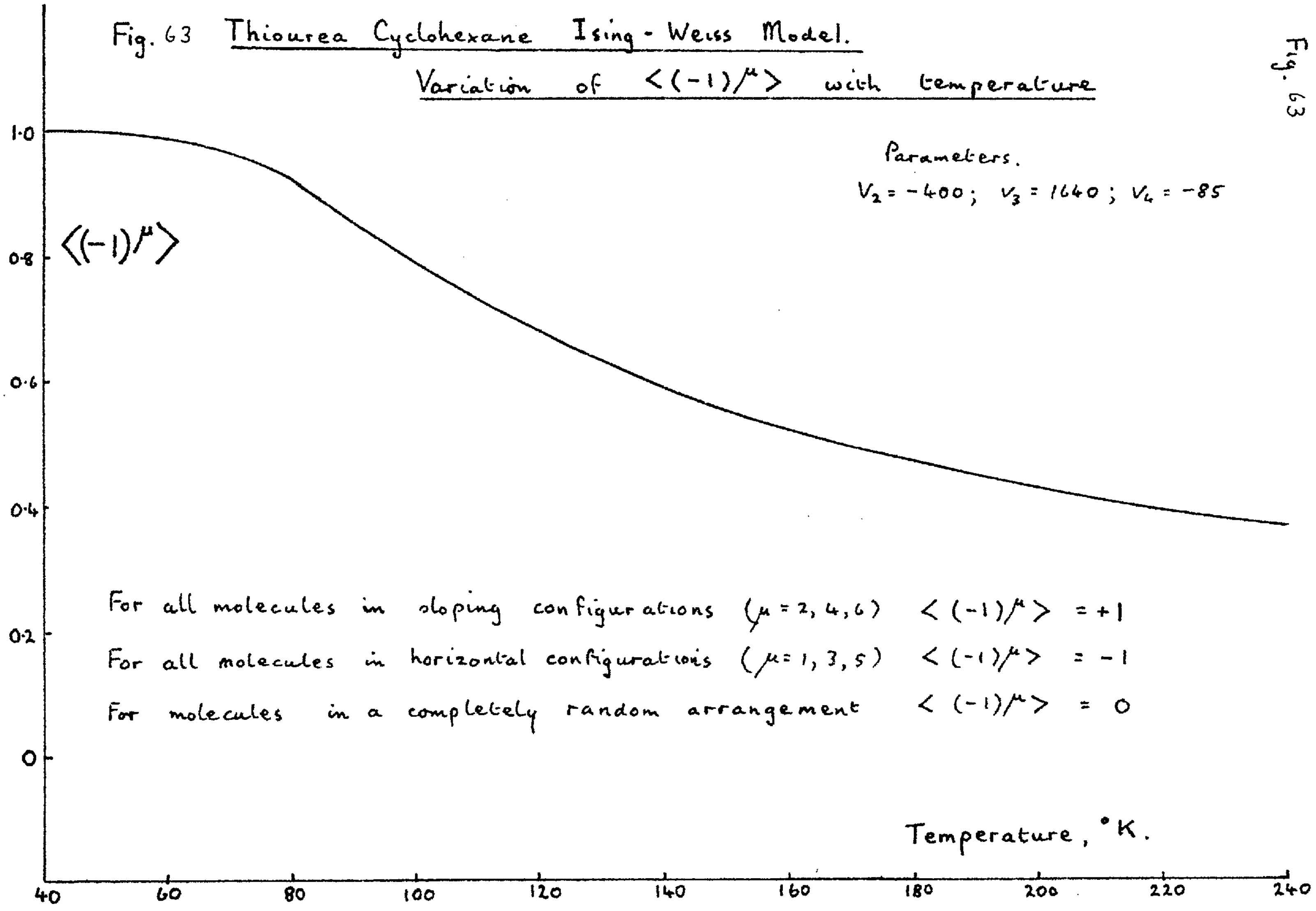
V_4 = -17, -85, -170

P(i) is the probability of a molecule having a configuration.

Fig. 62.

Fig. 63 Thiourea Cyclohexane Ising - Weiss Model.

Variation of $\langle(-1)^{\mu}\rangle$ with temperature



Parameters.

$V_2 = -400$; $V_3 = 1640$; $V_4 = -85$

For all molecules in sloping configurations ($\mu = 2, 4, 6$) $\langle(-1)^{\mu}\rangle = +1$

For all molecules in horizontal configurations ($\mu = 1, 3, 5$) $\langle(-1)^{\mu}\rangle = -1$

For molecules in a completely random arrangement $\langle(-1)^{\mu}\rangle = 0$

Fig. 63

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