TRANSITION TYPES IN HYDROCARBONS AND RELATED SUBSTANCES*

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More than 300 pure organic substances have been studied in detail by calorimetric methods. More than one-third of these compounds exhibit some type of thermal anomaly in the condensed phase. In 1940 Deffet[1] listed nearly 1,200 organic sustances in which polymorphism had been detected by either thermal or non-thermal methods, or both. Obviously, phase transformations other than melting are among the more common phenomena encountered in physical and thermodynamic studies of organic substances. Despite an abundance of experimental facts accumulated in the last 50 years, and despite the efforts of many able scientists to interpret these facts, satisfactory theoretical explanations of phase transformations in organic solids are rare.

Several recent reviews illustrate clearly the difficulties met in attempts to understand phase transformations either in terms of classical thermodynamic phase relations or of molecular and structural phenomena[2-4]. Theoretical treatments involving the use of statistical mechanics have yielded results in qualitative or, occasionally, quantitative agreement with experimental data for a few simple systems, most of which are composed of inorganic substances. So far these treatments are limited to two-dimensional cases, and even so, are quite complex. Partial interpretations of transitions of some molecular crystals have been made in terms of the order–disorder and structural transformations pre.umed to occur, but the common lack of adequate structural information usually makes such interpretations only tentative.

One of the reasons for the seemingly slow progress in developing theoretical interpretations of phase transformations may be that the theorist cannot be sure as to the nature of the phenomena that he must explain. The experimental data on phase transformations are scattered in the literature and often are reported in a confusing way. Different authors use the same terminology for what appear to be different phenomena, or different terminology for what appear to be similar phenomena. The purpose of this paper is to present in brief outline a systematic classification of the types of transitions that occur in hydrocarbons and related substances as an aid in eliminating some of the present confusion.

CLASSIFICATION OF TRANSITION TYPES

Jaffray[2], among others, discussed the difficulty of classifying phase transformations by relating them to either the macroscopic (thermodynamic) or microscopic theories of such phenomena. He presented a classificaton based on the geometrical form of the free energy and entropy curves below, at, and above a transition point. The classification given here is essentially

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that of Jaffray, but it is strictly phenomenological and includes some types not recognized as distinct by Jaffray. Because the classification is based entirely on observed heat capacity and enthalpy curves, only substances studied by calorimetric methods were considered.

From examination of results reported for the 95 compounds listed in *Table 1*, it was concluded that *seven* types of transformations in solid phases could be distinguished phenomenologically. Some of these types have been named in the literature, but the meanings attached to such terms as " first order ", " isothermal ", " second order ", " second kind ", " lambda ", and " higher order " are not uniform. For this reason, the types described in the following paragraphs are designated by numbers and/or letters so chosen as to have some mnemonic value.

Table 1. Solid–solid transitions in organic substances

Compound	Transition type*	Ref.†
Saturated hydrocarbons		
Methane	3N	5
Monodeuteromethane	3N(2)	6
Deuteromethane	3N(2)	7
n-Butane	1	8
2,2-Dimethylpropane	2I	9
2,2-Dimethylbutane	1(2)	10
2,3-Dimethylbutane	3I	10
2,2-Dimethylpentane	3N	11
2,2,3-Trimethylbutane	3N(2), 1	11
2,2,3,3,-Tetramethylbutane	2I	12
n-Nonane	2I	13
2,2-Diethylpentane	H,1(2)	11
n-Undecane	2I	13
n-Tridecane	2I	13
n-Pentadecane	2I	13
Unsaturated hydrocarbons		
2-Butyne	2N	14
Polyisobutene	G	15
3,3-Dimethyl-1-butene	2I	16
2,3-Dimethyl-2-butene	1	17
1-Decene	1	18
1-Undecene	1	18
1-Dodecene	3I	18
1-Hexadecene	3N	18
Cyclic hydrocarbons		
Cyclobutane	2N	19
Cyclopentene	G, 3I	20
Cyclopentane	1, 3I	21
Cyclohexene	1	20
Cyclohexane	3I	22
1,3,5-Cycloheptatriene	G, 2I	23
Cycloheptane	1(3)	23
1,1-Dimethylcyclopentane	3I	24
1,cis-2-Dimethylcyclopentane	1	24
Cyclo-octane	1(2)	23
1,1-Dimethylcyclohexane	1	25
1,cis-2-Dimethylcyclohexane	G, 1	25
cis-Hexahydroindan	1(2)	11
cis-Decahydronaphthalene	G, 1	26
n-Decylcyclohexane	H	11

* The number of transitions of each type is shown in parentheses if more than one occur.
† Only the most recent reference is listed.

TRANSITION TYPES IN HYDROCARBONS

Table 1—continued

Compound	Transition type*	Ref.†
Aromatic hydrocarbons		
1,3-Dimethylbenzene	H	27
1,4-Dimethylbenzene	H	27
1,3,5-Trimethylbenzene	H	28
1-Methylnaphthalene	1	26
2-Methylnaphthalene	2I	26
Pentamethylbenzene	1	29
Hexamethylbenzene	3N, H	30
Oxygen compounds		
Methanol	3I	31
Acetone	H	32
Furan	2I	33
n-Butanoic acid	2N	34
1,4-Dioxane	1	35
Cyclopentanol	1, H	36
n-Pentanol	H	37
2-Methyl-2-butanol	1	37
1-Sorbose	2N	38
Benzyl alcohol	H	39
Sulphur compounds		
Methanethiol	1	40
Thiacyclobutane	3I	41
1-Propanethiol	1	42
2-Propanethiol	2I	43
Thiophene	H(2), 3I	44
2-Methyl-2-propanethiol	3I,1(2)	45
2-Methylthiophene	G	46
3-Methylthiophene	G	47
Thiacyclohexane	2I, 3N, 1	48
2-Methyl-2-butanethiol	3N,2I	11
3,3-Bisthiaethyl-2,4-dithiapentane	1(2)	49
Benzenethiol	H	11
Cyclopentyl-1-thiaethane	3N, 1	11
Benzo(b)thiophene	G, 2I	50
Miscellaneous compounds		
Carbon tetrabromide	2N	51
Carbon tetrachloride	2I	52
Carbon tetrafluoride	2I	53
Chlorodifluoromethane	H	54
Sodium methoxide	H	55
Methylamine	H	56
Methylammonium chloride	1(2)	57
Chloropentafluoroethane	1	58
Polytetrafluoroethylene	3N,H	59
1,1,1-Trichloroethane	2I	60
1,1,1-Trifluoroethane	2I	61
Sodium acetate	H	62
1,2-Dibromoethane	2I	63
1,2-Dichloroethane	H	63
Dimethylcadmium	1	64
sym-Dimethylhydrazine	G	65
Dimethylaminediborane	2I	66
Propenenitrile	1	11
Octafluorocyclobutane	G,3N,2N(3)	67
Pyrrole	H	11
Pyrrolidine	2I	11
Undecafluoropiperidine	2I,1	11
n-Pentylammonium chloride	3N(2)	68
n-Hexadecafluoroheptane	1	69
Copper(II) acetonylacetone	H	70

* The number of transitions of each type is shown in parentheses if more than one occur.
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Type 1—The Type 1 transition illustrated in *Figure 1* is familiar as the so-called " isothermal " or " first order " transition, which is believed to occur entirely isothermally in the manner of melting for most pure substances.
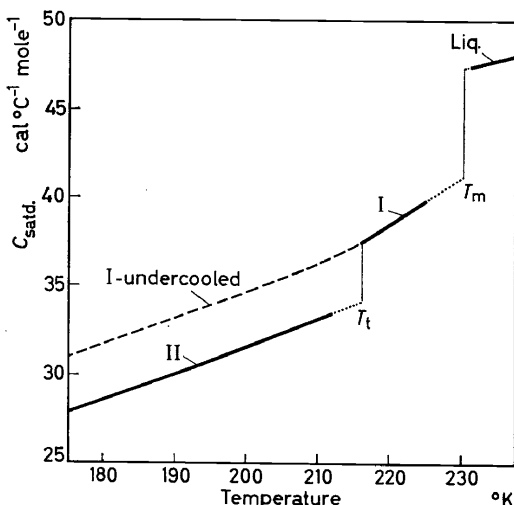

Figure 1. Type 1 transition in *cis*-decahydronaphthalene[26]: $T_m = 230 \cdot 18°K$, $\Delta H_m = 2268$ cal/mole; $T_t = 216 \cdot 1°K$, $\Delta H_t = 510 \cdot 6$ cal/mole

Thus, the heat capacity is " normal " immediately above and below the transition point, and the two crystalline phases involved are thermodynamically distinct. In fact, as the illustration shows, the high-temperature phase (crystals I) often may be undercooled, and occasionally the low-temperature phase (crystals II) may be superheated.
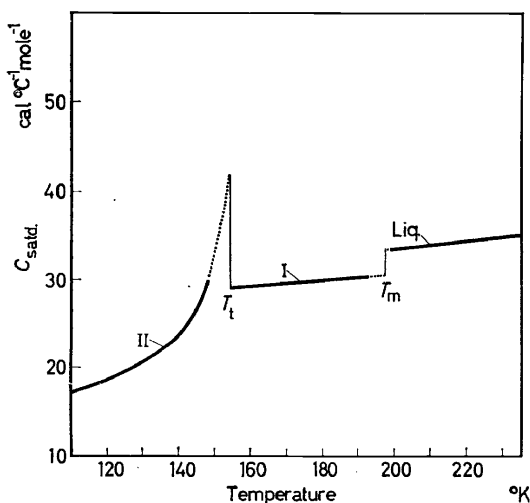
Figure 2. Type 2I transition in cycloheptatriene[23]: $T_m = 197 \cdot 92°K$, $\Delta H_m = 277 \cdot 4$ cal/mole; $T_t = 153 \cdot 98°K$, $\Delta H_t = 560 \cdot 9$ cal/mole

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Type 2I—The Type 2I (isothermal) transition is characterized by an upsweep in the heat capacity curve below the transition temperature, at which the remainder of the transformation proceeds isothermally. The heat capacity is " normal " above the transition temperature. An extreme example of this type is given in *Figure 2*. In other cases, the " pre-transition" effect shown by the heat capacity curve of crystals II is much less pronounced. Also, the heat capacity of crystals I at the transition point may be either greater or less than that of crystals II. As a Type 1 transition resembles the melting of a *pure* substance, so the Type 2I transition resembles the melting of an *impure* substance.

Type 3I—Transitions of Type 3I, illustrated in *Figure 3*, differ from those in Type 2I only in that the heat-capacity variation for crystals I shows that transformation continues *above* the point of isothermal transition in addition to beginning below that point. Comparison of *Figures 2* and *3* shows that this distinction is real from a phenomenological viewpoint.
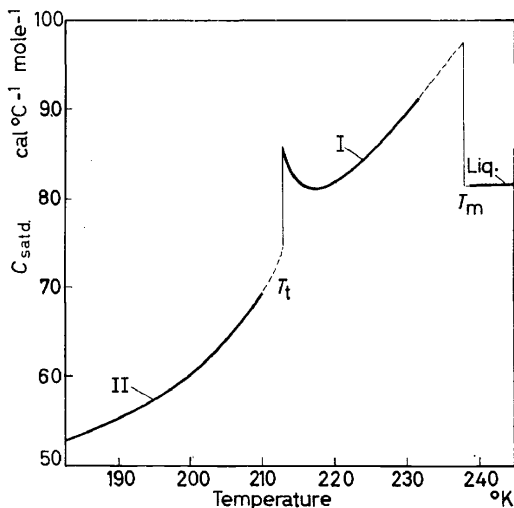

Figure 3. Type 3I transition in 1-dodecene[18]: $T_m = 237 \cdot 93°K$, $\Delta H_m = 4758$ cal/mole; $T_t = 212 \cdot 9°K$, $\Delta H_t = 1088$ cal/mole

Type 2N—*Figure 4* is an example of a Type 2N (non-isothermal) transition, so designated because of its apparent resemblance to a Type 2I transition. However, although the heat capacity may reach very high values at the transition point, the Type 2N transition appears to be entirely *non-isothermal*.

Type 3N—The Type 3N and Type 3I transitions are related in the same manner as those of Type 2N and Type 2I. As illustrated in *Figure 5*, the Type 3N transition occurs over a range of temperature both above and below that at which most of the transformation occurs, but at no point does the process proceed isothermally.
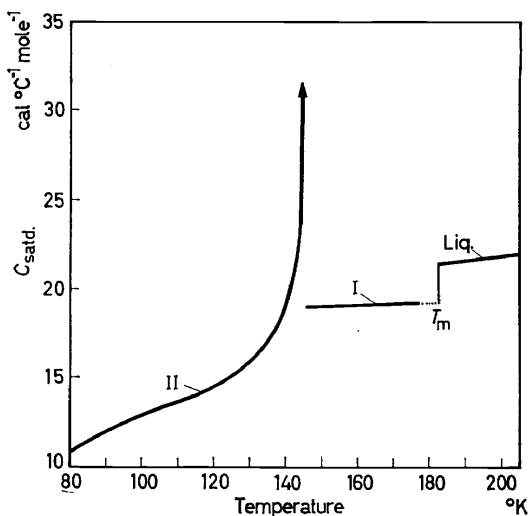
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Figure 4. Type 2N transition in cyclobutane[19]: $C_{max} = 876$ cal $°C^{-1}mole^{-1}$ at $145·54°K$; $T_m = 182·43°K$, $\Delta H_m = 260·1$ cal/mole

Type H—Transitions that are evidenced only by a maximum or " hump " in a continuous heat capacity curve are classed as Type H. The heat capacity curve shown in *Figure 6* is typical, but the hump often is much broader. The maximum heat capacity value usually is no more than twice the " normal " value.

Type G—Type G (glass-like) transitions, illustrated in *Figure 7*, are so designated because of their obvious resemblance to the glassy transitions
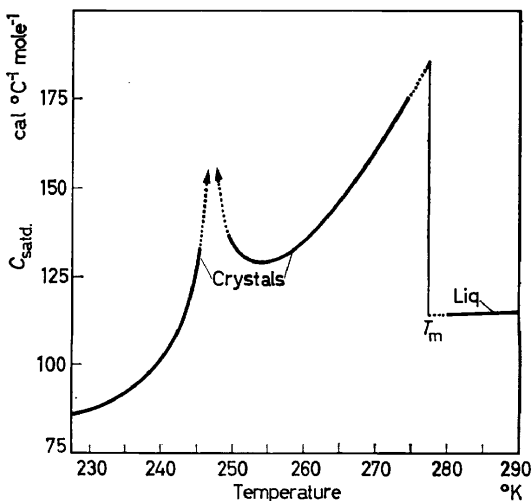

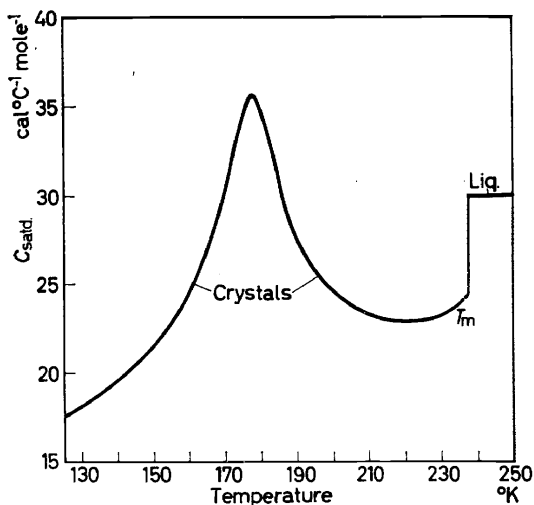*Figure 5.* Type 3N transition in 1-hexadecene[18]: $T_m = 277·51°K$, $\Delta H_m = 7216$ cal/mole

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Figure 6. Type H transition in 1,2-dichloroethane[63]: $T_m = 237 \cdot 2°K$, $\Delta H_m = 2112$ cal/mole

that occur in some under-cooled organic liquids. Indeed, both the true glass transitions in liquids and the Type G transitions in solids probably involve the same kind of " freezing-in " of molecular degrees of freedom. In some solids, the Type G transition may be neither so sharp nor so large as that in *Figure 7*. Also, although the slight peak in *Figure 7* is similar to those observed in some studies of glasses, it may not be real.
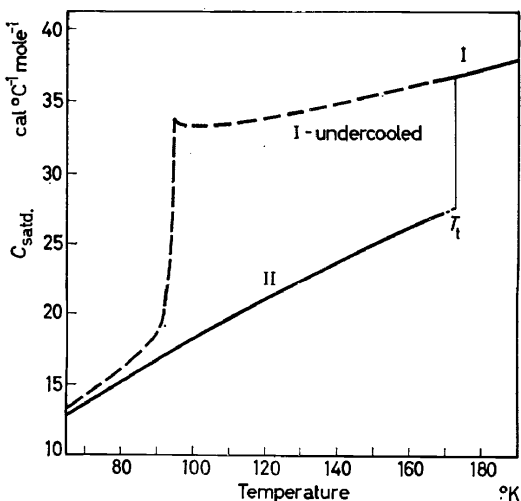

Figure 7. Type G transition in 1,*cis*-2-dimethylcyclohexane[25]: $T_t = 172 \cdot 50°K$, $\Delta H_t = 1973 \cdot 4$ cal/mole

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DISCUSSION

The classification given here was made with only incidental attention to possible interrelationships among the several types or to theoretical explanations that have been advanced for some of the types. This approach provides a fresh point of departure for further study, but an evaluation of the distinctions that have been drawn is necessary. As knowledge of phase transformations increases, it is likely that the number of distinct transition types will be recognized as smaller than the number distinguished here. Such simplification most probably will be the result of theoretical developments, for experimental methods already have been pushed nearly to the limit of their power of discernment.

Two effects limit experimental elucidation of the nature of phase transformations. The first, which might be eliminated and which ought to be the subject of more study, is the effect of impurities. Solid-insoluble impurities may have little effect on solid–solid phase transformations, but solid-soluble impurities could have a pronounced effect. Scott et al.[12] showed that the transition temperature of 2,2,3,3,-tetramethylbutane varies in samples of different purity. The second effect, which may not be subject to elimination, is that of the slow thermal equilibration so common in organic crystals. Experience in this Laboratory and elsewhere has shown that thermal equilibration in the vicinity of transition points may require more than 72 hours. Thus, accurate heat capacity measurements in the region of a phase transformation may be impossible, and it may not be feasible even to determine whether or not a transition is isothermal. The dotted portions of the curves in *Figures 1–7* indicate regions in which reliable heat capacity measurements could not be made.

The limitations of experimental investigations are responsible for some arbitrariness in this classification. There may be no real difference between transitions of Types 2I and 2N, Types 3I and 3N, or even Types 3N and H. On the other hand, *phenomenologically* similar types may be quite different in terms of detailed transformation processes. Thus, any theory or theories of phase transformations must account for both the *apparent* differences and the *apparent* similarities among the transition types that have been observed in hydrocarbons and related substances.

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