A CORRELATION OF THE ENTROPY OF FUSION OF MOLECULAR CRYSTALS WITH MOLECULAR STRUCTURE

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I. PURPOSE AND SCOPE

The increasing technological importance of crystallization as a separation process makes it worthwhile to provide the process engineer with the means to estimate the heat or the entropy of fusion of novel substances for which these data have not yet been determined experimentally. Heat of fusion data are also required for the calculation of the solubility of crystals as well as for the heat of sublimation of crystals, useful data for the correlation of elastic properties of solids (13, 15).

The purpose of the present correlation is to provide the means for estimating the heat of fusion from no more information than molecular structure and melting point. The scope of the method includes all molecular crystals. Owing to the very complicated problems of theory, the proposed method is almost entirely empirical.

II. GENERAL PRINCIPLES

Since the melting point (T_m) of a substance is not easily—if at all—predictable, but is easily determined experimentally, it will be assumed as given. This is an important qualification because calculation of the heat of fusion (ΔH_m) would call for a thorough knowledge of the crystal structure as well as of the expansion at the melting point (ΔV_m), neither of which is often available; however, the entropy of fusion (*i.e.*, $\Delta S_m = \Delta H_m/T_m$) is related to molecular structure in a manner that permits generalization with very little, if any, extra information.

Several reviews of the relations between the entropy of fusion and molecular structure have appeared in the literature (40, 57, 74, 75). Several of these also dealt with theoretical problems involved. Their contents will be assumed as known. The insights developed from theoretical analyses will be used in the construction of empirical correlations. An important consideration to keep in mind is the absence, if not impossibility, of an all-inclusive theory because of the large differences in mechanisms of fusion depending on differences in molecular and crystal structure.

Crystals composed of symmetrical molecules often "melt" in distinct stages; *i.e.*, the melting point is preceded by first-order solid–solid-phase transitions at T_{tr}. The incidence and location of T_{tr} (say, relative to T_m) are rarely predictable. An attempt to estimate the corresponding entropy of transition, ΔS_{tr}, from molecular and crystal symmetry considerations (45) has only been moderately successful. Hence, in the following only the entire melting and transition process will be treated; *i.e.*, the sum of all entropies of transition and of fusion

$$\Sigma\Delta S_{m,tr} \equiv \Delta S_m + \Delta S_{tr}(1) + \Delta S_{tr}(2) + \ldots$$

will be correlated with molecular structure.

Phenomenologically, the entropy of fusion (and/or transition) consists of two components: that due to the volume increase (ΔV_m), ΔS_m^v, and the entropy of fusion at constant volume, ΔS_m^j. The common name "configurational entropy of fusion" for ΔS_m^j should be avoided because of the tacit (popular) implication that it is the part of ΔS_m that is calculated by molecular theories

$$\Delta S_m^v = (\partial S/\partial V)_p \Delta V_m = \alpha K_0 \Delta V_m$$

TABLE I

COMPARISON OF ΔS_m AND ΔS_m^j WITH MOLECULAR STRUCTURE

Simple Molecules

	Ar	N_2	O_2	CH_4
$\Delta S_m^v/R$	0.90	0.57	0.36	
$\Delta S_m/R$	1.69	1.36	1.0	1.25
$\Delta S_m^j/R$	0.79	0.79	0.64	

Aryl Halides

	C_6H_5F	C_6H_5Cl	C_6H_5Br	C_6H_5I	p-$C_6H_4Cl_2$
$\Delta S_m^v/R$	2.10	1.42	1.60	1.83	3.16
$\Delta S_m/R$	5.87	5.10	5.26	4.90	6.70
$\Delta S_m^j/R$	3.77	3.68	3.69	3.56	3.54

Methylbenzenes

	C_6H_6	C_6H_5Me	*p*-Xylene	*m*-Xylene	*o*-Xylene
$\Delta S_m^v/R$	1.76	2.0	3.25	2.06	1.63
$\Delta S_m/R$	4.25	4.48	7.20	6.18	6.61
$\Delta S_m^j/R$	2.49	2.48	3.95	4.12	4.98

TABLE II

ENTROPY OF FUSION CALCULATED BY MEANS OF HSE THEORY

Substance	S_r/R	$\Sigma S_{tor}/R$	$\Sigma \Delta S_{m.tr}/R$ Calcd	$\Sigma \Delta S_{m.tr}/R$ Exptl
Benzene	8.91	5.40	4.51	4.25
Naphthalene	11.92	6.75	6.17	6.48

where α and K_0 are the expansion coefficient and zero-pressure bulk modulus, respectively. Since at T_m, $(\alpha K_0)_{liq} = (\alpha K_0)_{cryst}$, the choice of reference phase is immaterial.

Inspection of the ΔS_m^v and ΔS_m^j data of Table I shows the expected greater regularity among the ΔS_m^j data of a given group of compounds than among their straight entropy of fusion data. This phenomenon is especially striking among the low molecular weight substances Ar, N_2, and O_2 and among the aryl halides. Somewhat more surprising is the sequence of ΔS_m^j for benzene, toluene, and xylenes, where it should be remembered, however, that ΔV_m(toluene) is only an estimated value. Since the sparsity of ΔV_m data and the absence of any means of predicting this datum preclude the use of ΔS_m^j for engineering calculations, the present work is exclusively concerned with the more difficult task of correlating ΔS_m with molecular structure.

A very general molecular model for the melting process by Hirschfelder, Stevenson, and Eyring (HSE) (23) and the very similar treatment by Chihara and Shinoda (17) assume free rotation of the molecules in the liquid and arrive at

$$\Delta S_m = \Delta S_p + \Delta S_m(\text{rot})$$

where ΔS_p is the entropy contribution due to positional disordering of the crystal, and

$$\Delta S_m(\text{rot}) = S_r - S_{tor}$$

where S_r is the appropriate rotational contribution to gas-phase entropy. Most often

$$S_r = R \ln [\pi^{1/2}(T/39.6)^{3/2}10^{60}(I_1I_2I_3)^{1/2}/\sigma]$$

is the entropy contribution of the freely rotating rigid polyatomic nonlinear molecule, and

$$S_{tor} = \Sigma_n S_v$$

is the sum of the entropy contributions due to torsional oscillations in the crystal lattice. This term can be quite large. The appropriate libration frequencies are difficult to obtain, but a fair number of such frequencies have been measured (32), and a correlation permitting an estimate from a knowledge of the heat of sublimation and the moments of inertia of a molecule has been prepared.

According to Lennard-Jones (36) $\Delta S_p = 1.7R$, and according to HSE $\Delta S_p = R$. A hard-sphere model of solid and liquid by Longuet-Higgins and Widom (38) yields $\Delta S_m = 5.8R(V_L - V_s)V_c = 1.64R$ and is otherwise in fair accord with the triple point properties of rare gas solids. Globular molecules follow more nearly the HSE prediction.

A recent dislocation model of the melting process by Mizushima (48) yields ΔS_p as function of crystal defect characteristics which are well known in metals but generally unknown for molecular crystals. The same author concludes that the change in translational vibration frequency on melting leads to a significant contribution ΔS_{vibr} neglected by Lennard-Jones and HSE. One can estimate $\Delta S_{vibr} \approx {}^1/_2(R) \ln [\Delta H_s/(\Delta H_s - \Delta H_m)]$ because $\omega_{cryst} \sim (\Delta H_s/M)^{1/2}$ and $\omega_{liq} \sim (\Delta H_v/M)^{1/2}$.

Since the HSE theory assumes that molecules rotate freely in the liquid state, it should overestimate ΔS_m if the external rotation of molecules is hindered in the liquid state. The effect of hindered rotation in the liquid state on entropy is often expressed as the excess entropy of vaporization ΔS_v^j relative to a freely rotating model liquid at the same vapor volume, *i.e.*, at the same value of p/T (9), so that one should expect $\Delta S_m(\text{obsd}) = \Delta S_m(\text{HSE}) - \Delta S_v^j$. This supposition has been confirmed for several hydrocarbons, but more work needs to be done on applying this principle to polar compounds.

A comparison of the various theoretical estimates with experiment is shown on Tables II and III. While the agreement with experiment is quite satisfactory, the method is obviously too cumbersome for engineering application. However, the qualitative results of the theoretical analysis provide useful guide posts for the understanding of the data. In order to evade the issue of what dimensions to use for entropy, all data are given in terms of R, the universal gas constant (per mole).

III. EFFECT OF MOLECULAR STRUCTURE

A. RIGID MOLECULES

The data in Tables IV and V exhibit on the whole the parallel trend of $\Sigma \Delta S_{m,tr}$ and the moments of inertia of the molecules expected from theory. Notable excep-

TABLE III

ENTROPY OF FUSION OF RARE GAS CRYSTALS AND OF CRYSTALS COMPOSED OF GLOBULAR MOLECULES[a]

						Theory			
Rare gases		Ne	Ar	Kr	Xe	Lennard-Jones	HSE	L-H, W	
$\Delta S_m/R$		1.64	1.69	1.70	1.71	1.7	1.0	1.64	
Globular molecules (CX_4)	X =	H	F	Cl	Br	Me	SMe	CH_2OH	NO_2
$\Delta S_m/R$		1.25	0.94	1.2	1.36	1.52	1.44	1.59	1.74
Globular molecules (MH_4)	M =	C	Si	Ge					
$\Delta S_m/R$		1.25	0.91	0.94					
Globular molecules		Cyclohexane		Thiacyclohexane	1,4-Dioxane		Camphor		
$\Delta S_m/R$		1.12		1.01	1.04		1.4		

[a] All from ref 33 except where noted otherwise.

TABLE IV

TOTAL ENTROPY OF FUSION AND TRANSITION OF VARIOUS SIMPLE COMPOUNDS[a]

Diatomic molecules	H_2	N_2	NO	CO	O_2	F_2	Cl_2	Br_2	I_2
$\Sigma\Delta S_{m,tr}/R$	1.04	2.12	2.53	2.72	3.47	3.41	4.47	4.86	4.92
Diatomic molecules (associating)	HF	HCl	HBr	HI					
$\Sigma\Delta S_{m,tr}/R$	2.90	2.97	2.62	2.56					
Linear polyatomic molecules	FCN	HCN	$(CN)_2$	N_2O	CO_2	COS	CS_2		
$\Sigma\Delta S_{m,tr}/R$	4.0	3.89	3.98	4.32	4.66	4.24	3.28		
Nonlinear polyatomic molecules	H_2O	H_2S	H_2Se	SO_2	NH_3	PH_3	CH_4	SiH_4	GeH_4
$\Sigma\Delta S_{m,tr}/R$	2.65	3.30	4.55	4.51	3.48	3.61	1.61	2.13	1.99
Rigid single rings	Furan	Thiophene	Benzene	Pyridine	β-Sulfolene	Sulfolane			
$\Sigma\Delta S_{m,tr}/R$	4.08	5.01	4.25	4.25	4.86 (41)	4.55 (41)			
Rigid condensed double rings	Indene	Indane		Naphthalene		1,4-Dihydronaphthalene	Tetralin		Azulene
$\Sigma\Delta S_{m,tr}/R$	4.52 (69)	4.67 (69)		6.48		4.96	6.33		6.18
Rigid condensed rings	Acenaphthene	Phenanthrene		Anthracene	Chrysene				
$\Sigma\Delta S_{m,tr}/R$ (2)	6.85	6.02		7.09	7.5				

[a] From ref 33 except where noted otherwise.

TABLE V

COMPARISON OF TOTAL ENTROPY OF FUSION AND TRANSITION OF GEOMETRICALLY SIMILAR COMPOUNDS COMPOSED OF RIGID MOLECULES[a]

	$\Sigma\Delta S_{m,tr}/R$, X =						
Type	H	F	Cl	Br	I	Me	NO_2
CHX_3	...	4.0	5.29	4.95	4.97	4.97	...
CX_4	1.61	3.26 (28)	3.6	3.72	...	3.74[b]	4.60
C_2X_4	3.42	6.55	5.04	...	...	5.97	...
C_2X_6	3.85	6.19	5.98	...	...	5.01	...
o-Di-X-benzene	4.25	...	6.06	...	5.71	6.61	7.05
m-Di-X-benzene	4.25	...	6.15	5.96	6.25	6.18	6.76
p-Di-X-benzene	4.25	...	6.70	6.70	6.70	7.20	7.59

[a] All from ref 4, 33, and 71 except where noted. [b] For comparison: $\Delta S_m/R$ (spiropentane) = 4.66 (63).

tions are the hydrogen halide crystals and the series CO_2, COS, and CS_2. Here the interaction of all variables, T_m, I, and crystal libration frequencies and hindered external rotation in the liquid must be considered in order to understand the data. Strongly hindered rotation in the liquid reduces ΔS_m and must be expected when T_m/T_b is exceptionally small as in the case of CS_2, where $T_m/T_b = 0.50$ compared with the more usual 0.65. On the other hand, ΔS_m can be expected to be higher than "normal" if rotation is entirely free, as would always be the case when $T_m/T_b > 1.0$, keeping in mind that in the present context T_b is the temperature at $P_v = 760$ torr. Among the somewhat larger (organic) molecules one finds fortunately fewer such anomalous series; an example of such a series is that of the halobenzenes shown in Table I. These examples indicate that facile arguments cannot always be used in rationalizing observed entropy of fusion data. Yet very large differences in dipole orientation effects and cohesion forces do not matter if compounds are geometrically similar; nitrobenzene ($\Delta S_m/R = 5.24$), benzoic acid ($\Delta S_m/R = 5.27$), and their homomorph, isopropylbenzene ($\Delta S_m/R = 5.28$), set a good example for this behavior. In the section on hydrogen-bonded substances, more will be said on this subject.

The effect of symmetry is apparent from the sequence *ortho*, *meta*, *para* among the entropy data for the disubstituted benzene compounds of Table V.

Table VI

Effect of Molecular Symmetry on $\Sigma\Delta S_{m,tr}/R$[a]

Asymmetric polymethylbenzenes	1,2	1,2,3	1,2,3,4	1,3	1,2,4	1,2,3,5
$\Sigma S_{m,tr}/R$	6.61	5.03	4.65	6.18	6.88	5.16
Symmetric polymethylbenzenes	1,4	1,2,4,5	Hexamethyl[b]			
$\Sigma S_{m,tr}/R$	7.20	7.18	6.22			
Methylnaphthalenes	1	2	2,3	2,6 (29)		
$\Sigma S_{m,tr}/R$	5.95 (45)	7.10 (45)	6.3	7.60		

[a] From ref 4 except where noted. [b] As the methyl groups are squeezed out of their planar configuration, the molecule has lost the simple geometry of the disk-shaped benzene derivatives.

Table VII

Total Entropy of Fusion and Transition of Various Types of Inorganic Compounds[a]

			$\Sigma\Delta S_{m,tr}/R$ if X =					
No.	Shape	Molecule type	H	F	Cl	Br	I	Other molecules of the same shape
1	Plane triangle	BX_3		3.5				SO_3, 3.58; $OCCl_2$, 4.76
2	T-Shape	YX_3 (Y = Cl, Br)		5.11, 5.12				
3	Trigonal pyramid	MX_3 (M = P,[b] As, Sb)	3.6[c]	4.7	4.7	4.7		NMe_3, 5.3; $O\ddot{S}F_2$, 5.30
4	Tetrahedral	MX_4 (M = Si (6), Ge, Sn, Ti)	2.0 ± 0.1	. . .[d]	4.75 ± 0.2	5.1 ± 0.1	5.1	$FClO_3$, 3.68 (27); $OPCl_3$, 5.69; $Ni(CO)_4$, 6.7
5	Square pyramid	YX_5 (Y = Br, I)		4.2, 6.4				
6	Regular octahedron	YX_6 (Y = S, Te)		4.8				
7	Regular octahedron	MX_6 (M = Mo, W)		5.1	>5.5			PtF_6, 5.5
8	Regular octahedron	MX_6 (M = U, Np, Pu) (77)		6.9[e]				
9	Trigonal bipyramid	MX_5 (M = P, As, Sb)		7.5 ± 0.4	>4.4			$Fe(CO)_5$, 6.30 (35)
10	Trigonal bipyramid	MX_5 (M = Nb, Ta)			7.3 ± 1, 8.4 ± 0.8			

[a] All from ref 4, 33, 74, and 76 except where noted otherwise. For various linear and V-shaped molecules, see Table IV. [b] The available datum for a P-trihalide, PCl_3 ($\Sigma\Delta S_{m,tr}/R$ = 3.0), is probably wrong. [c] This is for PH_3; the available information on AsH_3, etc. appears to be incomplete. [d] For SiF_4, $\Delta S_m = 6.05R$ (see text). [e] The datum for NpF_6 differs slightly (6.44?).

Further examples are shown in Table VI. Another striking example of this symmetry effect is C_2F_6 ($\Delta S_m/R$ = 6.19) *vs.* C_2F_5Cl ($\Delta S_m/R$ = 5.25). This symmetry effect originates in part with the high packing density and melting temperature of symmetrical compounds, hence large ΔV_m and ΔS_m. The other part derives from the contribution to S_r made by the difference in symmetry number, as the moment of inertia product of *ortho-* and *para-*substituted benzene rings, for instance, is effectively equal.

The fusion entropy of cage-like molecules with nearly spherical symmetry, such as camphor and its many derivatives, are of the order 1.5 ± 0.5R (Table III). The great interest of these substances as solvents for cryoscopy led to the determination of their heat and entropy of fusion, but their solid–solid transitions have been examined only rarely. Hence, only the following few data are available.

	Camphor	Bicyclo[2.2.1]-heptane	Triethylene-diamine	3-Azabicyclo-[3.2.2]nonane
$\Sigma\Delta S_{m,tr}/R$	5.2	5.34(39)	7.05(73)	7.65(7,80)

More data are obviously required to produce a reasonably reliable correlation.

B. INORGANIC MOLECULAR CRYSTALS

There are two classes of inorganic molecular crystals: those composed of covalently bonded molecules, such as SO_2, and those composed of a central metal ion surrounded by monovalent ligands that completely shield the metal ion from interaction with nonbonded ligands. In the latter case a molecular crystal obtains when the shielded fraction A_r of the metal ion surface is larger than 0.8, where $A_r = (N_x/4)(r_1/r_2)^2$ when $l > r_2$ (the most frequent case), and $A_r = (N_x/4)[1 - (m^2/r_2^2)]$, when $l < r_2$, where N_x = number of ligand atoms or groups per metal ion, l = chemical bond distance between metal and ligand atom, r_1 and r_2 are the van der Waals radii of ligand and metal ion, respectively, and $m = (r_2^2 - r_1^2 + l^2)/2l$. To a good approximation $r_2 \approx 0.735R^{1/3}$, where R = molar refractivity increment of the metal ion in the Eisenlohr system. Insufficient shielding ($A_r < 0.8$), often found with fluorides and chlorides when $N_x < 5$, leads to ionic rather than molecular crystals with a correspondingly very different entropy of fusion.

One finds that to a first approximation the total entropy of fusion and transition of inorganic molecular crystals can be fitted into the known pattern of inorganic stereochemistry (22) as is evident from the rather spotty data in Table VII.

The first line of Table VII should be composed of the linear molecules of Table IV, where the anomalous cases of CS_2 (T_m/T_b = 0.50) and CO_2 (T_m/T_b = 1.1) have already been discussed. The second line should be V-shaped molecules, such as SO_2 ($\Sigma\Delta S_{m,tr}/R$ = 4.51), currently the only datum of that class. The plane triangles BF_3 and SO_3 would be excellent examples of the power of the shape generalization, were it not for the deviant phosgene. The sequence of the series of trigonal pyramid and of tetrahedral molecules

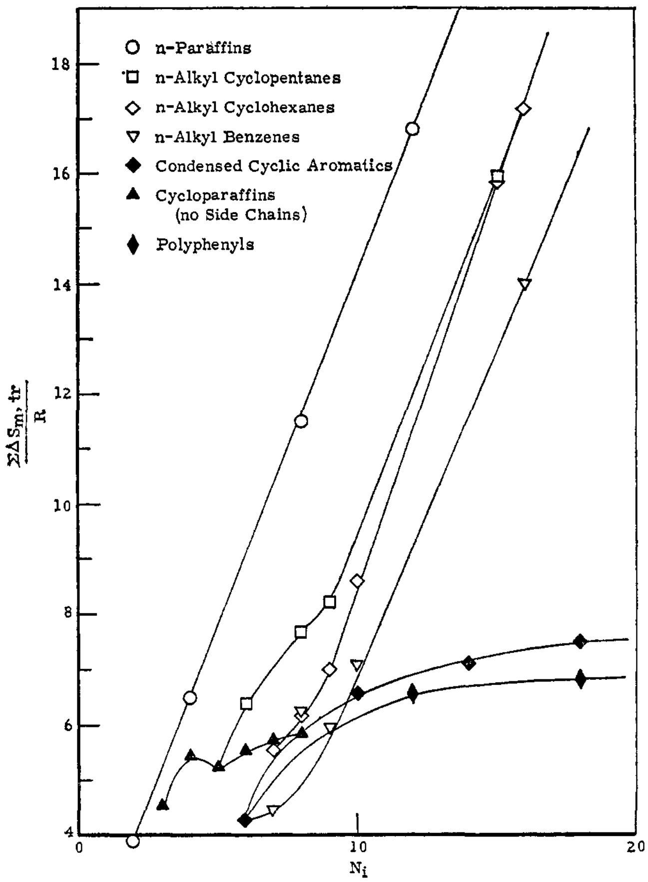


Figure 1.—Total entropy of fusion and transition *vs.* number of carbon atoms per molecule (N_1) for flexible (open symbols) and rigid (solid symbols) hydrocarbon molecules; polyphenyl data from ref 3.

exhibits, perhaps fortuitous, stepwise changes in $\Sigma\Delta S_{m,tr}$ with increasing ligand and/or molecule size. Provided $A_r > 0.8$ the constancy of $\Sigma\Delta S_{m,tr}$ is maintained in the tetrahedral series out to $ThBr_4$ and ThI_4 ($\Sigma\Delta S_{m,tr} \sim 5.0R$), while for $ThCl_4$, for which $A_r = 0.73$, a totally different behavior is encountered, the crystal being ionic and $\Delta S_m = 10.4R$.

The constancy of ΔS_m in the tetrahedral series is, in part, associated with the constancy of $T_m/T_b \approx 0.65$. When $T_m/T_b > 1.0$, ΔS_m becomes rather larger than average: with SiF_4 $T_m/T_b = 1.05$ and $\Delta S_m = 6.05R$ (53); with $ZrCl_4$ $T_m/T_b = 1.18$ and $\Delta S_m \approx 6.35R$ (54). The effect of moments of inertia on the over-all trend in the tetrahedral series is apparent from the extreme ends, from the low end with $FClO_3$ to the high value of $Ni(CO)_4$ (for which $T_m/T_b = 0.79$, not enough to have much effect).

A striking peculiarity of the MX_3 and MX_4 series is that for them $\Sigma\Delta S_{m,tr}$ is uniformly larger than it is for the corresponding halides of the first-row elements N and C by 1 to 1.5*R*. The CX_4 data are given in Table IV and $\Delta S_m(NF_3) = 3.1R$. This difference persists to the series M_2X_6, exemplified by $\Delta S_m(Si_2F_6) = \Delta S_m(C_2F_6) + 1.5R$. The primary difference between the higher metal tetrahalides and the CX_4 series is the occurrence of low-temperature solid–solid-phase transitions among all of the carbon compounds, and the absence of such transitions among the other members of the MX_4 series. The origin of the resulting decrement in $\Sigma\Delta S_{m,tr}$ will be discussed in the section on phase transitions.

Regular octahedra YX_6 and MX_6 (line 7) exhibit $\Sigma\Delta S_{m,tr}$ within the range expected from their moments of inertia and their crystal characteristics. However, those of the hexafluoro actinides are so much larger that one strongly suspects their structure to be somewhat elongated bipyramids rather than octahedra as deduced from electron and X-ray diffraction data (77). That X-ray and electron diffraction give unreliable data in this case because of excessive scattering by the heavy center atom has been pointed out by Smith (67); only neutron diffraction can resolve this question.

The best direct evidence for distortion of the actinide hexafluoride octahedra into elongated bipyramids by the crystal field comes from nmr spectroscopy (8). This notion is supported by the data for compounds of elongated bipyramidal structure in lines 9 and 10 of Table VII.

The foregoing correlation scheme for inorganic molecular crystals contains just enough systematic features to be useful for extrapolation purposes, and just enough deviations from gross regularities to prevent blindfolded generalizations.

C. FLEXIBLE MOLECULES

The chain segments of long-chain molecules execute torsional oscillations in the crystal and hindered rotations relative to each other in the liquid. The corresponding gain in entropy yields a rather constant increment for the entropy of fusion per chain link. The contrast between the resulting rapid rise in ΔS_m with molecular weight for long-chain compounds and the very slow rise with rigid molecules is shown on Figure 1.

The equations for the curves of various normal alkyl compounds are presented in Table VIII. The slopes of these curves fall into two groups apparently associated with the well-known differences in crystal structure, $\Delta S_m/R$ per methylene group = 1.2 ± 0.05 when orthorhombic, and 1.35 ± 0.05 when monoclinic. Less than one-quarter of this amount (0.25*R*) has been contributed by the volume change (42). The magnitude of this remainder, 0.93 to 1.1*R*, is near ln 3 as postulated by the theory of Aranow and co-workers (5) who ascribe the gain in entropy to the gain in the number of equivalent positions on melting. The third term in the equations accounts for the curvature near the parent compound.

A noteworthy aspect of the experimental data is the difference between odd- and even-numbered normal paraffins and their derivatives, which shows the strong

TABLE VIII

EQUATIONS RELATING THE TOTAL ENTROPY OF FUSION OF LONG-CHAIN COMPOUNDS TO THE NUMBER OF CARBON ATOMS PER MOLECULE[a]

Homologous series[b]	Formula, $\Sigma\Delta S_{m,tr}/R$ =
n-Paraffins (N_c = even)	$0.80 + 1.33N_c$
(N_c = odd)	$1.10 + 1.18N_c$
2-Methyl-*n*-alkanes	$-1.24 + 1.2N_c + 20/N_c^2$
2,2-Dimethyl-*n*-alkanes	$-6.26 + 1.33N_c + 83/N_c^2$
n-Alkylcyclopentane	$-5.1 + 1.30N_c + 131/N_c^2$
n-Alkylcyclohexane	$-6.3 + 1.45N_c + 56/N_c^2$
n-Alkylbenzene[c]	$-5.6 + 1.18N_c + 100/N_c^2$
n-Alkyl bromide (N_c = odd)	$2.4 + 1.38N_c + 0.54/N_c^2$
n-Alkanoic acid (N_c = even)	$-2.56 + 1.33N_c + 36/N_c^2$
n-Alkanoic acid (N_c = odd, >5)	$-2.7 + 1.25N_c$

[a] Generally *not valid* for the *first two* members of the series. [b] The available data for 1-alkenes and 1-alkanols are too irregular (and probably unreliable) for representation. [c] The datum for ethylbenzene is appreciably higher than predicted by this equation.

effect of crystal structure on the entropy of fusion (55, 75). In line with this is the identity of the increment per methylene group in polyethylene with that for odd-numbered normal paraffins with which it shares the orthorhombic crystal structure (47). The peculiar nonlinear initial rise of the ΔS_m *vs.* N_c curves of the alkylated ring systems parallels that for the number of external degrees of freedom per molecule for the same compounds in the liquid state (11) and is apparently due to the fact that short—hence, internally stiff—alkyl chains rotate so easily on the ring that their motion makes only a small contribution to the change in heat capacity and entropy.

The effect of *cis* or *trans* configuration in a hydrocarbon chain is qualitatively similar to that observed with internal double bonds in low molecular weight olefins but more pronounced (Table IX).

TABLE IX

TOTAL ENTROPY OF FUSION AND TRANSITION OF MODEL OLEFINS AND RELATED COMPOUNDS (4)

Compound	$\Sigma\Delta S_{m,tr}/R$	Compound	$\Sigma\Delta S_{m,tr}/R$
n-Butane	6.47	Diacetylene (20)	5.18
Butene-1	5.27	*n*-Hexane	8.82
cis-Butene-2	6.56	Hexene-1	8.43
trans-Butene-2	7.02	*cis*-Hexene-2	8.02
Butadiene-1,2	6.12	*trans*-Hexene-2	7.9
Butadiene-1,3	5.85	*cis*-Hexene-3	7.32
1,4-Pentadiene (39)	5.88	*trans*-Hexene-3	8.8
Butyne-1	4.89	*cis*-3-Me-pentene-2	5.84
Butyne-2	4.62	*trans*-3-Me-pentene-2	6.75

Flexible connections between rigid molecule fragments, such as phenyl or other ring systems, have about the same effect per link as similar groups in long-chain compounds, as is apparent from the data of Table X. In setting up models for this kind of effect, care should be taken to work with rotating groups of similar size, since, as the data show, very small groups derive no particular benefit from flexible connections.

TABLE X

TOTAL ENTROPY OF FUSION AND TRANSITION OF NONCONDENSED POLYCYCLIC AROMATIC COMPOUNDS (33)

Compound	$\Sigma\Delta S_{m,tr}/R$	Compound	$\Sigma\Delta S_{m,tr}/R$
Biphenyl	6.55	1,1-Diphenylethane	8.3
Diphenylmethane	7.44	1,2-Diphenylethane	11.36 (?)
Diphenyl ether	6.93	1,2-Diphenylethene (*trans*)	9.02
Diphenylethyne	7.76		

TABLE XI

EFFECT OF THE CENTRAL ATOM ON THE TOTAL ENTROPY OF FUSION AND TRANSITION OF VARIOUS COMPOUNDS[a]

Compound	$\Sigma\Delta S_{m,tr}/R$	Compound[b]	$\Sigma\Delta S_{m,tr}/R$
Me_2CH_2	4.95	Et_3CH	7.42
Me_2O	4.52	Me_4C	3.75
Me_2S	5.51	Me_4Si	4.77
Me_2Cd (37)	4.31	Me_4Sn	5.22
Et_2CH_2	7.02	Me_4Pb	5.36
Et_2O	5.70	Et_4C	5.76
Et_2S	8.46	Et_4Si	8.26
Me_3CH	4.82	Et_4Ge	8.26
Me_3N	5.05	Et_4Sn	7.70
Me_3In	5.2 (34)	Et_4Pb	7.40

[a] From ref 4 and 33 except where noted. [b] All values except for Et_3CH from ref 68.

Hindrance to rotation is a strong function of the nature and size of the central atom around which rotation takes place. This is brought out forcefully by the series of examples in Table XI, where the central carbon atom has been replaced successively by atoms of different sizes. The effect of the central atom and of the extent of alkyl substitution is dominated by the effect of these two variables on the mobility of the alkyl group in the liquid state and on the difference in mobility of the alkyl group between the crystalline and the liquid state. The mobility of the alkyl group in the liquid state is largely determined by the potential energy barrier to internal rotation. It would also determine the magnitude of ΔS_m if the alkyl groups were immobile or would perform only small amplitude torsional oscillations in the solid state. Nmr line-width determination easily establishes the alkyl group mobility in the solid state.

In the extreme case of virtually identical mobility of the methyl group in both phases as in the high-melting neopentane and dimethylcadmium, internal rotation makes no contribution to $\Sigma\Delta S_{m,tr}$. In the other extreme of nearly immobile methyl groups in the solid, as with the low-melting compounds of Table XI, it is apparent that in a given series S_{rr}, the contribution of hindered rotation, largely determines the trend of ΔS_m. Here the proximity of $\Sigma\Delta S_{m,tr}$ values to each other is far more surprising than their relatively small differences.

Addition of successive methylene groups should raise $\Sigma\Delta S_{m,tr}$ by a maximum of $1.2R/CH_2$ group. In the sequence Et_2CH_2, Et_3CH, Et_4C in Table XI, it is

TABLE XII

INCREASE OF ΔS_m BY REDUCING HINDRANCE TO INTERNAL ROTATION

Compound	$\Sigma\Delta S_{m,tr}/R$	Homomorph	$\Sigma\Delta S_{m,tr}/R$	δ	Ref
Ethyl acetate	6.68	2-Methylpentane	6.3	0.4	4, 33
Ethyl propionate	7.61	3-Methylhexane	7.4	0.2	4, 33
Acetaldehyde	4.57	Propene	4.10	0.5	4, 33
n-Butyraldehyde	7.55	Pentene-1	6.50	1.0	4, 33
Methyl cyanide	4.80	Propene	4.10	0.7	4, 58
Trifluoromethyl cyanide	4.64	Propene	4.10	0.5	4, 52
Cyanoacetylene	6.1	Diacetylene	5.18	0.9	20
Methylamine	4.12	Ethane	3.83	$0.3/NH_2$	4, 33
1,2-Diaminoethane	8.26	*n*-Butane	6.48	$0.9/NH_2$	4, 33
1,6-Diaminoethane	15.5	*n*-Octane	13.0	$1.25/NH_2$	4, 21
1,1-Dimethylhydrazine	5.60	2-Methylpropane	4.82	$0.8/NH_2$	4, 33
Hydrazine	5.56	Ethane	3.83	$0.85/NH_2$	4, 33
t-Butylamine	4.11	Neopentane	3.75	$0.4/NH_2$	4, 61
Aniline	4.75	Toluene	4.48	$0.3/NH_2$	4, 33
Methanethiol	4.73	Ethane	3.85	0.9	4, 33
Propanethiol	7.48	*n*-Butane	6.5	1.0	4, 33
n-Butanethiol	7.98	*n*-Pentane	7.02	1.0	4, 33
n-Pentanethiol	10.70	*n*-Hexane	8.62	2.1	4, 33
Benzenethiol	5.34	Toluene	4.48	0.9	4, 33
Dimethyl sulfone	6.80	Tetramethylmethane	3.75	3.0	4, 41
Methyl *t*-butyl sulfone	8.25	Hexamethylethane	5.01	3.2	4, 41
Diphenyl sulfone	10.9	2,2-Diphenylpropane	7.2	3.7	4, 41
Dimethyl sulfoxide	5.75	2-Methylpropene	5.38	0.4	4, 66

apparent that increased crowding sharply diminishes the increment per methylene group from $1.03R$ to $0.87R$ to $0.50R$, respectively. As expected, the reduced crowding in the sequence Et_4C to Et_4Si is accompanied by an increase in $\Delta S_m/CH_2$ group from $0.50R$ to $0.92R$. However, there are a few rather unexpected results. The excessively large increment for Et_2S ($1.47R/CH_2$ group) makes one or both of the ΔS_m values suspect as does the excessively low increment for Et_2O ($0.59R/CH_2$ group). In the latter case $\Delta S_m(Et_2O)$ appears to be far too low in comparison with $\Delta S_m(n\text{-}C_5H_{12})$. Equally unexpected are the very low increments for Et_4Sn ($0.62R/CH_2$) and Et_4Pb ($0.51R/CH_2$) in view of the nearly free rotation around the metal–carbon bonds. These data should either be checked or explained before use for further extrapolation. Extrapolation of $\Sigma\Delta S_{m,tr}$ for the series in Table XI beyond the ethyl derivative can probably be done quite safely with $1.2R/CH_2$ group added.

D. EFFECTS OF STRONG DIPOLE INTERACTIONS AND OF ASSOCIATION

The rotational contribution to the entropy of fusion has the magnitude $S_r(g) - S_{tor}(c)$ only if rotation in the liquid state is free. Any interference with free rotation should reduce the entropy of fusion correspondingly. The quantitative correctness of this effect has been demonstrated for long-chain hydrocarbons, where the entropy reduction due to hindered external rotation could be extracted from vapor pressure data (9). The same technique is not readily applicable to associating compounds. The possibility of expressing the effect of given types of dipole interaction upon ΔS_m in terms of an additive constant will be examined here. Theoretical analyses of the observed effects will be left to later efforts, especially in the field of hydrogen-bond studies.

A complicating feature in this analysis is the often simultaneous and opposing effect of a given polar group in hindering external and facilitating internal rotation. Aldehyde, carboxyl, and similar groups are typical in this respect. Often the facilitation of internal rotation is most important; then we obtain the enhancement in ΔS_m shown in Table XII. With low molecular weight esters we find an almost exact balancing of effects, and rather accurate predictions are made from the readily available data for the hydrocarbon homomorphs.

The expected depression of ΔS_m is found with the various groups assembled in Table XIII. The decrements are largely self-explanatory.

A plot of $\Sigma\Delta S_{m,tr}$ of the 1-bromo-*n*-alkanes *vs.* N_c reveals an alteration between odd and even numbers of carbon atoms per molecule for the first four members of the series, whereas the remaining oscillations in the curve appear to be experimental uncertainties rather than real. The opposite trend among the normal paraffins leads to the sharp change in δ with N_c noted in Table XIV. It is proposed here to accept the usual homomorph basis of calculation only up to *n*-propyl bromide, and thereafter to set $\Sigma\Delta S_{m,tr}/R = 1.81 + 1.49N_c$ for $N_c > 3$. Too few reliable data are available to develop similar relations for the other haloalkanes. The other seeming generalizations of Table XIV should therefore also be used with caution.

The dicyanoalkane data in the same table are wholly inconsistent with the monocyano data of Table XII,

TABLE XIII

REDUCTION OF ΔS_m BY DIPOLE INTERACTION[a]

Compounds	$\Sigma\Delta S_{m,tr}/R$	Homomorph	$\Sigma\Delta S_{m,tr}/R$	δ	Ref
Dimethyl ether	4.53	Propane	4.95	−0.42	4, 33
Dimethoxymethane	5.97	*n*-Pentane	7.02	−0.52/O	4, 46
Ethylene oxide	3.90	Cyclopropane	4.52	−0.42	4, 33
Trioxane	3.90	Cyclohexane	5.50	−0.53/O	4, 59
Acetone	3.91	2-Methylpropene	5.38	−1.5	4, 33
Methyl ethyl ketone	5.50	2-Methyl-1-butene	7.03	−1.5	4, 33
Dimethyl disulfide	5.88	*trans*-2-Butene[b]	7.02	−1.2	4, 33
Diethyl disulfide	6.62	*trans*-3-Hexene[b]	8.8	−1.2	4, 33
β-Sulfolene	4.86	4,4-Dimethylcyclopentene	(6.7)	(−1.8)	4, 41
Sulfolane	4.55	1,1-Dimethylcyclopentane	5.97	−1.4	4, 16

[a] Hindered external rotation in the liquid state. [b] The choice of these homomorphs was determined by the known stiffness of the S–S bond (barrier to rotation, ∼9.0 kcal/mole) and the geometry of the C–S–S–C bonds (62, 64).

TABLE XIV

HALIDES AND DICYANOALKANES

Compound	$\Sigma\Delta S_{m,tr}/R$	Homomorph	$\Sigma\Delta S_{m,tr}/R$	δ	Ref
Methyl chloride	4.43	Ethane	3.83	+0.60/Cl	4, 33
Methyl bromide	4.45			+0.62/Br	4, 33
$C(CH_2F)_4$	8.06	3,3-Diethylpentane		+0.58/F	4, 18
$C(CH_2Cl)_4$	7.40[a]			+0.41/Cl[b]	4, 18
$C(CH_2Nr)_4$	8.27			+0.63/Br	4, 18
Ethyl chloride	3.95	Propane	4.95	−1.0/Cl	4, 33
Ethyl bromide	4.57			−0.4/Br	4, 33
1,2-Dichloroethane	4.47	*n*-Butane	6.48	−1.0/Cl	4, 33
1,2-Dibromoethane	6.23			−0.13/Br	4, 33
Isopropyl chloride	4.85	Isobutane	4.84	0	4, 33
Isopropyl bromide	4.76			−0.1	4, 33
$(CN)_2$	3.98	Diacetylene	5.18	−0.6/CN	20, 33
1,2-Dicyanoethane	4.55	1,5-Hexadiene	8.4	−1.9/CN	79
1,3-Dicyanopropane	6.20	1,6-Heptadiene	9.6[b]	−1.7/CN	19

[a] This datum is questioned by its authors because crystals were poorly developed. [b] Estimated by correlation.

even though consistent with each other. Unfortunately not enough crystal structure data are available on the cyano compounds of the two tables, and no heat of fusion measurements could be found on a series of monocyanoalkanes which would yield a hint regarding the relation to molecular structure similar to that available for other alkanes. It is probable that there are two series of cyano increments just as there are two series of halo increments, but the distinguishing criteria have yet to be found.

The most consistent effects are those due to *hydrogen-bond formation.* They have been divided into those due to hydroxyl groups (Tables XV and XVI) and those involving nitrogen-containing groups (Table XVII). The effect of single aliphatic hydroxyl groups is straightforward, and perhaps remarkable only for its uniformity. Inconsistencies among the higher *n*-alkanols are most likely due to impurities (they are notoriously difficult to purify). The virtual absence of hydroxyl effects with phenol is unexplained at present.

The behavior of the polyols is particularly interesting. Many of these form continuous networks of hydrogen bonds in the solid crystal. Their liquid-state properties, especially their heat of vaporization, suggest that, in the liquid, extensive intramolecular hydrogen bonding takes place (10, 56). If one assumes that the vibration frequency of internal and external hydrogen bond is equal, then the maximum possible change in entropy is $\Delta S_m^v + S_r$. The rotational entropy contributions for the intramolecularly bonded ring systems, shown in Table XVI, of glycerol, erythritol, pentaerythritol, and mannitol are (in terms of R) about 11, 11.5, 13.5, and 14, respectively. Taking as a first approximation for all $\Delta S_m^v = 1.3R$, the value obtained for glycerol, then the maximum entropy of fusion for these polyols would be (in units of R) 12.3, 12.8, 14.8, and 15.3, respectively. Comparison of these numbers with the observed values in Table XVI suggests that (within the framework of our assumptions) intramolecular hydrogen-bond formation in the liquid state is far from complete for glycol but is surprisingly extensive for the three higher polyols. The entropy of fusion of the lower polyols is apparently well represented by that of their homomorphs and the decrement for a single hydroxyl group, the effect of the other groups having been neutralized by some degree of intramolecular hydrogen bonding.

Among the benzenediols, only the *ortho* isomer can and does form intramolecular hydrogen bonds at elevated temperature (10). However, at the melting

Table XV

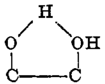
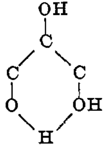
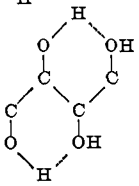
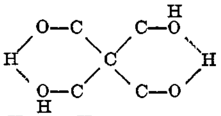
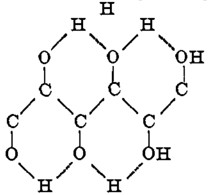
Reduction of Entropy of Fusion by Hydrogen Bonding[a]

Compound	$\Sigma\Delta S_{m,tr}/R$	Homomorph	$\Sigma\Delta S_{m,tr}/R$	δ
Methyl alcohol	2.68	Ethane	3.83	−1.15
Ethyl alcohol	3.84	Propane	4.97	−1.13
n-Propyl alcohol	4.27 (?)	*n*-Butane	6.48	?
Isopropyl alcohol	3.50	Isobutane	4.82	−1.32
n-Butyl alcohol	5.89	*n*-Pentane	7.04	−1.16
n-Pentyl alcohol	6.06	*n*-Hexane	8.82	−1.76
2-Methyl-2-butanol	3.64	2,2-Dimethylbutane	5.78	−2.14
n-Hexanol	8.23	*n*-Heptane	9.20	−0.97
n-Hexadecanol	19.79	*n*-Heptadecane	(21.0)	−1.21
Cyclohexanol	4.47	Methylcyclohexane	5.54	−1.1
Benzyl alcohol	4.20	Ethylbenzene	6.20[b]	−2.0[b]
Phenol	4.45	Toluene	4.48	0

[a] Hindering external rotation in the liquid with hydroxyl groups. From ref 4 and 33. [b] The reported entropy of fusion is out of line on a plot of $\Sigma\Delta S_{m,tr}$ *vs.* carbon number for the alkylbenzenes. The interpolated value of 5.4 yields the more normal decrement for alcohols, $\delta = -1.2$.

Table XVI

Total Entropy of Fusion and Transition of Various Polyols (4, 33)

Compound	$\Sigma\Delta S_{m,tr}/R$	Homomorph	$\Sigma\Delta S_{m,tr}/R$	δ
Glycol 	5.35	*n*-Butane	6.48	−1.1
Glycerol 	7.63	3-Methylpentane or Methylcyclopentane	(6.55)[a] 6.37	−1.1 −1.3
Erythritol 	13.08	2,3-Dimethylhexane		
Pentaerythritol 		Tetraethylmethane or Spirononane	5.76	
Mannitol 	14.70	3,4,5,6-Tetramethyloctane or Perhydropyrene	<10 <8	
1,2-Dihydroxybenzene	7.25	*o*-Xylene	6.61	+0.6
1,3-Dihydroxybenzene	6.67	*m*-Xylene	6.18	+0.4
1,4-Dihydroxybenzene	7.36	*p*-Xylene	7.20	+0.2

[a] Estimated.

Table XVII

Reduction of the Entropy of Fusion by Hydrogen Bonding with Nitrogen-Containing Groups

Compound	$\Sigma\Delta S_{m,tr}/R$	Homomorph	$\Sigma\Delta S_{m,tr}/R$	δ
Formamide	2.90	Propene	4.10	−1.3
Acetamide	4.97	2-Methylpropene	5.38	$-0.4/NH_2$
Urea	4.32	2-Methylpropene	5.38	$-0.6/NH_2$
Formanilide	5.45	*n*-Propylbenzene	5.90	−0.5
Benzamide	6.18	Isopropylbenzene	5.28	+0.9
Diphenylamine	6.60	Diphenylmethane	7.44	−0.8
α-Naphthylamine	4.98	1-Methylnaphthalene	5.95	−1.0
ϵ-Caprolactam	5.67 (55)	Methylcycloheptane[a]	5.7	0

[a] In analogy with the pair cyclohexane/methylcyclohexane, it is assumed that there is no change in $\Sigma\Delta S_{m,tr}$ in going from cycloheptane to methylcycloheptane.

point not enough freedom of rotation is gained thereby to raise ΔS_m appreciably. It differs, as the data of Table XVI show, only slightly more from the ΔS_m of its homomorph than the entropies of fusion of the other two isomers, which are almost certainly hydrogen bonded to their neighbors. The reason for this behavior is not obvious. As the data are quite old, the experiments bear repetition.

Substances which form defined dimers in the liquid state such as the fatty acids might be expected to exhibit comparatively simple regularities in the entropy of fusion. However, no clear-cut regularities are discernible with fatty acids with $N_c < 6$. The entropy of fusion of the lower unsaturated and of the aromatic monocarboxylic acids is reasonably predictable from that of their hydrocarbon homomorphs. The datum for *o*-phthalic acid suggests nearly free rotation of the intramolecularly hydrogen-bonded molecules. Extrapolation from this information to a wide variety of carboxylic acids appears hazardous at present.

Hydrogen bonds of amines cause two widely different effects on the entropy of fusion. The small lowering of ΔS_m by the comparatively weak hydrogen bond of primary amines is over-compensated by the fact that the barrier $V°(\text{C–NH}_2) < V°(\text{C–CH}_3)$, so that, as shown by the data of Table XII, δ is positive to the extent of $0.9R$ per primary alkylamine group. Once the rotation of the amino group is hindered, as in Me_2NH and α-naphthylamine, $\delta = -0.90R$ and $-1.0R$, respectively.

The entropy decrement of amide hydrogen bonds, shown in Table XVII, appears to be of the order $-0.5R$/amide NH_2. The excessive magnitude of the formamide increment may be due to the hydrogen-bond contribution of the C–H hydrogen. The internal amide NH bond appears to require no decrement, judging by the single example of ϵ-caprolactam.

E. HIGH POLYMERS

In the case of polymers, ΔS_m, $\Delta S_m{}^v$,and $\Delta S_m{}^j$ are always meant per repeating unit. This is so obvious that the frequently used notation ΔS_u, etc., has not been adopted in the present discussion.

The "configurational" entropy of fusion of polymeric crystals ($\Delta S_m{}^j \equiv \Delta S_m - \Delta S_m{}^v$) is taken as a function of the difference in the number of conformations accessible to the chain in the liquid as compared to the crystalline state (25, 42, 43). Correlation of ΔS_m with polymer structure is impeded by the dearth of pvT and ΔV_m data for polymers as compared to the fairly large amount of ΔS_m information available (43).

Hence it becomes worthwhile to generalize the few $\Delta S_m{}^v$ data on polymers for broader applicability. Those summarized by Kirshenbaum (25) can be cast into the empirical relation

$$\Delta S_m{}^v/R \approx 0.21n_c + 0.2n_o + 0.85n_p - 0.1n_e$$

where n_c, n_o, n_p, n_e are the numbers of aliphatic carbon atoms, ether oxygens, aromatic rings, and ester carboxyl groups per repeating unit, respectively.

The data of Table XVIII show that in those cases for which the $\Delta S_m{}^v$ correlation is suited, the functional group contributions $\Delta S_c(X) \equiv [\Delta S_m - \Delta S_m{}^v - n_m \cdot \Delta S_m{}^v(CH_2)]$ are somewhat more constant for a given group than are the uncorrected group contributions $\Delta S(X) \equiv [\Delta S_m - n_m \Delta S_m(CH_2)]$, where n_m = number of methylene groups per repeating unit. Nowhere does the correction cause a drastic change in trends. In view of the large experimental uncertainties in ΔS_m, not too much should be made of small differences in these data. Practically all functional groups shown reduce the entropy contribution of conformation changes (accompanying the phase change) below that of the methylene group (per unit volume).

In the case of hydrocarbons and slightly polar groups this drop in ΔS_m is due to rigidity of the backbone structure, while with strongly polar groups, this reduction is due to strong association in the melt phase. Conversion of $\Delta S_m(X)$ to δ by comparison with the appropriate (hydrocarbon) homomorph repeating unit yields the following series of increments.

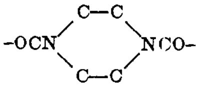
Functional group	—O—	F	Cl (isotactic)	Cl (syndiotactic)
δ (in units of R)	−0.6	−0.2−−0.5	−1.2	+0.4
Functional group	Cl (at C═)	—CN	$-\text{O}-\overset{\text{O}}{\overset{\Vert}{\text{C}}}-$	$-\overset{\text{H}}{\overset{\vert}{\text{N}}}-\overset{\text{O}}{\overset{\Vert}{\text{C}}}-$
δ (in units of R)	−1.5	−1.0	−3.8	−2.4−−3.5

Many of these increments are reassuringly similar to those obtained from data on low molecular weight compounds in Tables XIII and XIV. The difference between isotactic and syndiotactic poly(vinyl chloride) is surprisingly similar to that between the two classes of *n*-alkyl halides in Table XIV. However, the ester group decrement could not have been guessed from data on low molecular weight esters, the decrements of which rarely exceed $1.5R$ and are usually close to $0.5R$. The same applies to the amide group. These groups appear to interfere more strongly with the random conformation of the polymer coil than with the external rotation of monomeric molecules in their melts.

The attempt by Kirshenbaum (25) to formalize these relations by setting $\Delta S_c(X) = \sum_{j=0}^{j=n} R \ln N_t$ (where j = number of bonds other than alkane C–C bonds in the backbone chain (per repeating unit) and N_t = number of stable conformations in that bond relative to the preceding bond) cannot represent the facts in Table XVIII because $N_t < 1$ required by the several instances where $S_c(X) < 0$ is physically meaningless. Clearly, another approach is needed. The negative values of $\Delta S(X)$ and $\Delta S_c(X)$ more likely mean that the presence

TABLE XVIII

ENTROPY OF FUSION PER REPEATING UNIT FOR POLYMERS

Polymer	$\Delta S_m/R$	$(\Delta S_m - \Delta S_m^v)/R$	Functional group (X)	$\Delta S(X)/R$	$\Delta S_c(X)/R$	Ref
Polyethylene	1.18	0.93	...	...	...	25, 30
Polypropylene (isotactic)	2.1	1.45	>CMe	0.9	0.5	25, 30
Polybutene-1 (isotactic)	2.1	1.25	>CEt	0.9	0.3	25, 30
Polystyrene (isotactic)	2.1	1.0	$>CC_6H_5$	0.9	0.1	25, 30
Poly(vinyl fluoride)	1.6–1.9		>CF	0.4–0.7		60
Poly(vinyl chloride) (isotactic)	0.86		>CCl	−0.3		42
Poly(vinyl chloride) (syndiotactic)	2.49		>CCl	+1.3		26
Polyacrylonitrile	1.07		>CC≡N	−0.1		31
Poly(vinyl alcohol)	1.65		>COH	0.47		70
Polybutadiene, 1,4-*cis*-	3.87	3.0	-HC=CH-	1.5	1.1	49
Polyisoprene, 1,4-*cis*-	1.74	0.85	-HC=CMe-	−0.6	−1.0	42
Polyisoprene, 1,4-*trans*-	4.40	3.5	-MeC=C-	2.0	1.6	42
Polychloroprene, 1,4-*trans*-	2.86		-ClC=C-	0.5		42
Polyoxymethylene	1.8	1.5	-O-	0.6	0.57	25
Polyethylene oxide	2.9	2.35	-O-	0.5	0.5	25
Alkanedioic glycol esters	...	...	-OCO-	−1.7 ± 0.7	−1.2 ± 0.6	25
Terephthalic glycol esters	...	...	$-OOCC_6H_5COO-$	+2.6 ± 0.3	+2.4 ± 0.1	25
Poly(*p*-xylene)	5.60	4.3	$-C_6H_4-$	+3.2	+2.5	
Nylon 6	5.60		-NHCO-	−0.25		25
Nylon 66	10.3		-NHCO-	−0.75		25
Nylon 610	13.6		-NHCO-	−1.4		25
Sebacoyl piperazine	6.9			−2.5		42
Polytetrafluoroethylene	0.6		$>CF_2$	(0.6)		42
Polymonochlorotrifluoroethylene	1.25		>CClF	0.65 (rel to CF_2)		42

of the functional group has also reduced the number of conformations accessible to one or more methylene group adjacent to the functional group. Conversely, $\Delta S_c(X) > R \ln 3$ per rotatable bond in the functional group suggests that the presence of the functional group has made more conformations freely accessible to the neighboring methylene groups.

F. SUMMARY OF FUNCTIONAL GROUP INCREMENTS (δ)

For the convenience of the users of this review the functional group decrements have been summarized in Table XIX. The indicated error limits are only moderately meaningful because of the small sample sizes and because of the questionable quality of many of the experimental data from which they were derived. These increments are to be added to $\Sigma\Delta S_{m,tr}$ of the appropriately chosen hydrocarbon homomorph. The latter can be assumed to be generally available, or at least reasonably well estimated from the data and equations given in Tables V, VI, and VIII and in Figure 1.

The corresponding increments for polymers should be taken from column 5 of Table XVIII. Their uncertainty is of the same order as the considerable uncertainty of the experimental data. One of the major problems with several crystalline polymers is the absence of heat of transition data for solid–solid first-order transitions known to exist. Their calorimetry is difficult because of the slowness with which transitions proceed to completion.

TABLE XIX

ENTROPY OF FUSION CORRECTION (δ) DUE TO THE PRESENCE OF POLAR GROUPS

Polar group	Functional group	δ^a
Aliphatic ether	-O-	$-0.5^b \pm 0.1$
Aliphatic thioether	-S-	−1.0 ± 0.5
Aliphatic and diaromatic ketone	>C=O	−1.5 ± 0.1
Quinone	>C=O	−0.7 ± 2
Aliphatic aldehyde	-C(=O)H	+0.8 ± 0.3
Aliphatic ester	-OCO-	...
Aliphatic alcohol	(One OH group/ molecule)	−1.2 ± 0.2
Aliphatic primary amine	$-NH_2$	+0.9 ± 0.3
Aromatic amine (unhindered)[c]	$-NH_2$	+0.3
Aliphatic and aromatic secondary amine	>NH	−0.9 ± 0.1
Monocyanoalkane[d]	-C≡N	+0.7 ± 0.2
Dicyanoalkane	-C≡N	−1.8 ± 0.1
Alkaneamide	$-CONH_2$	−0.5 ± 0.1
Alkanethiol	-SH	+1.0 ± 0.1
Dialkyl disulfide	-SS-	−1.2
Dialkyl or diaryl sulfone	$-SO_2-$	+3.3 ± 0.3
Heterocyclic sulfone	$\diagdown SO_2 \diagup$	−1.4

[a] In units of *R*. [b] This is the most common value; a range *trans* −1.4 (vinyl and ethyl ether) to +0.2 (1,4-dioxane) is found with lesser frequency. [c] Hindered primary amine, $\delta = -0.9$. [d] For details on haloalkanes see Table XIV.

IV. THE HEAT OF FUSION

In the following procedures the melting point, T_m, is assumed to be known, so that the prediction of ΔH_m is reduced to the far simpler problem of estimating the entropy of fusion, ΔS_m. In order to avoid any confu-

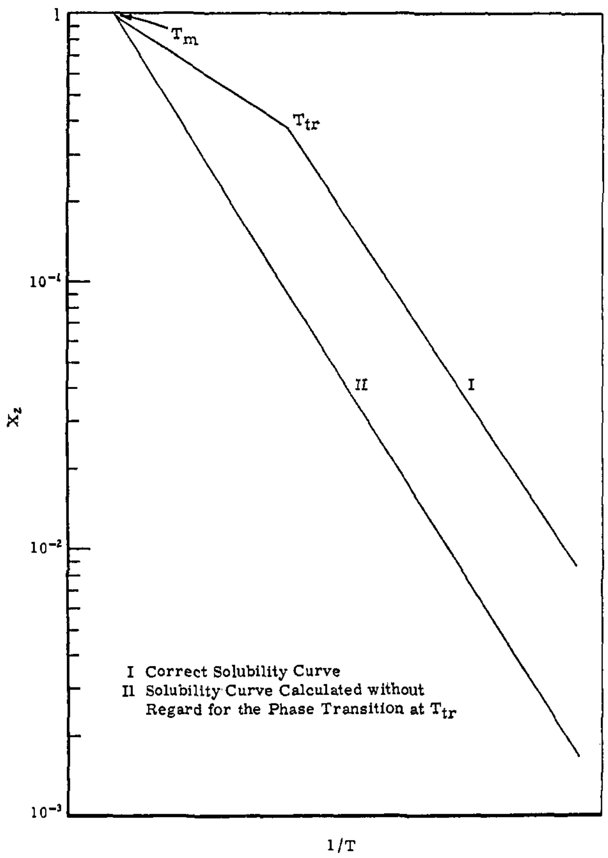


Figure 2.—Schematic illustration of the effect of disregarding solid–solid-phase transitions on solubility calculations.

sion of units, the entropy of fusion is given throughout in dimensionless units as $\Delta S_m/R$. Moreover, because of its greater ease of correlation with molecular structure, only the sum of the entropies of fusion and all first-order solid–solid-phase, transitions, $\Sigma\Delta S_{m,tr}/R$, has been presented.

Errors resulting from the ignorance of first-order solid–solid-phase transitions are serious only in two cases: for the heat balance of a crystallization plant which operates at T such that $T_m > T > T_{tr}$, and when ΔH_m is used for the calculation of solubility. Here ignorance of T_{tr} and of the associated subdivision of the total enthalpy change into ΔH_m and the various ΔH_{tr} can lead to a serious underestimate of solubility, as illustrated schematically in Figure 2.

The existence of a first-order solid–solid-phase transition point can be suspected when the melting point of a substance is substantially higher than those of most related compounds and when the substance is either spherically symmetrical or is a completely straight-chain compound. In those cases, one can guess that the important first-order transition point is at about the temperature where one expects the melting point to be in comparison with members of that particular series of compounds. (Comparison of first-order transition points with melting point of neighboring members within the C_6, C_7, or C_8 series of isoalkanes in the API-44 tables (4) is quite instructive in this respect.)

In the case of globular molecules, an approximate breakdown of $\Sigma\Delta S_{m,tr}$ is $\Delta S_m \approx R$ and $\Delta S_t \approx \Sigma\Delta S_{m,tr} - R$. With long-chain compounds very often $\Delta S_m \approx \Delta S_{tr}$.

V. The Heat Capacity Difference

The temperature coefficient $(\partial\Delta H_m/\partial T)_p = C_p(c) - C_p(liq)$. This difference is generally negative. The magnitude of $\Delta C_p = C_p(liq) - C_p(c)$ should be estimated from heat capacity data *only if experimental heat capacity data* are available. At present, there are no sufficiently reliable methods to estimate the heat capacity of liquids and molecular crystals to obtain a meaningful difference between the resulting uncertain data.

Thermodynamics show that at the melting point

$$\Delta C_p = C_v(liq) - C_v(c) + \left[\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial E}{\partial V}\right)_T\right]_{liq} - \left[\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial E}{\partial V}\right)_T\right]_c$$

Since the internal vibration contributions are virtually identical in both phases, one can replace $C_v(liq) - C_v(c)$ by the difference of the now readily calculated "lattice" contributions to $C_v(liq)$ and $C_v(c)$, C_v^{λ}, and C_v^{s}, as given in ref 14 and 15. With high-melting crystals comprised of rigid molecules, for which $T_m > 0.25\Delta H_s/fR$, where f = number of external degrees of freedom per molecule, one finds at T_m that $C_v(liq) \approx C_v(c)$, as shown in Table XX.

If one accepts Oriani's suggestion (51)—reasonably well borne out by experiment (Table XXI)—that at the melting point $(\partial E/\partial V)_{liq} = (\partial E/\partial V)_c$, then $\Delta C_p \approx (\partial E/\partial V)_{Tm}[(\partial V/\partial T)_{liq} - (\partial V/\partial T)_c] + (C_v^{\lambda} - C_v^{s})$.

Table XX

Heat Capacity Difference (in C_v) between Solid and Liquid at T_m

Substance	$[C_v(c) - C_v(liq)]/R$
Argon	0.57
Benzene	0
Naphthalene	0.1
Propane	−0.7
n-Heptane	−1.5
n-Hexadecane	−4.4
n-Paraffins above *n*-C_7	$[C_v(liq) - C_v(c)]/R = 1.5 + 0.29(N_c - 7)$

Table XXI

Comparison of $(\partial E/\partial V)_T$ in the Liquid and Crystalline States at the Melting Point

Substance	$(\partial E/\partial V_T)$, cal/cm^3 Liquid	Crystal	Ref
Benzene	92	119	
Naphthalene	93	103	
Glycerol	213	194	65

The expansion coefficient of liquids, and thus $(\partial V/\partial T)_{\mathrm{liq}}$ is generally available (keeping in mind that $d\rho/dT$ is independent of temperature at $T < 0.8T_b$). Should the expansion coefficient of the solid not be known, it can be estimated by methods given elsewhere (15). For nonpolar liquids (other than perfluorocarbons) and for nonassociating polar liquids, one can approximate $(\partial E/\partial V)_T$ of the liquid with sufficient accuracy for the present purpose by Hildebrand's rule $(\partial E/\partial V)_T \doteq \Delta E_v/V_L$ at the same temperature (1). Then $\Delta C_p = C_v(\mathrm{liq}) - C_v(\mathrm{c}) + \Delta E(\alpha_L - \alpha_c)$. The energy of vaporization ΔE_v can be estimated by means of the additive increments of ΔE_v given earlier (11). For associating liquids $(\partial E/\partial V)_T = T(\alpha/\beta)$ has to be estimated from experimental pvT data, extensive collections of which are now available (1).

VI. SOLID–SOLID-PHASE TRANSITIONS

The correlation of the total entropy of fusion and transition with molecular structure discussed in the previous sections leaves open the question of the incidence and location of first-order solid–solid-phase transitions for a given compound. Obviously, there can be no easy method to predict the freakish incidence of phase transitions such as that of *n*-butane, and the series of complicated multiple transitions among much higher molecular weight normal paraffins or among the alkylnaphthalenes. Even if the incidence of such transitions could be fitted into some scheme, the division of the total entropy of fusion and transition among the transitions would still be left for a separate accounting. Fortunately, however, one usually finds melting point and transition temperatures of long-chain compounds so close together that, for the purposes of heat balance calculations, the entire enthalpy change can be estimated for the melting point without great error. If crystallization in the process under design takes place reasonably distant from, say, <15° below the melting point, it is also safe to estimate the density change as being that due to fusion plus transition. However, the solubility calculated on the assumption of no phase transition may be very much too low if a solid–solid-phase transition does, in fact, take place more than a few degrees below the melting point.

The situation is somewhat more predictable for molecules with spherical symmetry. Here the entropy change at the melting point is most often of the order of $1.2 \pm 0.4R$. In some series, such as the carbon tetrahalides, one finds, as first pointed out by Trappeniers (72), the transition temperatures to be approximately constant fractions of the absolute melting point ($\sim 0.87T_m$). The fact that for tetramethylmethane $T_{tr}/T_m = 0.55$ shows that one dare not carry analogy very far with crystallization phenomena. Yet, one finds that $[T_{tr}/T_m(C_2Me_6)]/[T_{tr}/T_m(C_2X_6)] = [T_{tr}/T_m(CMe_4)]/[T_{tr}/T_m(CX_4)] = 0.63$, where for C_2X_6 (X = F, Cl) the lowest transitions are at $T_{tr}/T_m = 0.65 \pm 0.05$. No regularities have as yet been discovered among the alicyclic and heterocyclic aliphatic compounds of related structure. Even the incidence of transitions cannot be related from one cyclic compound to its analog. Hence, whenever nearly spherical symmetry or a very low measured entropy of fusion ($<3R$) leads one to suspect the incidence of solid–solid transitions, experimental observation of the transition should be resorted to.

VII. ENTROPY OF SOLID–SOLID-PHASE TRANSITIONS

In the cases where $\Delta S_m \approx R$, one would expect from the HSE theory that $\Delta S_{tr} \approx \Delta S_m(\mathrm{rot})$ (where T in $S_r = T_{tr}$); or in the cases where $\Delta S_m = R + \Delta S_m(\mathrm{rot})$ (C) and $\Delta S_{tr} = \Delta S_m(\mathrm{rot})$ (A, B) where the indicators A, B, C refer to the corresponding principal moments of inertia (in increasing sequence). The second case is found with many nonspherosymmetric molecules that exhibit solid–solid transitions, such as the monomethylnaphthalenes, tetramethylethylene, *n*-butane, etc. However, the more nearly spherosymmetric molecules CX_4 for which $\Delta S_m \approx R$ exhibit a deficiency $\Delta S_m(\mathrm{rot}) - \Delta S_{tr} \approx 1.5R$. Similar deficiencies are found in many cases involving solid–solid-phase transitions of crystals composed of highly symmetrical molecules (Table XXII). This suggests the possibility of a somewhat different approach to the calculation of ΔS_{tr}.

TABLE XXII

COMPARISON OF $\Sigma\Delta S_{m,tr}$ OF SIMILAR CRYSTALS WITH AND WITHOUT SOLID-SOLID-PHASE TRANSITIONS

With phase transitions	$\Sigma\Delta S_{m,tr}/R$	Without phase transitions	$\Delta S_m/R$
CCl_4	3.6	$SiCl_4$	4.6
CBr_4	3.7	$SnBr_4$	5.2
PtF_6	5.5	UF_6	6.9
Camphor	5.2	α-*d*-Bromocamphor	6.8
Furan	4.1	Thiophene	5.0

For solids, the molecules of which belong to certain restricted symmetry classes, ΔS_{tr} can be estimated if the transition is considered as an order–disorder transition, as has been shown by Guthrie and McCullough (78). The basic assumption then is that the molecules in the solid at $T > T_{tr}$ are in a state of definable disorder. Then

$$\Delta S_{tr}/R = \ln (N_2/N_1)$$

where N_1 and N_2 are the number of states of disorder statistically occupied in the low- and high-temperature states, respectively.

There is at present an element of arbitrariness in the counting of N_1 and N_2 even where the crystal structure of both states is known. The logic is most transparent in the case of molecules with tetrahedral symmetry, the data of which have been assembled in Table XXIII.

TABLE XXIII

COMPARISON OF ΔS_{tr} OF CRYSTALS COMPOSED OF TETRAHEDRAL MOLECULES ESTIMATED FROM ORDER–DISORDER THEORY WITH EXPERIMENTAL DATA (50, 78)

Substance	N_2/N_1[a]	Ln (N_2/N_1)	n_2/n_1[b]	Ln (n_2/n_1)	Ln (N_2/N_1) + ln (n_2/n_1)	$\Sigma\Delta S_{tr}/R$ (exptl)
CF_4	12	2.48	...	...	2.48	2.32
CCl_4	12	2.48	...	...	2.48	2.47
CBr_4	12	2.48	...	...	2.48	2.51
CMe_4	12	2.48	...	...	2.48	>2.22
CCl_3Me	12	2.48	4	1.38	3.86	4.0
t-BuCl	12	2.48	9	2.16	4.64	4.4
t-BuBr	12	2.48	9	2.16	4.64	(>3.8)
t-BuSH	12	2.48	9	2.16	4.64	4.3
$C(SMe)_4$	12	2.48	?		>2.48	2.8
$C(NO_2)_4$	12	2.48	?		>2.48	2.9
$C(CH_2OH)_4$	12	2.48	>64[c]	>4.2	>6.7	11.5

[a] N_1 assumed as 1; N_2 characteristic of low-temperature crystal structure. [b] n_2, number of extra orientations due to the methyl group. [c] Includes number of internal degrees of freedom gained in transition.

TABLE XXIV

COMPARISON OF ΔS_{tr} OF CRYSTALS COMPOSED OF SLIGHTLY ASYMMETRIC MOLECULES WITH AN ESTIMATE FROM ORDER–DISORDER THEORY (78)

Substance	Symmetrical analog	N_2/N_1[a]	Ln (N_2/N_1)	$\Sigma\Delta S_{tr}/R$ (exptl)
2,3-Benzothiophene	Naphthalene	4	1.38	1.38
Bicyclo[2.2.1]heptane	Bicyclo[2.2.2]octane	24	3.18	3.82
Cyclopentyl-1-thiaethane	...	2[b]	0.69	0.65

[a] N_1 assumed as 1. [b] N_1 assumed as 2 due to random distribution of molecules at lattice sites in two equivalent conformations.

For molecules of lower symmetry the assumption is made that the symmetry of the high-temperature state corresponds to that of the molecule's nearest symmetrical homomorph, as indicated by the data of Table XXIV. The minimum value of ΔS_{tr} to be expected in this case is $R \ln \sigma$, where σ is the symmetry number of the symmetrical homomorph of the unsymmetrical compound. Since first-order solid–solid-phase transitions occur only with crystals composed of fairly symmetrical molecules, the structural differences between the asymmetrical rotor and its symmetrical analog are usually small. In fact, one of the main difficulties here is the *a priori* predictability of the incidence of a transition. Few would have guessed that the substances in Table XXIV would even exhibit a first-order solid–solid-phase transition.

The entire scheme of accounting for ΔS_{tr} as a definable order–disorder phenomenon breaks down when the external change in order is accompanied by internal motions or when the rotational disorder in the high-temperature phase becomes too great. Examples for the former are the *t*-butyl halides and the methylchloroform of Table XXIII, which are still barely manageable and the pentaerythritol derivatives, which involve too many changes in internal and external mobility in the change from low- to high-temperature state for practical accountability. Examples of the excessive external mobility in the high-temperature state are the cycloalkanes in the range cyclobutane to cyclooctane.

One may summarize the present situation by the statement that in the absence of a well-founded theory the extensive available data provide a basis for guessing whether a solid–solid-phase transition is to be expected. In restricted cases one may also guess how to estimate ΔS_{tr} from crystallographic data and from molecular symmetry. But, in general, existing theoretical insight is, at best, suitable for *ex post facto* explanation of the observed magnitude of ΔS_{tr} rather than for prediction.

VIII. COMPARISON WITH PREVIOUS WORK

The oldest generalization is that due to Walden who suggested in analogy to Trouton's rule that $\Delta S_m \doteq 6.8R$. This strange finding was, of course, due to the fact that, at that time, most data had been obtained on coal tar derivatives, *i.e.*, on various substituted benzene and naphthalene derivatives. Aside from the HSE relation discussed earlier, the most elaborate scheme for the prediction of ΔS_m is that by Lüttringhaus and Vierk (40). They relate $\Sigma\Delta S_{m,tr}$ to the surface area per molecule, as measured on modified Stuart–Briegleb models. While these areas differ somewhat from those which were calculated from X-ray diffraction data (12), his results are given here in terms of the latter. Specifically, Lüttringhaus suggests that molecules be grouped in three categories: (1) long-chain molecules, $\Sigma\Delta S_{m,tr}/A_w \approx 1.8 \pm 0.1 \times 10^{-9}$ cal cm^{-2} °K^{-1}; (2) disk and ellipsoidally shaped molecules, $\Sigma\Delta S_{m,tr}/A_w \approx 1.3 \pm 0.2 \times 10^{-9}$ cal cm^{-2} °K^{-1}; and (3) tetrahedral and spherically shaped molecules, $\Sigma\Delta S_{m,tr}/A_w \approx 1.0 \pm$

0.2×10^{-9} cal cm^{-2} °K^{-1}. A_w is the area per mole of molecules in cm^2/mole, as given in ref 12. A basic difficulty of the Lüttringhaus scheme is the assumption that even for rigid molecules $\Sigma\Delta S_{m,tr} \sim A_w$, which is clearly at variance with the data in Tables IV–VII. The method can therefore not be expected to yield reliable results.

The first investigator to notice the strong shape dependence of ΔS_m, Pirsch (57), also observed that within a given family of compounds ΔS_m increases with increasing melting point, but he did not recognize the physical origin of this effect. He was primarily interested in the spherically symmetrical molecules with $\Delta S_m \approx R$ because of their utility as cryoscopic solvents. For those he found that $\Delta S_m/R = a[1 - (b/T_m)]$ with typically

	Tricyclo[2.2.1]-heptanes (camphors)	Tetracyclic dicyclopentadiene deriv	Pentacyclic *endo*-methylene phthalic anhydride deriv
a	4.05	3.85	3.60
b, °K	260	282	334

These correlations are based entirely on ΔH_m estimated from melting point depression, and can therefore not be given the same weight as calorimetric measurements.

For tetrahedral molecules, especially substituted methanes, Hood (24) proposed calculating two limiting values of $\Sigma\Delta S_{m,tr}$, using their symmetry number σ. He obtains a lower and an upper limit for $\Sigma\Delta S_{m,tr}$, depending on whether the molecule is assumed to rotate freely or to oscillate in the crystal at the melting point. A similar scheme has been proposed by Zeldovich to calculate the changes in melting point, etc., for different isomers of aromatic compounds (81). As the prediction method of Maslov (44) is restricted to narrowly defined families, it will not be discussed here.

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