Heat of Sublimation of Molecular Crystals

A Catalog of Molecular Structure Increments

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The heat of sublimation of many nonionic organic and inorganic compounds at their lowest first-order transition point has been separated into group increments. The group increments have been tabulated. Various aids are presented for the calculation of heats of sublimation from a minimum of experimental data. For many compounds, the heat of sublimation can be estimated using only the increments presented.

THE HEAT OF sublimation of crystalline solids is useful not only in thermochemical calculations but also as one of the more important correlating parameters for many thermal and mechanical properties of solids. The rapid accumulation of experimental data from which heats of sublimation can be derived has made it worthwhile, therefore, to develop means by which this information could be generalized and extended. Moreover, quite a few published data are seriously in error. This can be demonstrated most simply by suitable correlation methods, such as the one proposed here.

The scope of the present work has been limited to molecular crystals of organic substances and of inorganic hydrides, perhalides, and percarbonyls. Only those data which permit simple interpretation have been included for hydrogen bonded compounds. Data of multifunctional compounds indicating complicated interaction phenomena are considered outside the scope of the present summary and are the subject of a separate investigation.

GENERAL PRINCIPLES

Ideally the heats of sublimation of various compounds should be compared at 0° K. A serious obstacle to such comparison is the absence of generally reliable means to extrapolate ΔH_s to ΔH_s^1. A very approximate method is given in a later section. The magnitude of such uncertainty can easily be given. An uncertainty in $\Delta C_p = C_p(\text{solid}) - C_p(\text{vapor})$ of ± 2 cal. per ° K.-mole for a substance melting at 400° K. produces an error of the order of ± 800 cal. per mole in ΔH_s^1.

In this work, therefore, the lowest first-order transition temperature T_1 has been adapted as reference temperature. The reason for this choice is that crystals, the molecules of which acquire appreciable mobility above their first-order transition points are nearly like liquids before reaching their melting point. Comparison with ordinary solids at the melting point is then quite meaningless. We shall designate $\Delta H_s^1 = \Delta H_s$ at $T = T_1$. The best justification for this decision is the rather good correlatability of the resulting ΔH_s^1. This correlatability is limited primarily by the poor predictability of the packing density ρ^* or, more specifically, of the distribution of interaction distances in crystals. By "correlatability" is meant the additivity of ΔH_s^1 in terms of uniquely defined group increments:

$$\Delta H_s^1 = H_s^1(\text{R}\cdot) + H_s^1(\text{X}\cdot)$$

where $H_s^1(\text{R}\cdot)$ is the standard heat of sublimation increment for a given alkyl group R·, and $H_s^1(\text{X}\cdot)$ that of some functional group X·. Actually the relations are rarely that simple. If it is assumed that $H_s^1(\text{R}\cdot)$ derived from data of paraffinic hydrocarbons is always the same, it is found that generally:

$$H_s^1(\text{X}\cdot) \approx A - (B/N_c)$$

where N_c is the number of carbon atoms per molecule. The main reason for this decrease is probably the increasing effect of the hydrocarbon portion of the molecule on the crystal structure and on the packing density. The alternative choice, made by Davies (*13*), to consider $H_s(\text{X}\cdot)$ invariant and let the alkyl increment $H_s(\text{R}\cdot)$ vary from one homologous series to another was found to be less practical.

METHODS OF CALCULATION

Where the necessary data were available, the heat of sublimation of solids was calculated from the vapor pressure of the crystal by means of the Clausius-Clapeyron equations. However, in most instances the data were obtained by the scheme:

$$\Delta H_s^1 = \Delta H_v(\text{liq.}, T_a) + \int_{T_a}^{T_m} \Delta C_p^l dT + \Delta H_m + (T_m - T_1)\Delta C_p^s + \Delta H_{tr}$$

where $\Delta H_v(\text{liq.}, T_a)$ is, if possible, a calorimetric measurement or derived from an accurate vapor pressure value. The heat capacity difference ΔC_p^l and its temperature dependence were obtained either directly or from a previously established correlation (*8*).

The heat of fusion, ΔH_m and transition ΔH_{tr}, were taken from calorimetric measurements whenever possible. In the absence of reliable calorimetric data, a good approximation is:

$$\Delta H_m = T_m \sum \Delta S_{m,tr}$$

where T_m is the melting point of the compound in question and $\sum \Delta S_{m,tr}$ is the sum of the entropy of fusion and of transition, if any, of the nearest geometrical analog of the compound for which data can be found. Most often that will be its hydrocarbon homomorph, because most such data are available for hydrocarbons, but generally the more similar the geometrical analog is to the compound at hand, the safer is the estimate. This is especially true if one expects association in the liquid state. If one has $\sum\Delta S_{m,tr}$ for a lower homolog of the compound in question, it is generally safe to add 2.4 e.u. for each methylene group added. An analysis of methods for estimating ΔS_m is the subject of a separate investigation.

The estimation of ΔC_p between transition and melting point is not possible with any degree of exactness. However, the temperature interval in question is rarely large, so that errors have a comparatively small effect, and the assumption $\Delta C_p \approx 8$ cal. per mole ° K. is reasonably safe.

RESULTS

Globular Molecules. The series CH_4, $(CH_3)_2$, $(CH_3)_4C$, $[(CH_3)_3 \cdot C]_2$, . . . is of special interest because intermolecular contacts are restricted to those of primary hydrogen atoms. The data of Table I indicate that the contribution per primary hydrogen atom, $H_s^1(\cdot H_p)$, is quite uniformly 0.65 kcal. per mole, ethane being the only significant exception, probably because of the possibility of (somewhat attenuated) C—C/C—C interaction.

The magnitude of $H_s^1(\cdot H_p)$ is, of course, significantly larger than ½ $\Delta H_s^1(H_2)$ because the internuclear distance H . . . . H in hydrocarbon crystals is much shorter than it is in the hydrogen crystal (2.35 A. at 0° K. for the paraffins (*23*) compared with 3.76 A. in the H_2-crystal) and, more importantly, because the interaction is really between C—H bonds.

Table I. Heat of Sublimation of Globular Molecules

Compound	ΔH_s^1	ΔH_s/H Atom
CH_4	2.20	0.55
C_2H_6	4.90	0.82
$(CH_3)_4 \cdot C$	7.93	0.66
$[(CH_3)_3 \cdot C]_2$	11.74	0.65
$[(CH_3)_3 \cdot C]_2 \cdot CH_2$	12.87	0.645
$Et_4 \cdot C$	14.09	0.70
$[(CH_3)_3 \cdot Si]_2$	12.39	0.69
$(CH_2)_n$	2.0	1.0
$(CH_3)_4 \cdot Si$	9.22	0.77

Normal Paraffins. This is the best measured series of chemical compounds. The data calculated from vapor pressures could, therefore, be checked frequently against good calorimetric measurements. Whenever necessary, the calorimetric heats of vaporization were extrapolated to the melting point and transition points by means of the readily available ΔC_p data. All available data have been assembled in Table II.

This table shows the expected uniformity of increase of ΔH_s^1 with chain length after the first two members of the series, provided the comparisons are made within the series of odd and even numbered *n*-paraffins, respectively. These data yield a slightly higher increment per CH_2 group (2.0 kcal. per mole) than do Billmeyer's carefully calculated heat of sublimation data at 0° K., namely, 1.838 kcal. per mole (*6*), because ΔC_p^s becomes negative somewhere below the Debye temperature of the solid.

Branched Chain Paraffins. The primary effect of a branch in the paraffin backbone chain of a molecule is the conversion of a readily accessible C—H bond into an almost inaccessible C—C bond. Hence, the heat of sublimation decrement, Δ/b, per branch point (relative to the normal paraffin) should be of the order:

$$\Delta/b \approx -3/2\, H_s(CH_2) + 3H_s(H_p) \approx -1.1 \text{ kcal./mole}$$

in fair agreement with experimental observation. For *gem*-branch points, Δ/b is somewhat larger because of the increased shielding effect.

Cycloparaffins (Ring Structure Only). The heats of sublimation of the first three members of this series are, as the data of Table III show, slightly higher than estimated for the methylene group increments of the normal paraffins. All three have planar or nearly planar molecules, allowing close approach of nearest neighbors in the crystal lattice. The higher cycloalkanes with their well known puckered configuration pack so poorly that their lattice energy is distinctly lower than predicted from $H_s(CH_2)$. This effect is yet more pronounced for the condensed cyclic naphthenes. The high heat of sublimation of cyclotetradecane reported by Margrave (*29*) suggests that the very large rings are packed rather tightly in their crystals.

Alkyl Cycloparaffins. The ring increments $H_s(R\cdot)$ have been estimated by the relation:

$$H_s(R\cdot) = \Delta H_s^1 \text{ (alkyl cycloparaffins)} - H_s \text{ (alkyl group)}$$

where H_s(alkyl group), derived from normal and isoparaffin data, can be taken from the assembled increments of Table IV. The magnitude of the ring decrements for cyclopentane and cyclohexane reflects even more sharply than

Table II. Heat of Sublimation of *n*-Paraffins at Their Lowest First-Order Transition Temperature

		Kcal./Mole				
N	T_1, ° K.	$\sum\Delta H_{m,tr}$	$\Delta H_v(T)$	ΔH_s^1	ρ_s*	Ref.
1	90	. . .	. . .	2.20	0.553	(*2, 42*)
2	90	0.68	4.22	4.90	0.673	(*42, 50*)
3	86	0.84	5.97	6.81	. . .	(*39, 47*)
4	107	1.61	6.84	8.57	0.670	(*39, 42, 47*)
5	143	2.01	8.02	10.03	0.676	(*39, 42, 47*)
6	178	3.11	9.04	12.15	0.671	(*39, 42, 47*)
7	183	3.37	10.46	13.83	0.675	(*16, 39, 42, 47*)
8	216	4.96	11.31	16.27	0.679	(*16, 39, 42, 46*)
9	219	5.20	12.62	17.82	. . .	(*16, 39, 50*)
10	243	6.86	13.40	20.26	. . .	(*16, 39, 46*)
11	236.6	6.94	14.88	21.82	. . .	(*16, 39, 46*)
12	263	8.80	15.50	24.30	. . .	(*16, 39, 46*)
16	291	12.75	19.59	32.24	. . .	(*16, 36, 39, 46*)

Table III. Heat of Sublimation of Cycloparaffins

Compound	T, ° K.	Kcal./Mole ΔH_v	 $\sum \Delta H_{m,tr}$	 ΔH_s^1	Ref.
Cyclopropane	145	5.69	1.30	6.99	(*41, 52*)
Cyclobutane	145	7.04	1.67	8.71	(*37. 38*)
Cyclopentane	122	8.80	1.39	10.19	(*42, 50*)
Cyclohexane	186	8.91	2.22	11.13	(*39, 47*)
Cycloheptane	134	10.97	1.81	12.78	(*17*)
Cyclooctane	166	11.87	2.18	14.05	(*17*)
Cyclotetradecane	320	...	...	32.0[a]	(*29*)
trans-Decahydronaphthalene	241	12.37	3.44	15.82	(*28, 32*)
cis-Decahydronaphthalene	230	13.21	2.34	15.48	(*28, 32*)
trans-syn-trans-Perhydroanthracene	...	...	...	21.0[a]	(*29*)

[a] Heat of sublimation from vapor pressure of crystal.

Table III the difference is packing ability between these two ring types. The slight decrease in $H_s(R\cdot)$ with increasing size of alkyl group is probably also related to the packing problem and is a general phenomenon, as shown later.

Cage Molecules. In spite of their increasing importance in synthetic organic chemistry, surprisingly few data have been obtained on cage molecules. In fact, most available heat of sublimation data for cage molecules are on polar compounds. The heat of sublimation increments for hydrocarbon components of these cage molecules, presented in Table V, have been estimated from the heat of sublimation of the polar compounds. They should therefore be regarded as approximate only.

Olefins and Acetylenes. A noteworthy aspect of the 1-olefin increments of Table IV is the virtual identity with those of the *n*-paraffin of equal number of carbon atoms. The fact that this holds also for the conjugated olefin suggests that the occasionally postulated special interaction between conjugated double bonds (*18, 27*) is, if present at all, not very strong.

A peculiarity of the olefins is that chain branching at the double bond increases rather than decreases the standard heat of sublimation. The cause may be the improved packing possibilities owing to the nearly planar shape of the branch system and the absence of interfering hydrogen atoms. A high polarizability and a geometry well suited for tight packing cause the somewhat larger heat of sublimation increments of the acetylene group.

·Aromatic Ring Systems (Without Side Chains). Extensive data of widely varying quality have been obtained for this large class of compounds. The data have, therefore, been selected on the basis of the reputation of the experimentalists and their consistency with the well established data for benzene and naphthalene. The wide discrepancies in the literature are illustrated in Table VI. There is a

Table IV. Standard Heat of Sublimation Increments for Alkane and Cycloalkane Groups

Type	Fragment (R)	$H_s^1(R)$, Kcal./Mole
Aliphatic	$\cdot CH_3$ (=Me·)	2.45
	$>CH_2$	2.03
	·Et	4.28
	*n*Pr·	6.08
	iso-Pr·	5.32
	n-Bu·	8.14
	iso-Bu·	6.83
	sec-Bu·	7.21
	tert-Bu·	5.6
Cycloaliphatic	Cyclopentyl·	9.00[a]
	Cyclohexyl·	$8.5 + 0.70/N_B$
	Cyclohexylene:	8.3[a, b]
Monoolefinic	Vinyl·	4.14
	Vinylene: 1,1-	3.50
	Vinylene: 1,2-*cis*	3.90
	Vinylene: 1,2-*trans*	4.10
	Propenyl·	5.90
	Isopropenyl·	6.13
	n-Butenyl·	7.43
	iso-Butenyl·	7.80 8.00
Diolefinic	Allenyl·	(6.0)
Acetylenic	Ethynyl·	5.6[a]
	Ethynylene:	4.35[a]
	Propynyl·	6.64[a]

[a] Based on data from methyl derivatives only. [b] In 1,1-substitution, H_s (cyclohexylene) = 7.6 kcal./mole and the corresponding *gem*-group H_s ($Me_2C<$) = 3.2 kcal./mole.

Table V. Estimate of Standard Heat of Sublimation Increment of Cage Molecules

Substance	Ref.	Kcal./Mole ΔH_s^1	 Increments[a]
1,4-Ethylenepiperidine	(*11*)	12.20	$\bar{H}_s(CH_2 \text{ or } CH) = 1.45$ $\bar{H}_s(N:) = 2.25$
Triethylenediamine	(*15*)	13.00	
Hexaethylenetetramine	(25)	18.0	

[a] Weighted average.

Table VI. Range of Experimental Data for Standard Heats of Sublimation of Polyaromatic Hydrocarbons[a]

Substance	ΔH_s^1, Kcal./Mole	Ref.
Naphthalene	15.3	(*53*)
	15.4	(*1*)
	15.6	(*51*)
	16.2	(*19*)
	16.7	(*10*)
	16.8	(*29*)
Anthracene	21.7	(*20*)
	22.7	(*45*)
	23.4	(*10*)
	23.9	(*19*)
9,10-Diphenylanthracene	33.4	(*19*)
	37.2	(*45*)

[a] For other examples see the uncritical data collection by Jones (*22*).

trend toward more acceptable, or internally consistent, data with time. Hence, more recent data have, on the whole, been given greater weight than the older information. The steady increase of the observed heat of sublimation of a given compound as techniques are improved, reflects largely the reduction in the concentration of volatile (and gaseous) impurities. A careful test for thermodynamic consistency by Miller (*31*) leads to $\Delta H_s^1 = 17.014$ kcal. per mole for naphthalene, a value slightly higher than any of the data given in Table VI.

In the series benzene, biphenyl, 1,4-diphenylbenzene, one observes remarkable regularity, and that, rather exactly:

$$\Delta H_s^1 = 1.73\, N_{\mathrm{CH}} + 0.90\, N_{ct} \text{ kcal./mole}$$

when N_{ct} = number of tertiary carbon atoms on the ring. Substitution of two phenyl rings in the 1,3-position of a benzene ring does not reduce the packing density of the crystal significantly, but the heat of sublimation is reduced by virtue of a strong shielding effect, such that now:

$$\Delta H_s^1 = 1.73\, N_{\mathrm{CH}} + 0.30\, N_{ct} - 0.9\, N_{cm}$$

when N_{cm} = number of ring carbon atoms in *meta* substitution. The relation holds rather well for 1,3-diphenylbenzene and 1,3,5-triphenylbenzene and should, therefore, be of general validity. No data could be found for the heat of sublimation of 1,2-diphenylbenzene. The mutual shielding of the crowded, out-of-plane phenyl rings should cause appreciable reduction in ΔH_s^1. From the heat of vaporization data one might guess that the corresponding increment $N_{co} \approx -2$ kcal. per mole, yielding a guessed value of ΔH_s^1 (1,2-diphenylbenzene) $\approx$ 19.8 kcal. per mole.

The standard heat of sublimation of the condensed cyclic aromatics also follows rather simple trends which are, of course, related to the simple planar shape of these molecules and their easy parallel alignment in the crystal. A reasonably reliable relation for the *kata*-condensed series benzene, naphthalene, and anthracene, is:

$$\Delta H_s^1 = 1.73\, N_{\mathrm{CH}} + 1.35\, N_{ct}$$

For *peri*-condensed compounds, such as phenanthrene and chrysene, a shielding correction has to be made for the crowded ring carbon atoms (N_p) 1 and 8, such that:

$$\Delta H_s^1 = 1.73\, N_{\mathrm{CH}} + 1.35\, N_{ct} - 0.40\, N_p$$

Alkylaromatics. The standard heats of sublimation of various alkylated aromatic hydrocarbons indicate a sharp decrease in the magnitude of the ring increment with increasing length of the alkyl chain (Table VII). One of the reasons for this trend is probably the difficulty of accommodating a large alkyl chain and an aromatic ring in the same crystal structure. Once the alkyl chain reaches a certain size (approximately C_5), the ring has to accommodate itself to the arrangement of the chains in the crystal lattice.

The decreasing effect of chain branching and of multiple branches on the heat of sublimation increment of the ring system is somewhat smaller than one might have expected initially. It appears that only few substituents prevent close packing or close range interaction of neighboring aromatic rings.

General Observations on Hydrocarbons. The largest chemical differences between hydrocarbons are those associated with C—C bond order. Elaborate theories have been proposed which predict large effects of bond type, especially double bond conjugation on intermolecular forces (*18, 27*). However, when expressed as heat of sublimation increment per carbon atom, the differences arising from bond type are rather insignificant, as is shown by the data of Table VIII.

Nonpolar Halides. The replacement of all hydrogen atoms of a hydrocarbon by halogen atoms yields externally nonpolar molecules. The replacement of the C—H bond with a dipole moment of about 0.5 D. by a C—X bond with a dipole moment of 1.8 D. or more (*33*) adds a long range electrostatic repulsion term to the interaction energy equation. This term is important for the perfluoro compounds, is quite small for perchloro compounds, and probably negligible for perbromides and periodides. Owing to the increasing effect of electrostatic repulsion with increasing dipole density, $H_s(\cdot F)$ decreases with increasing number of CF_2 groups per molecule, as shown by the data of Table IX.

Only a small portion of the few chemically stable perchloro carbon compounds has been characterized by physical property measurements. The few available data have been assembled in Table X.

Table VII. Standard Heat of Sublimation Increments for Aromatic Rings

Type	Fragment (X)	H_s^1(X), Kcal./Mole
Monoalkylbenzenes	$\phi\cdot$	$8.40 + 1.60/N_B$
Dialkylbenzenes[a]	$\phi:$	$7.0 + 4.80/\sum N_B$[b]
Trialkylbenzenes[a]	$\cdot\phi:$	8.1[c]
Tetraalkylbenzenes[a]	$:\phi:$	6.8[c]
Hexaalkylbenzenes	$\vdots\phi\vdots$	4.6[c]
Monoarylbenzene	$\phi\cdot$	9.6
p-Diarylbenzene	$\phi:$	8.6
1,3,5-Triarylbenzene	$\cdot\phi:$	5.0
Monoalkylnaphthalene	Naphthyl·	15.0[c]
1,2-Dialkylnaphthalene	1,2-Naphthylene	14.2

[a] Averaged over position isomers, except for 1,3,5-trialkyl chains for which ΔH_s^1 is 0.8 kcal. lower than for the other isomers; it was therefore excluded from the averaging. [b] $\sum N_B$ = total number of carbon atoms in alkyl chains. [c] Derived from data on methyl derivatives only.

GROUP INCREMENTS

This section presents typical group increment data for the standard heat of sublimation (ΔH_s^1) of common chemical species. The use of the method is illustrated by the examples of Table XI which have been presented in the form in which increment addition is carried out. These examples indicate that the present method errs consistently on the high side. In evaluating this observation one should remember that incomplete degassing, the most common source of error in vapor pressure determinations on very nonvolatile substances, leads to lower-than-true heats of vaporization or sublimation. Another source of bias toward the high side, especially with molecules of complex shape, is the fact that most increments were obtained on molecules of simple shape which are packed more tightly in their crystals than are complex molecules. The next important improvement in the present method would be a correction for packing density. A meaningful test of the reliability of the present method could not be made because the

Table VIII. Comparison of Standard Heat of Sublimation Increments per Carbon Atom

Type	H_s^1, Kcal./Mole
Alkane (CH_2)	2.03
Olefin ($=CH_2$)	2.3
Allene ($=C=$)	2.0
Acetylene ($-C\equiv$)	2.2
Aromatic (CH)	1.73
Cage (CH_2)	1.45

Table IX. Standard Heat ot Sublimation of Perfluorocarbon Compounds

Substance	T_1, ° K.	Kcal./Mole $\Delta H_v(T_m)$	$\sum \Delta H_{m,tr}$	ΔH_s	X	H_s(X), Kcal./Mole	Ref.
CF_4	76	3.44	0.52	4.06	·F	1.02	*(14)*
C_2F_6	103	4.12	1.54	6.21	·F	1.03	*(35)*
n-C_5F_{12}	145	8.83	1.62	10.45	·F	0.87	*(5, 12)*
n-C_7F_{16}	180	10.17	3.25	13.79	·F	0.86	*(34)*
n-$C_{16}F_{34}$	...	...	...	25.01	·F	0.74	*(49)*
Cyclo-C_5F_{10}	115	6.49	2.03	9.13	·F	0.91	*(5, 12)*
Cyclo-C_6F_{12}	...	...	1.0[a]	10.4	·F	0.87	*(40)*
Cyclo-$C_6F_{11}\cdot CF_3$	234	9.75	2.58[a]	12.33	·F	0.88	*(40)*

[a] Assumed $\sum \Delta H_{m,tr} = T_m \Delta S_m$(cyclohexane and methylcyclohexane, respectively).

Table X. Standard Heat of Sublimation of Various Organic Perchloro Compounds

Substance	T_1, ° K.	$\Delta H_v(T_m)$	$\sum \Delta H_{m,tr}$	ΔH_s^1	X	H_s(X)	Ref.
CCl_4	226	8.45	1.70	10.34	Cl	2.6	*(47, 52)*
C_2Cl_6				14.1	Cl	2.35	*(21)*
Hexachlorocyclopentadiene	283	14.87	2.73	17.6	Cl	2.95	*(48)*
Hexachlorobenzene	403	...	...	21.4	Cl	2.82	*(44)*

increments have been derived from almost all available data, and too few data were left which are not contained in the increments.

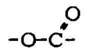
The method is safest to use when increments for hydrocarbon radicals are combined with increments for a given functional group, with proper allowance for the size of the hydrocarbon radical where indicated. Interactions of different functional groups with each other have not been worked out, except for the shielding effects of several identical functional groups in the same molecule, as indicated in the increment tables and best known for polychlorinated hydrocarbons. It is probably safe to consider different halogens in the same molecule as simply additive, as, for example, in 1-chloro-3-bromopropane. Care should be exercised when strongly electron withdrawing groups, such as trifluoromethyl, are next to another functional group (X), because they can cause a sharp change in the dipole moment and thus of H_s(X). Additivity can be assumed only after having been tested against known data for a compound similar to that for which the data are desired. The resulting correction, if any, can then be applied to the final calculation.

Table XI. Additivity of Increments[a]

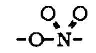
Combination	ΔH_s^1, Kcal./Mole Calcd.	Obsd.	Ref.
H_s(isopropenyl) + H_s(carboxylate) + H_s(methyl) = ΔH_s^1(methyl methacrylate)	14.7	14.2	*(26)*
$H_s(\cdot\dot{C}=O)_{ar}$ + H_s(phenylene) + $2H_s(\cdot O\cdot)$ + $2H_s$(methyl) = ΔH_s^1(*p*-acetylanisole)	19.5	18.6	*(1)*
$2[2H_s(CH_2) + H_s(\text{primary})(Cl)]$ + $H_s(S) = \Delta H_s^1(ClC_2H_4)_2S$	20.4[b]	20.2	*(3, 4, 33)*
H_s(naphthyl·) + $H_s(Cl_{ar})$ = ΔH_s^1(1-bromonaphthalene)	19.3[c]	18.9	*(26)*
$4[H_s(Br) + 2H_s(CH_2)]$ = $\Delta H_s^1(BrC_2H_4)_4C$	21.6[d]	20.1	*(26)*
$H_s(\cdot CCl_3) + 2H_s(Cl) + 2H_s$(phenylene) + H_s(CH)	33.3[e]	28.2	*(3, 4)*
= ΔH_s^1 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT)	30.1[f]	28.2	*(3, 4)*

[a] All examples are compounds not used in preparation of correlation. [b] Estimated $\Delta H_m = \Delta T_m[\Delta S_m(Et_2S) + \Delta S_m(1,2\text{-}EtCl_2) - \Delta S_m(\text{ethane})]$. [c] Assumed ΔS_m = 13.5 e.u. (typical for aromatic molecules of this type). [d] H_s(neopentyl quadruple radical) = 4.30 kcal./mole; not tabulated elsewhere. [e] Estimated ignoring all shielding effects. [f] Estimated taking shielding effects into consideration.

Resonance interaction of two adjacent groups (A—B) turns the two, in effect, into a new chemical entity, and there is no reason to expect any relation of the properties of group A—B to those of A and B. Typical instance are the esters


$-O-C(=O)-$

or


$-O-N(=O)=O$

the H_s increments of which are substantially smaller than the sum of the ether oxygen and carbonyl or nitro group, respectively, as is shown by the examples of Table XII.

While carbonyl and halide atoms (at two carbon atoms distance) in the same molecule might not show very strong deviations from increment additivity, hydroxyl or amino groups in the same molecule can interact so strongly, either by intra- or intermolecular hydrogen bonding, that additivity of increments can be precluded. However, the strength of the increment method is that even that type of interaction, when studied on correctly chosen model compounds for which data are available, can be transferred to the particular case for which no data are available. In short, the application of the present method requires some understanding of chemistry.

TableXII. Erroneous Estimates of Functional Group Increments

Wrong Method of Estimation	Increment, Kcal./Mole Estd.	Obsd.
$H_s(\cdot NO_2) + H_s(\cdot O\cdot) \rightarrow H_s(\cdot ONO_2)$	11.7-12.2	$H_s(\cdot ONO_2)$ = 9.6
$H_s(:C=O) + H_s(\cdot O\cdot) \rightarrow H_s(\cdot OC=O)$	7.7- 8.2	$H_s(\cdot OC=O)$ = 4-6

Table XIII. Standard Heat of Sublimation Increments for Group VII Compounds

Type	Fragment (X)	H_s^1(X), Kcal./Mole
Fluorides		
Polar Fluorides		
1-*n*-Alkyl fluorides	$\cdot F$	$2.43 + (0.60/N_c)$
n-Alkyl-1,1,1 trifluorides	$\cdot CF_3$	4.4
Aryl fluorides, mono-	$\cdot F$	1.90
di-, *p*-, *m*-		1.55
Benzotrifluoride	$\cdot CF_3$	3.2
Nonpolar Fluorides		
F_2(for comparison)	$\cdot F$	1.02
Inorganic perfluorides ($A_r > 0.8$)	$\cdot F$	1.1
n-Alkyl perfluorides	$\cdot F$	$0.74 + (1.70/N_F)$
n-Alkyl perfluorides (approx.)	$>CF_2$	1.48
Cycloaliphatic perfluorides	$\cdot F$	0.89
Chlorides		
Polar Chlorides		
1-*n*-Alkyl monochlorides[a]	$Cl\cdot$	$3.55 + (1.37/N_c)$
1,1-*n*-Alkyl dichlorides	$\cdot CHCl_2$	8.4
1,1,1-*n*-Alkyl trichlorides	$\cdot CCl_3$	8.5
Phenyl chloride, mono-, di-	$\cdot Cl$	3.5
Phenyl chloride, 1,2,4-tri-	$\cdot Cl$	2.8
Nonpolar Chlorides		
Cl_2(for comparison)	$\cdot Cl$	3.52
Aliphatic perchlorides	$\cdot Cl$	$1.87 + (2.90/N_{Cl})$
Hexachlorobenzene	$\cdot Cl$	2.82
Inorganic perchlorides with $A_r > 0.8$	$\cdot Cl$	2.7
Bromides		
Polar Bromides		
1-*n*-Alkyl monobromides[b]	$\cdot Br$	$4.12 + (1.62/N_c)$
Phenyl bromide	$\cdot Br$	4.28
Nonpolar Bromides		
Br_2(for comparison)	$\cdot Br$	5.24
CBr_4	$\cdot Br$	3.34
Inorganic perbromides with $A_r > 0.08$	$\cdot Br$	3.3 ± 0.2
Iodides		
Polar Iodides		
1-*n*-Alkyl monoiodides	$\cdot I$	$5.86 + (1.32/N_c)$
Phenyl iodide	$\cdot I$	5.03
Nonpolar Iodides		
Inorganic periodides with $A_r > 0.8$	$\cdot I$	4.6

[a] For secondary and tertiary monochlorides, $H_s(\cdot Cl)$ is the same as for primary monochlorides. The same increment also applies to other primary chlorides such as α, ω-dichlorides. [b] The same increment applies to other primary bromides such as α, ω-dibromides.

The order of the functional groups in this collection (Tables XIII to XVII) is largely that of the periodic table, going from right to left: halides, Group VI elements: oxygen, sulfur, selenium; Group V: arsenic, antimony, bismuth, nitrogen, phosphorus; Group IV (except carbon): silicon, germanium, tin, lead; Group III: and a few increments for metals in metal-organic compounds. Hydrogen bonded crystals are dealt with in the last section of the increment collection (Table XVIII to XX).

Metal Alkoxides. All reference to alkoxides of metals has been carefully avoided in this collection. The reason for this omission is twofold. There are neither melting points nor heat of fusion data available. Secondly, the fairly extensive heat of vaporization data collected by D.C. Bradley (*9*) show that coordinative bond formation between the central metal atom of one molecule and the oxygen atoms of neighboring molecules can make very large contributions to the cohesive energy of metal alkoxides with "small" alkyl groups and often leads to vapor phase dimerizations. These bonds are blocked by "large" and bulky alkyl groups. There are, thus, too many uncertainties at present to develop reliable correlations from rudimentary data.

Hydrogen Bonded Crystals. The most strongly directional interaction in molecular crystals derives from the hydrogen bond. The change in free energy of the system caused by shortening of hydrogen bonds is so large that it overcompensates even the penalty of loose packing. The best-known example is, of course, water, which gains in volume upon crystallization to form the open tridymite lattice. A somewhat less drastic case is phenol, where the hydrogen bonds are shortest when crystallizing in form of a helix (*30, 43*), although this means an over-all packing density of the solid of $\rho_s^* = 0.618$ compared with $\rho_s^* = 0.675$ for solid toluene, its hydrocarbon homomorph.

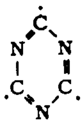
The standard heat of sublimation of hydrogen bonded substances should therefore be compared with that of its hydrocarbon homomorph at the same packing density to obtain a meaningful number for the hydrogen bond strength. Temporarily, the expedient has been adopted to ignore the packing density effect and proceed as before. The results (Table XXII to XXIV) are somewhat anomalous, in that now the hydrogen bond increments δ_s(X) of ΔH_s of many solids are often smaller than the corresponding increments for liquids at the same temperature (*7*). While probably quite suitable for the estimation of the heat of

Table XIV. Standard Heat of Sublimation Increments for Functional Groups Containing Some Group VI Elements

Type	Fragment (X)	$H_s(X)$, Kcal./Mole
Ether Oxygen		
Aliphatic	$\cdot O\cdot$	$1.55 + (2.36/N_c)$
Heterocycloaliphatic $\overset{\vert\text{—O—}\vert}{\text{C———C}}$	$\cdot O\cdot$	4.0
Heterocycloaliphatic	$\overset{\vert\text{—O—}\vert}{\text{C———C}}\cdot$	6.40
Heterocycloaliphatic (dioxane)	$\cdot O\cdot$	2.53
Aromatic [(phenyl)$_2$O]	$\cdot O\cdot$	1.0
Heteroaromatic (furan)	$\cdot O\cdot$	1.60
Carbonyl Oxygen		
Aldehyde (aliphatic)	$\cdot\overset{H}{C}=O$	6.40
Ketone (aliphatic)	:C=O	5.6
Ketone (diaromatic)	:C=O	(3.6)
Heteroaromatic ketone (quinone)	:C=O	6.0
Nonpolar carbonyl[a]	(C=O)	2.7
Carboxylate Ester Groups[b]		
Aliphatic	$\cdot\overset{O}{\overset{\Vert}{C}}—O\cdot$	$4.40 + (5.10^{c}/N_c)$
Heterocycloaliphatic (lactones)	$\cdot\overset{O}{\overset{\Vert}{C}}—O\cdot$	10.4
Heterocyclic Carbonates and Anhydrides		
Ethylene carbonates	$\cdot\dot{O}—\overset{O}{\overset{\Vert}{C}}—O\cdot$	13.1
Succinic (and similar anhydrides)	$\cdot\overset{O}{\overset{\Vert}{C}}—O—\overset{O}{\overset{\Vert}{C}}\cdot$	14.5
Phthalic (and similar anhydrides)	$\cdot\overset{O}{\overset{\Vert}{C}}—O—\overset{O}{\overset{\Vert}{C}}\cdot$	12.3
	Sulfur	
Thioethers		
S_8	$\cdot S\cdot$	2.90
Aliphatic (primary)	$\cdot S\cdot$	$4.28 + (1.60/N_c)$
Aliphatic[d]	$\cdot S\cdot$	Primary −0.1
Cycloaliphatic (hetero)	$\cdot S\cdot$	$4.60 \approx [(3.53 + (6.00/N_c)]$
Heteroaromatic (thiophene)	$\cdot S\cdot$	3.90
Disulfides		
S_8	$\cdot SS\cdot$	5.8
Aliphatic[d] (*sym*)	$\cdot SS\cdot$	$5.6 + (4.8/N_c)$
Thiols		
Aliphatic (primary)	$\cdot SH$	$5.26 + (1.05/N_c)$
Aliphatic (*sec*- and *tert*-)	$\cdot SH$	Primary −0.70
Aromatic	$\cdot SH$	5.10
Sulfur-Oxygen Compounds		
Sulfoxides (aliphatic)	:S=O	10.9[e]
Sulfones (aliphatic)	$O=\ddot{S}=O$	14.2[e] $[\approx 7.25 + (13.9/N_c)]$
Sulfites (aliphatic)	$(\cdot O)_2—S=O$	8.0[e, f]
Sulfates (aliphatic)	$(\cdot O)_2—S=(O)_2$	9.1[e, f]
	Selenium	
Se_6	$\cdot Se\cdot$	6.4[f]
Selenoethers (aliphatic)	$\cdot Se\cdot$	5.6[e]
Selenoethers (aromatic)	$\cdot Se\cdot$	(b)[e]
Selenoethers (heteroaromatic, selenophene)	$\cdot Se\cdot$	>4.3[e]
Selenohydride (aliphatic)	$\cdot SeH$	7.0[e]

[a] In metal carbonyl compounds. [b] All but formates. [c] Applicable also to esters of dicarboxylic esters, such as ethyl oxalate. [d] Restricted to aliphatic side chains with no more than one branch chain adjacent to a sulfur atom. [e] Datum of single compound. [f] Somewhat uncertain.

Table XV. Standard Heat of Sublimation Increments for Functional Groups Containing Group V Elements

Type	Fragment (X)	H_s(X), Kcal./Mole
Nitrogen		
Cyanide		
Aliphate monocyanide	$\cdot C \equiv N$	$6.18 + (2.24/N_c)$
α, ω-dicyanide	$\cdot C \equiv N$	6.34[a]
Percyanide (in cyanocarbon compounds)	$\cdot C \equiv N$	3.9
Nonbasic Nitrogen		
Alkylhydrazines	$—NMe_2$	5.56
Azo group	$—N=N—$	4.70
Triazine ring		9.0
Basic Nitrogen		
Aliphatic *tert*-amine	N:	0
Heteroaromatic pyridyl	N:	4.15
	pyridyl group	12.5
Nitro		
Aliphatic, mono-	$\cdot NO_2$	9.6[a]
per-[b]	$\cdot NO_2$	3.26[a]
Aromatic, mono-	$\cdot NO_2$	6.8
di-, *p*-, *m*-	$\cdot NO_2$	5.9, 5.2
tri-, (*sym*)	$\cdot NO_2$	5.3
Nitroxo		
Aliphatic, mono-	$\cdot ONO_2$	9.6[a]
di-	$\cdot ONO_2$	(7.4) ?
tri-	$\cdot ONO_2$	9.2[a]
tetra-	$\cdot ONO_2$	9.1 (80)[a]
Phosphorus		
White phosphorous (for comparison)	—P—	4.60
Phosphine	PH_3	4.10
Monoalkylphosphine (aliphatic)	$—PH_2$	4.75[c]
Dialkylphosphine	$>PH$	4.6[c]
Trialkylphosphine	$\overset{\vert}{—P—}$	2.93[c]
Trialkyl phosphate	$O=P(O—)_3$	~9.
Arsenic		
As_4(for comparison)	—As—	7.0
AsH_3(for comparison)	AsH_3	4.92
Dialkylarsine	$>AsH$	4.0[c]
Trialkylarsine	$\overset{\vert}{—As—}$	2.4[c]
Triarylarsine	$\overset{\vert}{—As—}$	~0[a]
Antimony		
SbH_3(for comparison)	SbH_3	6.05
Trialkylstibine	$\overset{\vert}{—Sb—}$	3.3
Triarylstibine	$\overset{\vert}{—Sb—}$	2.0[c]
Bismuth		
Trialkylbismuthine	$\overset{\vert}{—Bi—}$	4.4[c]

[a] Datum of a single compound. [b] As in tetranitromethane. [c] Approximate value, from data for single compound.

Table XVI. Standard Heat of Sublimation Increments for Functional Groups Containing Silicon, Germanium, Tin, and Lead

Type	Fragment (X)	H_s(X), Kcal./Mole
	Silicon	
Silane	$-\mathrm{SiH_3}$	3.56
	$-\mathrm{SiH_2}-$	2.93
Silyl Compounds		
Alkyl	$-\overset{\vert}{\underset{\vert}{\mathrm{Si}}}-$	-0.60
	$-\mathrm{SiMe_3}$	6.47
Siloxanes		
Alkyl (linear)	$-\mathrm{O}-$	1.21[a]
Alkyl (cyclic)	$-\mathrm{O}-$	0.4[a]
Silicates		
Tetraalkyl	$\mathrm{Si(O-)_4}$	-1.0
	Germanium	
Germanes	$\cdot\mathrm{GeH_3}$	4.39
	Tin	
Stannanes		
Tetraalkyl	$-\overset{\vert}{\underset{\vert}{\mathrm{Sn}}}-$	1.5
	Lead	
Plumbanes		
Dialkyl	$>\mathrm{PbH_2}$	3.0
Tetraalkyl	$-\overset{\vert}{\underset{\vert}{\mathrm{Pb}}}-$	2.5

[a] Calculation based on $H_s(-\mathrm{SiMe_3})$ of previous line, not on the use of H_s(Me) of Table IV.

Table XVII. Standard Heat of Sublimation Increments of Groups Containing Aluminum, Gallium, Indium, Zinc, Cadmium, and Mercury

Type	Fragment (X)	H_s(X), Kcal./Mole
Trialkylaluminum	$-\overset{\vert}{\mathrm{Al}}-$	. . .[a]
Trialkylgallium	$-\overset{\vert}{\mathrm{Ga}}-$	$1.40 + (6.60/N_c)$
Trialkylindium	$-\overset{\vert}{\mathrm{In}}-$	6.3[b]
Di-*n*-alkylzinc	$-\mathrm{Zn}-$	$3.90 + (3.00/N_c)$
Di-*n*-alkylcadmium	$-\mathrm{Cd}-$	6.95[c]
Di-*n*-alkylmercury	$-\mathrm{Hg}-$	7.4[c]
Diarylmercury	$-\mathrm{Hg}-$	10.0[d]

[a] Tri-*n*-alkylaluminum compounds are generally dimers in liquid and vapor phase, and $\Delta H_s \approx 6[\Delta H_s(\text{alkyl}) - 0.2]$. [b] From data on one compound (trimethyl). [c] From data on one compound (dimethyl). [d] From data on one compound (diphenyl).

Table XVIII. Standard Heat of Sublimation Increments of Hydrogen Bonding Groups Containing Oxygen

		Kcal./Mole	
Type	Framgent (X)	H_s(X)	δ_s(X)
$\mathrm{H_2O_2}$ (for comparison)	$\cdot\mathrm{OH}$	7.80	. . .
n-Alkanols-1	$\cdot\mathrm{OH}$	8.20	5.75
tert-Alkanols	$\cdot\mathrm{OH}$	6.90	4.65
Primary alkane polyols	$\cdot\mathrm{OH}$	7.5	5.1
Phenols	$\cdot\mathrm{OH}$	6.4-7.2	4.0-4.6
n-Alkanoic and dioic acid	$\mathrm{O{=}\overset{\vert}{C}{-}OH}$	11.5	5.5
Phenyl carboxylic acid	$\mathrm{(O{=}\overset{\vert}{C}OH)_{ar}}$	12.4	(6.5)

Table XIX. Standard Heat of Sublimation Increments for Hydrogen Bonding Groups Containing Nitrogen

Type	Fragment (X)	H_s(X), Kcal./Mole
Hydrazine ($\mathrm{N_2H_4}$) (for comparison)	$\cdot\mathrm{NH_2}$	7.00
Monoalkylamine (or unsymmetrical dialkylhydrazine)	$\cdot\mathrm{NH_2}$	6.35
Monoarylamine	$\cdot\mathrm{NH_2}$	6.50
Dialkylamine (or monoalkylhydraryl group)	$>\mathrm{NH}$	4.50
Heterocycloaliphatic	$>\mathrm{NH}$	4.80
Heteroaromatic (pyrrole, carbazole)	$>\mathrm{NH}$	7.3
Heteroaromatic (pyrazole, etc.)	$=\mathrm{N}-\overset{\vert}{\mathrm{N}}\mathrm{H}$	11.0
Heteroaromatic (1,2,3-triazole, etc.)	$-\mathrm{N}=\mathrm{N}-\overset{\vert}{\mathrm{N}}\mathrm{H}$	14.2
Heteroaromatic (tetrazoles)	$=\mathrm{N}-\mathrm{N}=\mathrm{N}-\overset{\vert}{\mathrm{N}}\mathrm{H}$	21.6
Heteroaromatic (imidazoles)	$-\mathrm{N}=\mathrm{C}-\overset{\vert}{\mathrm{N}}\mathrm{H}$	16.5

sublimation of many hydrogen bonded substances, these increments should be used with care. They should not be used to estimate hydrogen bond strength without making allowance for the effects of packing density.

The amount of detailed information available on hydrogen bond strengths in crystals is so large that its presentation would go far beyond the scope of the present summary. The increments given should be considered as "samples" only. A separate study is required to do justice to the very interesting interactions observed in hydrogen bonding systems.

COMPARISON WITH OTHER METHODS

Few methods have been proposed to estimate the heat of sublimation of molecular crystals. The best known method is perhaps that by Klages (*24*), who proposed the correlations:

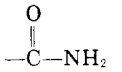
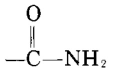
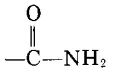
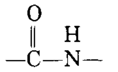
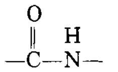
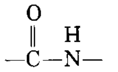
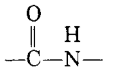
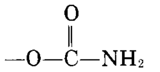
$$\Delta H_s \text{ (at 25° C.) for nonpolar or slightly polar compounds} = 5.4 + 0.036\, T_b \text{ kcal./mole}$$

$$\Delta H_s \text{ (at 25° C.) for hydrogen bonded compounds} = 6.8 + 0.045\, T_b \text{ kcal./mole}$$

where T_b is the atmospheric boiling point. The main deficiency of this method is its dependence on the atmospheric boiling point, which is often either unknown or experimentally inaccessible for the high boiling compounds, the heat of sublimation of which is often of greatest interest. The entropy of sublimation at the melting point $\Delta H_s/T_m$, analogous to Trouton's constant, is not sufficiently constant to be of practical utility. Only Aihara (*1*) has presented a group increment system similar to the one proposed here. However, he restricted his scheme to a small group of compounds, and not all his increments agree with more extensive experimental data.

There are good reasons to suppose the energy of sublimation $\Delta E_s^1 = \Delta H_s^1 - RT_1$ to be a better datum for correlations than ΔH_s^1. In a trial run, the improvements of increment uniformity proved to be too small to warrant the additional complication. In the preparation of precision correlations, however, the use of ΔE_s^1 might well be considered.

Table XX. Standard Heat of Sublimation Increments for Hydrogen Bonding Groups Containing Nitrogen and Oxygen

Type	Fragment (X)	$H_s(X)$, Kcal./Mole
Aliphatic amides (N_c = even)	 $-\overset{O}{\overset{\|}{C}}-NH_2$	$12.4 + [3.7/(N_c\text{-}1)]$
Aliphatic amides (N_c = odd)	 $-\overset{O}{\overset{\|}{C}}-NH_2$	$10.2 + [8.3/(N_c\text{-}1)]$
Aryl amide	 $-\overset{O}{\overset{\|}{C}}-NH_2$	13.4
Aliphatic-*N*-methyl amides	 $-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-$	$7.6 - 0.35(N_c\text{-}1)$
Aryl-*N*-alkyl amides	 $-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-$	8.6
Benzanilide	 $-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-$	6.0
Heterocycloaliphatic amides (lactams)	 $-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-$	10.5
Aliphatic carbamates	 $-O-\overset{O}{\overset{\|}{C}}-NH_2$	~15

NOMENCLATURE

A_r = fraction of perhalide molecule surface not covered with halogen atom
= $N_x/4[1 - (m^2/r_2^2)]$ if $r_2 > l$
= $N_x/4[(r_1/r_2)^2$ if $l = r$
where N_x = number of halogen atoms per molecule; r_1, r_2 are van der Waals radii of halogen and central atoms, respectively; l = bond distance between halogen and central atom; and $m = (r_2^2 - r_1^2 + l^2)2l$
A, B = empirical constants
b = number of branches per molecule
C_p = heat capacity at constant pressure, cal./mole-° K.
ΔC_p^1 = C_p(liquid) – C_p(gas), cal./mole-° K.
ΔC_p^s = C_p(solid) – C_p(gas) cal./mole-° K.
$H_s^1(H_p)$ = standard heat of sublimation increment per primary hydrogen atom in molecule, kcal./mole
H_s^1(R) = standard heat of sublimation increment for hydrocarbon fragment ·R, kcal./mole
H_s^1(X) = standard heat of sublimation increment for fragment X, kcal./mole
ΔH_m = heat of melting, kcal./mole
ΔH_s = heat of sublimation, kcal./mole
ΔH_s^1 = standard heat of sublimation = ΔH_s at $T = T_1$, kcal./mole
ΔH_{tr} = heat of transition, kcal./mole
ΔH_v = heat of vaporization, kcal./mole
$\sum\Delta H_{m,tr}$ = sum of heats of fusion and all solid/solid transitions, kcal./mole
N = number of carbon atoms
N_B = number of carbon atoms in alkyl branch chain
N_c = number of carbon atoms per molecule
N_{CH} = number of carbon atoms in CH groups
N_{cm} = number of carbon atoms in *meta*-substitution
N_{Cl} = number of carbon atoms in group containing Cl
N_F = number of carbon atoms in group containing F
N_{ct} = number of tertiary carbon atoms in aromatic ring
N_p = number of carbon atoms in *peri*-condensed compounds
ΔS_m = entropy of fusion, e.u.
ΔS_{tr} = entropy change accompanying a solid/solid transition, e.u.
$\sum\Delta S_{m,tr}$ = sum of entropies of fusion and all solid/solid transitions, e.u.
T_a = temperature at which heat of vaporization has been determined, ° K.
T_b = normal atmospheric boiling point, ° K.
T_m = melting temperature, ° K.
T_1 = lowest temperature at which solid/solid transition occurs in a substance, ° K.
δ_s(X) = ΔH_s^1(RX) – ΔH_s^1 (homomorph), kcal./mole; e.g., the hydrocarbon homomorph of phenol is toluene (7)
Δ = ΔH_s^1 (*n*-paraffin) – ΔH_s^1 (isomer) at constant N_c, kcal./mole
ρ_s^* = packing density of solid at $T_1 = V_w/V_1$ where V_w = van der Waals volume of molecule (8) and V_1 = molal volume of solid at $T = T_1$, dimensionless

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Measurement of Total Pressures for Determining Liquid-Vapor Equilibrium Relations of the Binary System Isobutyraldehyde-*n*-Butyraldehyde

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THE HYDROFORMYLATION of propylene (oxo synthesis) leads to the simultaneous formation of the two C_4-aldehydes, *n*-butyraldehyde and isobutyraldehyde. If they are to be chemically converted into other products, these two aldehydes must be completely separated and, for this purpose their liquid-vapor equilibrium diagram is needed.

Bologna and Albonico (2) have published some data relating to this equilibrium, but the thermodynamic activity coefficients (γ_1 and γ_2) that can be calculated from these data are above unity in the case of one constituent and below unity for the other. This is incompatible with the Duhem-Margules slope law.

The determination of this equilibrium is very difficult, since the use of dynamic apparatus, such as that of Othmer, requires that the products under examination be maintained at boiling point for some considerable time. Aldehydes undergo rapid oxidation and polycondensation reactions under the conditions.

To avoid such reactions, we have resorted to a method based upon the measurement of total pressures. This permits numerous measurements when the required temper-

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