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1. Introduction

Evaporation enthalpies for both the solid and liquid phase, ΔH_g , ΔH_v , are important thermodynamic properties of the condensed phase. Most frequently, evaporation enthalpies are used to correct heats of formation data to a standard state,¹⁻³ but since these quantities are a measure of the magnitude of the interactions in the condensed phase, various other types of studies desire an evaluation or estimation of ΔH_g and ΔH_v .⁴⁻⁸ Some examples include the use of ΔH_g in a variety of studies of intermolecular interactions in the solid state such as for estimating lattice energies via atom-atom potentials,^{4,7} and studies of molecular motion in solids,^{7c} as a measure nature of the differences in interaction between chiral solids and their racemic modifications,⁵ and for estimating transport properties of various chemicals such as pesticides and other commercial preparations in the environment.^{6,8}

We became interested in measuring latent heats nearly a decade ago in order to correct heats of combustion data to the gas phase. Since most of our interests at that time centered around highly strained molecules, the general low long term stability of many of these molecules precluded the possibility of interesting other research groups in making these measurements for us. Furthermore, as we learned subsequently, very few groups in North America were active in this area at that time. We therefore decided to explore some potential methods of making these measurements ourselves.

Our initial attempts were focused on the construction of a mass effusion apparatus. After some preliminary effort, we realized the extent of commitment necessary in both resources

and time to make reliable measurements and abandoned this approach.

The sublimation apparatus described by Melia and Merrifield⁹ and used to measure vapor pressures and heat of sublimation of tris(acetylacetonato) complexes of Sc(III), V(III) and Cr(III) appeared to be, from our perspective, an attractive alternative. Our initial efforts in this area were focused on demonstrating the applicability and versatility of this technique and on defining this method's inherent limitations.¹⁰ As we have pursued our own interests and have responded to the requests of colleagues for specific measurements, it has been necessary to continually modify the apparatus. The modifications in general have been in response to the need to measure increasingly lower vapor pressures. We have been able to extend the range of this technique to measure vapor pressures over a range of pressures from 10⁵ to 10⁻³ Pa. The description which follows in the next section, briefly describes the basic principles of head space analysis (HSA) as we have applied it to measure vapor pressures and heats of sublimation, and reports on the results of our efforts to expand the dynamic range of this technique. A portion of this work has not yet been reported. A subsequent section deals with our application of this technique to study differences in solid state interactions which occur between chiral and racemic solid modifications. The final section contains a comprehensive summary of the heats of sublimation which have been reported for organic compounds in the time period 1910-1983.

2. The Measurement of Vapor Pressure By Head Space Analysis

A. Basic Principles

Head space analysis has been used by a number of research groups in recent years to measure equilibrium vapor pressures.⁹⁻¹³ A typical apparatus is shown in Fig. 2-1. The experiment in general can be performed either isothermally or under steady state conditions. By keeping the ballast and sample compartment at the same temperature, equilibrium will be achieved when

$$P(\text{condensed phase}, T_1) = P(\text{vapor}, T_1)$$

sample compartment ballast chamber 2-1

where P represents the vapor pressure of the sample at temperature T_1 . This is basically the experimental procedure described by Melia and Merrifield.⁹ An analysis of the contents in the ballast tank of known volume followed by treatment of this quantity by the ideal gas law yields the experimental vapor pressure of the compound in question. Although satisfactory results can be obtained by performing these experiments isothermally, we have found that small temperature fluctuations in the constant temperature bath can often be sufficient to cause condensation of the vapor in the ballast tank. This a potential source of error can be introduced at this point if the experiments are performed in this manner. Additional limitations will be described below. In our experience, the probability of condensation increased when the volatility of the sample decreased and the working temperature increased.

An alternative procedure to the one described above is to maintain the ballast chamber at a higher temperature than the sample compartment. A steady state will be achieved when the pressures in the two compartments are equal.

$$P(\text{condensed phase}, T_1) = P(\text{vapor}, T_2) \text{ where } T_2 > T_1$$

sample compartment ballast chamber

By an appropriate design of the apparatus, Fig. 2-2, heat flow between the two compartments can be restricted and thermal equilibrium maintained in each respectively. In this mode, condensation of the vapor in the ballast tank is inappreciable and as will be described below, adsorption of sample on the surface of the vessel can be minimized and/or corrected.

Analysis of the vapor density in the ballast compartment can be achieved either by direct or indirect methods. In cases where the vapor pressure is high, or the analytical technique sufficiently sensitive, direct measurement as a function of temperature is possible. Two examples whose heat of sublimation have been determined in this manner include anthracene (by fluorescence^{14,15}) and urea (by infrared¹⁶); for a more detailed listing the reader is referred to Section 4. The major advantages of direct head space analysis in the case in which these experiments can be performed. Disadvantages often include the limited temperature range in which the detector response remains linear with concentration, the fact that vapor pressures cannot be obtained directly from these results and perhaps most significantly, the propensity

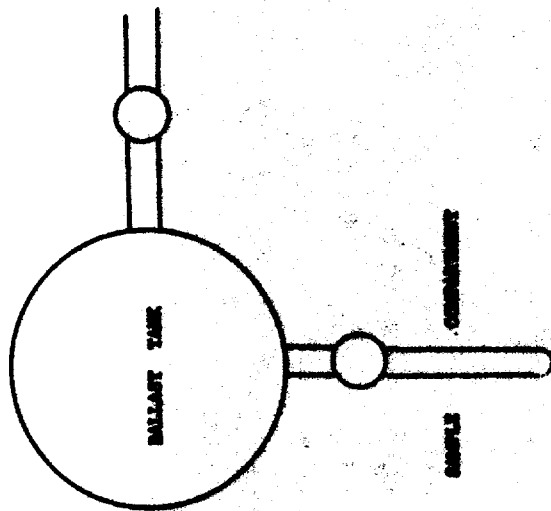


Figure 2-1. Apparatus for isothermal indirect head space analysis.

to employ excessively high temperatures in order to obtain a suitable vapor density to detect spectroscopically.

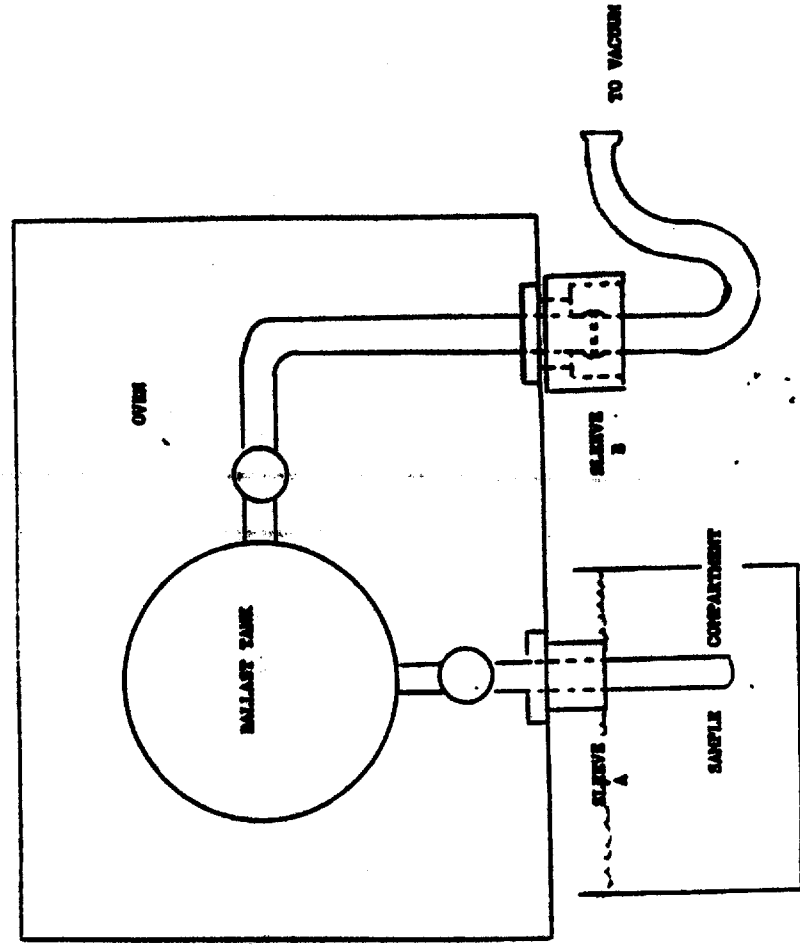
Vapor in the ballast tank can be analyzed indirectly either by transfer of the contents of ballast compartment and/or condensation of the vapor followed by quantitative analysis of the contents by a variety of spectroscopic techniques. Advantages of indirect analysis include a wider flexibility in the choice of analytical tools, increased sensitivity and sample size arising from analysis of the entire contents of the ballast tank rather than from a small cross section, the ability to use a lower temperature as a result of the increase in effective sample size, access to a broader temperature range for measurement and the capability of correcting for adsorbed substrate (*vide infra*). The major disadvantage to the indirect method is the increase in time and effort that needs to be expended as a consequence of the additional steps required.

Use of the gas laws under ideal conditions (low pressure, high temperature) affords a relationship for converting directly to vapor pressure. When the experiment is performed in the isothermal mode the contents and volume of the ballast tank, the temperature of the ballast tank and molecular weight all serve to define the sample's vapor pressure. In the steady state mode these quantities serve to define the vapor pressure in the ballast tank. The condition of steady state requires this pressure to equal the vapor pressure of the sample at the lower sample temperature. 10

B. A Description of the Apparatus

Our apparatus at its current stage of development is shown in Fig. 2-2. It can be built with only a modest investment in time

Figure 2-2. Apparatus for indirect steady state head space analysis (not drawn to scale).



C. The Measurement of Vapor Pressures

A. Description of the Procedure

The measurement of vapor pressures by the method of head space analysis requires a period of time to establish equilibrium (isothermal experiment) or a steady state. Although a period of hours has been allowed to achieve this result⁹, it is remarkable how quickly it is achieved. Figure 2-3 describes the results of allowing an evacuated sample of diphenylacetylene (approximately 500 mg) to reach steady state with its vapor in a 12 liter ballast tank at a background pressure of approximately .2 Pa. Two sets of experiments are reported which correspond to sample temperatures of 287 and 317.5 K reaching steady state vapor pressures with a ballast tank maintained at 383 K. These results indicate that a steady state is reached after only a few hundred seconds. Similar results have been obtained with a variety of other substances. In general we have used 600s as a standard time interval to establish the steady state.

A similar type of experiment can be performed to evaluate the time necessary for complete transfer of the contents from the ballast tank to the collection tube. In this instance however, the time necessary for transfer depends on a variety of factors including the geometry of the vacuum system, the diameter of the vacuum line and the pumping speed of the forepump and diffusion pumps used. When measuring vapor pressures above 0.1 Pa at a ballast temperature of 350 K, (1 Pa at a ballast temperature of 300 K) comparison of the total amount of sample collected

and equipment. The ballast tank consists of a 12 L flask which is connected to the sample compartment and vacuum system by means of 10 mm teflon stopcocks. The apparatus is housed in a plywood oven lined with aluminum foil and is heated by four 250 watt infrared lamps. These heaters are sufficient to maintain oven temperatures up to 300 K and provide uniform heating of the ballast tank. The lamps are controlled by a variable transformer. A fan further insures temperature uniformity within ± 2 K.

The interfaces between the oven and sample compartment and oven and collection tube are fitted with aluminum sleeves and heated with 100 watt cartridge heaters. Their temperatures are controlled electronically at a temperature intermediate between the temperatures of the oven and sample compartments. Sleeve A prevents the condensation of vapor at the interface between the constant temperature bath and oven while sleeve B assures that condensation of vapor occurs only after entering the collection tube. An O ring seal connects the collection tube to the ballast tank and can be partially heated by sleeve B if necessary. The collection U tube which is easily removed by means of the O ring seals is generally cooled in a liquid nitrogen trap to ensure complete condensation.

The vacuum system employed depends in part on the vapor pressure range to be measured. For pressures above 10^{-1} Pa, only an efficient forepump is necessary. For measurements below 10^{-1} Pa, pumping speed becomes increasingly important as will be discussed below.

as a function of time also becomes invariant with time. In our system this has generally occurred after 500 s of collection. However if this experiment is performed differently or if the sample size is small, corresponding to a vapor pressure below the limiting pressures indicated above, sample size does continue to vary with time. By monitoring the amount of sample collected over designated time intervals, results such as those shown in Fig. 2-4 for diphenylacetylene are obtained. The ordinate represents the fraction of the total amount of diphenylacetylene collected as a function of time for a single "steady state equilibration" between a ballast tank at 385 K and a sample at 317.5 K.

The amount of recovered diphenylacetylene was monitored sequentially at various times over a period of 2×10^4 s. These results can be interpreted as two competing first order processes characterized by rate constants which differ roughly by an order of magnitude. The rapid process can be described as the transfer of vapor from the ballast compartment and is characterized by a rate constant which is a measure of the pumping speed of the vacuum system. The slower process is best described as the desorption of diphenylacetylene off the surface of the ballast tank and subsequent transfer to the collection tube. Both processes obey first order kinetics. When this experiment was repeated using the same sample temperature but at a higher a ballast tank temperature, the amount of material collected in the first 600s remained essentially constant but the amount of material collected in subsequent time intervals decreased. At a constant ballast temperature but higher sample temperature (higher steady state pressure) the quantity of sample collected during the first 600s

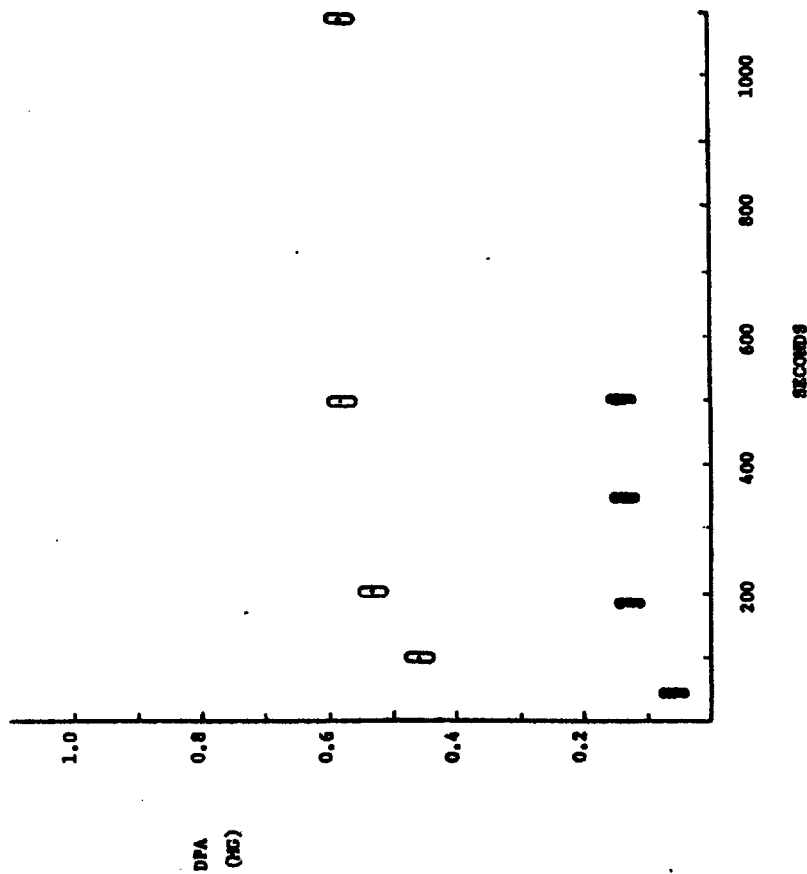


Figure 2-3. Rate of equilibration of diphenylacetylene (DPA, 500 mg) with a 12 L ballast tank. Sample temperature a) 317 K, b) 287 K.

and that collected subsequently both increased but with the former contributing more significantly to the increase.

These results are consistent with the interpretation cited above and offer an explanation of the curvature observed in log P vs $1/T$ plots when measuring vapor pressures around 0.1 Pa^{10} . Even in cases where curvature is not observed, the proportional increase in contribution of adsorbed sample to the total as the vapor pressure decreases explains why the heats of sublimation measured by this technique tend to be a few % lower than those measured by other methods. In addition some simple modifications to the experimental procedure for improving accuracy and for possible expansion of the range of this method into the sub-Pascal region become apparent from these results.

The results in Figure 2-4 indicate that quantitative transfer (99%) of the vapor can be achieved after 600s. Since this period of time is reflective of the pumping speed of vacuum system and not of the sample, it should remain invariant to the nature of the sample being measured and need be determined only once for each system. By limiting the period of collection to 600s, the contribution of adsorbed substrate to the total collected can be minimized. This is demonstrated for diphenylacetylene whose vapor pressure as a function of temperature is reported in Fig. 2-5. The data collected in the 10^1 to 10^{-1} Pa range serves to establish the slope of the line in the Clapeyron relationship of log vapor pressure vs $1/T$ (K^{-1}). As can be seen in the diagram, the apparent vapor pressure levels off below 10^{-1} Pa at approximately 4×10^{-2} Pa if the time for collection of the sample is in excess of 1200 s (circles). By restricting the collection period to 600 s in the

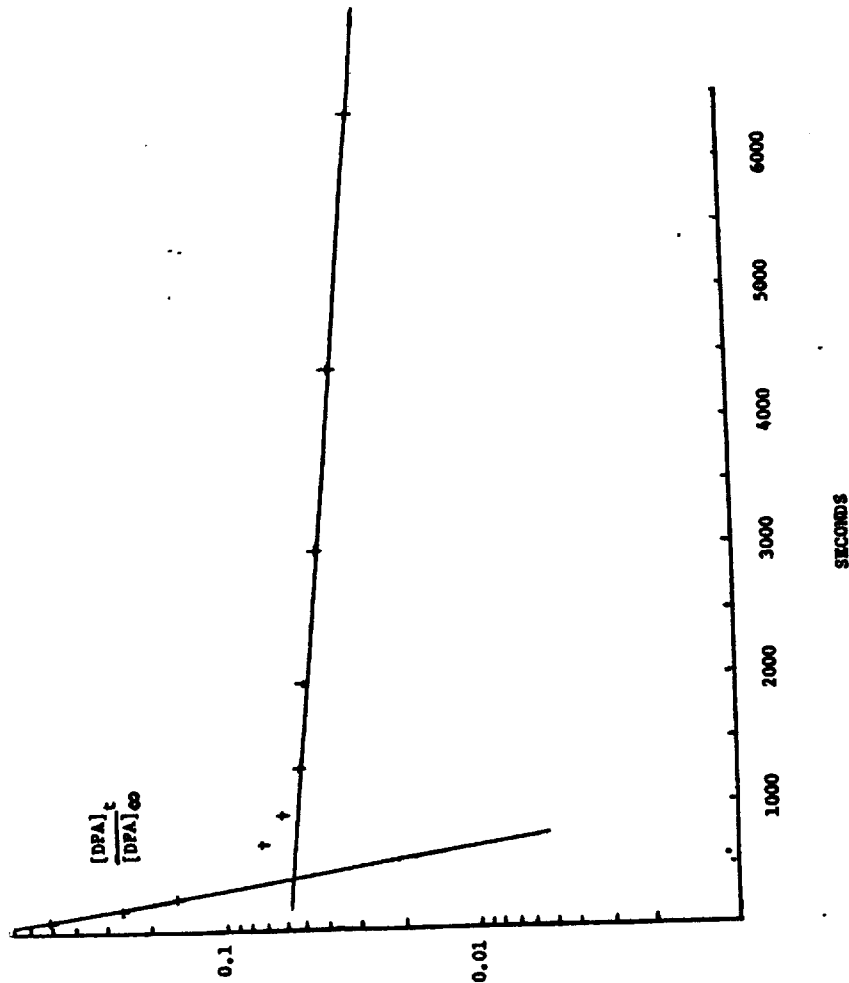


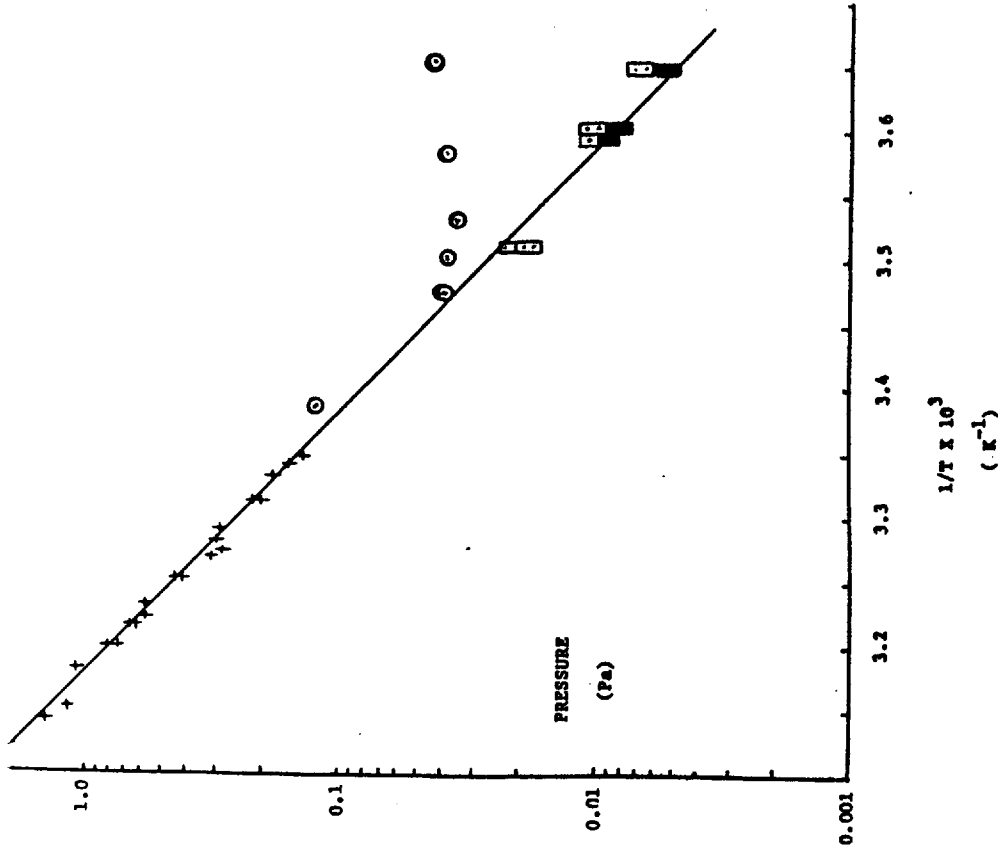
Figure 2-4. The fraction of diphenylacetylene collected from a 12 L ballast tank as a function of time.

10^{-2} Pa region and correcting the data for the contribution of adsorbed substrate in the 10^{-3} Pa region, linearity can be observed from 1 to 10^{-3} Pa. Estimation of the amount of adsorbed substrate contributing to the first 600s was achieved in this instance by two consecutive 600 s collections. The difference between the quantities obtained in these two collections then serves as a more accurate estimate of diphenylacetylene's true vapor pressure at the corresponding sample temperature. Such a correction appears reasonable as long as the contribution of adsorbed material is small.

Extension of the range of this technique much below 10^{-3} Pa would require extensive modification of the vacuum system. An increase in pumping speed by at least an order of magnitude is technologically possible and would be an additional technical improvement necessary to extend the range any further. However, as currently set up this technique is capable of measuring vapor pressures from 10^5 to 10^{-3} Pa, and covers a sufficiently broad range of vapor pressures to measure the vapor pressures and heats of sublimation of most typical organic molecules.

D. Reliability of the Method

The usefulness of any technique used to measure vapor pressures and heats of sublimation depends ultimately on the reliability of the measurements obtained. Comparisons of previous heat of sublimations obtained by indirect head space analysis, as described above, are provided Table 1. Agreement obtained by this method is generally within 5% of the literature values. As noted above, these results are usually a few percent lower than accepted values. A reasonable explanation of the origin of this error is based on



the contributions that adsorbed substrate makes to the total sample collected. Previous measurements did not correct for these contributions and since these contributions are proportionately higher at the lower vapor pressures, slightly lower heats of sublimation resulted. By a more careful timing of the collection period, it is likely that improvement in the accuracy of this method can be realized.

Table 1: A Comparison of Heats of Sublimation Determined By Indirect Head Space Analysis with Literature values

Compound	Head Space Analysis ΔH_s (kJ/mol) (Ref)	Literature ^a ΔH_s (kJ/mol) (Ref)
dl-camphor	51.5±2.6 (10)	51.8±8 (84) 53.6 (85)
biphenyl	76.±4 (10)	50.7 (86) 77.9±.3 (87) 80.4±1.6 (88) 83.6±2.5 (89)
phenol	65.3±3.3 (10)	69.7±.9 (90) 68.7±.5 (91)
naphthalene	67.8±3.5 (10)	67.8 (92) 72.6±.1 (35) 72.8±.3 (37)
2,2,4,4-tetramethyl- 1,3-cyclobutanedione	70.3±3.5 (10)	72.5±.1 (36) 72.2±.6 (93)
thymol	89.1±4.5 (10)	91.2±4.1 (92)
tetrahydrofulvalene	92±6.3 (4)	95.3±1 (94)
dl-dimethyl tartrate	112.±5.6 (5)	113.8 (33)

a. Typical values are included for comparisons; for a complete list see table 5

3. Heat of Sublimation of Chiral Systems

A. Introduction

Some years ago we became aware of a report in which fractional sublimation of a partially resolved optically active material led to optical fractionation of the mixture.¹⁷ A search revealed a few other similar reports scattered in the literature.¹⁸⁻²⁰ Since fractional sublimation can be a potentially useful technique for enhancing "optical purity", we decided to employ the vapor pressure apparatus we developed in an effort to gain a better understanding of the effect which was being observed. We embarked on a program of systematically investigating the vapor pressure and heats of sublimation of a variety of chiral solids. A parallel course of study was initiated by a colleague who examined the composition of the sublimate as a function of the optical purity of the initial mixture for d-l mixtures whose phase diagram was known.²¹

B. Origin of the Effect - Heats of Vaporization and Fusion

Enthalpies of sublimation can be directly related to the corresponding enthalpies of fusion, ΔH_{fus} , and vaporization, ΔH_v , by equation 3-1. This relationship is exact for enthalpies obtained at the same temperature, *eq.* the fusion temperature, or when corrected for heat capacity differences between the condensed and gas phases. The enthalpy of sublimation of a solid at temperature T is given by:²²

$$\Delta H_s(T) = \Delta H_{fus}(T_M) + \Delta H_v(T_V) + \int_T^{T_M} Cp(c)dT + \int_T^{T_V} Cp(l)dT + \int_{T_V}^{T_Y} Cp(g)dT, \quad 3-1$$

where Cp represents the heat capacity of the solid (c), the liquid (l), and the vapor (g), and T_M and T_Y represents the normal melting and boiling points respectively. Neglecting for the moment the heat capacity contributions which are small (see Section 4B), the major contributors to $\Delta H_s(T)$ are $\Delta H_{fus}(T_M)$ and $\Delta H_v(T_V)$. Comparison of the heats of sublimation of the racemic pair, $\Delta H_s^R(T)$, to one of the enantiomers, $\Delta H_s^E(T)$, leads to the conclusion that any differences between $\Delta H_s^R(T)$ and $\Delta H_s^E(T)$ are likely to be the result of differences in the corresponding heats of evaporation and/or fusion, equation 3-2.

$$\Delta H_s^R(T) - \Delta H_s^E(T) = (\Delta H_v^R(T_V) - \Delta H_v^E(T_V)) + (\Delta H_{fus}^R(T_M) - \Delta H_{fus}^E(T_M)). \quad 3-2$$

Heats of vaporization usually make up the largest contribution to $\Delta H_s(T)$ and differences between enantiomer and racemic mixture in the liquid state might be expected. However most available evidence suggests that this term contributes only minor differences to $\Delta H_s^R(T) - \Delta H_s^E(T)$. Examples of studies which have tried to identify the nature and magnitude of the differences in interactions between liquid enantiomers and their racemic counterparts include: identical densities and dielectric constants for 2-octanol,²³ and a heat of mixing (d + l \rightarrow dl) of only 13 J/mol,^{24,25} identical vapor pressures and boiling points of (d) and (dl)-2-butanol,²⁴⁻²⁶ heats of mixing for 2-(p-nitrophenyl)butane and α -methylbenzylamine of 1.88 J/mol²⁴ and 9.6 J/mol²⁴ respectively; excess molar volumes for limonene, fenchone and α -methylbenzylamine which are small,²⁷ heats of mixing of solutions of enantiomers of α -methyl- γ -ethylsuccinic acid (CHCl₃, 298 K),²⁵

α -methyl- α -isopropylsuccinic acid (CHCl_3 , 298 K),²⁵ tartaric acid²⁸ (H_2O , 298 K) and threonine²⁸ (H_2O , 298 K) of 140, 209, 2.0 and 5.5 J/mol, respectively. In contrast a standard free energy difference of 2.76 kJ/mole at 296 K has been recently reported for hydrogen bonding between homodimers (R \rightarrow R; S \rightarrow S) and heterodimers (R \rightarrow S; S \rightarrow R) in 2-butanol.²⁹ Studies of hydrogen bonding in racemic and (R)-2,2,4-trimethylpentane-3-ol however show differences of only 200 J/mol.³⁰

Although some of these results do not necessarily preclude differences in $\Delta H_v(T)$ and in vapor pressure, they are indicative of similarities in $\Delta H_v(T_v)$ for both the d and dl, particularly in cases where strong intermolecular forces are not involved. Experimental results obtained in our laboratory support this contention. The vapor pressure of d and dl ephedrine (mp 312, 352 K) measured at 354.4 K gave results of 71.9 \pm 1 and 69.1 \pm 2.5 Pa respectively.³¹ The vapor pressures of liquid l and dl-menthol (mp 316, 301 K, respectively) have been measured from 324-343 K. The results which are shown in Fig. 3-1 do not suggest any substantial difference in either vapor pressure or enthalpy of vaporization, $\Delta H_v^R(T_v) - \Delta H_v^S(T_v)$.³¹

Heats of fusion of enantiomers and their racemates generally make up only about 25% of the total contribution to $\Delta H_f(T)$ for typical organic solids. Here however differences are observed between the two forms as demonstrated in Tables 2A and B except in certain circumstances. Chiral molecules crystallize in one of three general categories. Molecules of a given chirality either prefer to cohabit the crystal with other molecules of the same chirality (Case A, conglomerate), of opposite chirality (Case B,

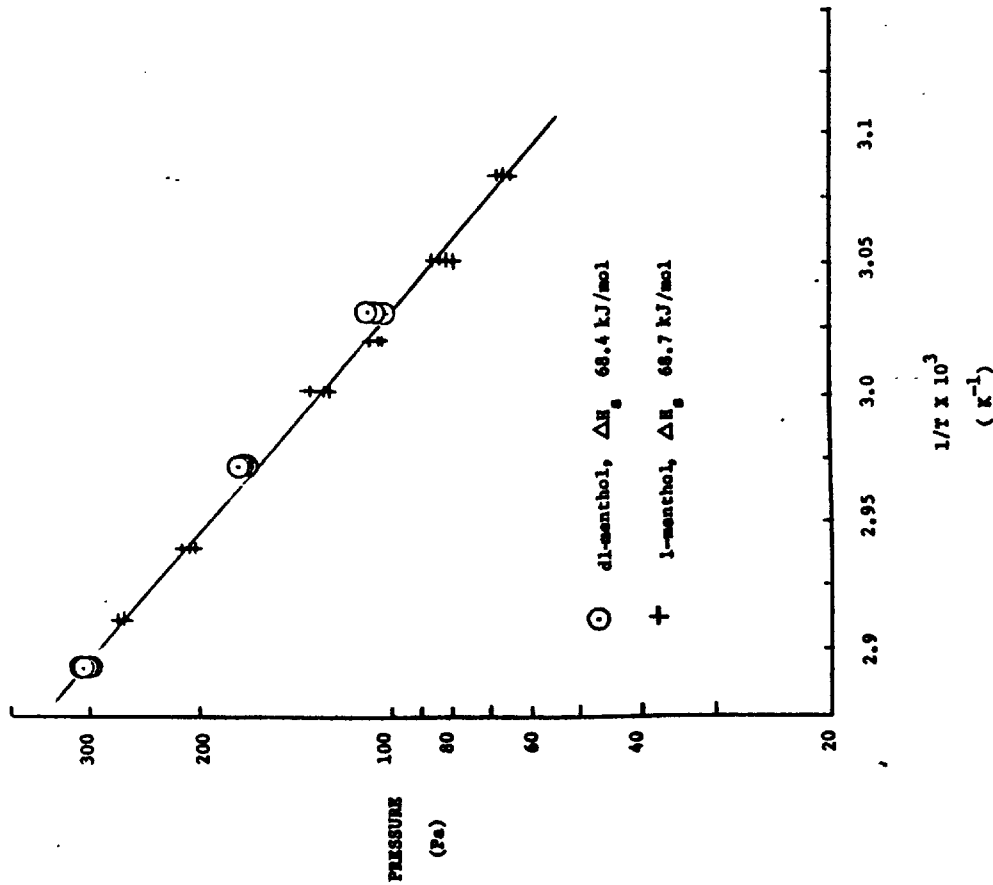


Figure 3-1. Log P vs 1/T for (dl), (l)-menthol in the liquid state.

racemic compound formation) or the crystal lattice does not differentiate chirality (Case C, solid solution). Approximately 5-10% of all organic substances crystallize in the form of conglomerates. Formation of solid solutions also appears to be rare. The bulk of organic molecules prefer to form racemic compounds in which the d and l are present in a 1:1 ratio although a few cases are known with different stoichiometry.²² Examples exist in each category, as demonstrated in Tables 2 and 3 which clearly document the dependence of a variety of physical properties such as melting point, density and heat of fusion on the d-l composition of the solid, even in solid solutions (*vide infra*). Consequently, referring back to equation 3-2, if differences in ΔH_f and vapor pressure are to be expected, these differences for the most part should be reflective of any differences observed between heats of fusion for enantiomer and racemate. Of significance to this discussion is whether these differences can be correlated with other physical properties and whether they can be of use in resolution studies.

C. Heats of Sublimation

Until our own work, we are aware of only two previous studies of the heat of sublimation on both enantiomer and racemate. Both studies measured the heat of sublimation of d and dl-dimethyl tartrate. The conclusions reached by examination of these results were inconclusive. One study found a difference of 6.74.6 kJ/mol between (d) and (dl)-dimethyl tartrate³² while the other found a difference of only 0.75kJ.³³ Substantial differences in the vapor pressures between the two compounds were observed in the latter case.

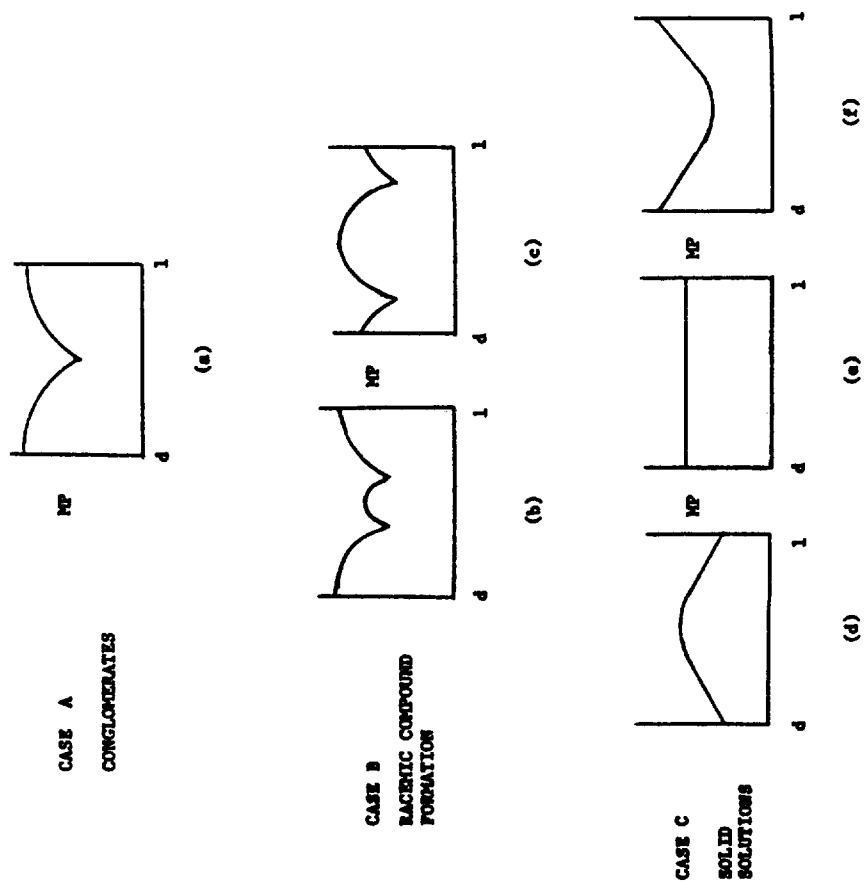


Figure 3-2. Typical phase diagrams for enantiomers and their racemates.

Table 2A: Heats of Fusion of Some Representative Chiral Solids

Compound	MP (K)	ΔH_f (kJ/mol)	Phase Diagram Case
mandelic acid ^{22,79}			
racemic	392	25.5	B
active	406	26.4	
menthyl 3,5-dinitrobenzoate ⁵			
racemic	427	30.6	A
active	401	34.5	
carvone oxime ⁵			
racemic	364	16.8	C
active	344	15.0	
3-(<i>m</i> -chlorophenyl)- hydracrylic acid ^{22,79}			
racemic	340	23.8	A
active	368	28.0	
2-(<i>o</i> -chlorophenoxy)- propionic acid ^{22,79}			
racemic	388	32.1	B
active	369	26.8	

Table 2B: Differences in the Heats of Solution of Racemic and Optically Active Solids⁹⁵

Compound	$\Delta H_{sol}(\text{DL}) - \Delta H_{sol}(\text{ACTIVE})$ 298 K (kJ/mol solute)	Phase Diagram
alanine	+2.0±.2	
glutamic acid ^a	+4.1±.2	A
histidine	+1.5±0.2	
threonine ^a	-0.17±.13	A
tartaric Acid	+9.4±.3	B
valine	+2.3±.01	

a. It is interesting and perhaps surprising that although glutamic acid and threonine both form conglomerates,^{22 a} reversal in sign is observed between the two.

The crystalline systems which we chose to investigate are representative of the most common phase diagrams observed in chiral organic solids. (d), (dl)-Dimethyl tartrate was chosen for reasons mentioned above as an example of a system whose phase diagram exhibits compound formation (Case B). The melting point at the dl composition is greater than for pure enantiomer, Fig. 3-2c. (dl), (l)-Menthhol is an example of a similar case in which the melting of pure enantiomer is greater than for the (dl)-compound, Fig. 3-2b. (d), (dl)-Carvone oxime was chosen as an example of a system which forms a solid solution, Case C, Fig. 3-2d. This system is unusual however. Although the crystal lattice does not differentiate chirality, the physical properties are reflective of the (d)-(l) composition of the solid with the racemic composition exhibiting a maximum in the melting point. Other important crystalline systems which have not yet been examined include conglomerates, Case A, Fig. 3-2a, ideal solid solutions and solid solutions exhibiting a minimum in the melting point, Case C, Fig. 3-2e,f.

Table 3 summarizes a variety of physical constants measured for the materials mentioned above. First it should be noted that the differences in ΔH_g and vapor pressure observed between enantiomer and racemate, are nearly the same magnitude as the experimental uncertainties associated with these numbers. This is particularly true of the results of d-dimethyl tartrate for which data was collected over a temperature span of only 10 K. However since comparisons between enantiomer and racemate are relative numbers, comparison of ΔH_g and vapor pressures are believed to be qualitatively significant. This conclusion is further reinforced by the agreement obtained from heats of

Table 3. Some Physical Constants of Enantiomers and Their Racemates^a

Compounds	MP	ΔH_g	ΔH_{fus}	ΔH_v	ΔH_g (calc)	V.P. ^d	Case
	K	kJ/mol	kJ/mol	kJ/mol	kJ/mol	Pa	(T) (R)
l-menthol	316	95.8±5	11.9	68.7 ^c	80.6	6.5	(298)
dl-menthol	301	78.7±4	10.3	68.4 ^c	78.7	6.4	(298) B
d-dimethyl tartrate	322	77.4±8	17.4	64.3 ^b	81.7	1.4	(320)
dl-dimethyl tartrate	360	112.4±6	27.0	62.8 ^b	89.8	0.4	(320) B
d-carvone oxime	344	90.8±5	15.0			12.9	(345)
dl-carvone oxime	364	101.7±5	16.8			1.8	(325)
						8.6	(345) C
						1.0	(325)

- a. data from reference 5 unless otherwise noted
 b. from reference 96
 c. see Fig. 3-1
 d. vapor pressure at the corresponding temperature, column 8.

sublimation calculated from the heats of fusion and vaporization, column 6, according to the first two terms of equation 3-1. Heats of sublimation estimated in this manner by ignoring heat capacity corrections for enthalpies obtained at higher temperatures, can generally be considered as a lower limit for ΔH_g (vide infra).

Several trends become evident upon examination of the data in Table 3. Heats of sublimations differences between enantiomer and racemate are paralleled by similar differences in the heats of fusion. The crystalline form with the highest melting point exhibits the greatest ΔH_g , ΔH_{fus} and generally the lowest vapor pressure.

Thus although there is not enough data to clearly establish this trend, it does suggest that fractionation of optically pure materials can occur and predictions about the composition of the vapor are possible from examination of the appropriate phase diagram. Eutectic compositions generally exhibit the lowest heats of fusion (see results for menthyl 3,5-dinitrobenzoate, Table 2A) and therefore should be the most volatile. Depending on the initial optical purity relative to the composition of the closest eutectic, fractional sublimation can lead to optical enrichment of either the sublimate or the residual sample. This has been demonstrated for *d*, *dl*-mandelic acid (phase diagram, Fig. 3-1b) by starting at optical purities on each side of the eutectic composition.²¹ In both cases the eutectic composition sublimed preferentially.

In summary, heats of sublimation and heats of fusion are expected to vary depending on the phase diagram. Fractional sublimation is not expected in general to lead to optically pure material except perhaps in cases where conglomerates and certain

types of solid solutions are involved. However if the eutectic composition lies close to either the pure enantiomer or the *dl* pair, substantial optical enrichment of the sublimate or residual substrate is possible as has been reported.¹⁷⁻²¹ Additional experimentation is necessary to confirm the trends noted in this work. Demonstration of the feasibility of optical purification or enrichment of racemates by fractional sublimation relative to more conventional techniques such as recrystallization would also be worthwhile and could prove to be of considerable practical utility in many studies involving resolutions.

D. Vapor Pressures of Conglomerates

As noted previously, differences in vapor pressures have been observed between enantiomer and racemic compound. In the case of conglomerates in which the eutectic composition corresponds to a 1:1 ratio of *d* to *l*, the vapor pressure of the eutectic should correspond to twice the vapor pressure of a single enantiomer ($v_d + v_l = 2v_{dl}$) since a conglomerate is a physical mixture of *dd* and *ll*. The inverse of this statement suggest that if at a particular temperature the vapor pressure of a racemic compound equals twice the vapor pressure of pure enantiomer, this should correspond to the transition temperature for the racemic compound to conglomerate transformation. Whether this is a necessary and sufficient condition for the existence of polymorphism of the type just described has not yet been experimentally demonstrated. Implied by the above is that a chamber consisting of physically distinct crystals of *d* and *l* should grow at the expense of racemic compound (*dl*) at a temperature in which the vapor pressure of the

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dl just exceeds the sum of the vapor pressures of each respective enantiomer.

The relatively rare occurrence of conglomerates coupled with their potential usefulness in resolutions-conglomerates can often be resolved by physical methods²² - has prompted the development of methods to aid in their detection. Ironically it was just such considerations of vapor pressure that led Meyerhoff in 1904 to propose the so-called "double solubility" rule which is of considerable value in detecting conglomerates.³⁴ The rule predicts that the solubility of conglomerates will be greater or equal to the sum of the solubilities of each enantiomer. The success of the rule is based on the similarities between vapor pressure and solubility and on the mathematic relationships which describe their temperature behavior under ideal conditions, the Clapeyron and Schroder-Van Larr equations. This topic has recently been reviewed.^{5,22}

of the literature (Table 5) reveals that a number of substances have been used as standards for heat of vapor pressure measurements. The most frequently used materials such as benzoic acid, naphthalene, benzophenone, xerrocene, and anthracene. A more detailed listing can be found in Table 5. These compounds have been chosen as standards for a variety of reasons, including availability in pure form, long term thermal stability and ease of measurement. Recent work has afforded very accurate measurements for naphthalene³⁵⁻³⁷ and benzoic acid.³⁶⁻³⁸ Both have been recommended as standards for both vapor pressure and ΔH_v measurements.³⁹ Some objections to the use of benzoic acid however, have recently been raised.³⁶

From our perspective, selection of standards is long overdue and more standards are needed. The measurement of vapor pressures or heats of sublimation of substances with vapor pressures in the 1 Pa range is relatively straightforward. The experiment becomes progressively more difficult as the vapor pressure decreases. The ability of a technique to accurately measure vapor pressures or ΔH_v in one pressure region does not in itself guarantee the same degree of accuracy in a different pressure region.⁸¹ An examination of the data in Table 5 supports such a conclusion. The precision in heats of sublimation reported for many compounds often exceeds their accuracy. This suggests that the systematic errors revealed by comparison of the results obtained by different methods are a function of pressure and/or temperature. Only by establishing a series of standards whose vapor pressures cover the entire vapor

Pressure region experimentally accessible and temperature range commonly employed, can the accuracy of a technique within a given pressure and temperature range be assessed. This series of standards would serve the same general purpose as the series of melting point standards that are used to standardize thermometers.

B. Heats of Sublimation Corrections to A Standard State

Enthalpies of sublimation at 298 K or 0 K are often required for a variety of studies, including correcting heats of formation to a standard state and for standardizing atom-atom potentials used in the calculations of lattice energies. Enthalpies measured at other temperatures can be corrected to the reference temperature, T_R , by correcting for the differences in heat capacities at constant pressure, ΔC_p , between the gas and condensed phase, $C_p(g)$ and $C_p(c)$, respectively. Since many enthalpies are measured over a range of

$$\Delta H(298, 0 \text{ K}) = \Delta H_g(\bar{T}_M) + \Delta H(T_R) - \int_{298, 0}^{\bar{T}_M} C_p dT \quad 4-1$$

temperatures, corrections are customarily from the mean temperature of this range, \bar{T}_M . If a phase transition occurs between \bar{T}_M and the reference temperature, the enthalpy change of this transition, $\Delta H(T_R)$ must also be included.

Since heat capacity corrections are generally small and often comparable in magnitude with the uncertainty associated with the heat of sublimation measured varying degrees of approximation have been used to correct to 298 or 0 K. Recent technological advancements in the measurement of heats of sublimation, has afforded data for which these corrections are more significant.

If the heat of sublimation is accurately known and the heat capacity data is available, corrections to a standard state, T_R , simply involves integrating the $\Delta C_p dT$ term.

Assuming ΔC_p to be independent of temperature, yields

$$\Delta H(T_R) = \Delta H(\bar{T}_M) + \Delta H(T_R) + \Delta C_p (\bar{T}_M - T_R) \quad 4-2$$

Since C_p does vary with temperature, mean values can be used for $C_p(g)$ and $C_p(c)$ in evaluating ΔC_p in equation 4-2 for the temperature range $\bar{T}_M - T_R$.

Often heat capacities for both the gas and condensed phase are not known. The heat capacity of the condensed phase can be measured directly, for example by Differential Scanning Calorimetry. Reasonable estimates of $C_p(g)$ can be obtained by bond additivity or group additivity methods and by structural methods employing statistical mechanics. Specific details on these estimation techniques for $C_p(g)$ have been described in detail by Benson.⁴⁰

Vapor pressures which have been measured over a significantly large temperature range, show some curvature in $\ln P$ vs $1/T$ plots. In this instance ΔC_p can be extracted by fitting the results to the equation:^{41,42}

$$R \ln P_2/P_1 = - \frac{\Delta G^0(T_R)}{T_R} + \frac{\Delta H^0(T_R)}{T_R} + \Delta C_p(T_R) \left[\frac{T_R}{T} - 1 + \ln \frac{T}{T_R} \right] \quad 4-3$$

where T_R refers to a reference temperature, P_0 is a standard pressure (1 Pa), $\Delta C_p(T_R)$ is the value of $C_p(g) - C_p(c)$ at T_R and $\Delta G^0(T_R)$ and $\Delta H^0(T_R)$ are the standard thermodynamic functions

evaluated at the reference temperature. Generally the usual temperature range studied is not sufficiently large enough to observe curvature; the only parameters which can be evaluated from equation 4-3 in such circumstances are $\Delta G^0(T_R)$ and $\Delta H^0(T_R)$.

An alternative and more approximate method that has been used to correct heats of sublimation is to treat the gas as ideal and to assume that the Dulong-Petit value holds for the solid. 4,43,44

The molar heat capacity of the gas at constant volume, $C_v(g)$, can be partitioned into translational, rotational, vibrational and electronic components:

$$C_v(g) = C_v(\text{trans}) + C_v(\text{rot}) + C_v(\text{vib}) + C_v(\text{elec})$$

where $C_v(\text{trans}) = 3/2 R$, $C_v(\text{rot}) = 3/2 R$ (R for linear molecules), $C_v(\text{vib}) = (3N-6)R$ ((3N-5) R for linear molecules), where N is the number of atoms in the molecule and $C_v(\text{elec}) \approx 0$.

Treating a mole of gas containing N atoms/molecule, as a solid of N vibrating atoms, where $M = N \times A$ (A = Avogadro's number), the total vibrational degree of freedom for the solid is 3M. The molar heat capacity according to the Dulong-Petit treatment is 3R, which for N atoms gives a total heat capacity of $3RM/A = 3RN$. Substituting into equation 4-1 for the heat capacities of solid and gas and noting that:

$$C_p(g) = C_v(g) + R,$$

$$C_v(s) \approx C_p(s)$$

yields:

$$\Delta H_g(T_R) = \Delta H_g(\bar{T}_M) + \Delta H(T_M) - \int_{T_R}^{\bar{T}_M} [R+3R + (3N-6)R-3RN]dT, \quad 4-4$$

which upon simplification:

$$\Delta H_g(T_R) = \Delta H_g(\bar{T}_M) + \Delta H(T_M) + \int_{T_R}^{\bar{T}_M} 2R dT, \quad 4-5$$

and integration results in

$$\Delta H_g(T_R) = \Delta H_g(\bar{T}_M) + 2R(\bar{T}_M - T_R) + \Delta H(T_M). \quad 4-6$$

Equation 4-6 states that heats of sublimation will always increase with decreasing temperature. In order for this condition to hold, according to equation 4-1 the heat capacity of the solid must be greater than for the corresponding gas. Examination of Table 5, shows in cases where ΔH_g is reported at two temperatures, an increase is observed with decreasing temperature. Other methods of estimating heat capacities are described in Section C.

C. Estimation of Heats of Sublimation

The difficulty in obtaining reliable heats of sublimation data has prompted the development of techniques that can be used to estimate ΔH_g in cases where such data is not readily available. One of the earliest methods was application of Walden's Rule⁴⁵, equation 4-8, and Trouton's Constant⁴⁶, equation 4-9, to evaluate the heats of fusion and

4-7

$$\Delta H_B(298) \approx \Delta H_{fus}(T_M) + \Delta H_V(T)$$

A similar method has been used to determine ΔH_B for diphenyl disulfide and dibenzyl disulfide.⁵¹ $\Delta H_V(298)$ in this instance was estimated by the additivity method of Laidler.⁵² Heats of fusion were estimated by Walden's Rule and adjusted to 298 K using Sidgwick's approximation:⁵³

4-8

$$\frac{\Delta H_{fus}(T_M)}{T_M} \approx 56.5, \text{ J/K}$$

T_M

4-9

$$\frac{\Delta H_V(T_B)}{T_B} \approx 92, \text{ J/K}$$

T_B

vaporization, where T_M and T_B represent the melting and boiling points respectively. An alternative approach to estimating ΔH_V in equation 4-7 was developed by Klages⁴⁷ who proposed that for non-polar and slightly polar compounds,

4-10

$$\Delta H_V(298) = 22.6 + 0.151(T_B - 298), \text{ kJ/mol,}$$

and for hydrogen bonded compounds,

4-11

$$\Delta H_V(298) = 28.5 + .188(T_B - 298), \text{ kJ/mol.}$$

The major limitations to equations 4-9, 10, 11 are that normal boiling points for solids are often unknown or inaccessible.

Results reported for acridine (mp 384, bp 619 K) and phenazine (mp 445, bp 612 K) according to equations 4-7, 8, 9 are 78.7 and 81.4 kJ/mol,⁴⁸ whereas equations 4-8 and 4-10 give 92.8 and 95.2 kJ/mol for ΔH_B respectively. These results can be contrasted to the experimentally determined values of 91.6±2.5⁴⁹ and 99.9±2.5⁵⁰ (90.4±4.7⁴⁹) kJ/mol for each respectively.

$$\Delta H_f(298) = \Delta H_f(T_M) + 0.013(298 - T_M). \quad 4-12$$

Experimental comparisons are not available for these compounds.

Other equations used to correct $\Delta H_{fus}(T_M)$ and $\Delta H_V(T)$ to 298 K include⁵⁴

$$\Delta H_{fus}(298) = \Delta H_{fus}(T_M) - \Delta Cp(lc)(T_M - 298), \quad 4-13$$

$$\Delta H_V(298) = \Delta H_V(T) - \Delta Cp(gl)(T - 298), \quad 4-14$$

$$\Delta H_V(298) = \Delta H_V(T) \left[\frac{T_C - T}{T_C - T_B} \right]^{.38}, \quad 4-15$$

where $\Delta Cp(lc)$ is the molar heat capacity between liquid (l) and solid (c), $\Delta Cp(gl)$ is the same difference between gas and liquid, and T_C is the critical temperature. The heat capacities required in equations 4-13, 14 for solids and liquids can be estimated using a form of Kopp's law. The heat capacity of a solid or liquid can be approximated by the sum of the heat capacities of the constituent atoms. Values for the following atoms in solids and liquids have been assigned:⁵⁵ C, 7.5 (11.7); H, 9.6 (18); B, 11.3 (19.7); Si, 15.9 (24.3); O, 16.7 (25.1); F, 20.9 (29.3); P, S, 22.6 (31.0); and 25.9 (34.3) J/K for heavier atoms. Values in parenthesis

are for liquids. Heat capacities of the corresponding gas phase can be estimated as described in Section 4-B or by other methods.⁵⁶ Methods of estimating the critical temperature required in Watson's equation, equation 4-15,⁵⁷ are described by Thomson.⁵⁸ All

required knowledge of the normal boiling point. Other semi-empirical rules have been developed for estimating heat capacities of a variety of organic compounds.⁵⁹

Numerous successful methods have been developed for estimating $\Delta H_v(298)$ of liquids, particularly hydrocarbons.^{52,53,56-58,60-70} These methods vary in the empirical parameters required. Some methods depend on experimental parameters (e.g. critical properties) and others only require knowledge of molecular structure. The relative magnitudes of ΔH_v and ΔH_{fus} observed for many organic compounds suggest that the better the estimation of ΔH_v , the closer will equation 4-7 approximate experimental values of ΔH_g . Application of these methods to estimate $\Delta H_v(298)$ of solids together with a better assessment of $\Delta H_{fus}(298)$ should improve the accuracy of equation 4-7. The obstacles imposed by crude estimations of $\Delta H_{fus}(T_M)$ ^{56,71}, such as Walden's rule, can be circumvented by direct experimental measurement. Using current instrumentation, this measurement can be accomplished quickly and accurately and is experimentally accessible for many organic solids. In cases where fusion cannot be observed directly, ΔH_{fus} may be available by other techniques such as the temperature dependence on solubility (Schroder-Van Larr equation, section 3).²²

An alternate method of estimating heats of sublimation by molecular structure increments has been developed by Bondi.⁷² The method assumes additivity in group increments to yield the

total sublimation energy,

$$\Delta H_g(RX) = \Delta H_g(R) + \Delta H(X) \quad 4-16$$

Group increments have been tabulated and the methods is quite useful for rough estimates of ΔH_g , particularly in cases where molecular instability is involved.⁶

The vaporization energy, $\Delta E(s)$, where

$$\Delta E(s) = \Delta H_g - RT,$$

of condensed polynuclear aromatic hydrocarbons was found to vary linearly with the number of carbon atoms in the molecule.⁷³

The average contribution was found to be 6.3 kJ/mol per carbon atom. A similar additivity was observed by Alhara for a variety substituted aromatics and group contributions were derived.⁷⁴ Although the accuracy of the sublimation enthalpies used to derive the two relationships described above has been questioned,⁶¹ these results do support the concept of group additivity at a qualitative level. The sublimation enthalpies of planar aromatic hydrocarbons have been correlated with molecular structure most recently by Morawetz,⁶¹ and bond contributions by type have been tabulated.

Other accurate but also more restrictive relationships for some simple homologous series have been developed.⁷⁵ The relationships are of the form:

$$\Delta H_g = A + B(n),$$

where A is a measure the contribution to ΔH_g of the functional group and B is a constant which reflects the sensitivity of ΔH_g to homologating an alkyl side chain. Some examples of the type of systems investigated include molecules of the type, ROH, RCO₂H, RCO₂CH₃, and RCONH₂, where R = C_nH_{2n+1} and n is incremented by two. Relationships have been observed for both the even and odd series but are restricted to those members of the series which are iso-structural (i.e. members of the same polymorphic form).⁷⁵ Similar relationships have been established for even and odd alkanes,⁶³

$$\begin{array}{ll} \Delta H (298) \approx -8.58 + 0.95 (n_c), & (\text{even } n_c; \text{ kJ/mol}) \quad 4-18 \\ \Delta H (298) \approx 26.6 + 0.95 (n_c), & (\text{odd } n_c; \text{ kJ/mol}) \quad 4-19 \\ \Delta H (298) \approx 4.1 + 0.24 (n_c), & (\text{even } n_c; \text{ kJ/mol}) \quad 4-20 \end{array}$$

where n_c is the number of carbon atoms in the molecule. The differences observed for even and odd members of these series appears to result from differences in crystal structure, particularly from packing differences in the end group layers in the crystal.^{62,78} Equations 4-16, 4-19 and 4-20 appear to have been established by two independent but parallel studies of lattice energies of normal alkanes. Equations 4-18 and 4-19 were derived from experimental heats of sublimation of even normal alkanes from C₁₂ to C₂₀ and odd alkanes C₁₃ to C₁₉ respectively & H_g calculated for liquids from equation 3-1).⁶¹ Equation 4-20 was derived from a relationship similar to equation 4-17 established for lattice energies of even n-alkanes up to C₁₆ by Mnyukh (for triclinic structures, A=-12.45, B=-8.39 kJ/mol).⁷⁶ Using crystal structure data for C₁₈H₃₈ and C₃₂H₆₆, together with a Lennard-Jones 6-12 potential,

equation 4-20 was derived and compared to ΔH_g values obtained by an alternative estimation technique.⁷⁷

The approximate nature of the assumption of group additivity in heats of sublimation is particularly dramatized in the ΔH_{fus} and ΔH_g results reported in Section 3, Tables 2 and 3. Differences of several kJ/mol are routinely observed in ΔH_{fus} between racemic and active forms of the same chiral molecule and differences up to 16 kJ/mol have been measured.⁷⁹ These differences are clearly due to differences in packing. Similar deviations from group additivity has also been observed in the chlorobenzenes.⁸⁰ The dependence of ΔH_g on molecular packing in the crystal suggests that estimations of ΔH_g by the methods of group additivity are likely to remain either qualitative or highly restrictive.

D. Heats of Sublimation Compendium. Table 5

The most frequent use of heat of sublimation data is to correct heats of formation to a standard state. Compendia on heats of formation usually include references for heats of sublimation and are a valuable reference source for this information.^{1,2,3} However these compendia are sources for heats of formation; the available information on heats of sublimation is not exhaustive nor is the coverage inclusive of all available data. Heat of sublimation data has not been compiled since 1960,⁸² and since results are diffusely scattered in the literature, an exhaustive search was initiated to update this information.

This compendium has resulted in the collection of over 800 organic compounds whose heats of sublimation has been reported in the time frame, 1910-1983 and has attempted to list all determina-

tions reported for each substance. A few organometallic compounds are also included but the list here is for from comprehensive. Coverage for organics is comprehensive for the time frame 1910-1983 and includes data reported in the sublimation compendium by Jones (1960),⁸² and thermochemical compendia of Cox and Pilcher (1970),² Pedley and Rylance (1977),¹ and the chemical literature. Estimates of heats of sublimation are with a few exceptions, not included.

The compounds in Table 5 are arranged in alphabetical order with the usual exception of carbon and hydrogen. The sequencing within a given elemental composition is in terms of monoatomic increments in reverse alphabetical order. Column 2 lists the chemical name of each substance. Occasionally, a trivial name is also included for purposes of ease of identification. Other identifying information is included, if available, such as the space group, or melting point if the compound was known to exhibit polymorphism at the time of measurement. Otherwise, reference to column 3 which refers to the temperature range in which the measurement were made, serves to experimentally define the most probable crystalline modification used. Absolute configurations and/or sign of rotation are included for chiral molecules when possible.

In a few cases where ΔH_g for a molecular complex have been reported, such complexes are listed under the molecular formula of the member which would be listed first. Thus the molecular complex formed from tetrathiafulvalene - 7,7,8,8-tetracyanoquinodimethane ($C_6H_4S_4C_{12}H_4N_4$) is listed under $C_6H_4S_4$.

The experimental heats of sublimation in kJ/mol are listed in column 4 along with the experimental uncertainty if reported. Column 5 lists the temperature to which this heat of sublimation refers. In

many cases the temperature reported in this column is simply the mean temperature of the experiments. In other cases, heat capacity corrections to the standard state (298 K) are included. The reader is referred to the original literature for specific details regarding the experimental or approximate nature of these corrections.

In a few instances, the heats of sublimation reported in column 4 are prefaced with a U. This implies that in our estimation these results are considered unreliable. Criteria used in this evaluation include comparisons with other literature values reported for the same substance, and in cases where comparisons were not directly available, how well a given technique reproduced literature values when such comparisons could be made.

Column 6 abbreviates the technique used in the reported measurement. The reader is referred to Table 4 for a definition of the abbreviation used.

The final column in Table 5 lists the reference(s) to the original work, which are arranged chronologically in the reference section following the table. Recent improvement in equipment and design as

well as the development of techniques for simultaneous analysis, generally afford results which are more reliable than earlier ones. Consequently the entries in the table for each substance are arranged in reverse chronological order. In addition, reference to one of the compendia previously mentioned is included when possible as an additional source to the original literature, thereby significantly reducing the chances of citation error. In those cases where the original literature was not consulted, the Chemical Abstracts reference is included in the reference.

Table 4 List of Abbreviations Used in Table 5

Abbreviation	
A	calculated from the vapor pressure data reported by the method of least squares
B	calculated from the sum of the heats of vaporization and fusion
BG	Bourdon Gage
C	calorimetric determination
DBM	dibutyl phthalate manometer
DM	diaphragm manometer
E	estimated
GS	gas saturation, transpiration
HSA	head space analysis
I	isoteniscope
IPH	inclined piston manometry
KG	Knudsen gage
LE	Langmuir evaporation
ME	Mass effusion-Knudsen effusion
MG	McLeod Gage
MH	mercury manometer
NA	not available at the time of publication
QF	quartz fiber
QR	quartz resonator
RG	Rodebush Gage
T	tensimeter
TCH	thermal conductivity manometer
TE	torsion effusion
TGA	thermal gravimetric analysis
TSGC	temperature scanning gas chromatography
V	viscosity gage
VG	MKS Baratron Vacuum Gauge

a. A description of many of the instruments and techniques listed in this table can be found in reference 83.

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