Enthalpies of Sublimation after a Century of Measurement:
A View as Seen through the Eyes of a Collector

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Measurements of sublimation enthalpy are reviewed from an empirical perspective. Some of the reasons responsible for the lack of agreement between measurements are discussed and some general advice is given to prospective users of the sublimation enthalpy data.

1. Introduction

Measurements of sublimation enthalpies and vaporization enthalpies have been made for over a century.[1] These measurements are useful for adjusting enthalpies of formation of solids to a gaseous standard state and for evaluating environmental transport properties. Sublimation enthalpies are also useful for studies of polymorphism and predictions of molecular packing in the solid state. Yet despite the longevity in interest in these measurements and the significant technological improvements in instrumentation and assessment of purity, examination of recent data still show significant discrepancies in data published by different laboratories and by different techniques. Agreement between laboratories is often not within the precision cited. It is the objective of this article to discuss some of the reasons responsible for the apparent inaccuracies and disagreement, and to try to provide to the user of this data, the author's opinion of the quality of some of the data generated by the various types of measurements. The opinions expressed are those viewed through the eyes of an individual who has been collecting this data for approximately 30 years and not necessarily of one who has had hands-on experience with all the techniques discussed below.

2. Sublimation Enthalpies of Organic Compounds

2.1　How good is the data?

To get some idea of the quality of the sublimation data in the literature, measurements summarized in a recent compendium were examined.[2] Since sublimation enthalpies are temperature dependent, data reported at T 298.15 K were used whenever possible. Otherwise, data at the same temperature or at similar temperatures ($\pm$ 15 K) were collected and analyzed. Compounds for which at least three independent measurements reported since 1950 were considered. A total of 451 measurements reported on 80 compounds were identified. A summary of the results can be found in **Fig.1**. Literature values are plotted against the mean for each compound considered. The standard deviation associated with the difference between the mean and each experimental value was $\pm$ 6.7 kJ mol^{-1}. As can be seen in the figure, a number of measurements are clearly outliers. Removing data at variance with the mean by more than 18 kJ mol^{-1} ($\pm$ 3σ), and recalculating the mean results in **Fig.2**. The number of compounds considered remained the same but the amount of data was reduced to 442 entries. The standard deviation associated with these data points was $\pm$ 4.9 kJ mol^{-1} ($\pm$ σ). The data was further analyzed by considering the magnitude of the sublimation enthalpy. A total of 45 compounds (299 measurements) were characterized by a mean sublimation enthalpy of less
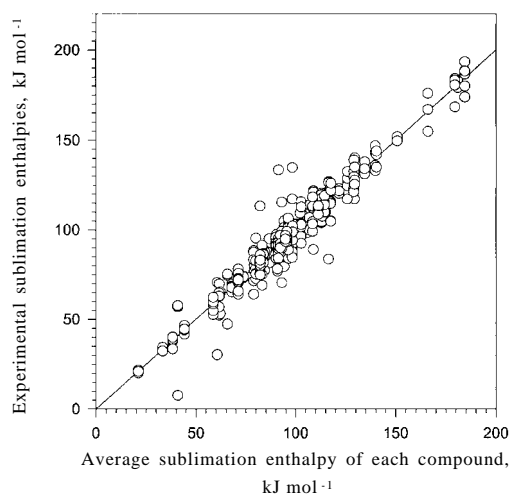
Fig.1 A total of 451 experimental sublimation enthalpy measurements on 80 organic compounds as a function of their mean. The equation of the line is given by: $\Delta H_{sub}(T)_{expt}$ (0.999 ± 0.011) $\Delta H_{sub}(T)_{mean}$ (0.092 ± 6.75) correlation coefficient: r^2 0.943.
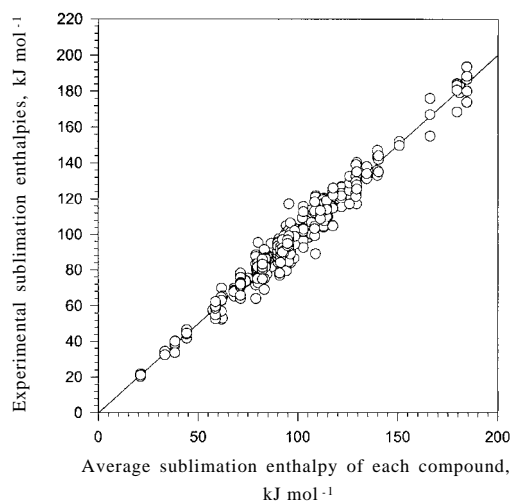

Fig.2 A total of 442 experimental sublimation enthalpy measurements on 80 organic compounds as a function of their mean. The equation of the line is given by: $\Delta H_{sub}(T)_{expt}$ (0.999 ± 0.008) $\Delta H_{sub}(T)_{mean}$ (0.008 ± 4.9) correlation coefficient: r^2 0.969.

than 100 kJ mol ^{1}; the standard deviation was $\pm$ 4.6 kJ mol ^{1}. The uncertainty increases to 5.6 kJ mol ^{1} for 35 compounds (143 measurements) characterized by a sublimation enthalpy in excess of 100 kJ mol ^{1}.

2.2 Why is there disagreement?

There are probably several likely reasons responsible for the apparent lack of agreement found between many measurements. All measurements of sublimation enthalpy and vaporization enthalpy are based on mass transport and as such are dependent directly or indirectly on vapor pressure. The difficulties in measuring low vapor pressures in the Pascal and sub-Pascal region have previously been noted.[3] To some extent, the lack of a sufficient number of standards that exhibit appropriate vapor pressures over the typical range of temperatures used in experimental measurements is partially responsible. Recently a series of standards have been proposed;[4] however, sufficient quality data to adopt a set of primary standards covering a range of vapor pressures and sublimation enthalpies were not available; as a consequence, it was necessary to assign secondary and tertiary standards. It is not clear what impact, if any, these standards will have on future measurements. What is clearly necessary for any substantive improvement in the quality of measurements in the low-pressure region, is the identification and adoption of a set of primary standards. At present, benzoic acid, naphthalene, ferrocene and anthracene have been recommended as primary standards and of these, only anthracene poses any sort of challenge to the instrumentation. Most standards are ideal in the sense that they are quite volatile, readily available and easy to measure; they are in some ways different from the properties of many materials of interest today.

The results in **Fig.2** suggest that uncertainties associated with sublimation (and vaporization) enthalpy measurements in the literature are related to the magnitude of their value, but the relationship is not necessarily linear. Compounds that have large sublimation/ vaporization enthalpies generally have low vapor pressures at ambient temperatures, thus requiring the measurements to be performed at elevated temperatures. As noted above, standards for the calibration of the instruments under these conditions are not available, and as such, authors reporting these measurements can be considered as having ventured into "unchartered waters".

Some of the discrepancies observed in the literature for sublimation enthalpy measurements may be due to the occurrence of polymorphism and solid-solid phase transitions. These may or may not be related. Although differences in sublimation enthalpies of polymorphic

forms are usually small,[2] this may not always be the case. The occurrence of phase transitions can easily be checked by differential scanning calorimetry (dsc). The detection of polymorphism is trickier; polymorphs usually have different infrared spectra, and their physical properties such as melting point may differ. Their ease in detection depends in part on whether the polymorphs are enantiotropic (inter-convertible) or monotropic (non-interconvertible modifications) in the solid state.[5,6] Enantiotropic polymorphic transitions, in so far as they affect sublimation enthalpies can be detected by dsc. Monotropic forms can be more difficult to detect since only one modification may be present. The occurrence of polymorphism emphasizes the importance of providing additional physical property identification when reporting sublimation enthalpy measurements; this includes recrystallization solvents and methods used in purification, as well as melting point. All other things equal, measurements reported in articles that provide this auxiliary information should be weighted more heavily than those that do not.

Chirality is also a factor that may influence the sublimation enthalpy and can be responsible for polymorphism. Various solid-liquid phase diagrams are known for chiral molecules.[7] What little work has been reported in this area suggests differences in sublimation enthalpy between chiral and racemic modifications[8,9] and examples of polymorphism in chiral systems are well known.[7]

The third and probably the most important reason, is due to systematic errors associated with the measurements. Every technique has some systematic error inherent in the method; in some cases the error is more significant than others. Measurements by more than 43 different techniques are identified in the compendium recently published.[2] It is not surprising given this number of different techniques, that some variance in the reported results is observed.

Despite the large number of different techniques used to measure sublimation and vaporization enthalpies, all measurements can be included into one of several categories. They are either "equilibrium vapor pressure" measurements conducted over a range of temperatures, direct "isothermal" calorimetric measurements of the enthalpy necessary to transport a fixed amount of material or an indirect measurement. Indirect measurements in this article, include measurements obtained by combining fusion and vaporization enthalpies and measurements of other properties related to mass flow. Within each category, examination of the experimental data suggests a priority of ranking with regards to the accuracy of each method. Accuracy in this context is taken to mean how well the results of a given technique (within the uncertainties cited) compares with other measurements conducted by other techniques or other laboratories.

2.3 Assessment of the Measurements

Several general statements can be made with regards to the quality of the available data. Measurements conducted in the past 40 yrs are usually better than earlier values. This is not a reflection of the quality of earlier work, but simply a consequence of the technological improvements in the instrumentation used to make the measurements and the technology used to assess purity. Measurements performed by laboratories specializing in sublimation/vaporization measurements should be weighed more heavily than those measurements performed on an *ad hoc* basis. This does not necessarily imply that all measurements reported by a thermochemical laboratory are of equal quality. However systematic errors are more likely to be uncovered and experiments repeated, if necessary, by a laboratory that specializes in these measurements. Unfortunately, the number of such laboratories has decreased dramatically in recent years, particularly in the United States. As a result of the lack of sustained funding, many laboratories specializing in thermochemical measurements have closed.[10]

Sublimation enthalpies vary with temperature. Although they are not as temperature dependent as vaporization enthalpies, values reported in the literature at substantially different temperatures cannot be directly compared. Simple but reasonably reliable equations for adjusting sublimation enthalpies of organic compounds to a common temperature are available.[2] In addition, sublimation enthalpies increase with decreasing temperature; discordance can be easily identified in two values if the sublimation enthalpy reported at the lower temperature is smaller than the value reported at the higher temperature. The difficulty that remains is the identification of the most reliable value.

The measurement of sublimation/vaporization enthalpy by each laboratory is a unique experiment. There

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are no commercial instruments available that have been designed to make low pressure measurements,[11] not, at least, without significant modifications. Experiments performed by the same method, Knudsen effusion for example, are unique, since the construction of each Knudsen effusion apparatus differs. Consequently, evaluation of each experimental technique is ultimately a reflection of the resources and expertise available at the laboratory making the measurements.

Before describing some of the techniques used to measure sublimation enthalpies, it might be useful to consider the enthalpic window available to sublimation enthalpy measurements. This window can be defined pragmatically as the lowest and highest value possible. Sublimation enthalpy is the sum of the fusion and vaporization enthalpy. This relationship, a rigorous thermodynamic property for enthalpies measured at the same temperature, yields an approximate value when combining vaporization and fusion enthalpies measured at different temperatures. Vaporization enthalpy is the largest in terms of its magnitude. A convenient estimate of the window's lower limit is to use a simple approximation for the vaporization enthalpy of organic compounds at T 298.15 K. This approximation is given by equation 1. The term n_c refers to the number of carbon atoms. This equation:

$$\Delta_l^g H_m (298.15 \text{ K})$$
$$(4.64 \pm 0.13) n_c \quad (2.93 \pm 0.8); \quad r \quad 0.965 \quad (1)$$

is a simplification of an equation used to estimate the vaporization enthalpy of hydrocarbons.[12] With the exception of fluorine, all other functional groups[13] in the molecule contribute as much or more as each carbon to the vaporization enthalpy of the molecule. Using a value for n_c that is a sum of both the number of carbon atoms and functional groups, it is possible to arrive at an approximate estimate of the vaporization enthalpy and this number can serve as an excellent lower minimum for the sublimation enthalpy at T 298.15 K. At the other extreme, an estimate of the upper limit to the sublimation enthalpy can be obtained by considering the homolytic bond strength of the weakest bond in the molecule. Barring peculiar frequency factors, the measured sublimation enthalpy cannot exceed the magnitude of the weakest bond in the molecule. Though the crystal lattice may be able to stabilize molecules in its interior,

evaporation is predominately a surface phenomena and the measurement of sublimation enthalpy is an "equilibrium" measurement. Molecules that have sufficient energy to sublime in this energy regime will also have sufficient energy to dissociate, no matter what the temperature of measurement. Sublimation enthalpies reported in the literature that approach or exceed bond dissociation enthalpies should be viewed cautiously and with some skepticism.

2.4 General Assessment of the Methods

Before describing some of the methods used to measure sublimation enthalpies, it should probably be emphasized that some of the comments expressed below are subjective and simply reflect the opinions of the author formed in the process of compiling sublimation enthalpy data. Among the most reliable methods for measuring "equilibrium vapor pressure" as a function of temperature are Knudsen or mass effusion and torsion effusion methods. Mass effusion measurements have been used for a long time by many investigators;[14] torsion effusion has been used less frequently and is more recent.[15] Mass effusion measurements appear reliable provided the measurements are made in the region of molecular flow. Depending on the effusion cell, this results in experimental vapor pressures in the vicinity of 1 Pa. An additional consideration is the range of temperatures used in the measurement of vapor pressure. Measurements made over a large range of temperatures (over 30 K) risk venturing into the transition region between molecular and hydrodynamic flow. Equations that can correct measurements that have ventured into the transition region have been reported but do not appear to have been used to any great extent in organic systems.[16]

Torsion effusion is a complimentary method to mass effusion and has often been measured simultaneously.[17,18] In torsion effusion, two orifices of a Knudsen cell are configured in an anti-periplanar arrangement such that the effusing vapor creates a torque on a fiber (or wire) to which the cell or cells are suspended. As noted by De Kruif and Blok, absolute calibration of the torsion effusion apparatus is very time consuming, necessitating the need of standards. Standardization is simplified significantly, if both torsion and mass effusion are measured simultaneously. The combined measurements offer the additional advantage

of providing vapor pressure information that is dependent (mass effusion) and independent (torsion effusion) on the molar mass of the effusing vapor.[19] This information can be useful in assessing the presence of molecular association in the vapor.

Calorimetric methods are another reliable means of obtaining sublimation enthalpies. Two kinds of calorimeters have been built and utilized, adiabatic[20-22] and conduction.[23] Adiabatic calorimeters have been used extensively in the measurement of vaporization enthalpies and sublimation enthalpies of volatile liquids and solids. Conduction calorimeters, such as the Calvet calorimeter, are among the most of reliable of calorimeters built for substances exhibiting low vapor pressures.[24-26] In this instrument, a sample and reference cell are used both equipped with Knudsen cells. The sample is allowed to sublime while the calorimeter is maintained at a constant temperature. The heat flow relative to the reference cell is measured by the output of two balanced thermopiles surrounding the sample and reference compartments. The thermopiles are connected in a parallel arrangement so that their output cancels when both cells are in thermal equilibrium.

It should be noted that sublimation enthalpies reported in the literature measured calorimetrically that have been standardized only by the Joule effect[27] appear to be lower than similar measurements made on other instruments and techniques, generally by a few per cent. The origin of this discrepancy is presently unknown. Caution has been expressed by Wadsö,[21] who noted the relative ease with which reproducible results can be obtained calorimetrically; also noted is the propensity to introduce systematic errors in these measurements, whose origin can often be difficult to explain.[16] An extensive use of standards is recommended.

Sublimation enthalpy measurements have also been reported on drop calorimeters. In this instance, a sample and reference vessel are dropped into a heated conduction microcalorimeter, evacuated and the output measured. While this method is not an equilibrium method, results on standards of ± 4 kJ mol^{-1} have been reported.[28] Measurements of this type should, in general, be treated as being less quantitative than other calorimetric measurements and the uncertainties cited above should probably be considered as lower limits.

A number of sublimation enthalpies have been reported by various modifications of commercial differential scanning calorimeters (dsc) and thermal gravimetric analysis (tga) instruments; measurements reported by these techniques, particularly the earlier ones run in temperature scan mode appear to be less accurate than those measured on the calorimeters described above. Dsc measurements run isothermally under vacuum appear to be more promising.[29]

Transpiration or gas saturation is another popular technique for measurement of vapor pressure. In this experiment an inert gas is passed over the sample in question and the amount of material transported as a function of temperature is quantified. The technique is generally applied under conditions of temperature and pressure where the ideal gas law is applicable. If the experiments are performed properly, the vapor pressure calculated is independent of the flow of carrier gas, assuring conditions of equilibrium. Advantages of this technique include the large temperature range accessible to these types of measurements and the flexibility in the analytical methods used to quantitate the mass transferred. Results using this technique are generally accurate to ± 5 %. The vapor pressure and sublimation enthalpy of many pesticides and other chlorinated hydrocarbons have been measured by this technique.[30]

Head space analysis is another technique that has been used by various investigators. In this experiment, the vapor in equilibrium above the solid is either measured directly by an absorption technique,[31] or indirectly.[32] In a modification of indirect head space analysis, a steady state is reached between a solid at one temperature and vapor at a higher temperature; the vapor is transferred, condensed and analyzed separately.[33] In these experiments, the amount of vapor is analyzed as a function of temperature. Adsorption on the surface is a potential problem in both the direct and indirect methods. In head space analysis, the vapor can be maintained at a higher temperature than the solid until a steady state is achieved. The time for transfer and condensation of the vapor can be carefully monitored and controlled in indirect head space analysis to minimize the transfer of adsorbed material. This technique is capable of providing results with an accuracy of ± 5 % for compounds exhibiting a vapor pressure down to about 1 Pa. Experimental results tend to be lower by a few % relative to other techniques. This has been attributed to a small contribution of

adsorbed material to the amount of vapor transferred; adsorbed material appears to make a larger contribution to the total material transferred at lower temperatures than at higher temperatures resulting in a slightly lower sublimation enthalpy.[33]

Despite the general reliability of these measurements, examples of unreliable measurements can be found in the literature even by laboratories specializing in these measurements. While it is not the intent of this article to single out unreliable measurements, except perhaps in a general sense, reputable laboratories, having recognized measurements that are problematic, have often made efforts to correct the measurements. Readers are encouraged to reach their own assessment by scanning the entries available.[2]

Indirect measurement of sublimation enthalpy is a third general method that has been used by researchers. These methods are generally quite varied. Some of these methods are also capable of both good precision and accuracy; the track record of other methods, however, leaves something to be desired. A quartz resonator is an example of an indirect method of measuring vapor pressure. In this experiment, the frequency of the quartz crystal is affected by the thickness of material (to be measured) deposited on its surface. The performance of this method when compared to the results obtained by other methods is mixed.[2] Measurements by Langmuir evaporation is another method with a poor past record.[2]

Sublimation enthalpy is the sum of the fusion and vaporization enthalpy when both are measured at the same temperature. An approximate value for the sublimation enthalpy can be obtained by adding the two experimental enthalpies when they are referenced to different temperatures. This method has seen limited use in the past since the vaporization enthalpies of many solids are not available. The availability of a compendium of experimental vaporization enthalpies may be useful in this respect.[34] Adjusting both enthalpies to the same temperature, T 298.15 K, improves the quality of the calculation. A protocol for adjusting of both vaporization and fusion enthalpies with temperature for many organic compounds has been reported.[34,35] In addition, experimental methods to obtain the vaporization enthalpies at T 298.15 K of compounds that are solids at this temperature by gas chromatography have been developed and these enthalpies should prove useful in completing
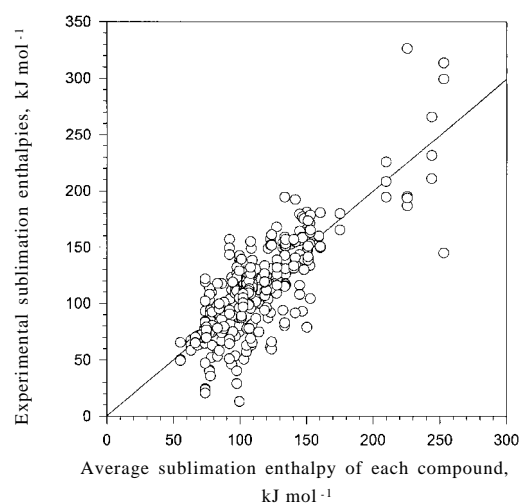

Fig.3 A total of 442 experimental sublimation enthalpy measurements on 80 organo-metallic compounds as a function of their mean. The equation of the line is given by: $\Delta H_{sub}(T)_{expt}$ (0.999 ± 0.034) $\Delta H_{sub}(T)_{mean}$ (0.337 ± 23.9) correlation coefficient: r^2 0.662.

thermodynamic cycles.[36] In addition, sub-cooled vaporization enthalpies can also serve as excellent lower values for sublimation enthalpy. Fusion enthalpies of solids adjusted for temperature decrease as the temperature is lowered (because the heat capacity of the liquid phase exceeds the heat capacity of the solid). Therefore the contribution they make at T 298.15 K is less than their contribution to the sublimation enthalpy at the melting point. Whether the indirect method is used to obtain sublimation enthalpies or simply to confirm or identify the best experimental value, the use of the indirect method can be a useful asset when dealing with enthalpy changes associated with phase changes.

3. Sublimation Enthalpies of Organo-metallic Compounds

3.1 How good is the data?

The comments expressed until now in this article have focused primarily on organic compounds. Despite the fact that an organo-metallic compound, ferrocene is one of the primary standards, and with some exceptions, the uncertainties associated with the sublimation enthalpies of organometallic compounds are of particular concern. To provide the reader with some idea of the quality of the sublimation enthalpy data on organo-metallic

compounds in the literature, a brief evaluation of these measurements is also included.[2] The analysis is similar to what has been reported for organic compounds with one major exception. Much of the sublimation enthalpy data reported for organo-metallic compounds has not been adjusted to T 298.15 K. Consequently it was necessary to include measurements conducted at different temperatures in the mean. Since sublimation enthalpies are temperature dependent; inclusion of measurements referenced to different temperatures should introduce a larger variability in their reproducibility than measurements adjusted to a common temperature. Compounds for which at least three independent measurements reported since 1950 were considered. Very few measurements on organo-metallic compounds have been reported prior to the mid 1960's. A total of 395 measurements reported on 80 compounds were identified. A graphical summary of the results can be found in **Fig.3**. Literature values are plotted against their mean for each compound considered. The standard deviation between the mean and experimental value was ± 23.9 kJ mol⁻¹ (± σ). As can be seen in the figure, the scatter for many compounds is so large that it is impractical to use statistical criteria to identify outliers. Furthermore, the magnitude of the uncertainty is beyond what could reasonably be attributed to the differences resulting from measurements referenced to different temperatures. Omission of temperature adjustments would be expected to contribute a few kJ mol⁻¹ to the overall uncertainty. The actual uncertainty is nearly three times what would be expected based on the results reported above for organic compounds.

3.2 Why is there disagreement?

A number of the measurements on organometallic compounds have been conducted by mass effusion, torsion effusion and by drop calorimetric methods; methods that have given good reproducible results with organic compounds. Also noted are a substantial number of measurements recorded by less reliable methods such as dsc and dta. However, the use of less reliable methods does not seem to be sufficient to explain the scatter. The reasons for the large uncertainty are not totally clear, but low volatility and thermal instability of some of the organo-metallic compounds as well as the lack of appropriate standards must also play a role. In any event,

users of this data must be very cautious.

4. Summary

In evaluating literature data, the reader must take several factors into consideration. These include the nature of the compound, its purity, how well it has been characterized, its relative volatility and how well the technique used to make the measurements has performed with other similar compounds. The past performance of the laboratory reporting the results should also be considered. In many cases, experimental sublimation enthalpies can be confirmed by constructing thermochemical cycles. The availability of compiled data should prove useful in this respect.[2,34,37]

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