

# Heat Capacity Corrections to a Standard State: A Comparison of New and Some Literature Methods for Organic Liquids and Solids

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Received February 8, 1992; revised July 21, 1992; accepted August 14, 1992

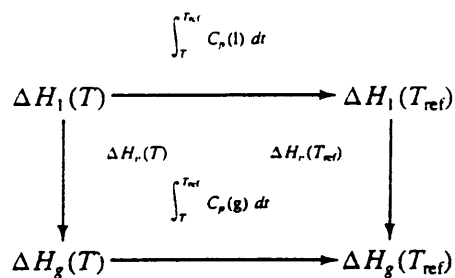
The estimation methods commonly used to correct phase change enthalpies to the standard state are compared where possible to experimental measurements. Heat capacity corrections for liquid-gas equilibria are found to correlate with molecular structure, and we suggest an improved method for estimating these corrections using group methods. A similar improvement for estimating heat capacity corrections for solid-gas equilibria using group methods is also proposed. Heat capacity corrections for liquid-solid equilibria are examined. These corrections were found to be comparable in magnitude to the experimental error associated with heat capacity measurements, so it was not possible to obtain any meaningful correlations.

**KEY WORDS:** Heat capacity; comparison of estimation methods.

Many thermochemical measurements that involve phase changes are performed at temperatures other than 298 K. Corrections to a standard state require information on the heat capacity differences of the two phases involved over the temperature interval separating the experiment and the standard state [1]. Several methods, some theoretical, others totally empirical, have been developed and used to correct for heat capacity differences between liquid and gas, solid and gas, and solid and liquid phases. Some of these methods provide heat capacity differences between phases directly and do not require absolute heat capacities. In this study, we have examined the predictions of some of these relationships and have compared the results, whenever possible, to experimental heat capacity differences. In a few cases where experimental data are not available, absolute heat capacities have been estimated by means of group additivity methods [2, 3] and differences between phases calculated.

## PHASE CHANGE ENTHALPIES

Vaporization enthalpy,  $\Delta H_v(T)$ , measured at an experimental temperature  $T$ , is related to the vaporization enthalpy at a standard state,  $\Delta H_v(T_{ref})$ , by the following diagram:



The terms g and l represent the gas and liquid states respectively. The enthalpy of a gaseous or liquid substance varies with temperature according to its heat capacity (Eqs. (1) and (2)):

$$\Delta H_l(T_{ref}) = \Delta H_l(T) + \int_T^{T_{ref}} C_p(l) dt \quad (1)$$

$$\Delta H_g(T_{ref}) = \Delta H_g(T) + \int_T^{T_{ref}} C_p(g) dt \quad (2)$$

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The difference between standard enthalpies in the gas and liquid state is given by Eq. (3). This difference is the standard vaporization enthalpy,  $\Delta H_v(T_{\text{ref}})$ . Likewise,  $\Delta H_g(T) - \Delta H_l(T) = \Delta H_v(T)$ . Since vaporization enthalpies measure the enthalpy changes between the gas and liquid phases at a fixed temperature,  $T$ , corrections to 298 K or any other temperature require temperature corrections to the enthalpy of both phases involved. The temperature corrections take the form of heat capacity differences of the two phases and are expressed by Eq. (4) for vaporization enthalpies. Similar corrections are necessary for other phase change enthalpies.

$$\Delta H_g(T_{\text{ref}}) - \Delta H_l(T_{\text{ref}}) = \Delta H_g(T) - \Delta H_l(T) + \int_T^{T_{\text{ref}}} C_p(\text{g}) dt - \int_T^{T_{\text{ref}}} C_p(\text{l}) dt \quad (3)$$

$$\Delta H_v(T_{\text{ref}}) = \Delta H_v(T) + \int_T^{T_{\text{ref}}} C_p(\text{g}) dT - \int_T^{T_{\text{ref}}} C_p(\text{l}) dT \quad (4)$$

Treating the heat capacities as constant over the temperature range of the correction and noting that the integration limits for both are the same reduces Eq. (4) to the form usually used when applying these corrections, Eq. (5). Equations (6) and (7) can be derived similarly, and correct for the effects of temperature on sublimation and fusion enthalpy measurements, respectively.

$$\Delta H_v(T_{\text{ref}}) = \Delta H_v(T) - [C_p(\text{l}) - C_p(\text{g})][T_{\text{ref}} - T] \quad (5)$$

$$\Delta H_s(T_{\text{ref}}) = \Delta H_s(T) - [C_p(\text{c}) - C_p(\text{g})][T_{\text{ref}} - T] \quad (6)$$

$$\Delta H_{\text{fus}}(T_{\text{ref}}) = \Delta H_{\text{fus}}(T) - [C_p(\text{c}) - C_p(\text{l})][T_{\text{ref}} - T] \quad (7)$$

The magnitude of the heat capacity depends on the phase and generally decreases in the order liquid > solid > gas. For measurements above ambient temperatures, corrections to the standard state increase vaporization and sublimation enthalpies and decrease fusion enthalpies. Corrections of thermochemical data to a standard state do not necessarily require condensed-phase and

gas-phase heat capacities but only differences between them. Several methods have been developed to estimate such differences, and these are described here.

## VAPORIZATION ENTHALPY CORRECTIONS

A general method that has been used to correct vaporization enthalpies to 298 K is Sidgwick's rule (Eq. (8)) [1, 4]:

$$\Delta H_v(298 \text{ K}) = \Delta H_v(T) - 54.4(298 - T); \text{ J/mole} \quad (8)$$

In Eq. (8),  $T$  is the temperature of measurement or mean temperature of measurement if  $\Delta H_v(T)$  has been obtained from a Clausius-Clapeyron treatment of vapor pressures. The difference in heat capacity between a liquid and gas phase is described by a constant, 54.5 J/(mole K) and is independent of structure. A relationship similar to Eq. (8) was observed independently by Shaw [5], who noted that  $C_p(\text{l}) - C_p(\text{g}) \approx 50.2$  J/(mole K) ( $\Delta C_p(\text{lg})$ ) for a large variety of different organic liquids at 298 K.

We have examined the differences in heat capacity between liquid and gas phases,  $C_p(\text{l}) - C_p(\text{g})$ , of 289 liquids at 298 K. The experimental data were obtained from the compilations of Domalski and Hearing [6, 7], Domalski, Evans, and Hearing [8] (289 liquids and 143 gases), and Stull, Westrum, and Sinke [9]. In order to compare the experimental results to those predicted by Eq. (8), we have summarized the distribution of experimental values in the histogram of Fig. 1. The distribution interval was chosen to reflect standard errors ( $\pm 1$  standard deviation) associated with the experimental measurements. The typical experimental error in liquids was obtained by calculating the standard error associated with a total of 877 independent measurements reported on 219 different liquids [6, 7]. The standard deviation associated with these duplicate and often multiple determinations was 8 J/mole. The combined value of 12 J/mole also reflects an estimated uncertainty in gas-phase heat capacities of 4 J/(mole K) [3].

As illustrated in Fig. 1, 187 out of the 289 compounds (65%) fall within an uncertainty of  $\pm 12$  J/(mole K) of 54 J/(mole K). The mean value of all 289 compounds was 64.2 J/(mole K), and the standard deviation of the mean was 32.2 J/(mole K). For purposes of comparison, we have also calculated heat capacity differences between liquid and vapor phases at 298 K for 114 compounds that are solids at room temperature. Since there is no experimental  $C_p(\text{l})$  data available for

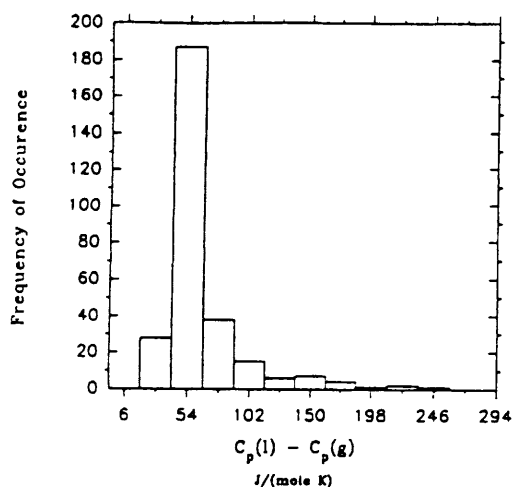


Fig. 1. The distribution of the experimental liquid heat capacities of 289 organic liquids about 54 J/(mole K) using a distribution interval of  $\pm 1$  standard deviation (24 J/mole).

these compounds at 298 K, liquid heat capacities were calculated by using group additivity parameters previously described [2] and experimental values for the gas phase were obtained from the afore mentioned sources. The distribution of heat capacity differences between the liquid and gas phases observed for these solids is presented in Fig. 2. Using the same protocol as previously described (distribution interval  $\pm 1$  standard deviation: 48 J/(mole K) (gas phase uncertainty: 4 J/(mole K)); liquid state uncertainty: 20 J/(mole K) (1 standard deviation for calculated  $C_p(l)$  values of solids) [2]), the results in Fig. 2 show a much broader distribution in the

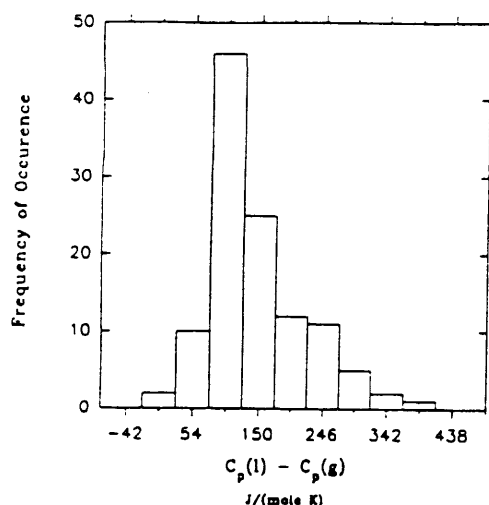


Fig. 2. The distribution of  $C_p(l) - C_p(g)$  of 114 organic solids about 54 J/(mole K) using a distribution interval of  $\pm 1$  standard deviation (48 J/mole);  $C_p(l)$  values are estimated from group additivity tables and  $C_p(g)$  values are literature values.

liquid-gas heat capacity differences for solids than was observed in Fig. 1. A mean value of 134 J/(mole K) and a standard deviation of 71 J/(mole K) were obtained. The mean and standard errors are roughly twice each respective value observed for compounds that are liquids at 298 K. The significant differences observed between solids and liquids prompted us to try to identify the cause(s) of the discrepancies observed in the two figures.

We have found that heat capacity differences between liquid and gas phases vary quite regularly with increasing molecular size. For hydrocarbons as an example, if  $\Delta C_p(lg)$  is plotted against the number of carbons atoms in the molecule, a good linear correlation is obtained. A total of 158 hydrocarbons (24 solids, 134 liquids) resulted in a linear correlation characterized by an intercept of 6.69 J/(mole K), a slope of 6.89 J/(mole K, carbon atom), a correlation coefficient of 0.9406, and a standard deviation of 14.5 J/(mole K). The heat capacity differences of simple hydrocarbon derivatives also correlated to the number of carbon atoms in the molecule provided a group contribution to  $\Delta C_p(lg)$  was included for the functional group in question. Although this approach successfully correlated  $\Delta C_p(lg)$  terms of many hydrocarbon derivatives, sufficient experimental data on compounds containing a variety of functional groups are lacking, and this limitation prompted us to search for an alternative approach.

The correlation observed between molecular size and  $\Delta C_p(lg)$  suggested an approach which proved equally successful. We have found that the experimental liquid-gas-phase heat capacity differences can also be correlated with the heat capacity of the liquid,  $C_p(l)$  calculated from the group values previously reported [2]. The attractiveness of this approach is that group values for a large variety of functional groups are already available. Using experimental heat capacities only for liquids, a plot of 289 experimental  $\Delta C_p(lg)$  values against the calculated heat capacity of the liquid,  $\Delta C_p(l)_c$ , resulted in a linear correlation characterized by the following parameters:

$$\Delta C_p(lg) = 10.58 + 0.26 C_p(l)_c; \quad (9)$$

correlation coefficient, 0.886

Using this equation, we are able to reproduce the experimental  $\Delta C_p(lg)$  values of the 289 liquids used in this correlation with a standard deviation of 15 J/(mole K). The heat capacity of the 114 solids of Fig. 2 which were not used in the correlation were reproduced with a standard deviation of 25 J/(mole K). The use of Eq. (9) and the group additivity tables [2] reduced the standard de-

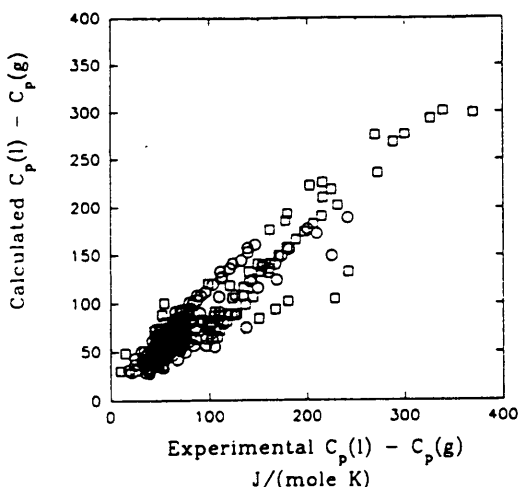


Fig. 3. Calculated and experimental heat capacity differences of 289 organic liquids (circles) and 114 solids (squares) using Eq. (9).

viations of both liquids and solid to roughly one-third their previous value. A summary of these results for both solids and liquids is provided by Fig. 3, which compares calculated and experimental heat capacity differences for both liquids and solids. Entries by circles refer to liquids, and those by squares refer to solids at 298 K. Heat capacity differences between liquid and gas phases for solids were not used in deriving Eq. (9) because the  $C_p(l)$  term used for these compounds was the calculated value.

### VAPORIZATION ENTHALPIES AS A FUNCTION OF TEMPERATURE

The use of heat capacity information for the gas and liquid phases estimated or measured at 298 K is only useful for correcting vaporization enthalpies measured at other temperatures if it is assumed that either the heat capacities are independent of temperature or that the heat capacity curves of the liquid and gas phases closely parallel each other as a function of temperature. To test how well  $\Delta C_p(lg)$  values at 298 K correct  $\Delta H_v(T)$  values to the standard state,  $\Delta H_v(298\text{ K})$ , we have examined the changes observed in  $\Delta H_v(T)$  as a function of temperature for 126 different compounds over the temperature range typical of these corrections (roughly 260 to 400 K). Experimental vaporization enthalpies measured or evaluated at different temperatures were obtained from the critically reviewed compilation of Majer and Svoboda [10]. The differences in  $\Delta\Delta H_v$ , usually referenced to  $\Delta H_v(298\text{ K})$  or the temperature closest to 298 K, were compared to the differences calculated using

both experimental and calculated  $\Delta C_p(lg)(298\text{ K})$  values and the corresponding temperature differences  $\Delta T$ . The amount of experimental data available in this compendium [10] varies considerably from compound to compound. To minimize the bias resulting from the uneven distribution of this data, heat capacity corrections were included for a minimum of two to a maximum of four temperatures for each compound. Temperatures were chosen to cover the temperature range 260 to 370 K as uniformly as possible, with the exception that  $\Delta H_v(T)$  values measured close to the boiling point were not used. (The heat capacity of the liquid phase increases rapidly above the boiling point as the critical temperature and pressure are approached, resulting in a vaporization enthalpy of zero at the critical temperature and pressure.) The results of using experimental  $\Delta C_p(lg)$  values and temperature differences to correct for heat capacity effects between liquid and gas phases are shown in Fig. 4. Enthalpy differences calculated using  $\Delta C_p(lg)(298\text{ K})[T - T_{ref}]$  correlate quite well with enthalpy differences measured from vaporization enthalpies for most compounds (circles), except for those compounds that are capable of forming strong hydrogen bonds (squares), i.e., alcohols, carboxylic acids, and primary and secondary amines. Even in cases with hydrogen bonding, significant deviations from the correlation were not observed in all cases. The equation generated by a least-squares treatment of all the data is characterized by an intercept of  $-0.23\text{ kJ/mole}$ , a slope of 0.868, a correlation coefficient of 0.927, and a stan-

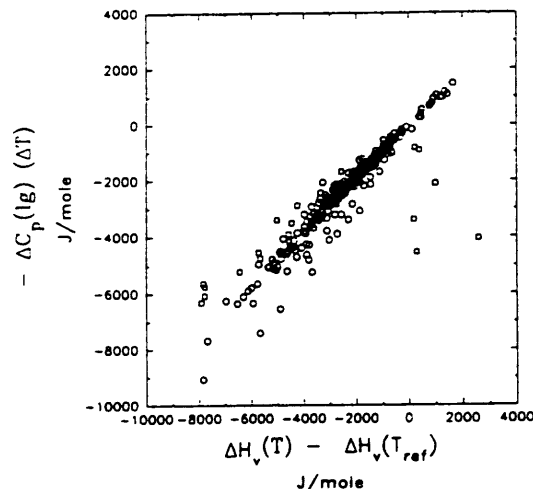


Fig. 4. A comparison of heat capacity corrections using experimental heat capacity values at 298 K and those from vaporization enthalpies measured as a function of temperature; squares represent values of compound that form strong hydrogen bonds, and circles represent all other compounds.

## Heat Capacity Corrections to a Standard State

standard error of 0.61 kJ/mole. The correlation improves if compounds that form such hydrogen bonds (15/126) are excluded from the data base. An intercept of 34.9 J/mole, slope of 0.986, correlation coefficient of 0.9785, and standard error of 0.33 kJ/mole are obtained.

Substituting calculated values of  $\Delta C_p(\text{lg})$  in place of experimental ones provided a similar correlation. Using all the data, an intercept of  $-0.25$  kJ/mole, a correlation coefficient of 0.8946, a slope of 0.885, and a standard error of 0.77 kJ/mole are obtained. An intercept of 46.7 J/mole, slope of 1.06, correlation coefficient of 0.96718, and standard error of 0.49 kJ/mole are obtained if the compounds forming hydrogen bonds are excluded from the correlation.

Use of the term  $\Delta C_p(\text{lg})[T - T_{\text{ref}}]$  to correct for heat capacity changes with temperature introduces an error that is directly proportional to the temperature change. Some idea of the magnitude of this uncertainty can be obtained from Fig. 5, which illustrates the increase in scatter observed with increases in  $T - T_{\text{ref}}$ . The vertical axis compares heat capacity differences obtained from the temperature dependence of vaporization enthalpy measurements ( $\Delta H_v(T) - \Delta H_v(T_{\text{ref}})$ ) and experimental heat capacities ( $C_p(\text{lg})(T - T_{\text{ref}})$ ). The squares represent values measured for compounds that can form hydrogen bonds, while the circles include all others.

Numerous other methods have also been developed to correct vaporization enthalpies with temperature [1] (for a comprehensive listing of those methods see Ref. 11). Most are empirical and require either critical properties or other parameters that are not generally available and must be estimated themselves.

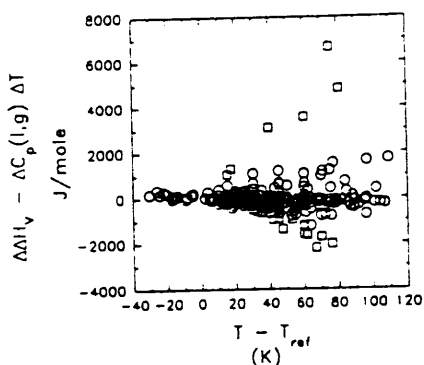


Fig. 5. Differences in heat capacity corrections as obtained from vaporization enthalpies and heat capacity values as a function of temperature.

## SUBLIMATION ENTHALPY CORRECTIONS

A simple relationship that has been used to estimate heat capacity differences between solids and gases and to correct sublimation enthalpies with temperature is given by Eq. (10) [12]:

$$\Delta H_s(298 \text{ K}) = \Delta H_s(T) - 2R(T - 298 \text{ K}) \quad (10)$$

This equation is derived from a theoretical treatment of the heat capacity of solids and gases [13]. The terms  $T$  and  $R$  refer to the temperature and gas constant (8.314 J/(mole K)), respectively. A difference of 16.6 J/(mole K) is predicted for each compound, regardless of structure. A similar relationship but characterized by a temperature coefficient of  $6R$  (50 J/mole) has been suggested by Pedley [14], while temperature coefficients of 40 J/mole have been used by Melia and Merrifield [15], and de Kruif *et al.* [16] have used a value of 60 J/mole for a series of amino acids and small peptides.

The usefulness and accuracy of these relationships were tested by obtaining experimental heat capacity differences between the solid and gas phases for 117 compounds. Gas-phase data was obtained from the collection by Stull, Westrum, and Sinke [9], and some additional values were estimated using both the Domalski-Hearing tables for hydrocarbons [7] and the Benson tables [3] for hydrocarbon derivatives. Heat capacity values for solids were obtained from the compendium by Domalski and Hearing [6].

The experimental values are characterized by a mean value of 32.7 J/(mole K) and a standard deviation of 45.7 J/(mole K). The distribution of values for each of the models described is illustrated in the histograms of Fig. 6 for a distribution interval of 54 J/mole. This interval was chosen to represent  $\pm 1$  standard deviation in the uncertainty of the experimental data. For solids an uncertainty of 23 J/(mole K) was calculated from 284 independent experimental measurements reported in 102 different solids and an additional 4 J/(mole K) reflects the estimated uncertainty in gas-phase heat capacities. Comparison of the four histograms of Fig. 6 suggests that using the mean value of 32 J/mole for the temperature coefficient in Eq. (10) would give the most symmetrical distribution.

In an attempt to improve the correlation, we decided to see if heat capacity differences for solids,  $C_p(\text{c}) - C_p(\text{g})$ , were also a function of molecular size and composition as observed for liquids. Plotting experimental heat capacity differences against the calculated heat capacity of the solid ( $C_p(\text{c})$ ) resulted in the follow-

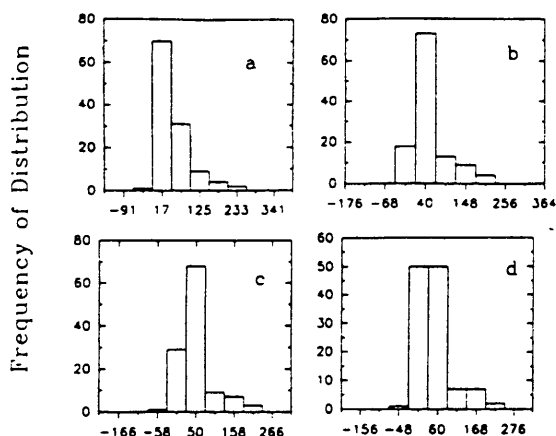


Fig. 6. The distribution of  $\Delta C_p(\text{cg})$  values of 114 organic solids about (a)  $2R$  (17 J/mole), (b) 40 J/mole, (c)  $6R$  (50 J/mole), (d) 60 J/mole using a distribution interval of  $\pm 1$  standard deviation (54 J/mole).

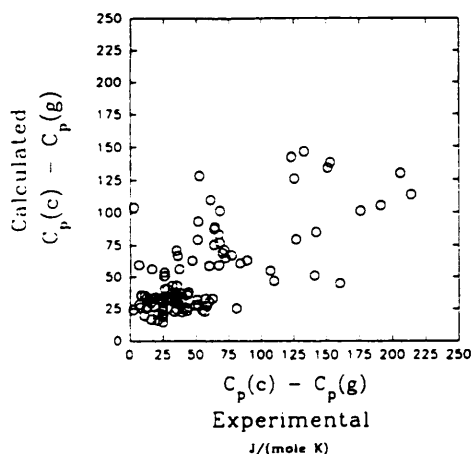


Fig. 7. Calculated and experimental heat capacity differences of 114 organic solids using Eq. (11).

ing correlation:

$$\Delta C_p(\text{cg}) = 0.75 + 0.15 C_p(\text{c});$$

correlation coefficient, 0.698 (11)

A comparison of  $C_p(\text{c}) - C_p(\text{g})$  calculated with the aid of Eq. (11) and experimental  $C_p(\text{c}) - C_p(\text{g})$  values is shown in Fig. 7. The standard deviation between experimental and calculated results is 33 J/(mole K), an improvement over using a modified version of Eq. (10). The significantly larger standard deviation in the correlation observed for solids (33 J/(mole K)) as compared to liquids (14.5 J/(mole K)) closely parallels the estimated experimental uncertainties in each case (27 compared to 12 J/(mole K), respectively).

## FUSION ENTHALPY CORRECTIONS

Corrections of fusion enthalpies to 298 K requires heat capacity information for both the solid and liquid phases. A general method that has been used to correct fusion enthalpies, also proposed by Sidgwick, is given by Eq. (12) [1, 4]. The correction in Eq. (12) is very similar in form to the term in Eq. (8) but opposite in sign. The term  $T_{\text{fus}}$  represents the melting point of the solid.

$$\Delta H_{\text{fus}}(298 \text{ K}) = \Delta H_{\text{fus}}(T_{\text{fus}}) + 54.4(298 - T_{\text{fus}}); \text{ J/mole} \quad (12)$$

Another approximate method that has been used to estimate the heat capacity difference between solids and liquids is Kopp's law [11b, 13]. Kopp's law treatment assumes additivity of atomic properties. Values for the following atoms in solids have been assigned: 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/(mole K); values in parenthesis are for liquids. Heat capacity differences between condensed phases can easily be calculated. In a modified version of this law, each atom in the molecule is assumed to contribute 8.3 J/(mole K) to the total heat capacity difference between liquid and solid [11b].

The heat capacities of 117 organic solids were used to test the accuracy of these two methods. Experimental heat capacities of these solids at 298 K were obtained from the compendium by Domalski and Hearing [6], and the heat capacities of the liquid state at 298 K for these compounds, not generally available, were estimated by using the group additivity tables developed [2].

Application of Kopp's law or the modified version to this group of 117 solids revealed the approximate nature of this estimation. Heat capacity differences between the liquid and solid at 298 K,  $\Delta C_p(\text{lc})$ , were generally overestimated by approximately 250% and 300% by Kopp's law and the modified version, respectively. Estimates using Eq. (10) were considerably better. The results shown in Fig. 8 illustrate the distribution in  $\Delta C_p(\text{lc})$  values obtained. The distribution interval (86 J) was chosen to represent the combined uncertainty of calculated liquid (20 J/(mole K)) and experimental solid heat capacities (23 J/mole). The average of the 117  $\Delta C_p(\text{lc})$  values was 84.4 and the standard deviation was 56.7 J/(mole K). Only minor improvements were achieved by correlating  $\Delta C_p(\text{lc})$  to calculated  $C_p(\text{c})$  values ( $\Delta C_p(\text{lc}) + 0.135 C_p(\text{c}) + 40.7$ ; standard devia-

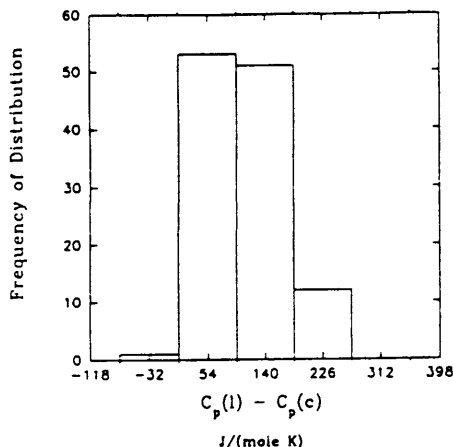


Fig. 8. The distribution of  $C_p(l) - C_p(c)$  of 114 solids;  $C_p(l)$  values are calculated from group additivity tables, and  $C_p(c)$  are experimental values.

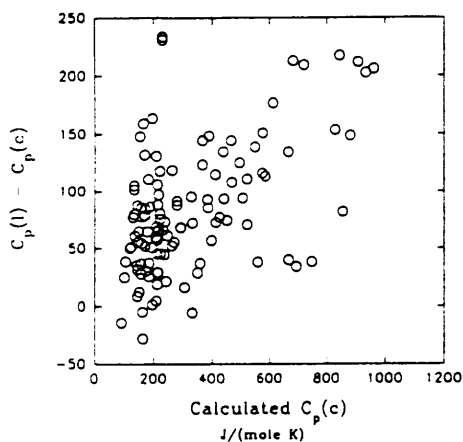


Fig. 9. Attempts of correlating  $C_p(l) - C_p(c)$  to calculated  $C_p(c)$  values.

tion, 49.4; correlation coefficient, 0.504) as shown in Fig. 9. The lack of success can be attributed to magnitude of the combined error, which is as large as the  $\Delta C_p(lc)$  term.

The reader should be cautious in using Eq. (12). Correction of the enthalpy of fusion of benzyl methyl sulfone to 298 K provides an example of the approximate nature of this correction and the hazards associated with extrapolations over a large temperature range. An enthalpy of fusion of 25.1 kJ/mole measured at the melting point (400 K), was corrected to 8.8 kJ/mole at 298 K by using this relationship [17]. Accordingly, at approximately 140 K, the fusion enthalpy of this material is predicted to vanish.

## SUMMARY

Vaporization enthalpies can be corrected to a standard state by using Sidgwick's equation (Eq. (8)). This relationship works best for liquids (standard error 32.2 J/(mole K)) and less so for solids (standard error 71 J/(mole K)). We have shown that improvement can be realized by using Eq. (9) and calculating the heat capacity of the liquid phase by using group values recently reported [2] (standard error for liquids, 15; solids, 25 J/mole).

Sublimation enthalpies can be corrected to the standard state by using Eq. (10) (standard error 45.7 J/(mole K)). This relationship generally underestimates the correction. In the text, we document that some improvement can be achieved by using Eq. (11) and calculating the heat capacity of the solid by using group additivity tables [8] (standard error 33 J/(mole K)).

The corrections of fusion enthalpies to a standard state using Eq. (12) should be used with great caution. Our results suggest that the corrections for many compounds are small, and in many cases the experimental uncertainty is as large as the effect. Ignoring the heat capacity corrections may result in a smaller error than the error introduced by using Eq. (12).

## ACKNOWLEDGMENTS

We would like to thank the IRQ fund of the University of Missouri-St. Louis for partial support of this work.

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