New Methods for Estimating the Heats of Formation, Heat Capacities, and Entropies of Liquids and Gases

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Using group additivity values to estimate $\Delta_{vap}H°(298)$ and the Kistiakowsky equation to estimate both $\Delta_{vap}S°(T_b)$ and $\Delta_{vap}H°(T_b)$ at the boiling point (T_b), it is shown how an average value of $\Delta_{vap}C_p°$ can be obtained which can then be used to calculate values of $\Delta_{vap}S°(298)$. This latter can then be used in conjunction with $S°(g,298)$ to calculate $S°(l,298)$. Alternatively, where values of $S°(l,298)$ are available but not $S°(g,298)$ the latter can be calculated. The method applies to regular liquids, even those with relatively large dipoles but not to H-bonded liquids. The accuracy of estimated values of $S°(l,298)$ are 0.45 ± 0.16 cal/(mol K) with a maximum deviation of 1.0 cal/(mol K) for an assortment of 14 selected compounds and 0.3 ± 0.12 for another 17 liquids for which groups are not available but $\Delta_{vap}H°(298)$ and $\Delta_{vap}S°(298)$ are. Here the largest deviation is 1.9 cal/(mol K). Calculated values of $C_p°(l,298)$ are much less accurate, ±3 cal/(mol K) with a maximum deviation of 9.0 cal/(mol K). It is also shown that the best average value of $C_p°$ to use in calculating changes in $\Delta H°$ and $\Delta S°$ in a specified temperature interval, T_1 to T_2, is the arithmetic mean of the initial and final values, $[C_p°(T_1) + C_p°(T_2)]/2$. Changes are recommended in some of the group values for calculating $\Delta_{vap}H°(298)$ and also in the group $O-(C)_2$ for calculating gas-phase entropies of ethers and for $N-(C)_2(H)$ for calculating entropies of secondary amines.

Introduction

Group additivity provides great facility in estimating the thermochemistry of gas-phase reactions for species whose thermochemistry has not been measured.[1,2] To have equal facility in dealing with the much larger realm of condensed phase reactions it is important to have methods for evaluating the relevant thermochemistry of species in the liquid state. A major step in this direction was taken by Ducros and co-workers[3−6] who showed that group additivity could be used to estimate heats of vaporization of organic and metal organic compounds at 298 K with good precision. This made possible the evaluation of $\Delta_fH°_{298}(l)$ for those compounds for which gas-phase group values were available. One method for doing this has been described by Benson and Cohen.[1] In the present paper, we will describe another method whereby $S°(l,298)$ can be estimated from gas-phase data on $S°(g,T_b)$ and the Kistiakowsky equation[7] for the relation between the entropy of vaporization at the boiling point and the boiling point. It is an improvement on the Trouton relation that $\Delta S°_{vap}(T_b) = 21$ eu at the boiling point (1 eu = 1 cal/(mol K)):

$$\Delta_{vap}S(T_b) = \frac{\Delta_{vap}H(T_b)}{T_b} = 8.75 + R \ln T_b \qquad (1)$$

To eliminate the apparent dependence of the logarithmic term on units we will rewrite the Kistiakowsky equation referenced to 298 K:

$$\Delta_{vap}S(T_b) = \frac{\Delta_{vap}H(T_b)}{T_b} = 20.06 + R \ln\left(\frac{T_b}{298\ \mathrm{K}}\right) \qquad (2)$$

To apply this equation to obtain both $\Delta_{vap}H(T_b)$ and $\Delta_{vap}S(T_b)$ we need only know T_b. For any given substance this can usually be obtained from literature or else can be estimated with good accuracy from a method described by Joback,[8]

$$T_b = 198 + \sum \Delta T_{bi} \qquad (3)$$

where ΔT_{bi} is the ith group increment in the species for which T_b is to be estimated. The method has a mean absolute error of 13 K. The errors are much smaller if we exclude structured liquids such as water and alcohols.[13] These latter also show gross deviations from Trouton's rule and the Kistiakowsky equation.

Heat of Formation and Entropy of Liquids at Their Boiling Points

The Kistiakowsky equation provides a method of estimating the entropy and enthalpy of vaporization of nonstructured liquids at their boiling points. Where appropriate groups and/or direct data are known for $S°(g,T_b)$ and $\Delta_fH°(g,T_b)$ both heats of formation and absolute entropies can be estimated at the boiling point for the liquids.

From thermodynamics we can write the general equation for the change in entropy with temperature at constant pressure. Since this can be done for both gas and liquid phases, we can also write for the change of entropy of vaporization

$$\Delta_{vap}S°(T_b) = \Delta_{vap}S°(298) + \int_{298}^{T_b} \frac{\Delta_{vap}C_p°}{T}\,dT \qquad (4)$$

$$= \Delta_{vap}S°(298) + \langle\Delta_{vap}C_p°\rangle \ln\left(\frac{T_b}{298}\right) \qquad (5)$$

where $\langle\Delta_{vap}C_p°\rangle$ is the suitably taken average of $\Delta_{vap}C_p$ over

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TABLE 1: Heats of Vaporization at 298 K at T_b and $\langle\Delta_{vap}C_p^\circ\rangle$

compound	bp (K)[a]	$\Delta_{vap}H^\circ(298)$[b]	$\Delta_{vap}H^\circ$(bp)[c]	$-\langle\Delta_{vap}C_p^\circ\rangle$[d]
n-C_5H_{12}	309	6.30	6.24	5.4
n-C_6H_{14}	342	7.50	6.95	12.5
n-$C_{10}H_{22}$	447	12.20	9.34	19.2
cyclohexane	354	7.80	7.22	10.3
1,3,5-trimethylbenzene	438	11.4	9.1	16.4
diphenylmethane	537	16.4	11.4	18.9
diethyl ether	308	6.3	6.2	10
di-*n*-propyl ether	364	8.6	7.45	17.4
n-butyl methyl ether	344	7.6	7.00	13.0
diethyl ketone	375	9.22	7.69	19.9
tert-butyl mercaptan	337	7.37	6.84	13.5
1,2-dichloroethane	357	8.52	7.28	21.2
1,2-dibromoethane	404.5	10.2	8.36	17.3
bromobenzene	429	10.7	8.9	11.4

[a] Values from: *CRC Handbook of Chemistry and Physics*, 72nd ed.; CRC Press: Boca Raton, FL, 1987. [b] Calculated from groups (kcal/mol). [c] Calculated from the Kistiakowsky eq 2. [d] Calculated from eq 9 (cal/(mol K)).

the temperature interval T_b-298. Note that since the molar heat capacities of liquids are always greater than that of their vapors, $\Delta_{vap}C_p$ will always be negative. Since the Kistiakowsky equation gives us the value of $\Delta_{vap}S^\circ(T_b)$, eq 5 will give us the desired value of $\Delta_{vap}S^\circ(298)$ if we know $\langle\Delta_{vap}C_p^\circ\rangle$.

We can use the Kistiakowsky equation to obtain $\Delta_{vap}H^\circ(T_b)$ and group additivity to obtain $\Delta_{vap}H^\circ(298)$. Again from thermodynamics we can write a relation similar to eq 4 to relate them:

$$\Delta_{vap}H^\circ(T_b) = \Delta_{vap}H^\circ(298) + \int_{298}^{T_b}\Delta_{vap}C_p^\circ\,dT \quad (6)$$

$$= \Delta_{vap}H^\circ(298) + \langle\langle\Delta_{vap}C_p^\circ\rangle\rangle(T_b - 298) \quad (7)$$

Note again that since $\Delta_{vap}C_p^\circ$ is negative $\Delta_{vap}H^\circ$ will decrease with increasing temperature. $\langle\langle\Delta_{vap}C_p^\circ\rangle\rangle$ and $\langle\Delta_{vap}C_p^\circ\rangle$ represent different averages over the temperature interval T_b-298. If for the moment we ignore this difference and equate them,

$$\langle\Delta_{vap}C_p^\circ\rangle \approx \langle\langle\Delta_{vap}C_p^\circ\rangle\rangle \quad (8)$$

then we can use eq 7 to obtain $\langle\langle\Delta_{vap}C_p\rangle\rangle$ and so $\langle\Delta_{vap}C_p\rangle$:

$$\langle\langle\Delta_{vap}C_p^\circ\rangle\rangle = \frac{\Delta_{vap}H^\circ(T_b) - \Delta_{vap}H^\circ(298)}{T_b - 298} \quad (9)$$

and substituting this value into eq 6 in place of $\langle\langle\Delta_{vap}C_p^\circ\rangle\rangle$ permits us to calculate $\Delta_{vap}S^\circ(298)$ from $\Delta_{vap}S^\circ(T_b)$.

$$\Delta_{vap}S^\circ(T_b) - \Delta_{vap}S^\circ(298) = \frac{[\Delta_{vap}H^\circ(T_b) - \Delta_{vap}H^\circ(298)]}{T_b - 298}\ln\left(\frac{T_b}{298}\right) \quad (10)$$

In Table 1 are presented relevant data for a number of organic, regular liquids. The values of $\Delta_{vap}H^\circ(298)$ are calculated from group additivity[6−9] using a modified choice of group values as will be discussed later, while values of $\langle\Delta_{vap}C_p^\circ\rangle$ are calculated with the use of eq 9.

Table 2 presents for these same liquids their gas-phase entropies at 298 K calculated by group additivity using the values of ref 10; their entropies of vaporization at 298 K using eq 10 and from these $S^\circ(l,298)$. The last column of Table 2 shows experimental values of $S^\circ(l,298)$[11] which can be compared with the calculated values shown in column 4.

Table 3 contains for these same compounds the values of C_p°(g,298) calculated by group additivity using the increments of ref 10 and the values of $C_p^\circ(l,298)$ calculated from these values and the calculated values of $\langle\Delta_{vap}C_p^\circ\rangle$ from Table 1. The last column lists the experimental values[11] of $C_p^\circ(l,298)$ for comparison.

Table 4 contains some of the group additivity values of Ducros et al.[3−5] for estimating $\Delta_{vap}H^\circ(298)$ for the compound in Table 1 together with the modified values selected by the author and used here.

In Table 5 are given data for 17 compounds for which groups are not available. These are taken from the compilations of ref 15 labeled by an (S) and ref 16 labeled by a (J). For these compounds we use the reported values of $\Delta_{vap}H^\circ(298)$ instead of trying to estimate them from groups.

Discussion

Some time ago the author was able to derive a theoretical relation between $\Delta_{vap}C_p^\circ$ and the temperature coefficient of the heat of vaporization[12] which suggested that $\Delta_{vap}C_p^\circ$ would have values at 298 K around 12 cal/(mol K). Subsequently, Shaw[17] showed that for an astonishingly large and diverse group of liquids an average value would be 12 ± 3 cal/(mol K). He also calculated tables of group additivity values which were very accurate in estimating values of $C_p^\circ(l,298)$ for a large number of liquids. They suffer from the same limitations as group additivity, namely, an incomplete database.

The calculation of $\langle\Delta_{vap}C_p^\circ\rangle$ presented here depends on a relatively small difference in estimated $\Delta_{vap}H^\circ(298)$ and an also estimated $\Delta_{vap}H^\circ(T_b)$. Literature values of $\Delta_{vap}H^\circ(298)$ are generally extrapolated from measured values and are probably not more accurate than 0.1−0.2 kcal/mol. Thus, when $\Delta\Delta_{vap}H^\circ \le 0.5$ kcal/mol the uncertainty may be as high as 30% and 15% for $\Delta\Delta_{vap}H^\circ \le 1.0$ kcal/mol. This is reflected in the values of $\langle\Delta_{vap}C_p^\circ\rangle$ shown in Table 1. They tend to be low for smaller values of $\Delta\Delta_{vap}H^\circ$ as in the cases of *n*-pentane, diethyl ether, and cyclohexane. In these cases, the boiling points are close to 298 so that the large uncertainty in $\langle\Delta_{vap}C_p^\circ\rangle$ introduces a much smaller uncertainty in the estimated value of $S^\circ(l,298)$. Equation 5 shows that this result is due to the very small values of ln(T_b/298) when T_b is not very different from 298. This is the case for about half of the liquids used and for half of the groups it will be seen (Table 2) that their values of $\Delta_{vap}S^\circ(T_b)$ are not very different from the Trouton value at 300 K of 20.4 cal/(mol K).

The sensitivity of eq 10 for calculating $\Delta_{vap}S^\circ(298)$ to the magnitude of (T_b-298) can be examined numerically by expanding ln(T_b/298) in a power series. First making use of the identity we write

$$\frac{T_b}{298} = \frac{T_b}{T_b - \Delta T} = \left(1 - \frac{\Delta T}{T_b}\right)^{-1} \quad (11)$$

where $\Delta T = T_b - 298$.

Then

$$\ln(T_b/298) = -\ln\left(1 - \frac{\Delta T}{T_b}\right) = \frac{\Delta T}{T_b} + \frac{1}{3}\left(\frac{\Delta T}{T_b}\right)^2 + \frac{1}{3}\left(\frac{\Delta T}{T_b}\right)^3 + \ldots \quad (12)$$

and substituting the first two terms of this series into eq 10, we find

TABLE 2: Calculated and Experimental Values of $S°(l, 298)$

compound	$S°(g,298)^a$	$\Delta_{vap}S°(298)^b$	$S°(l,298)$	$S°(l,298)^d$exp
n-C_5H_{12}	83.3	20.4	62.9	62.8
n-C_6H_{14}	92.6	22.1	70.5	70.8
n-$C_{10}H_{22}$	130.4	28.2	101.7	101.8
cyclohexane	71.7	22.2	49.5	48.8
1,3,5-trimethylbenzene	92.5	27.1	65.4	65.4
diphenyl methane	105.0	32.3	72.7	72.1
diethyl ether	83.3 [81.8]^c	20.4	62.9 [61.4]^c	60.4
di-*n*-propyl ether	102.1 [100.6]^c	23.9	78.2 [76.7]^c	77.4
n-butyl methyl ether	93.7 [92.2]^c	22.2	71.5 [70.0]^c	70.6
diethyl ketone	89.2	25.1	64.1	63.6
tert-butyl mercaptan	80.7	22.0	58.7	58.9
1,2-dichloroethane	74.2	24.2	50.0	49.8
1,2-dibromomethane	80.2	26.0	54.2 [52.7]^e	53.4
bromobenzene	77.8	25.0	52.8 [51.3.]^e	52.4

^{a} Calculated using group additivity.[10] All values in units of cal/(mol K). ^{b} Calculated from eq 5 using $\langle\Delta_{vap}C_p\rangle$ from Table 1. ^{c} Values calculated with the change in the group value of $S°(g,298)[O-(C)_2]$ from 8.7[14] to 7.2. ^{d} Data from ref 11. ^{e} Calculated with reassigned groups in Table 4.

TABLE 3: Estimated and Experimental Values of $C_p°(l,298)$ and $C_p°(g,298)$

compound	$C_p°(g,298)^a$	$C_p°(l,298)^b$	$C_p°(l,298)$ exp^c
n-C_5H_{12}	28.9	40.9	40.3
n-C_6H_{14}	34.4	46.9	46.4
n-$C_{10}H_{22}$	56.4	75.6	75.2
cyclohexane	27.2	41.8 (39.2)^d	37.4
1,3,5 trimethylbenzene	36.3	52.7 (48.3)^d	50.0
diphenyl methane	43.5	62.4	66.9
diethyl ether	25.8	35.8 (37.8)^d	41.2
di-*n*-propyl ether	36.8	54.2	53.0
n-butyl methyl ether	31.8	44.8	46.1
diethyl ketone	30.4	50.3 (42.4)^d	45.6
tert-butyl mercaptan	29.1	42.6 (41.1)^d	41.8
1,2-dichlorethane	17.8	39.0 (29.8)^d	30.8
1,2-dibromomethane	18.2	35.4 (30.2)^d	30.8
bromobenzene	24.0	35.4 (36.0)^d	36.1

^{a} Values calculated using group additivity increments from ref 10. ^{b} Values calculated using $\langle\Delta_{vap}C_p\rangle$ from Table 1 and $C_p°(g,298)$ of column 2 of this table. ^{c} Experimental values taken from ref 11. ^{d} Value in parentheses calculated using $\Delta_{vap}C_p°(298) = 12$ cal/(mol K).

$$\Delta_{vap}S°(T_b) - \Delta_{vap}S°(298) = \left[\frac{\Delta_{vap}H°(T_b) - \Delta_{vap}H°(298)}{T_b}\right]\left[1 + \frac{\Delta T}{2T_b}\right] \quad (13)$$

For $\Delta T = 50$ K, $T_b = 348$ K and the term $\Delta T/2T_b = 0.07$ so that omitting it completely in eq 13 would produce only a 7% error in our calculation of the entropy change.

The most important result of the present work is the excellent agreement of the calculated and observed values of $S°(l,198)$ shown in Table 2 (columns 4 and 5). For the 14 selected compounds the average absolute deviation (AAD) is 0.55 cal/(mol K) and the standard deviation is 0.27 within the accuracy of measurement. The maximum deviation is 2.5 cal/(mol K) for diethyl ether.

When the original estimation of group additivity values were made[14] some 30 years ago gas-phase entropies were known for only one ether, dimethyl ether. This has not changed since. The group value $O-(C)_2$ was therefore taken from the entropy for dimethyl ether. If we now include in our database the three ethers presented here as providing a larger set and the optimum value for all four values used, then we would revise the group value, $\Delta S°[O-(C)_2]$ from 8.7 to 7.2 eu. This would give the values shown in brackets in column 4 in Table 2. The AAD is now 0.45 cal/(mol K) with a standard deviation of 0.16 cal/(mol K). The maximum deviation is then 1.0 cal/(mol K).

This new group value for $DS[O-(C)_2]$ can be compared with the more broadly based group entropy value for $C-(C)_2(H)_2 = 9.42$ eu and the less accurate $N-(C)_2(H) = 8.94$ eu. A decrease of $O-(C)_2$ seems reasonable. Note that the $N-(C)_2(H)$ group is also based on a single compound $HN(CH_3)_2$.

TABLE 4: Group Additivity Increments for Estimating $\Delta_{vap}H°(298)$ kcal/mol

group	Ducros value	modified value
$C-(C)(H)_3$[(a)]	1.35	1.50
$C-(C)_2(H)_2$	1.19	1.15
$C-(C)_3(H)$	0.72	0.40
$C-(C)_4$	0.0	−0.40
cyclopentane	0.66	1.00
cyclohexane	0.45	0.90
ortho	0.35	0.35
meta	0.12	0.0
C_B-H	1.35	1.35
C_B-C	0.98	0.80
$C-(C_B)(C)(H)_2$	1.02	1.02
$C-(C_B)(C)_2(H)$	0.23	
$C_d-(H)_2$	1.15	
$C_d-(H)(C)$	1.22	
$C_d-(C)_2$	1.15	
allenic C_d	1.84	
$C_d-(C_d)(H)$	1.49	
$C_d-(C_d)(C)$	1.27	
$C-(C_d)(C)(H)_2$	1.21	
$C-(C_d)(C)_2(H)$	0.62	
$C-(C_d)(C)_3$	0	
$C-(C_d)_2(H)_2$		1.23
$C-(C_B)_2(H)_2$		0.85
$C-(C)(O)(H)_2$	1.10	1.00
$O-(C)_2$	1.60	1.30
$C-(C)_2(O)(H)$	0.70	
$C-(C)_3(O)$		0.20
$C-(C)(H)_2(Br)$	$4.6\,2 + g_1$[b]	5.10
$C-(C)(H)_2(Cl)$	$3.95 + g_2$[b]	4.26

^{a} The values for all methyl groups are assigned: $C-(H)_3(X) = 1.35$ (1.50 MV). ^{b} The terms g_1 and g_2 are very complex corrections (involving numbers of nearest and next nearest neighbors) to the numerical values shown. The modified values require no corrections.

The insertion of an $O-(C)_2$ group into propane in place of the $C-(C)_2(H)_2$ [methylene group] is accompanied by the loss of 2H atoms. In addition, there are small changes in the external moments of inertia which amount to about −0.5 cal/mol K. The four bends associated with the 2H contribute about −1.0, thus further supporting the net loss in $S°_{298}$ of 1.5 cal/(mol K) or more suggested above. Using the accurate 9.42 for $C-(C)_2(H)_2$ and the improved 7.2 for $O-(C)_2$ obtained here, we can interpolate a revision of $N-(C)_2(H)$ to 8.3 eu.

Perhaps most surprising are the agreements of the estimates of $\Delta_{vap}S°(298)$ with experimental values shown in Table 5. For these 19 compounds, some of them with very large dipole

TABLE 5: Comparison of Calculated and Observed Values of $\Delta_{vap}S°(298)$ for Compounds for Which Groups Are Not Available

compound[a]	T_b (K)[b]	$\Delta_{vap}H°(298)$	$\Delta_{vap}H°(T_b)$[c]	$-\langle\Delta_{vap}C_p°\rangle$[d]	$\Delta_{vap}S°(T_b)$[c]	$\Delta_{vap}S°(298)$[e]	$\Delta_{vap}S°(298)$[f]
CCl_4(S)	349	7.75	7.11	12.5	20.37	22.4	22.5
$CHCl_3$(S)	335	7.4	6.80	16.2	20.29	22.2	22.2
CH_2Cl_2(S)	313	6.9	6.31	39	20.16	22.1	21.9
CH_3I(S)	316	6.63	6.38	14	20.18	21.0	21.8
CH_3NO_2(S)	374	9.2	7.67	20.1	20.51	24.7	24.7
CS_2(S)	319	6.6	6.46	12	20.20	21.0	20.7
BBr_3(J)	364	8.2	7.5	10.6	20.46	22.6	22.8
B_5H_9(J)	335	7.3	6.8	13.5	20.29	21.9	21.9
Br_2(J)	333	7.39	6.75	18.3	20.28	22.3	22.4
$TiCl_4$(J)	409	10.2	9.3	8.1	20.69	23.3	24.5
WF_6(J)	290	6.4	6.4	0	20.01	20.0	21.9
CH_2CCl_2(S)	310	6.3	6.24	5	20.14	20.6	20.7
CH_3CN(S)	355	8.30	7.25	18.4	20.41	23.6	22.4
C_2H_5CN(S)	370	8.6	7.6	13.9	20.49	23.5	23.3
Ethyl Acetate(S)	350	8.6	7.1	28.8	20.38	25.4	24.7
Pyrrolidine(S)	362	9.0	7.4	25	20.45	25.0	25.2
Iodobenzene(S)	462	11.9	9.7	13.4	20.94	26.8	26.5

[a] Data labeled (S) are taken from reference 15; (J) from ref 16. [b] Same source as Table 1. [c] Calculated from eq 2. [d] Calculated from eq 9. [e] Calculated from eq 10. [f] Taken from measured data of (S) or (J).

moments, the deviations are AAD = 0.3 ± 0.12 cal/(mol K). The largest deviations are 1.2 cal/(mol K) for Ti Cl_4 and CH_2-CCl_2 and 1.9 cal/(mol K) for WF_6. The estimated values of $\langle\Delta_{vap}C_p°\rangle$ for a number of the compounds such as CH_2Cl_2, 39 cal/(mol K); CH_2CCl_2, 5 cal/(mol K); and WF_6, 0 cal/(mol K) must be considered unreliable and a result of their very low boiling points. Changing them by factors of 2 or using a mean value of 12 cal/(mol K) for $\langle\Delta_{vap}C_p°\rangle$ would have very little effect on the calculated values of $\langle\Delta_{vap}S°(298)$ in Table 5. [See prior discussion on the insensitivity of $\langle\Delta_{vap}S°(298)$ to $\langle\Delta_{vap}C_p°\rangle$].

The values of $C_p°(l,298)$ calculated using values of $C_p°$(g,298) from group additivity[10] and $\langle\Delta_{vap}C_p°\rangle$ from Table 1 are not in nearly so good agreement with the experimental values shown in Table 3. Here, the mean absolute deviation is 3.0 cal/(mol K) with a maximum deviation of 9.0 cal/(mol K). The use of the empirical rule that $\Delta_{vap}C_p°(298) = -12.0$ cal/(mol K) does only marginally better than $\langle\Delta_{vap}C_p°\rangle$ with a mean absolute deviation of 2.7 cal/(mol K). However, the maximum deviation changes to 11.4 cal/(mol K). It is not likely that this situation will change until there is a greater database for the use of group additivity for estimating either $C_p°(l,298)$ or $C_p°$(g,298).

A last point concerns the different averages of $\Delta_{vap}C_p°$ from eq 5 for $\Delta_{vap}S_p°$ and eq 6 for $\Delta_{vap}H_p°$. The author has shown that if $C_p°$ can be written as a quadratic function of temperature, then the average value of $\langle C_p°\rangle$ is very close to the arithmetic mean of the lowest and highest temperature of the interval chosen (ref 10, p 21).

$$\langle C_p°\rangle = \frac{C_p°(T_i) + C_p°(T_f)}{2} \tag{14}$$

When $\langle C_p°\rangle$ is a linear function of temperature, eq 14 is exactly true.

It is now of interest to show that this is also true for the use of eq 5. Rewriting eq 4:

$$\Delta_{vap}S°(T_b) - \Delta_{vap}S°(298) = \int_{298}^{T_b} \Delta_{vap}C_p° \, d(\ln T) \tag{15}$$

Integrating by parts

$$= [\Delta_{vap}C_p°]\ln T\Big|_{298}^{T_b} - \int_{298}^{T_b} (\ln T)\, d(\Delta_{vap}C_p°) \tag{16}$$

Let us note that over any expected temperature interval, let us say for an example, 300−600 K, ln T changes very little in absolute value, namely from 5.70 to 6.40, about 11%. If we write the integral in eq 16 as

$$\int_{298}^{T_b}(\ln T)\, d(\Delta_{vap}C_p°) = \langle \ln T\rangle \int_{298}^{T_b} d(\Delta_{vap}C_p°) \tag{17}$$

$$= \frac{(\ln T_b + \ln 298)}{2}[\Delta_{vap}C_p°]\Big|_{298}^{T_b} \tag{18}$$

$$\frac{(\ln T_b + \ln 298)}{2}(\Delta_{vap}C_p°(T_b) - \Delta_{vap}C_p°(298)) \tag{19}$$

and combine it with the term between limits in eq 16 we find

$$\Delta_{vap}S_p°(T_b) - \Delta_{vap}S_p°(298) = \left[\frac{\Delta_{vap}C_p°(T_b) - \Delta_{vap}C_p°(298)\ln 298}{2}\right] + \left[\frac{\Delta_{vap}C_p°(298)\ln T_b - \Delta_{vap}C_p°(T_b)\ln 298}{2}\right] \tag{20}$$

$$= \left[\frac{\Delta_{vap}C_p°(T_b) + \Delta_{vap}C_p°(298)}{2}\right]\ln(T_b/298) \tag{21}$$

$$= \langle\Delta_{vap}C_p°\rangle \ln(T_b/298) \tag{22}$$

But this is now precisely the result we obtained in eq 14 for $\langle C_p°\rangle$ over an arbitrary temperature interval. This result ensures us that instead of taking a precise integrated average as called for in the integrals in eqs 5 and 7, we can use an average value of $\Delta_{vap}C_p°$ which is the arithmetic mean of the values at the end points.

If we were just looking at the value of $C_p°$ for a single compound over an arbitrary temperature interval, the quadratic term might be significant so that the average in eq 14 is not exact. However, the usual use of $\langle C_p°\rangle$ is generally for a chemical equation where $\Delta C_p°$ for the overall reaction is much less than for any single molecule involved in the equation, and in such cases the linear temperature dependence of $\Delta C_p°$ is quite good.

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