Sublimation Vapor Pressures as Evaluated by Correlation-Gas Chromatography

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Vapor pressures of the liquid phase obtained by correlation-gas chromatography are used in conjunction with experimental fusion enthalpies to calculate sublimation vapor pressures of a number of compounds including n-alkanes, polyaromatic hydrocarbons, aromatic heterocyclic compounds, and polycyclic hydrocarbons. Vapor pressures at the fusion temperature, T_{fus}, calculated from vapor pressure equations generated by this technique and obtained by extrapolation, are used to evaluate vaporization enthalpies at T_{fus}. The sublimation enthalpy at T_{fus} is obtained from the sum of the experimental fusion enthalpy and vaporization enthalpy. The vapor pressure at T_{fus}, used as an approximation of the triple-point vapor pressure, combined with the sublimation enthalpy and a heat capacity adjustment is used to calculate sublimation vapor pressures as a function of temperature. Calculated sublimation vapor pressures extrapolated to near ambient temperatures compare with experimental values to within a factor of three.

Introduction

Correlation-gas chromatography is a useful technique for the reliable evaluation of both vaporization enthalpies and liquid-phase vapor pressures of materials that are either solid or liquid at the temperatures of interest.[1−15] Vaporization enthalpies and vapor pressures are not measured directly but are evaluated in relation to established values by correlation. For compounds that are crystalline solids at room temperature and above, the vapor pressures obtained model the expected vapor pressure of the supercooled liquid and have been referred to as hypothetical vapor pressures. These vapor pressures are also useful. Large polyaromatic hydrocarbons, for example, are relatively nonvolatile and are often found adsorbed on particulate matter. The partitioning between the adsorbed material and the vapor is frequently described empirically on the basis of the vapor pressure of the subcooled liquid.[10,16−19] Also of interest, however, is the corresponding vapor pressure of the crystalline solid. This article describes a protocol that can be used to evaluate the vapor pressure of the crystalline material by combining the vapor pressure equation of the liquid obtained by correlation-gas chromatography with a fusion enthalpy measurement obtained by calorimetry. This protocol does not provide sublimation vapor pressure values as accurate as those measured directly. However, it serves quite adequately if a vapor pressure within a factor of two or three of the experimental value will or must suffice.

Methodology

Vaporization enthalpies are evaluated in a series of isothermal runs by plotting the time that an analyte spends on the column, t_a, in the form of $\ln(t_a/t_o)$ against reciprocal temperature. The slope of the line measures the enthalpy of transfer of the solute from the stationary phase to the gas phase, $\Delta_{\text{sln}}{}^{\text{g}}H_{\text{m}}(T_{\text{m}})$, divided by the gas constant. The term t_a refers to the adjusted retention time and is obtained as the difference between the experimental retention time of an analyte and that of a nonretained reference such as methane; t_o represents the reference time, 1 min. Since the adjusted retention time is inversely proportional to the vapor pressure of the analyte off of the column, this plot is analogous to a Clausius−Clapeyron treatment of vapor pressure. The enthalpy of transfer calculated from the slope, $\Delta_{\text{sln}}{}^{\text{g}}H_{\text{m}}(T_{\text{m}})$, is a sum of two terms, the vaporization enthalpy and the enthalpy of interaction of the solute with the column. It has been found to correlate linearly with the vaporization enthalpy of the analyte. Thus, if a series of analytes with known vaporization enthalpies are included in a mixture along with others, this linear correlation allows an evaluation of any additional analytes included in the mix whose vaporization enthalpies are unknown. The proper selection of standards is immensely important. In general, hydrocarbons, for example, serve as suitable standards for other hydrocarbons, and hydrocarbon derivatives serve similarly, provided the number and type of functional group remains constant. An exception to this rule has been found.[2] Whether a compound containing a particular functional group is a suitable standard should be determined empirically in separate experiments using analytes with known vaporization enthalpies.

Liquid vapor pressures can be evaluated in a similar manner. The adjusted gas chromatographic retention times for each analyte in the form $\ln(t_o/t_a)$ are also found to correlate linearly with $\ln(p/p_o)$ of a series of suitable liquid standards. Regardless of whether the analytes are solids or liquids, the correlation between $\ln(t_o/t_a)$ and $\ln(p/p_o)$ of the liquid standards as a function of temperature provides a measure of the vapor pressure of the liquid phase of each analyte. The vapor pressures of the target analytes are evaluated from each correlation equation as a function of temperature. Since vapor pressure is a sensitive function of temperature, the correlation between $\ln(t_o/t_a)$ (calculated from the slope and intercept of each analyte) and $\ln(p/p_o)$ of the liquid standards should be performed at regular temperature intervals over the desired temperature range. The correlation between $\ln(t_o/t_a)$ and $\ln(p/p_o)$ of the standards should remain linear, and the correlation coefficient should remain relatively unchanged ($r^2 > 0.98$; < 0.01 change in r^2) over the entire temperature range. The resulting values of $\ln(p/p_o)$ of the target molecules calculated from each correlation equation are generally fit to a polynomial. Over the typical pressure range

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Table 1. Constants of Equation 1 Evaluated by Correlation-Gas Chromatography, $p_o = 101325$ Pa[a]

		A	B	C	D
$C_3H_3N_3$	1,3,5-triazine	−257351031	2117318	−10229	17.168
$C_4H_4N_2$	pyrazine	−324948325	2615598	−11549	17.976
$C_8H_6N_2$	quinazoline	62950222	−1019158	−2388.44	8.073
C_8H_8	cubane[b]	23505091	−601478	−2091.0	7.31
$C_{10}H_8N_2$	2,2-dipyridine	81725946	−1192650	−2825.4	8.6
$C_{10}H_8N_2$	2,4-bipyridine	89785141	−1256837	−3110.7	8.95
$C_{10}H_8N_2$	4,4-dipyridine (anh)	87876825	−1240024	−3205.1	9.104
$C_{10}H_8N_2$	4-phenylpyrimidine	82739965	−1191247	−3078.9	8.993
$C_{10}H_{16}$	adamantane[b]	36493822	−738753.1	−1971.7	6.788
$C_{12}H_8N_2$	4,7-phenanthroline	123705710	−1579330	−3296.6	8.741
$C_{12}H_8N_2$	1,7-phenanthroline	121578810	−1558844	−3192.8	8.625
$C_{12}H_{18}$	hexamethylbenzene	85376172	−1283535	−2488.3	8.474
$C_{13}H_{10}$	fluorene	281912268	−3039484	2358.69	3.348
$C_{13}H_{11}N$	9-methylcarbazole	119137845	−1531860	−3317.9	8.855
$C_{13}H_{12}$	diphenylmethane	115104919	−1585090	−1317.6	7.085
$C_{14}H_{10}$	anthracene	95758558	−1413713	−3073.7	8.359
$C_{16}H_{10}$	pyrene	272098419	−3361297	2143.07	3.095
$C_{17}H_{12}$	2,3-benzofluorene	244120458	−3097766	780.11	4.616
$C_{18}H_{12}$	chrysene	248993159	−3249677	497.8	5.04
$C_{18}H_{12}$	1,2-benzanthracene	282250431	−3627106	1948.44	3.323
$C_{18}H_{12}$	triphenylene	268335766	−3471270	1311.11	4.051
$C_{18}H_{14}$	*p*-terphenyl	175908596	−2525730	−1277.4	7.319
$C_{19}H_{16}$	triphenylmethane	76236040	−1716465	−2378.2	7.648
$C_{20}H_{12}$	perylene	335699657	−4269274	2557.59	2.961
$C_{20}H_{12}$	benzo[a]pyrene	362132280	−4462435	3363.69	1.852
$C_{20}H_{12}$	benzo[e]pyrene	361778001	−4467131	3358.28	1.935
$C_{20}H_{12}$	benzo[k]fluoranthene	340115134	−4248262	2729.01	2.689
$C_{22}H_{14}$	1,2:5,6-dibenzanthracene	423491901	−5187595	4420.35	1.118
$C_{22}H_{14}$	1,2:3,4-dibenzanthracene	422327238	−5189597	4340.62	1.277
$C_{24}H_{18}$	1,3,5-triphenylbenzene	353704496	−4572620	2525.49	3.679
$C_{24}H_{18}$	*p*-quaterphenyl	375623111	−4787612	2943.2	3.038

[a] From refs 1, 2, 4, and 10. [b] Evaluated in this work using the data reported in ref 8 using over the temperature range where $T = (298.15$ to $440)$ K.

of interest, p/p_o at $T = 298.15$ K to the boiling temperature, we have found that fitting the data to a third-order polynomial, eq 1, reproduces liquid $\ln(p/p_o)$ values quite well with temperature.

$$\ln(p/p_o) = A(T/\mathrm{K})^{-3} + B(T/\mathrm{K})^{-2} + C(T/\mathrm{K})^{-1} + D \tag{1}$$

To evaluate the vapor pressure of a solid, both the sublimation enthalpy of the solid, $\Delta_{cr}{}^{g}H_m(T)$, and at least one vapor pressure value are necessary, as shown in eq 2. The sublimation enthalpy can be obtained by combining the experimental fusion enthalpy with the vaporization enthalpy ($\Delta_l{}^{g}H_m(T_{fus})$) evaluated at the fusion temperature (T_{fus}), shown in eq 3 by using eq 1. Since the fusion temperature and the triple-point temperature are closely related numerically, we have used the fusion temperature as an approximate triple-point temperature and the vapor pressure evaluated at this temperature as the pressure common to both solid and liquid. To account for the fact that the vapor pressures of the solid will be extrapolated as a function of temperature, and that sublimation enthalpy is also a function of temperature, a heat capacity adjustment has also been included, in eq 4. The heat capacity term, eq 5, has been evaluated empirically and has been successful in adjusting sublimation enthalpies with temperature.[20,21]

$$\ln(p_2/p_1) = -\Delta_{cr}^{g}H_m(T)/R[1/T_2 - 1/T_1] \tag{2}$$

$$\Delta_{cr}^{g}H_m(T_{fus}) = \Delta_{l}^{g}H_m(T_{fus}) + \Delta_{cr}^{l}H_m(T_{fus}) \tag{3}$$

$$\Delta_{cr}^{g}H_m(T) = \Delta_{l}^{g}H_m(T_{fus}) + \Delta_{cr}^{l}H_m(T_{fus}) + \Delta_{cr}^{g}C_p(T_{fus} - T) \tag{4}$$

$$\Delta_{cr}^{g}C_p = (0.75 + 0.15C_{p,cr}(298.15\ \mathrm{K})) \tag{5}$$

In eq 2, R refers to the gas constant, and $C_{p,cr}(298.15$ K) in eq 4 refers to the heat capacity of the solid at $T = 298.15$ K, which has been estimated using a group additivity approach.[22]

Table 2. Constants of Equation 1 Evaluated by Correlation-Gas Chromatography for Alkanes, $p_o = 101325$ Pa[a]

		A	B	C	
		K^3	K^2	K	D
$C_{21}H_{44}$	heneicosane	199890000	−2907500	−98.135	6.6591
$C_{22}H_{46}$	docosane	217130000	−3117600	110.72	6.5353
$C_{23}H_{48}$	tricosane	233860000	−3322000	310.77	6.4198
$C_{24}H_{50}$	tetracosane	250720000	−3528600	530.15	6.282
$C_{25}H_{52}$	pentacosane	267380000	−3730700	741.19	6.15
$C_{26}H_{54}$	hexacosane	282440000	−3919300	910.53	6.07
$C_{27}H_{56}$	heptacosane	300920000	−4125300	1198.8	5.811
$C_{28}H_{58}$	octacosane	313890000	−4312000	1279.4	5.884
$C_{29}H_{60}$	nonacosane	328710000	−4504300	1431.2	5.841
$C_{30}H_{62}$	triacontane	344040000	−4699800	1601.6	5.77
$C_{31}H_{64}$	hentriacontane	360370000	−4900200	1791.2	5.679
$C_{32}H_{66}$	dotriacontane	375240000	−5092100	1947.2	5.63
$C_{33}H_{68}$	tritriacontane	389830000	−5280900	2098	5.585
$C_{34}H_{70}$	tetratriacontane	404350000	−5467900	2249.5	5.537
$C_{35}H_{72}$	pentatriacontane	417460000	−5648000	2363.8	5.544
$C_{44}H_{90}$	tetratetracontane	550110000	−7346700	3778.6	5.117
$C_{46}H_{94}$	hexatetracontane	564510000	−7599200	3810.6	5.224
$C_{50}H_{102}$	pentacontane	613300000	−8260200	4268.3	5.143
$C_{54}H_{110}$	tetrapentacontane	509590000	−7716700	1772.4	7.41
$C_{60}H_{122}$	hexacontane	730610000	−9844800	5365.4	4.957

[a] From refs 5, 7, and 9.

All vaporization enthalpies and the vapor pressures at the fusion temperature were calculated using eq 1 where $p_o = 101.325$ kPa. Constants used with this equation are provided in Tables 1 and 2. All constants listed for the compounds in these two tables were generated by correlation-gas chromatography using other reliable literature vapor pressures as references.[1,2,4,5,10] The constants of eq 1 reported for adamantane and cubane in Table 1 are new and were calculated using existing data previously published over the temperature range $T = (298.15$ to $440)$ K at 20 K intervals. The data that included octane, naphthalene, undecane, and decane as

Table 3. Phase Change Properties of Various Compounds Used to Calculate Sublimation Vapor Pressures

		$\Delta_{cr}{}^{l}H_m(T_{fus})$ kJ·mol^{-1}	$T_{fus}{}^{a}$ K	$C_{p,cr}(298\ K)^{b}$ J·mol^{-1}·K^{-1}	$\Delta_l{}^{g}H_m(T_{fus})^{c}$ kJ·mol^{-1}	$\Delta_{cr}{}^{g}H_m(T_{fus})^{d}$ kJ·mol^{-1}
$C_3H_3N_3$	1,3,5-triazine	14.56	353	94.2	36.85	51.41
$C_4H_4N_2$	pyrazine	12.95	324.2	97.8	39.06	52.01
$C_8H_6N_2$	quinazoline[e]	16.95	364	149.8	57.45	74.40
C_8H_8	cubane[f]	8.70	405	93.6	38.53	47.23
$C_{10}H_8N_2$	2,2′-dipyridine	20.4	345.2	184.8	63.86	84.26
$C_{10}H_8N_2$	2,4′-bipyridine	17.4	322.8	184.8	69.14	86.54
$C_{10}H_8N_2$	4,4′-dipyridine (anh)	16.1	377.5	184.8	65.91	82.01
$C_{10}H_8N_2$	4-phenylpyrimidine	18.8	334.1	184.8	66.43	85.23
$C_{10}H_{16}$	adamantane[g]	13.8	543.2	194.4	36.35	50.15
$C_{12}H_8N_2$	4,7-phenanthrolene	18.2	350.3	202	77.26	95.46
$C_{12}H_8N_2$	1,7-phenanthrolene	21.8	445.5	202	69.47	91.27
$C_{12}H_{18}$	hexamethylbenzene[h]	20.59	438.4	270.5	58.32	78.90
$C_{13}H_{10}$	fluorene	19.58	387.9	198.6	63.98	83.56
$C_{13}H_{11}N$	9-methylcarbazole	17.15	362.5	211.7	75.27	92.42
$C_{13}H_{12}$	diphenylmethane	19.01	298.3	218.9	67.08	86.09
$C_{14}H_{10}$	anthracene	29.4	488.9	209	63.66	93.06
$C_{16}H_{10}$	pyrene	17.36	423.8	227.2	76.33	93.69
$C_{17}H_{12}$	2,3-benzofluorene	23.4	489.7	250.6	73.35	96.75
$C_{18}H_{12}$	chrysene	26.2	531.4	261	75.59	101.79
$C_{18}H_{12}$	1,2-benzanthracene	21.4	434.3	261	86.57	107.97
$C_{18}H_{12}$	triphenylene	24.74	471	261	81.53	106.27
$C_{18}H_{14}$	*p*-terphenyl	35.4	486	279	78.5	113.9
$C_{19}H_{16}$	triphenylmethane	20.7	367.2	297	83.47	104.17
$C_{20}H_{12}$	perylene	31.87	550.9	279.2	80.05	111.92
$C_{20}H_{12}$	benzo[a]pyrene[i]	17.3	454	279.2	91.71	109.01
$C_{20}H_{12}$	benzo[e]pyrene[j]	16.6	454	279.2	91.97	108.57
$C_{20}H_{12}$	benzo[k]fluoranthene	27.5	489.3	278.6	86.3	113.8
$C_{22}H_{14}$	1,2:5,6-dibenzanthracene	31.17	544.2	313	86.14	117.31
$C_{22}H_{14}$	1,2:3,4-dibenzanthracene	25.8	553.5	313	85.48	111.28
$C_{24}H_{18}$	1,3,5-triphenylbenzene	32.4	447	366	105.02	137.42
$C_{24}H_{18}$	*p*-quaterphenyl	57.6	586.7	388	84.04	141.6

[a] Fusion enthalpies and temperatures from references cited in 1, 2, 21, and 28 unless noted otherwise. [b] Estimated: ref 22. [c] Calculated using eq 1. [d] The sum of $\Delta_{cr}{}^{l}H_m(T_{fus})$ and $\Delta_l{}^{g}H_m(T_{fus})$. [e] Ref 46. [f] A transition [$\Delta_{cr}{}^{cr}H_m$(394 K) (5.94 kJ·mol^{-1})] has also been reported.[29] [g] Ref 30. [h] A transition [$\Delta_{cr}{}^{cr}H_m$(483 K) (1.84 kJ·mol^{-1})] has also been reported.[28] [i] A broad transition [$\Delta_{cr}{}^{cr}H_m$(390 K) (8.50 kJ·mol^{-1})] has also been reported.[32] [j] A broad transition [$\Delta_{cr}{}^{cr}H_m$(426 K) (2.50 kJ·mol^{-1}) has also been reported.[32]

Table 4. Phase Change Properties of Alkanes Used to Calculate Sublimation Vapor Pressures

		$\Delta_{cr}{}^{cr}H_m(T_t)$ kJ·mol^{-1}	$T_t{}^{a}$ K	$\Delta_{cr}{}^{l}H_m(T_{fus})$ kJ·mol^{-1}	$T_{fus}{}^{a}$ K	$C_p(cr)^{b}$ J·mol^{-1}·K^{-1}	$\Delta_l{}^{g}H_m(T_{fus})$ kJ·mol^{-1}	$\Delta_{cr}{}^{g}H_m(T_{fus})^{a}$ kJ·mol^{-1}
$C_{21}H_{44}$	heneicosane	16.6	304.4	47.7	313.2	584.3	104.4	152.1
$C_{22}H_{46}$	docosane	29.0	315.2	48.8	316.8	611.2	108.8	186.6
$C_{23}H_{48}$	tricosane	21.7	315.6	53.1	320.4	638.1	113.1	187.9
$C_{24}H_{50}$	tetracosane	31.7	320.7	54.4	323.6	665	117.3	203.4
$C_{25}H_{52}$	pentacosane	26.7	320.3	57.1	326.3	691.9	121.4	205.2
$C_{26}H_{54}$	hexacosane	33.8	326	69.0	329.2	718.8	125.5	228.3
$C_{27}H_{56}$	heptacosane	26.8	326.3	61.1	331.7	745.7	128.7	216.6
$C_{28}H_{58}$	octacosane	35.1	330.5	65.1	334.2	772.6	133.9	234.1
$C_{29}H_{60}$	nonacosane	30.8	330.8	68.2	336.2	799.5	138.4	237.4
$C_{30}H_{62}$	triacontane	37.0	332.2	68.3	338.2	826.4	142.8	248.1
$C_{31}H_{64}$	hentriacontane	36.6	336.5	73.3	341.1	853.3	146.8	256.7
$C_{32}H_{66}$	dotriacontane	40.8	337.2	75.8	342.5	880.2	151.4	268.0
$C_{33}H_{68}$	tritriacontane	37.9	340.9	79.5	344.3	907.1	155.7	273.1
$C_{34}H_{70}$	tetratriacontane	48.0	342.2	79.4	345.6	934	160.1	287.5
$C_{35}H_{72}$	pentatriacontane	41.1	344.2	86.3	347.7	960.9	164.5	291.8
$C_{44}H_{90}$	tetratetracontane	18.2	357.7	149.6	358.7	1203	202.7	370.5
$C_{46}H_{94}$	hexatetracontane			176.0	360.7	1473.4	210.6	386.6
$C_{50}H_{102}$	pentacontane			162.4	365.2	1601	226.1	388.5
$C_{54}H_{110}$	tetrapentacontane			177.2	368.1	1728.6	240.2	417.4
$C_{60}H_{122}$	hexacontane			193.2	372.4	1920	263.8	457.0

[a] Fusion enthalpies, transition enthalpies, and the corresponding temperatures from ref 23. [b] Estimated: ref 22.

standards were used.[8] All vaporization enthalpies at the mean temperature $T = T_{fus}$ were calculated using extrapolated vapor pressures generated over a 30 K range at $T = 5$ K intervals centered at the fusion temperature. Experimental fusion enthalpies, fusion temperatures, estimated heat capacities, and vaporization enthalpies evaluated at $T = T_{fus}$ are provided in Tables 3 and 4; the resulting sublimation enthalpies at T_{fus} are reported in last column.

Many of the n-alkanes listed in Table 4 and a few compounds in Table 3 as noted in the footnotes have additional solid−solid phase transitions occurring between $T = 298.15$ K and T_{fus}.[23] For these compounds, eqs 2 and 3 were used to evaluate the vapor pressure at the phase transition. Below this temperature, the total phase change enthalpy, $\Delta_{cr}{}^{g}H_m(T)_{tpce}$, in eq 6, was substituted for $\Delta_{cr}{}^{g}H_m(T)$ in eqs 2 and 4, and the vapor pressure, p_t, calculated at the phase transition temperature, T_t, was used

Table 5. Coefficients of a Second-Order Polynomial for Some Polycyclic Aromatic Hydrocarbons and Related Substances and a Comparison of Sublimation Vapor Pressures with Literature Values

				T	T	$p(T)_{\mathrm{calc}}$	$p(T/\mathrm{K})_{\mathrm{lit}}$	
	A'	B'	C'	K range	K	Pa	Pa	lit.
1,3,5-triazine	−172558	−5214.9	15.491	353 to 298	228.4	2.6	1.0	33
quinazoline	−256864	−7351.4	18.041	321 to 298	298.2	7.5	8.0	46
2,2′-dipyridine	−321989	−8285	19.097	345 to 298	298.2	0.46	na[a]	
2,4′-bipyridine	−315978	−8455.7	19.148	323 to 298	298.2	0.29	na[a]	
4,4′-dipyridine (anh)	−339518	−8102	17.392	378 to 298	298.2	0.13	na[a]	
4-phenylpyrimidine	−315452	−8372.9	19.211	334 to 298	298.2	0.41	na[a]	
4,7-phenanthrolene	−353817	−9481.7	19.289	350 to 298	298.2	$7 \cdot 10^{-3}$	na[a]	
1,7-phenanthrolene	−395301	−9328.4	17.919	446 to 298	298.2	$1.9 \cdot 10^{-3}$	na[a]	
cubane	−171490	−4841.8	11.825	394 to 262	298.2	177		
					262	10.8	*1.4*	34
					239	1.1	*0.04*	34
adamanatane	−414570	−4735.8	11.029	543 to 298	303.5	11.7	30.4	30
hexamethylbenzene	−674270	−6563	15.695	438 to 298	298.2	0.113	0.152	31
fluorene	−370051	−8191	17.636	388 to 298	298.2	0.085	0.086	35
9-methylcarbazole	−370649	−9103.4	18.48	362 to 293	312.8	0.056	0.052	36
diphenylmethane	−306268	−8309	20.487	298 to 268	283.3	0.32	0.33	37
anthracene	−421165	−9674.8	18.544	489 to 298	353.6	0.5	0.5	38
					350.4	0.37	0.38	39
					327.8	0.034	0.036	40
pyrene	−437893	−9305	17.412	424 to 298	298.2	$7.5 \cdot 10^{-4}$	$6.0 \cdot 10^{-4}$	41
2,3-benzofluorene	−509066	−9798.9	17.523	490 to 298	370.7	0.3	0.09	40
chrysene	−552868	−10502	17.878	531 to 298	408.4	1.5	0.5	38
1,2-benzanthracene	−498970	−10832	19.621	434 to 298	388.2	0.9	0.5	38
triphenylene	−1244858	−4768.7	9.514	471 to 298	397.7	1.1	0.5	38
p-terphenyl	−567491	−11617	21.856	486 to 298	384.3	0.5	0.39	42
triphenylmethane	−534935	−9660.2	20.258	367 to 298	323	0.039	0.035	43
perylene	−601489	−11694	18.791	551 to 298	400.5	0.07	0.016	40
benzo[a]pyrene	−839460	−9441.9	16.351	454 to 390				
	444617	−12525	21.294	390 to 298	298	$6.9 \cdot 10^{-7}$	$9 \cdot 10^{-7}$	41
benzo[e]pyrene	−960644	−8832.8	15.642	454 to 326				
	−538242	−13102	23.344	326 to 298	360	$3.4 \cdot 10^{-3}$	$2.9 \cdot 10^{-3}$	44
benzo[k]fluoranthene	−573526	−11602	19.553	498 to 298	397.2	0.17	0.065	45
1,2:3,4-dibenzanthracene	−662367	−11482	17.624	554 to 298	442.1	0.8	0.5	38
1,2:5,6-dibenzanthracene	−659858	−12144	18.939	544 to 298	452.2	1.5	0.5	38
1,3,5-triphenylbenzene	−718438	−6717.2	9.0422	447 to 298	418.3	1.5	0.42	39
p-quaterphenyl	−756680	−15192	24.169	587 to 287	298	$4.8 \cdot 10^{-11}$	na[a]	

[a] na = not available.

as the reference pressure and temperature (p_1, T_1 in eq 1) for calculations at temperature below T_t.

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(T)_{\mathrm{tpce}} = \Delta_{\mathrm{cr}}^{\mathrm{cr}}H_{\mathrm{m}}(T_{\mathrm{t}}) + \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(T) \qquad (6)$$

Results

The results of applying eqs 1 to 6 to calculate sublimation vapor pressures are reported in column 7 of Table 5. Sublimation vapor pressures from the literature are provided for comparison. The compounds in this table consist mostly of aromatic solids whose vapor pressures have been measured directly by various experimental techniques. Several independent measurements of anthracene at various temperatures were located and are also included. Columns 2 to 4 of Table 5 provide the constants to be used in conjunction with eq 7 to predict sublimation vapor pressures over the temperature range indicated in column 5 of the table; as with eq 1, $p_{\mathrm{o}} = 101.325$ kPa.

$$\ln(p/p_{\mathrm{o}})_{\mathrm{sub}} = A'(T/\mathrm{K})^{-2} + B'(T/\mathrm{K})^{-1} + C \qquad (7)$$

Evaluated vapor pressures obtained by using this protocol vary from approximately $p = (3 \text{ to } 2 \cdot 10^{-7})$ Pa, and with the exceptions of cubane, calculated pressures fall within a factor of three of the literature values. The literature vapor pressures for cubane at $T = (262 \text{ and } 239)$ K are reported in italics since subsequent work has shown that the sublimation enthalpy calculated using vapor pressures measured in this temperature range are significantly in error.[8,24] The estimated vapor pressure of cubane at $T = 298$ K, 177 Pa, is approximately a factor of 16 times more volatile than naphthalene, 10.9 Pa,[25] consistent with the observed volatility of solid cubane at this temperature.[26] The results obtained for adamantane are unique in the sense that the vapor pressure calculated at the melting temperature is predicted to exceed 1 atm ($\ln(p/p_{\mathrm{o}}) = 0.88$ at $T = 543$ K (sealed

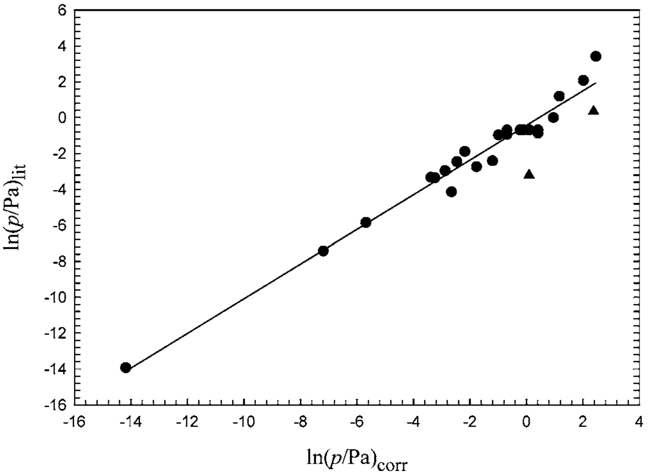

Figure 1. Logarithmic comparison of literature sublimation vapor pressures with those evaluated by correlation-gas chromatography of the compounds in Table 5. The triangles represent the results for cubane at $T = (262 \text{ and } 239)$ K. Excluding the results for cubane, the equation of the line is given by: $\ln(p/\mathrm{Pa})_{\mathrm{lit}} = (0.965 \pm 0.036)\ \ln(p/\mathrm{Pa})_{\mathrm{corr}} - (0.436 \pm 0.14)$; $r^2 = 0.9700$.

Table 6. Coefficients of a Second-Order Polynomial for the n-Alkanes and a Comparison of Vapor Pressures With Previous Estimates

	A'	B'	C'	T / K range	T / K	$p(T)_{\mathrm{calc}}$ / Pa	$p(T)_{\mathrm{lit}}$[23] / Pa
heneicosane	−1017189.2	−11804.0	31.270	308 to 304	308	0.0019	0.0018
docosane	−6787618.9	31641.7	−49.713	315 to 298	308	$4.1 \cdot 10^{-4}$	$5 \cdot 10^{-4}$
tricosane	521753.0	−25999.1	58.355	315 to 298	308	$1.2 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$
tetracosane	1113614.8	−17564.1	46.823	321 to 298	308	$3.0 \cdot 10^{-5}$	$2.8 \cdot 10^{-5}$
pentacosane	−1157818.0	−17539.7	45.887	320 to 298	308	$8.0 \cdot 10^{-6}$	$6.7 \cdot 10^{-6}$
hexacosane	748469.1	−32284.0	72.128	326 to 298	308	$1.7 \cdot 10^{-6}$	$1.6 \cdot 10^{-6}$
heptacosane	846882.0	−31513.4	68.031	332 to 298	308	$9.4 \cdot 10^{-7}$	$4.1 \cdot 10^{-7}$
octacosane	−1309617.6	−20312.9	52.162	330 to 298	308	$1.1 \cdot 10^{-7}$	$9.4 \cdot 10^{-8}$
nonacosane	−1352755	−20489.5	51.989	330 to 298	308	$3.2 \cdot 10^{-8}$	$2.5 \cdot 10^{-8}$
triacontane	−1405152.6	−21508.4	54.428	332 to 298	308	$7.6 \cdot 10^{-9}$	$5.5 \cdot 10^{-9}$
hentriacontane	−3155034.9	−11474.8	38.727	337 to 298	308	$1.6 \cdot 10^{-9}$	$1.5 \cdot 10^{-9}$
dotriacontane	−1506877.9	−23420.7	59.116	337 to 298	308	$5.7 \cdot 10^{-10}$	$3.2 \cdot 10^{-10}$
tritriacontane	−1557809.0	−23820.0	59.417	340 to 298	308	$1.2 \cdot 10^{-10}$	$9.4 \cdot 10^{-11}$
tetratriacontane	−1609564.1	−25285.0	63.143	342 to 298	308	$2.5 \cdot 10^{-11}$	$1.9 \cdot 10^{-11}$
pentatriacontane	−1662341.4	−25570.7	63.298	344 to 298	308	$6.7 \cdot 10^{-12}$	$5.7 \cdot 10^{-12}$
tetratetracontane	−2115444. 9	−32887.8	78.762	358 to 298	298.2	$9.4 \cdot 10^{-20}$	na[a]
hexatetracontane	−2594217.4	−32295.5	78.891	361 to 298	298.2	$3.6 \cdot 10^{-21}$	na[a]
pentacontane	−2843139.7	−31379.4	74.738	365 to 298	298.2	$7.4 \cdot 10^{-23}$	na[a]
tetrapentacontane	−3078572.1	−33743.9	79.893	368 to 298	298.2	$3.3 \cdot 10^{-25}$	na[a]
hexacontane	−3435063.4	−36841.0	86.235	372.4	298.2	$1 \cdot 10^{-28}$	na[a]

[a] na = not available.

tube)). Also included in this table are a few predicted sublimation vapor pressures.

Some idea of the comparison between experimental and calculated values is also provided as a logarithmic comparison in Figure 1. The equation of the line obtained by a linear regression is given in the caption below the figure and does not include the two values for cubane reported in Table 5. The triangles in this figure represent the vapor pressure comparisons of cubane at the two temperatures mentioned above.

The forms of polynomials 1 and 7 have been chosen to allow the reader to distinguish between experimental data and data obtained by correlation. The use of a third-order polynomial to model what curvature is observed in plots of the logarithm of sublimation vapor pressure against $1/T$ did not seem justified in view of the more approximate nature of the sublimation vapor pressure calculated by this protocol. Experimental sublimation vapor pressures are usually expressed in the form of the Antoine or Clausius−Clapeyron equations. Experimental liquid vapor pressures have included a number of additional formulations, all of which differ from the form of eqs 1 and 7.

The n-alkanes in Table 6 are reported separately since experimental sublimation vapor pressure values are not available for these compounds. A number of predictive methods have been reported. Vapor pressures of the corresponding liquid, evaluated by correlation-gas chromatography, and experimental fusion enthalpies have been reported.[5,7,9,23] For comparison with our calculations, the method reported by Pouillot et al. has been chosen.[27] The following relationships have been proposed by these workers for estimating sublimation vapor pressures of the n-alkanes $C_{20}H_{42}$ to $C_{35}H_{72}$ over the temperature range of $T = (308 \text{ to } T_{\mathrm{fus}})$ K:

$$\ln p_{\mathrm{sub}} = A + B/T \tag{8}$$

for even numbered n-alkanes

$$A = 12.31 + 1.87N$$
$$B = -67.54 - 1013.7N$$

for odd numbered n-alkanes

$$A = 11.35 + 1.78N$$
$$B = -34.63 - 978.3N$$

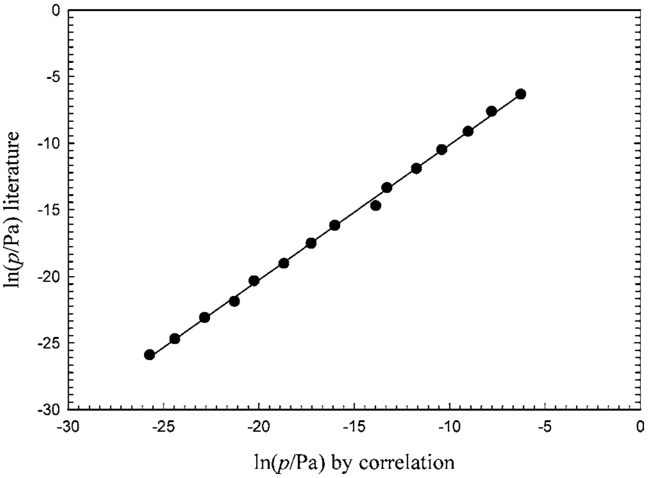

Figure 2. Logarithmic comparison of sublimation vapor pressures of the n-alkanes of Table 6 estimated using the method of Pouillot et al. with those evaluated by correlation (this work). The equation of the line is given by: $\ln(p/\mathrm{Pa})_{\mathrm{lit}} = (1.014 \pm 0.010) \ln(p/\mathrm{Pa})_{\mathrm{corr}} + (0.019 \pm 0.17)$; $r^2 = 0.9987$.

We have used these equations to generate the values reported in the last column of Table 6 at $T = 308$ K. As can be seen in the last two columns in Table 6, the comparisons between the vapor pressures calculated by the protocol described above and the values estimated using the method of Pouillot et al. are remarkably very good. The excellent correlation is also evident in Figure 2 which compares the two sets of values in logarithmic form. As noted above for Table 5, columns 2 to 4 of Table 6 report the constants to be used in conjunction with eq 7 to predict the sublimation vapor pressures of these n-alkanes over the temperature range listed in column 5 of the table. Since most of the n-alkanes exhibit phase transitions close to the fusion temperature, only the constants representing the vapor pressure/temperature dependence between $T = (T_t$ and 298.15 K) are reported in columns 2 to 4 of this table. A few additional predictions are also included in this table.

Summary

A protocol that has been used in evaluating vaporization enthalpies and vapor pressures of liquids has been expanded to include a manner for evaluating the sublimation vapor pressures of those materials that are solids at room temperature. The method appears to reproduce experimental sublimation vapor pressures within a factor of three.

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