1 ## ORIGINAL RESEARCH

2 # An examination of the vaporization enthalpies and vapor
3 # pressures of pyrazine, pyrimidine, pyridazine,
4 # and 1,3,5-triazine

5 **Dmitri Lipkind · James S. Chickos**

8 **Abstract** The vaporization enthalpies and liquid vapor
9 pressures from $T = 298.15$ K to $T = 400$ K of 1,3,5-tri-
10 azine, pyrazine, pyrimidine, and pyridazine using pyridines
11 and pyrazines as standards have been measured by corre-
12 lation-gas chromatography. The vaporization enthalpies of
13 1,3,5-triazine $(38.8 \pm 1.9$ kJ mol$^{-1})$ and pyrazine
14 $(40.5 \pm 1.7$ kJ mol$^{-1})$ obtained by these correlations are in
15 good agreement with current literature values. The value
16 obtained for pyrimidine $(41.0 \pm 1.9$ kJ mol$^{-1})$ can be
17 compared with a literature value of 50.0 kJ mol^{-1}. Com-
18 bined with the condensed phase enthalpy of formation in
19 the literature, this results in a gas-phase enthalpy of for-
20 mation, $\Delta_f H_m$ (g, 298.15 K), of 187.6 ± 2.2 kJ mol^{-1} for
21 pyrimidine, compared to a value of 195.1 ± 2.1 calculated
22 for pyrazine. Vapor pressures also obtained by correlation
23 are used to predict boiling temperatures (BT). Good
24 agreement with experimental BT (± 4.2 K) including
25 results for pyrimidine is observed for most compounds with
26 the exception of the pyridazines. The results suggest that
27 compounds containing one or two nitrogen atoms in the
28 ring that are suitable standards for correlating various
29 heterocyclic compounds provided the nitrogen atoms are
30 isolated from each other by carbon. Pyridazines do not
31 appear to be evaluated correctly using pyridines and pyr-
32 azines as standards.
33

34 **Keywords** Pyridine · Pyrazine · Pyrimidine ·
35 Vaporization enthalpy · Enthalpy of formation ·
36 Vapor pressure
37

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Introduction 38

Pyrazine, pyrimidine, pyridazine, and 1,3,5-triazine are the 39
parent compounds of a diverse series of heterocyclic 40
compounds, members of which are important components 41
of many natural products and biological systems. Yet 42
despite their structural and electronic similarity to benzene 43

pyrazine   pyrimidine   pyridazine   1,3,5-triazine
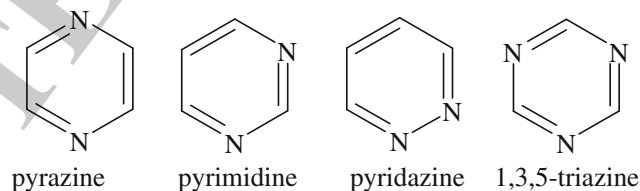
and pyridine, relatively few experimental thermodynamic 44
studies of these parent materials and their derivatives have 45
been reported [1]. In an effort to demonstrate the applica- 46
bility of correlation—gas chromatography to obtain 47
reliable vaporization enthalpies and vapor pressures of 48
diazine and triazine derivatives, this article focuses on the 49
vaporization enthalpies and vapor pressures of the parent 50
heterocyclic compounds. Previous study on the phenyl- 51
pyridine isomers demonstrated that if necessary the 52
vaporization enthalpies of hydrocarbons could be used as 53
standards to determine the vaporization enthalpies of ter- 54
tiary amines using gas chromatography [2]. The lack of 55
sufficient vapor pressure data on aromatic diazines and 56
triazines prompted a study of the vaporization enthalpies of 57
the parent heterocycles in an effort to demonstrate that 58
pyridine derivatives can act as suitable vaporization stan- 59
dards for systems containing more than one nitrogen atom. 60
Unlike aromatic diazines and triazines, a substantial 61
amount of quality data is available for pyridine and its 62

derivatives, many of which are found environmentally in heavy petroleum [3]. While this study does validate the assumption that pyridines can be used as suitable vaporization enthalpy and vapor pressure standards, it also reveals a specific instance where this presumption is probably invalid. This study demonstrates that gas chromatographic retention time measurements of pyridine derivatives can used in obtaining vaporization enthalpies and vapor pressures of nitrogen heterocycles, provided the nitrogen atoms are separated from each other by one or more carbon atoms. The vaporization enthalpy and vapor pressure measurements obtained for pyridazine and its derivatives by correlation-gas chromatography could not be validated. This study also brings into question the accuracy a previous calorimetric measurement of the vaporization enthalpy of pyrimidine [4]. To the best of our knowledge, this is the only experimental value reported for pyrimidine.

This study is intended to validate the use of pyridine and its derivatives for use as standards for future correlations of aromatic diazines, triazines, and other materials containing multiple tertiary nitrogen atoms. Some of the aromatic heterocycles studied are crystalline solids at $T = 298.15$ K. Vaporization enthalpies of crystalline materials are quite useful hypothetical properties. Combined with fusion enthalpies, they can provide sublimation enthalpies for compounds that are too non-volatile to be measured by conventional methods provided the samples survive the journey through a gas chromatograph. This sum can be used to provide independent confirmation of the magnitude of a sublimation enthalpy measurement [5, 6].

Correlation-gas chromatography is also a simple and reliable manner in which vapor pressures and vaporization enthalpies of the liquid or sub-cooled liquid can be derived [5, 6]. Since each analyte moves according to its vapor pressure on the column, measurement of the temperature dependence of its elution time provides a convenient measure of both the interaction of the analyte with the column and its volatility. The magnitude of this interaction energy, referred to as the enthalpy of transfer from the stationary phase of the column to the gas phase $\Delta_{sln}^g H_m(T_m)$, can be expressed thermodynamically as the sum of two terms, the vaporization enthalpy of the liquid and the enthalpy of interaction of the liquid with the column ($\Delta_{sln} H_m(T_m)$ (Eq. 1).

$$\Delta_{sln}^g H_m(T_m) = \Delta_{vap} H_m(T_m) + \Delta_{sln} H_m(T_m). \quad (1)$$

The magnitude of $\Delta_{sln}^g H_m(T_m)$ is due mainly to the vaporization enthalpy of the compound. $\Delta_{sln}^g H_m(T_m)$ has been found to correlate linearly with $\Delta_{vap} H_m(T)$, where T may differ from the mean temperature of measurement, T_m, and is often the reference temperature of 298.15 K. By including a series of standards with known vaporization

enthalpies and vapor pressures in a mixture containing the compounds of interest, the vaporization enthalpies and vapor pressures of these compounds can be evaluated. For organic compounds containing functional groups, it has been necessary to demonstrate independently that the vaporization enthalpy of the standards correlate with the enthalpies of transfer. Hence the need for standards with similar functionality. Tertiary amines and hydrocarbons have previously been used as suitable standards for pyridines [2]. In this article, we demonstrate that nitrogen heterocycles containing one or more isolated nitrogen atoms can be successfully correlated with each other. The one exception observed, pyridazine and its derivatives, with two nitrogens adjacent to each other, emphasizes the importance of empirically demonstrating the existence of such a correlation.

Plots of $\ln(t_o/t_a)$ versus $1/T$ over a $T = 30$ K range results in a linear relationship with the slope of the line equal to— $\Delta_{sln}^g H_m(T_m)/R$, where R is the gas constant. The term t_o is a reference time, 1 min, and t_a represents the adjusted retention time. The adjusted retention time of an analyte is evaluated as the difference between the actual retention time measured, t, and the retention time of the unretained reference, often the solvent, $t_a = t - t_{ref}$. A correlation coefficient (r^2) of <0.99 is usually indicative of some retention of the unretained reference on the column. In addition, $\ln(t_o/t_a)$ of each analyte has also been found to correlate linearly with the vapor pressure of the pure liquid phase of each analyte at a given temperature [5, 6]. Thus the same series of experiments can be used to evaluate vapor pressures if the mixture contains components with known vapor pressures.

Experimental

All compounds used in this study were obtained from a various commercial sources and used as is. All were analyzed by gas chromatography and most found to have purities of >99%. Since all were analyzed as mixtures, the initial purity of these materials is not as important as in studies where the thermochemical properties are highly dependent on purity. Pentane and cyclopentane were used as solvents. Correlation gas chromatography experiments were performed on an HP 5890 Gas Chromatograph controlled by an HP Chemstation and equipped with split/splitless capillary injection ports and flame ionization detectors at a split ratio of approximately 50/1. The compounds were run isothermally on a 30-m SPB 5 column. Temperature was controlled to ±0.1 K. Helium was used as the carrier gas. Methane was used as a non-retained reference. Adjusted retention times, t_a, were calculated by subtracting the measured retention time of the non-retained

165 reference from the retention time of each analyte as a
166 function of temperature, over a 30-K range at 5 K intervals.
167 Column temperatures were controlled by the gas chro-
168 matograph and were monitored independently by using a
169 Fluke digital thermometer. Temperature maintained by the
170 gas chromatograph was constant to ±0.1 K. Enthalpies of
171 transfer were calculated as the negative product of the
172 slope of the line obtained by plotting $\ln(t_o/t_a)$, versus $1/T$
173 and the gas constant, R. All plots of $\ln(t_o/t_a)$, versus $1/T$,
174 where $t_o = 1$ min, were characterized with correlation
175 coefficients, $r^2 > 0.99$. Unless noted otherwise, p_o is
176 101.325 kPa. The uncertainties (±σ) reported in the last
177 column of these tables were calculated from the uncertainty
178 in the slope and intercept of the equations listed at the
179 bottom of each respective table. These uncertainties reflect
180 the potential error in the absolute value of the vaporization
181 enthalpy.
182 The vaporization enthalpies of the compounds used as
183 reference materials and for comparison are provided in
184 Table 1. The vaporization enthalpies for pyrazine, 2-methyl
185 and 2,4-dimethylpyrazine and 2,4,6-trimethylpyridine
186 obtained from reference [7] were calculated from the vapor
187 pressure data provided in that article; The vaporization
188 enthalpy used for pyrazine was an average of the value
189 obtained from references [8, 7]. The value for 2,4,6-tri-
190 methylpyridine obtained from reference [9] was calculated
191 from the Antoine constants reported for the global fit using

192 Eq. 2. These constants can be found in the footnote of
193 Table 1. Heat capacities at $T = 298.15$ K were estimated
194 by a group additivity procedure [10] and vaporization
195 enthalpies were adjusted to $T = 298.15$ K using Eq. 3 [11].

$$\Delta_{vap}H_m(T_m) = RB[T_m/(T_m - C)]^2 \quad \text{where } T_m = 371 \text{ K,}$$
(2)

$$\Delta_{vap}H_m(298.15\,\text{K}) = \Delta_{vap}H_m(T_m/\text{K}) \\ + \left[[10.58 + 0.26C_p(\text{l})]/\text{J mol}^{-1}\,\text{K}^{-1}\right] \\ \times [T_m/\text{K} - 298.15]/1000.$$
(3)

197

199 Vaporization enthalpy values for 1,3,5-triazine and also
200 for pyrazine were calculated using a thermochemical cycle,
201 Eq. 4, and the data provided in Table 2. Sublimation and
202 fusion enthalpies were adjusted to $T = 298.15$ K using
203 Eqs. 5 and 6, respectively. These values are included for
204 reference only.

$$\Delta_{vap}H_m(298.15\,\text{K}) = +\Delta_{sub}H_m(298.15\,\text{K}) \\ - \Delta_{fus}H_m(298.15\,\text{K}),$$
(4)

$$\Delta_{sub}H_m(298.15\,\text{K}) = \Delta_{sub}H_m(T_m/\text{K}) \\ + \left[[0.75 + 0.15C_p(\text{cr})]/\text{J mol}^{-1}\,\text{K}^{-1}\right] \\ \times [T/\text{K} - 298.15]/1000,$$
(5)

206

208
209

$$\Delta_{fus}H_m(298.15\,\text{K}) = \Delta_{fus}H_m(T_{fus}) + \left[[0.15C_p(\text{cr}) - 0.26\,C_p(\text{l})/\text{J} - 9.83)]/\text{J mol}^{-1}\,\text{K}^{-1}\right][T_{fus}/\text{K} - 298.15]/1000.$$
(6)

Table 1 The vaporization enthalpies (kJ mol^{-1}) used as standards or for reference

	$\Delta_{vap}H(T_m)$ (kJ mol^{-1})	T_m (K)	C_pl (298.15 K) (J mol K^{-1})	$\Delta_{vap}H$ (298.15 K)	References
Pyridine				40.21 ± 0.1	[12]
Pyrazine[a]				41.02 ± 0.13	[8]
Pyrazine[a]	37.8	352	128.6	40.15 ± 0.24	[7]
Pyrazine				42.0 ± 0.85[b]	[4, 7]
Pyrimidine				50.00 ± 0.25	[4]
Pyridazine				53.47 ± 0.42	[4]
1,3,5-Triazine				41.8 ± 0.5[b]	[18, 19]
2-Methylpyrazine	42.0	340	157	44.1 ± 2.0	[7]
2,5-Dimethylpyrazine	43.6	357	185.4	47.04 ± 1.9	[7]
3-Picoline				44.47 ± 0.16	[13]
2,6-Lutadine				45.31 ± 0.16	[14]
2,4,6-Trimethylpyridine	47.2	356	214.9	51.0 ± 1.0	[7]
2,4,6-Trimethylpyridine[c]	46.2	371	214.9	51.1	[9]

[a] The mean value, 40.58 kJ mol^{-1}, from references [7, 8] was used in the correlations

[b] Value from Table 2 using Eq. 4

[c] Antoine equation $\ln(p/\text{kPa}) = A - B/(T/\text{K} - C)$; $A = 14.0622$, $B = 3446.6$, $C = 78.881$

Table 2 Vaporization enthalpies calculated from sublimation enthalpies

	$\Delta_{sub}H(T_m)$ (kJ mol^{-1})	T_m (K)	$\Delta_{sub}H$ (298 K) (kJ mol^{-1})	$\Delta_{fus}H$ (T_{fus}) (kJ mol^{-1})	T_{fus} (K)	C_p (298.15 K) (J mol^{-1} K^{-1})		$\Delta_{fus}H_m$ (298 K) (kJ mol^{-1})	References
						cr	l		
Pyrazine	56.3 ± 0.5	298	56.3 ± 0.5	15.6 ± 0.32[a]	326	97.8	128.6	14.82 ± 0.41	[4, 8]
Pyrazine	56.2 ± 1.0	303	56.3 ± 1.0	15.6 ± 0.32[a]	326	97.8	128.6	14.82 ± 0.41	[7, 8]
1,3,5-Triazine	54.8	313	55.0 ± 0.12	14.56 ± 0.01	353	94.2	127.5	12.97 ± 0.53	[18, 19]

[a] Includes a phase transition of 0.9 kJ mol^{-1} at $T = 300.5$ [8]

Table 3 Parameters of the Wagner equation (Eq. 7)

	A_W	B_W	C_W	D_W	T_c (K)[a]	p_c (kPa)	Φ	Θ	References
Pyrazine	−7.97194	3.11079	−3.23885	−2.76341	627	6700	2.5	5.0	[8]
Pyridine	−6.82447	0.47569	0.02974	−4.19797	620	5650	2.0	4.0	[12]
3-Picoline	−8.216177	4.684186	−4.363634	−3.415866	644.5	4680	2	4.8	[13]
2,6-Lutidine	−8.09336	2.51161	−3.40513	−3.23131	624	3850	2.5	5.0	[14]

[a] $T_r = T/T_c$

Table 4 Parameters of the third-order polynomial (Eq. 8) used as standards

	A (T^3)	B (T^2)	C (T)	D	References
2-Methylpyrazine	−1729170077	15000207	−48064.622	53.233	[7]
2,5-Dimethypyrazine	−1686812742	14141074	−44477.036	48.362	[7]
2,4,6-Trimethylpyridine	−78931184.8	128347	−4404.98	10.181	[7]

[a] Constants derived from vapor pressure measurement reported in reference [7]

Vapor pressure data used for pyrazine [8], pyridine [12], 3-picoline [13], and 2,6-lutidine [14] have been calculated from the parameters reported for the Wagner equation (Eq. 7). Vapor pressures for 2-methylpyrazine [7], 2,5-dimethylpyrazine [7], and 2,4,6-trimethylpyridine [7] were obtained from the original article and fit to a third-order polynomial, Eq. 8, known to provide reasonable vapor pressure values upon extrapolation [5, 15].

$$\ln(p/p_c) = (1/T_r)\big[A_W(1 - T_r) + B_W(1 - T_r)^{1.5} + C_W(1 - T_r)^{\Phi} + D_W(1 - T_r)^{\Theta}\big], \quad (7)$$

$$\ln(p/p_o) = A(T/K)^{-3} + B(T/K)^{-2} + C(T/K)^{-1} + D. \quad (8)$$

The constants needed to calculate $\ln(p/p_o)$ for the Wagner equation: p_c, T_r, A_W, B_W, C_W, D_W, Φ, Θ, and the third-order polynomial: A, B, C, and D are provided in Tables 3 and 4. The retention times measured for the six mixtures studied are reported in Table 5.

Results

The enthalpies of transfer measured for each mixture are reported in Table 6. The equation characterizing the correlation between enthalpies of transfer and vaporization enthalpy, Eqs. 9–14, is given below each run. Uncertainties were calculated from the uncertainty associated with the slope and intercept of each equation. The results of the six runs are summarized in Table 7. The uncertainties listed in column 8 of this table are the averages of the uncertainties reported for each compound in Table 6. A comparison of the values obtained for each of the compounds whose vaporization enthalpy was treated as an unknown documents for their reproducibilities. This includes 1,3,5-triazine, pyrimidine, 4-methylpyrimidine, pyridazine, and 3-methylpyridazine. The correlation coefficients, r^2, of Table 6 also suggest that the enthalpies of transfer and vaporization enthalpies of the pyrazines and pyridines used as standards correlate linearly with each other. Comparison of the vaporization enthalpy in Table 1 calculated for 1,3,5-triazine from the sublimation and fusion enthalpies to the value in Table 7 suggests that pyridines and pyrazines can also be used as reasonable standards for 1,3,5-triazines. What is presently not known is whether this correlation also applies to pyrimidines and pyridazines. Comparison of the values in column 8 of Table 7 to the literature values reported in the last column of this table for pyrimidine and pyridazine suggests that the correlation may not be

Table 5 Retention times for runs 1–6

Run 1	342.3 (t/min)	347.4 (t/min)	352.3 (t/min)	357.5 (t/min)	362.5 (t/min)	367.5 (t/min)	372.6 (t/min)
Methane	2.716	2.709	2.731	2.782	2.817	2.847	2.883
Pentane	2.922	2.893	2.898	2.928	2.951	2.967	2.994
Pyrazine	4.225	4.008	3.856	3.757	3.672	3.599	3.548
Pyridine	4.351	4.117	3.951	3.84	3.745	3.663	3.604
2-Methylpyrazine	5.784	5.301	4.932	4.66	4.435	4.246	4.1
3-Picoline	6.809	6.151	5.644	5.257	4.938	4.674	4.467
2,5-Dimethylpyrazine	8.813	7.764	6.944	6.317	5.809	5.392	5.062
Pyridazine	8.91	7.886	7.047	6.418	5.921	5.497	5.15

Run 2	342.3 (t/min)	347.4 (t/min)	352.3 (t/min)	357.5 (t/min)	362.5 (t/min)	367.5 (t/min)	372.6 (t/min)
Methane	2.709	2.721	2.758	2.795	2.826	2.821	2.89
Pentane	2.912	2.899	2.922	2.937	2.958	2.942	2.993
Pyrazine	4.217	4.018	3.88	3.77	3.68	3.572	3.548
Pyrimidine	4.426	4.195	4.028	3.897	3.787	3.664	3.627
2-Methylpyrazine	5.782	5.32	4.964	4.683	4.446	4.222	4.102
3-Picoline	6.809	6.174	5.677	5.284	4.95	4.65	4.468
2,5-Dimethylpyrazine	8.821	7.798	6.99	6.359	5.825	5.37	5.065

Run 3	337.9 (t/min)	342.9 (t/min)	348 (t/min)	353 (t/min)	358.1 (t/min)	363.2 (t/min)	368.2 (t/min)
Methane	2.676	2.712	2.73	2.79	2.811	2.844	2.873
Cyclopentane	3.119	3.103	3.074	3.099	3.088	3.089	3.099
1,3,5-Triazine	3.754	3.642	3.537	3.496	3.43	3.389	3.359
Pyrazine	4.46	4.235	4.039	3.925	3.798	3.706	3.634
Pyrimidine	4.71	4.443	4.214	4.072	3.923	3.813	3.726
2-Methylpyrazine	6.367	5.804	5.34	5.01	4.708	4.474	4.287
3-Picoline	7.639	6.843	6.198	5.727	5.31	4.982	4.719
2,6-Lutidine	8.473	7.504	6.726	6.143	5.642	5.249	4.933
2,5-Dimethylpyrazine	10.146	8.855	7.826	7.039	6.379	5.86	5.441
Pyridazine	10.231	8.957	7.959	7.148	6.486	5.964	5.535

Run 4	342.9 (t/min)	348 (t/min)	353.1 (t/min)	358.1 (t/min)	363.2 (t/min)	368.3 (t/min)	373.3 (t/min)
Methane	2.819	2.584	2.866	2.877	2.918	2.918	2.983
Pentane	3.029	2.774	3.034	3.033	3.057	3.049	3.1
1,3,5-Triazine	3.778	3.418	3.593	3.516	3.48	3.418	3.428
Pyrazine	4.39	3.937	4.034	3.895	3.806	3.7	3.674
Pyridine	4.52	4.051	4.132	3.981	3.88	3.766	3.732
2-Methylpyrazine	6.004	5.274	5.15	4.83	4.594	4.371	4.246
3-Picoline	7.067	6.154	5.885	5.445	5.114	4.814	4.626
2,6-Lutadiene	7.757	6.701	6.316	5.791	5.39	5.036	4.805
2,5-Dimethylpyrazine	9.15	7.828	7.239	6.549	6.017	5.56	5.137
Pyridazine	9.336	7.941	7.373	6.655	6.124	5.672	5.245

Run 5	372.8 (t/min)	367.7 (t/min)	362.6 (t/min)	357.5 (t/min)	352.5 (t/min)	347.5 (t/min)	342.5 (t/min)
Methane	3.044	2.982	2.958	2.934	2.922	2.904	2.87
s-Triazine	3.482	3.472	3.508	3.559	3.619	3.705	3.827
Pyrazine	3.73	3.756	3.838	3.944	4.069	4.229	4.439
Pyrimidine	3.815	3.855	3.953	4.078	4.225	4.415	4.662
2-Methylpyrazine	4.304	4.423	4.623	4.874	5.183	5.564	6.055
4-Methylpyrimidine	4.412	4.548	4.772	5.051	5.396	5.822	6.369

Table 5 continued

Run 5	372.8 (*t*/min)	367.7 (*t*/min)	362.6 (*t*/min)	357.5 (*t*/min)	352.5 (*t*/min)	347.5 (*t*/min)	342.5 (*t*/min)
3-Picoline	4.689	4.868	5.147	5.497	5.923	6.453	7.134
2,6-Lutidine	4.868	5.087	5.419	5.837	6.356	6.998	7.824
2,5-Dimethylpyrazine	5.304	5.605	6.039	6.585	7.28	8.125	9.215
Pyridazine	5.397	5.701	6.142	6.69	7.395	8.244	9.334
2,4,6-Trimethylpyridine	6.761	7.352	8.171	9.206	10.561	12.195	14.328
3-Methylpyridazine	6.989	7.606	8.453	9.513	10.911	12.594	14.763

Run 6	372.7 (*t*/min)	367.8 (*t*/min)	362.7 (*t*/min)	357.7 (*t*/min)	352.6 (*t*/min)	347.5 (*t*/min)	342.5 (*t*/min)
Methane	3.025	3.013	2.981	2.952	2.918	2.897	2.863
s-Triazine	3.466	3.495	3.528	3.576	3.637	3.713	3.808
Pyrazine	3.711	3.777	3.853	3.953	4.077	4.229	4.419
Pyrimidine	3.794	3.873	3.965	4.084	4.231	4.411	4.635
2-Methylpyrazine	4.285	4.449	4.645	4.892	5.198	5.574	6.048
4-Methylpyrimidine	4.392	4.575	4.794	5.07	5.412	5.833	6.367
3-Picoline	4.666	4.895	5.169	5.513	5.938	6.461	7.12
2,6-Lutidine	4.845	5.117	5.445	5.858	6.371	7.009	7.819
2,5-Dimethylpyrazine	5.283	5.638	6.071	6.616	7.295	8.143	9.228
Pyridazine	5.376	5.734	6.172	6.726	7.41	8.266	9.362
2,4,6-Trimethylpyridine	6.73	7.391	8.208	9.244	10.55	12.202	14.34
3-Methylpyridazine	6.963	7.643	8.492	9.572	10.913	12.617	14.818

253 applicable to these compounds. Since to our knowledge
254 there are no other vaporization enthalpies reported for
255 pyrimidines and pyridazines in the literature for compari-
256 son, it was decided to attempt to predict the vapor pressures
257 of these compounds in an effort to verify the applicability
258 of the slopes and intercepts reported in Table 6 for mea-
259 suring vaporization enthalpies.

260 It has been demonstrated previously that the equations
261 governing the temperature dependence of retention time
262 along with some experimental vapor pressures can be used
263 to predict the vapor pressures of compounds whose values
264 are unknown in the cases where enthalpies of transfer and
265 vaporization enthalpies correlate [6]. In this instance, the
266 vapor pressures of pyrimidine and pyridazine are not
267 known; however their boiling temperatures (BT) are known
268 and a comparison of predicted BT to the experimental
269 values would be a good indicator of whether the results of
270 these equations can be trusted.

271 Table 8 illustrates the correlation obtained between
272 $\ln(t_o/t_a)$ and $\ln(p/p_o)$ at $T = 298.15$ K. Values of $\ln(t_o/t_a)$
273 were calculated using the slope and intercept of each
274 compound appearing in Table 6 in runs 1–6. Values of
275 (t_o/t_a) for each compound were averaged and the natural
276 logarithm of $(t_o/t_a)_{av}$, $\ln(t_o/t_a)_{av}$ (column 2, Table 8) was
277 correlated with $\ln(p/p_o)$ calculated from Eqs. 7 and 8 and
278 the constants reported in Tables 3 and 4. The resulting

279 correlation equation, Eq. 15, was used to calculate $\ln(p/p_o)$
280 for each material. This process was repeated from
281 $T = 298.15$ to $T = 400$ K at 10 K intervals. The correla-
282 tion coefficient at $T = 298.15$ K is typical of the values
283 obtained over this temperature range. The resulting $\ln(p/p_o)$
284 values for each entry were then plotted against $1/T$ and fit
285 to Eq. 8. The A, B, C, and D constants resulting from this
286 fit are reported in Table 9. These constants were then used
287 in conjunction with Eq. 8 to predict BT. The last two
288 columns in this table compare the normal BT calculated
289 using these constants and literature values. With the
290 exception of pyridazine and 3-methylpyridazine, the BT of
291 the remaining compounds are reproduced with a standard
292 deviation of ± 4.2 K. 1,3,5-Triazine has the largest error in
293 BT. However its vaporization enthalpy is within experi-
294 mental error of the literature value as noted in Table 7.
295 This material has the shortest retention times measured and
296 it is likely to have the largest uncertainty in the slope and
297 intercept of all the compounds studied. If the BT of 1,3,5-
298 triazine is omitted, the standard deviation is reduced to
299 ±2.5 K. Several literature values are reported for the BT of
300 pyrimidine. Values range from 395.2 to 397.2 K in rea-
301 sonable agreement with the value predicted by Eq. 8. This
302 suggests that the vapor pressures obtained for pyrimidine as
303 a function of temperature are reasonable, which in turn
304 confirms the magnitude of the vaporization enthalpy

Table 6 Vaporization enthalpies calculated by correlation of $\Delta^g_{sln}H_m$ (357 K) with $\Delta_{vap}H_m$ (298.15 K) for runs 1–6

Run 1	Slope (K)	Intercept	$\Delta^g_{sln}H_m$ (357 K) (kJ mol^{-1})	$\Delta_{vap}H_m$ (298.15 K) (kJ mol^{-1})	
				Lit[a]	Calc
Pyrazine	−3457	9.692	28.74	40.58	40.4 ± 1.2
Pyridine	−3452.7	9.599	28.70	40.16	40.4 ± 1.2
2-Methylpyrazine	−3896	10.291	32.39	44.08	43.8 ± 1.3
3-Picoline	−4003.4	10.866	33.28	44.47	44.6 ± 1.3
2,5-Dimethylpyrazine	−4336.3	10.266	36.05	47.04	47.1 ± 1.5
Pyridazine	−4230.2	10.539	35.17		46.3 ± 1.4

$$\Delta^g_l H_m(298.15\ \text{K})/\text{kJ mol}^{-1} = (0.914 \pm 0.040)\Delta^g_{sln}H_m(357\text{K}) - (14.17 \pm 0.25),\ r^2 = 0.9942 \quad (9)$$

Run 2	Slope (K)	Intercept	$\Delta^g_{sln}H_m$ (357 K) (kJ mol^{-1})	$\Delta_{vap}H_m$ (298.15 K) (kJ mol^{-1})	
				Lit[a]	Calc
Pyrazine	−3477.9	9.754	28.91	40.58	40.6 ± 1.2
Pyrimidine	−3548.9	10.316	29.5		41.2 ± 1.2
2-Methylpyrazine	−3914.2	10.337	32.54	44.08	43.8 ± 1.3
3-Picoline	−4020.2	10.91	33.42	44.47	44.6 ± 1.3
2,5-Dimethylpyrazine	−4353.2	9.831	36.19	47.04	47.1 ± 1.4

$$\Delta^g_l H_m(298.15\ \text{K})/\text{kJ mol}^{-1} = (0.883 \pm 0.039)\Delta^g_{sln}H_m(357\text{K}) - (15.1 \pm 0.20),\ r^2 = 0.9960 \quad (10)$$

Run 3	Slope (K)	Intercept	$\Delta^g_{sln}H_m$ (353 K) (kJ mol^{-1})	$\Delta_{vap}H_m$ (298.15 K) (kJ mol^{-1})	
				Lit[a]	Calc
1,3,5-Triazine	−3271.3	9.613	27.2		39.1 ± 2.0
Pyrazine	−3496.5	9.776	29.07	40.58	40.7 ± 2.1
Pyrimidine	−3566.4	9.852	29.65		41.2 ± 2.2
2-Methylpyrazine	−3935.8	10.349	32.72	44.08	43.7 ± 2.4
3-Picoline	−4053.3	10.402	33.7	44.47	44.5 ± 2.5
2,6-Lutidine	−4242.7	10.806	35.27	45.31	45.8 ± 2.6
2,5-Dimethylpyrazine	−4378.3	10.953	36.4	47.04	46.8 ± 2.7
Pyridazine	−4280.2	10.65	35.58		46.1 ± 2.6

$$\Delta^g_l H_m(298.15\ \text{K})/\text{kJ mol}^{-1} = (0.883 \pm 0.039)\Delta^g_{sln}H_m(353\text{K}) - (15.1 \pm 0.20),\ r^2 = 0.9960 \quad (11)$$

Run 4	Slope (K)	Intercept	$\Delta^g_{sln}H_m$ (358 K) (kJ mol^{-1})	$\Delta_{vap}H_m$ (298.15 K) (kJ mol^{-1})	
				Lit[a]	Calc
1,3,5-Triazine	−3235.2	9.48	26.9		39.1 ± 1.6
Pyrazine	−3463.1	9.651	28.79	40.58	40.6 ± 1.7
Pyridine	−3460.8	9.564	28.77	40.16	40.6 ± 1.7
2-Methylpyrazine	−3895.5	10.207	32.39	44.08	43.5 ± 1.9
3-Picoline	−4002.1	10.23	33.27	44.47	44.2 ± 1.9
2,6-Lutadiene	−4201.3	10.66	34.93	45.31	45.5 ± 2.0
2,5-Dimethylpyrazine	−4464	11.17	37.11	47.04	47.3 ± 2.1
Pyridazine	−4371.3	10.877	36.34		46.7 ± 2.1

$$\Delta^g_l H_m(298.15\ \text{K})/\text{kJ mol}^{-1} = (0.806 \pm 0.056)\Delta^g_{sln}H_m(358\text{K}) - (17.38 \pm 0.42),\ r^2 = 0.9807 \quad (12)$$

Run 5	Slope (K)	Intercept	$\Delta^g_{sln}H_m$ (358 K) (kJ mol^{-1})	$\Delta_{vap}H_m$ (298.15 K) (kJ mol^{-1})	
				Lit[a]	Calc
s-Triazine	−3220.5	9.476	26.77		38.5 ± 2.0
Pyrazine	−3453.4	9.65	28.71	40.58	40.3 ± 2.0
Pyrimidine	−3520.0	9.711	29.26		40.8 ± 2.1

Table 6 continued

Run 5	Slope (K)	Intercept	$\Delta_{sln}^g H_m$ (358 K) (kJ mol^{-1})	$\Delta_{vap} H_m$ (298.15 K) (kJ mol^{-1})	
				Lit[a]	Calc
2-Methylpyrazine	−3896	10.231	32.39	44.1	43.7 ± 2.3
4-Methylpyrimidine	−3949.6	10.293	32.84		44.1 ± 2.3
3-Picoline	−4008.7	10.268	33.33	44.47	44.6 ± 2.4
2,6-Lutidine	−4210.9	10.708	35.01	45.31	46.2 ± 2.5
2,5-Dimethylpyrazine	−4354.2	10.878	36.2	47.04	47.3 ± 2.6
Pyridazine	−4264.7	10.598	35.46		46.6 ± 2.5
2,4,6-Trimethylpyridine	−4758.8	11.467	39.56	51.0	50.4 ± 2.8
3-Methylpyridazine	−4665.1	11.156	38.78		49.7 ± 2.8

$$\Delta_l^g H_m(298.15\,\text{K})/\text{kJ mol}^{-1} = (0.930 \pm 0.071)\Delta_{sln}^g H_m(358\,\text{K}) - (13.61 \pm 0.59),\ r^2 = 0.9771 \qquad (13)$$

Run 6	Slope (K)	Intercept	$\Delta_{sln}^g H_m$ (358 K) (kJ mol^{-1})	$\Delta_{vap} H_m$ (298.15 K) (kJ mol^{-1})	
				Lit[a]	Calc
s-Triazine	−3262.3	9.589	27.12		38.6 ± 2.1
Pyrazine	−3480.5	9.727	28.94	40.58	40.3 ± 2.1
Pyrimidine	−3545	9.785	29.47		40.8 ± 2.2
2-Methylpyrazine	−3924.5	10.307	32.63	44.08	43.8 ± 2.4
4-Methylpyrimidine	−3980.5	10.376	33.09		44.2 ± 2.4
3-Picoline	−4028.9	10.322	33.5	44.47	44.6 ± 2.4
2,6-lutidine	−4232.5	10.765	35.19	45.31	46.2 ± 2.6
2,5-Dimethylpyrazine	−4376.4	10.935	36.38	47.04	47.3 ± 2.7
Pyridazine	−4294.1	10.675	35.7		46.7 ± 2.6
2,4,6-Trimethylpyridine	−4770.2	11.496	39.66	51	50.4 ± 2.9
3-Methylpyridazine	−4688.1	11.216	38.98		49.7 ± 2.8

$$\Delta_l^g H_m(298.15\,\text{K})/\text{kJ mol}^{-1} = (0.941 \pm 0.07)\Delta_{sln}^g H_m(358\,\text{K}) - (13.1 \pm 0.59),\ r^2 = 0.9765 \qquad (14)$$

[a] See Table 1

Table 7 A summary of the vaporization enthalpies of runs 1–6 and comparison with literature values

	$\Delta_{vap} H_m$ (298.15 K) (kJ mol^{-1})							
	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Average	Lit
1,3,5-Triazine			39.1	39.1	38.5	38.6	38.8 ± 1.9	41.8 ± 0.5
Pyridine	40.4			40.6			40.5 ± 1.5	40.2 ± 0.1
Pyrazine	40.4	40.6	40.7	40.6	40.3	40.3	40.5 ± 1.7	41.5 ± 0.2
Pyrimidine		41.2	41.2		40.8	40.8	41.0 ± 1.9	50.0 ± 0.3
2-Methylpyrazine	43.8	43.8	43.7	43.5	43.7	43.8	43.7 ± 1.9	44.1 ± 2.0
4-Methylpyrimidine					44.1	44.2	44.2 ± 2.4	
3-Picoline	44.6	44.6	44.5	44.2	44.6	44.6	44.5 ± 2.0	44.5 ± 0.2
2,6-Lutidine			45.8	45.5	46.2	46.2	45.9 ± 2.4	45.3 ± 0.1
2,5-Dimethylpyrazine	47.1	47.2	46.8	47.3	47.3	47.3	47.2 ± 2.2	47.0 ± 0.2
Pyridazine	46.3		46.1	46.7	46.6	46.7	46.5 ± 2.2	53.5 ± 0.4
2,4,6-Trimethylpyridine					50.4	50.4	50.4 ± 2.9	51.0 ± 1.0
3-Methylpyridazine					49.7	49.7	49.7 ± 2.8	

measured. This result raises a red flag concerning the vaporization enthalpy of this material reported previously in the literature [4]. Unlike pyrimidine, the BT measured for pyridizine and 3-methylpyridizine are more than 40 K lower than literature values. This suggests that pyridines and pyrazines are not suitable standards to use for aromatic

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Table 8 Results obtained by correlating $\ln(t_o/t_a)_{av}$ with $\ln(p/p_o)$ at $T = 298.15$ K

	$\ln(t_o/t_a)_{av}$	$\ln(p/p_o)$	$\ln(p/p_o)$
1,3,5-Triazine	−1.352		−3.03
Pyridine	−2.012	−3.593	−3.67
Pyrazine	−1.934	−3.704	−3.60
Pyrimidine	−2.095		−3.75
2-Methylpyrazine	−2.836	−4.476	−4.47
4-Methylpyrimidine	−2.964		−4.60
3-Picoline	−3.173	−4.822	−4.8
2,6-Lutadiene	−3.425	−4.891	−5.04
2,5-Dimethylpyrazine	−3.728	−5.38	−5.34
Pyridazine	−3.714		−5.32
2,4,6-Trimethylpyridine	−4.499	−6.128	−6.08
3-Methylpyridazine	−4.5		−6.08

$$\ln(p/p_o) = (0.97 \pm 0.04)\ln(t_o/t_a)_{av} - (1.72 \pm 0.095) \quad r^2 = 0.9906 \qquad (15)$$

Table 9 Parameters for Eq. 8 and predicted BT obtained by correlating $\ln(t_o/t_a)$ with $\ln(p/p_o)$ from $T = 298.15$ K to $T = 400$ K

	$A\ (T^3)$	$B\ (T^2)$	$C\ (T)$	D	BT (K) Calc	BT (K) Lit
1,3,5-Triazine	−257351030.9	2117317.87	−10228.618	17.168	372.8	385.2
Pyridine	−322093844.2	2565357.61	−11299.75	17.523	390.4	388.2
Pyrazine	−324948325	2615598.11	−11549.026	17.976	387.2	388.2
Pyrimidine	−346777640	2784315.59	−12027.135	18.35	390.9	395
2-Methylpyrazine	−454046742.1	3627796.62	−14472.256	20.391	407	408.2
4-Methylpyrimidine	−470354160.6	3751479.12	−14813.823	20.636	410.1	413
3-Picoline	−487718452.4	3862725.41	−15041.819	20.602	416.3	417.2
2,6-Lutadiene	−545016214.7	4354009.32	−16618.099	22.279	418.6	416.2
2,5-Dimethylpyrazine	−590317407.4	4713687.79	−17672.686	23.186	424.6	428.2
Pyridazine	−566482741.6	4483588.67	−16846.004	22.116	427.7	481
2,4,6-Trimethylpyridine	−703998173.6	5610818.05	−20286.539	25.402	439.5	443.8
3-Methylpyridazine	−680672239	5381295.73	−19448.99	24.294	443.6	487.2

[a] Literature BT are from SciFinder Scholar listed under Experimental Properties provided by each parent name

Table 10 A comparison of experimental and theoretical gas phase enthalpies of formation; all enthalpies in kJ mol⁻¹

	$\Delta_f H_m$ (c, 298 K) lit[a]	$\Delta_c^g H_m$ (298 K) lit	$\Delta_f H_m$ (g, 298 K) lit	$\Delta_c^g H_m$ (298 K) this work	$\Delta_f H_m$ (g, 298 K) this work	$\Delta_f H_m$ (g, 298 K) theoretical[f]
Pyrimidine	146.6 ± 1.2	50.0 ± 0.3[b]	196.6 ± 1.2	41 ± 1.9[d]	187.6 ± 2.2	181.2 ± 2.7
Pyrazine	139.8 ± 1.2	56.3 ± 0.5[c]	196.1 ± 1.3	55.3 ± 1.7[e]	195.1 ± 2.1	201.4 ± 3.6

[a] Enthalpy of formation of the condensed phase [4]

[b] Vaporization enthalpy [4]

[c] Sublimation enthalpy [4]

[d] Vaporization enthalpy

[e] Sum of the vaporization and fusion enthalpies at $T = 298.15$ K

[f] From reference [16]

1,2-diazines and that the vaporization enthalpies reported in Table 7 for these materials are not to be trusted.

In addition to the vaporization enthalpy of pyrimidine and the sublimation enthalpy of pyrazine, Tjebbes [4] also reported the enthalpies of combustion and formation of these diazines. The study of Tjebbes together with the results of this work is summarized in Table 10. While we are not aware of any further experimental values reported

for these two diazines, theoretical calculations by Wiberg et al. [16] on a series of azines concluded that the experiment value for pyrimidine in the literature was in error. They calculated a gas-phase enthalpy of formation of 181.2 ± 2.7 kJ mol^{-1} for pyrimidine at the 6-31G** level of theory, the last column in Table 10. Accepting the condensed phase enthalpy of formation measured by Tjebbes [4], and the vaporization enthalpy obtained by correlation gas chromatography, this results in an experimental enthalpy of formation of 187.6 ± 2.2 kJ mol^{-1} for pyrimidine, in considerably better mutual agreement with the theoretical calculations. In an unrelated study, Rai and Siepmann [17] recently used transferable potentials developed with explicit hydrogen representation, TraPPE-EH, to generate a force field for modeling phase equilibria. They calculate a vaporization enthalpy of 44.0 kJ mol^{-1} for pyrimidine, in good agreement with 41 ± 1.9 kJ mol^{-1} measured in this study. They also calculate a vaporization enthalpy of 39.9 kJ mol^{-1} for pyrazine that compares with a value of 40.5 ± 1.7 obtained by correlation-gas chromatography.

In conclusion, the results obtained by correlation-gas chromatography do substantiate the conclusion reached by Wiberg et al. concerning the discrepancy observed for pyrimidine. Results for pyrazine reported by Tjebbes and others appear to be entirely consistent with the results of this study. Our results also clearly indicate that while pyridines and pyrazines can be used as suitable standards for pyrimidines and triazines, different standards are necessary to evaluate vapor pressures and vaporization enthalpies of the 1,2-diazines. Further study is necessary in developing an understanding of why some of the physical properties of pyridazines differ as much as they do from their other diazine relatives.

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