

# An Examination of the Thermodynamics of Fusion, Vaporization, and Sublimation of Several Parabens by Correlation Gas Chromatography

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**ABSTRACT:** The vaporization, fusion, and sublimation enthalpies of methyl, ethyl, propyl, and butyl paraben are reported and compared with literature values. The vaporization enthalpies were measured by correlation gas chromatography and the fusion enthalpies by differential scanning calorimetry. Adjusted to  $T = 298.15$  K, these enthalpies were combined to yield the sublimation enthalpy. The results compare favorably to some of the literature values but do not support the reversal in magnitude of both the vaporization and sublimation enthalpy previously reported for propyl and butyl paraben. The following fusion and vaporization enthalpies were measured for methyl through to butyl paraben, respectively:  $\Delta H_{\text{fus}}(T_{\text{fus}})$   $26.3 \pm 0.1$  (398.6 K),  $26.5 \pm 0.1$  (388.5 K),  $27.3 \pm 0.1$  (368.8), and  $25.9 \pm 0.3$  (340.7 K)  $\text{kJ}\cdot\text{mol}^{-1}$ ;  $\Delta H_{\text{vap}}$  (298.15 K)  $79.5 \pm 0.5$ ,  $84.0 \pm 0.5$ ,  $89.7 \pm 0.6$ , and  $95.8 \pm 0.6$   $\text{kJ}\cdot\text{mol}^{-1}$ . The results are believed to be accurate to  $\pm 4$   $\text{kJ}\cdot\text{mol}^{-1}$ . © 2011 Wiley-Liss, Inc. and the American Pharmacists Association J Pharm Sci 100:1847–1855, 2011

**Keywords:** parabens; sublimation; vaporization; fusion enthalpies; correlation gas chromatography

## INTRODUCTION

Parabens, esters of 4-hydroxybenzoic acid, are widely used in cosmetics, pharmaceutical formulations, and as antimicrobial preservatives in a wide variety of consumer products (Fig. 1). As a consequence, considerable interest has focused on them, most recently on their thermochemical properties. A number of studies have reported measurements of their phase change enthalpies. However, some of these properties have not been very well characterized with respect to temperature. The vaporization and sublimation enthalpies of the parabens as reported in the literature are reported in Table 1. The term NA refers to reference temperatures that were not readily available. Also surprising is the apparent reversal in the magnitude of the vaporization enthalpy observed for propyl and butyl paraben reported both by Perlovich et al.<sup>1</sup>

and Chatterjee et al.<sup>2</sup> Such behavior in homologous series is to our knowledge rare and indicative of the onset of some new interaction in either the condensed or gas phase.<sup>3</sup> The sublimation enthalpies reported by Perlovich et al.<sup>1</sup> are reported at  $T = 298.15$  K but the enthalpy calculated from a plot of  $\ln(p)$  against  $1/T$  from data provided in the article reproduced the cited values at the mean temperature of measurement. Similarly, Chatterjee et al.<sup>2</sup> also report vaporization enthalpies of three parabens but do not indicate the reference temperature. Both Refs. 2 and 6 in Table 1 are reported by Chatterjee et al.; only the more recent value has been considered. Evaluation of the vaporization enthalpies from the Antoine constants reported in the article also indicated that these enthalpies are referenced to the mean temperature of measurement.<sup>2</sup> As noted above, the continuing pharmaceutical interest in these compounds have prompted us to investigate their vaporization enthalpies by correlation gas chromatography and their fusion enthalpies by differential scanning calorimetry (DSC).

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**Table 1.** Literature Vaporization and Sublimation Enthalpies

	$\Delta H_{\text{vap}}(T_m)$ [kJ·mol <sup>-1</sup> ]	$T_m$ /K	$\Delta H_{\text{sub}}(298\text{ K})$ [kJ·mol <sup>-1</sup> ]	Method <sup>a</sup>	Ref.
Methyl paraben	73.5	298	98.8	T	1
	81.5	461		NA	4
	83.1	298.15		CGC	5
Ethyl paraben	74.2 <sup>b</sup>	NA	100.9	TGA	2
	74.5	298		T	1
	72.6	NA		TGA	6
	78.8 <sup>b</sup>	NA		TGA	2
Propyl paraben	96.5	298	123.7	T	1
	76.5	479		TGA	6
	76.0 <sup>b</sup>	NA		TGA	2
Butyl paraben	81.8	298	108.4	T	1
	72.2	NA		TGA	6

<sup>a</sup>TGA, thermal gravimetric analysis; T, transpiration; NA, not available; CGC, correlation gas chromatography.

<sup>b</sup> Calculated from the Antoine Constants at the temperature reported.

Correlation gas chromatography is a simple method for evaluating both vaporization enthalpy and vapor pressure regardless of whether the target substance is a solid or liquid, provided appropriate standards are used with reliable vaporization enthalpies and liquid vapor pressures. The technique is particularly well suited for measuring vaporization enthalpies of homologous series.<sup>3,7-9</sup> The standards are injected simultaneously with the target substances along with an unretained analyte, which measures elution time. Because each analyte moves through the column according to its vapor pressure on the column; measurement of the temperature dependence of its adjusted retention time,  $t_a$ , provides a convenient measure of both its volatility and interaction with the column. The adjusted retention time is evaluated as the difference between the measured retention time of each analyte and that of a nonretained reference. Because the vapor pressure of each analyte is inversely proportional to its adjusted retention time,  $t_a$ , a plot of  $\ln(t_0/t_a)$  versus  $1/T$  run isothermally, usually over a

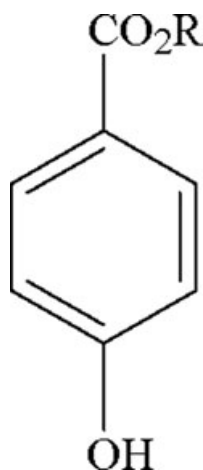
$T = 30\text{ K}$  range, results in a linear relationship with a slope equal to the negative of the enthalpy of transfer of the analyte from the column to the gas phase,  $\Delta H_{\text{trn}}(T)$ , divided by the gas constant, a typical Clausius–Clapeyron plot. The term  $t_0$  refers to a reference time, 1 min, and  $t_a$  is the time each analyte spends in the column. The enthalpy of transfer can be related to the following thermodynamic relationship:

$$\Delta H_{\text{trn}}(T_m) = \Delta H_{\text{vap}}(T_m) + \Delta H_{\text{intr}}(T_m) \quad (1)$$

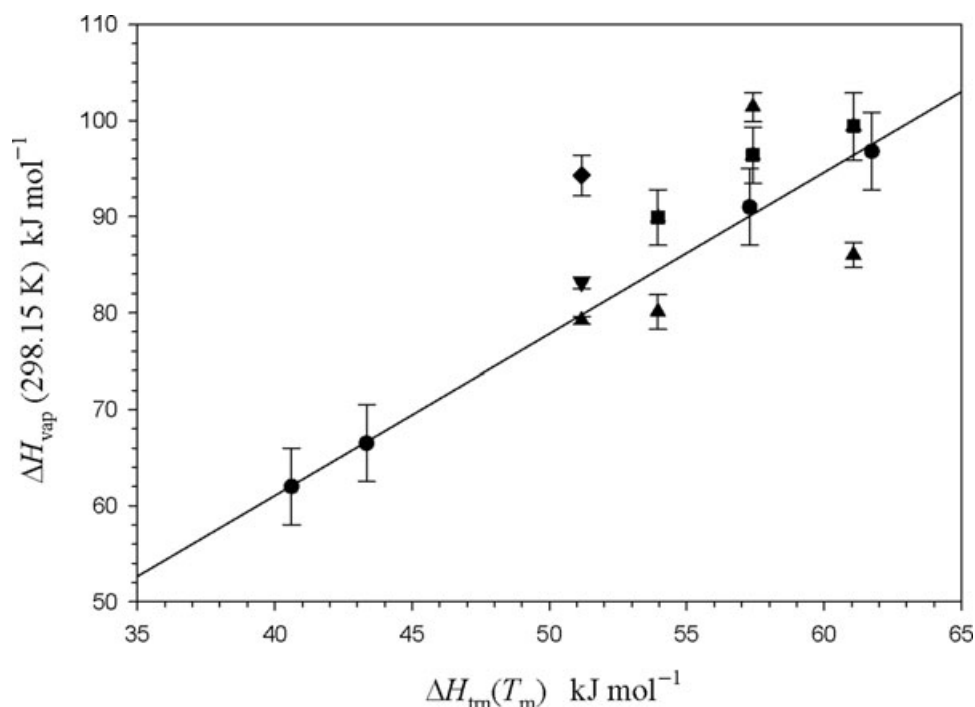
where  $\Delta H_{\text{vap}}(T_m)$  refers to the vaporization enthalpy and  $\Delta H_{\text{intr}}(T_m)$  refers to the interaction of each analyte with the column measured at some mean temperature,  $T_m$ . The enthalpy of transfer,  $\Delta H_{\text{trn}}(T_m)$ , has been found to correlate linearly with  $\Delta H_{\text{vap}}(T)$ . A study of how the magnitude of  $\Delta H_{\text{trn}}(T_m)$  compares with  $\Delta H_{\text{vap}}(T_m)$ , both measured at  $T_m$ , suggests that the  $\Delta H_{\text{vap}}(T_m)$  makes the largest contribution to  $\Delta H_{\text{trn}}(T_m)$ .<sup>10</sup> Temperature  $T$  usually differs from  $T_m$ . The quality of the correlation obtained is determined both by the quality of data available for the standards and selection of the appropriate standards. Selection of the proper standards is of paramount importance. Additional details regarding the relationships between  $\Delta H_{\text{trn}}(T_m)$ ,  $\Delta H_{\text{vap}}(T_m)$ , and  $\Delta H_{\text{intr}}(T_m)$  have been reported.<sup>10</sup>

## MATERIALS AND METHODS

All compounds used in this study were obtained from Aldrich Chemical Co. Milwaukee WI and used as purchased. All compounds were analyzed by gas chromatography and found to have purities of 98% mass fraction or better. Because all compounds were analyzed as mixtures, which are separated by the chromatography, the initial purity of these materials is not as critical as in studies wherein the thermochemical properties are highly dependent on purity. Correlation gas chromatography experiments were



**Figure 1.** The structure of the parabens investigated by correlation gas chromatography and DSC. R = methyl, ethyl, propyl and butyl



**Figure 2.** A comparison of the vaporization enthalpies at  $T = 298.15$  K as a function of the enthalpies of transfer measured at  $T = 448$  K for run 4 by correlation gas chromatography. The uncertainty of the standards assumed to be  $\pm 4$  kJ·mol<sup>-1</sup> (●, line): standards; ▲, ref. 1; ■, ref. 2; ◆, ref. 4; ▼, ref. 5.

performed on an HP 5890 Gas Chromatograph, Santa Clara CA, equipped with a flame ionization detector and run at a split ratio of approximately 100/1. Retention times were recorded on an HP Chemstation. The compounds were run isothermally on a 0.25 mm, 30 m DB5 MS column. Although enthalpies of transfer do depend on the nature of the column used and the various instrumental parameters used such as flow rate and temperature, the results following the correlation remain independent of the experimental conditions within the reproducibility of the results. Helium was used as the carrier gas. At the temperatures of these experiments, the retention time of the methylene chloride, used as solvent, generally increased with increasing temperature. This is a consequence of the increase in viscosity of the carrier gas with temperature; it is the criterion that has been used to confirm that the reference was not being retained in the column. Adjusted retention times,  $t_a$ , were calculated by subtracting the measured retention time of the nonretained reference from the retention time of each analyte as a function of temperature, at  $T = 5$  K intervals over a  $T = 30$  K range. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke digital thermometer. Temperature maintained by the gas chromatograph was constant to  $\pm 0.1$  K. Enthalpies of transfer were calculated as the product of the slope of the line obtained by plotting  $\ln(t_o/t_a)$  versus  $1/T$  and

the gas constant  $R$ . All plots of  $\ln(t_o/t_a)$  versus  $1/T$ , where  $t_o = 1$  min, were characterized by correlation coefficient,  $r^2$ , above 0.99. The uncertainties ( $\pm\sigma$ ) reported in the last column of Table 7 were calculated from the uncertainty in the slope and intercept of the equations listed at the bottom of each respective run. These uncertainties reflect the potential error in the absolute value of the vaporization enthalpy and are a measure of the precision of the measurements. Although the results are highly reproducible, the absolute error is also dependent on the quality of the data used as reference. Because some of the reference data were obtained from the Handbook of the Thermodynamics of Organic Compounds, which does not include references, it is difficult to assess the quality of the original data. The absolute uncertainty in our vaporization enthalpies is believed to be roughly  $\pm 4$  kJ·mol<sup>-1</sup>.

Equations 2, 3, and 7 described below were used to adjust sublimation/fusion and vaporization enthalpies to  $T = 298.15$  K, if necessary. The temperature-independent terms in Eqs. 2 and 3 were generated by correlating the observed difference between the heat capacity of the condensed and gas phase with the estimated heat capacity of the respective condensed phase. Gas phase heat capacities were those from Stull et al.<sup>11</sup> and condensed phase heat capacities were obtained from Domalski and Hearing.<sup>12</sup> Equation 3, used to adjust fusion

**Table 2.** Experimental Retention Times of the Parabens and Standards

	(t/min)						
Run 1 (T/K)	433.3	438.2	443.1	448.1	453.1	458	463.2
CH <sub>2</sub> Cl <sub>2</sub>	3.08	3.102	3.13	3.155	3.178	3.212	3.247
Ethyl	4.226	4.11	4.019	3.943	3.881	3.838	3.808
3-hydroxyhexanoate							
Methyl salicylate	4.906	4.707	4.545	4.41	4.298	4.207	4.138
Ethyl salicylate	5.651	5.342	5.089	4.878	4.702	4.556	4.443
Methyl paraben	8.842	7.99	7.296	6.734	6.275	5.881	5.573
Ethyl paraben	11.038	9.792	8.788	7.971	7.304	6.755	6.316
Propyl paraben	15.797	13.677	11.975	10.61	9.506	8.587	7.857
Butyl paraben	23.632	19.987	17.096	14.796	12.954	11.43	10.223
Phenyl salicylate	25.324	21.63	18.648	16.234	14.273	12.64	11.321
Benzyl salicylate	41.971	35.061	29.502	25.153	21.662	18.637	16.262
Run 2 (T/K)	433.3	438.2	443.2	448.1	453.1	458	462.9
				(t/min)			
CH <sub>2</sub> Cl <sub>2</sub>	3.08	3.093	3.112	3.129	3.146	3.163	3.184
Ethyl	4.228	4.097	3.996	3.91	3.84	3.781	3.734
3-hydroxyhexanoate							
Methyl salicylate	4.909	4.692	4.519	4.372	4.252	4.147	4.059
Ethyl salicylate	5.654	5.325	5.059	4.836	4.652	4.493	4.358
Methyl paraben	8.854	7.963	7.253	6.674	6.206	5.806	5.467
Ethyl paraben	11.042	9.765	8.739	7.903	7.225	6.663	6.195
Propyl paraben	15.809	13.636	11.909	10.52	9.403	8.478	7.708
Butyl paraben	23.648	19.93	17.007	14.673	12.817	11.293	10.036
Phenyl salicylate	25.343	21.573	18.548	16.103	14.124	12.486	11.116
Benzyl salicylate	42.108	34.921	29.329	24.932	21.446	18.497	15.998
Run 3 (T/K)	433.4	438.2	443	448	453.1	458	463
				(t/min)			
CH <sub>2</sub> Cl <sub>2</sub>	3.054	3.076	3.099	3.121	3.146	3.169	3.201
Methyl salicylate	4.875	4.674	4.508	4.364	4.249	4.153	4.081
Ethyl salicylate	5.618	5.306	5.049	4.827	4.648	4.499	4.381
Methyl paraben	8.767	7.917	7.226	6.649	6.183	5.802	5.494
Ethyl paraben	11.005	9.754	8.747	7.901	7.229	6.681	6.231
Propyl paraben	15.767	13.639	11.94	10.526	9.407	8.501	7.753
Butyl paraben	23.587	19.936	17.051	14.679	12.817	11.321	10.091
Phenyl salicylate	25.253	21.555	18.576	16.104	14.125	12.515	11.179
Benzyl salicylate	41.806	34.885	29.407	24.849	21.292	18.442	15.998
Run 4 (T/K)	433.3	438.2	443.2	448.1	453	458	463
				(t/min)			
CH <sub>2</sub> Cl <sub>2</sub>	3.059	3.081	3.103	3.128	3.151	3.18	3.209
Methyl salicylate	4.877	4.682	4.512	4.373	4.258	4.167	4.093
Ethyl salicylate	5.618	5.315	5.053	4.837	4.658	4.514	4.394
Methyl paraben	8.770	7.928	7.231	6.663	6.197	5.819	5.509
Ethyl paraben	10.993	9.765	8.745	7.917	7.247	6.700	6.25
Propyl paraben	15.743	13.651	11.932	10.546	9.429	8.524	7.78
Butyl paraben	23.547	19.955	17.037	14.708	12.849	11.348	10.128
Phenyl salicylate	25.224	21.577	18.573	16.135	14.156	12.545	11.215
Benzyl salicylate	41.665	34.898	29.344	24.89	21.346	18.46	16.086

enthalpies, is simply the difference between Eqs. 2 and 7. The uncertainties associated with the temperature-independent term of Eq. 7 is  $16 \text{ J mol}^{-1} \text{ K}^{-1}$  and the uncertainties associated with the use of Eqs. 2 and 3 are 30% of the total temperature adjustment.

### Fusion Enthalpies of the Parabens

The fusion enthalpies of the parabens studied were measured on a PerkinElmer DSC 7 instrument

(PerkinElmer, Inc., Waltham, Massachusetts). The instrument was calibrated using indium metal as a standard. The results of triplicate measurements are reported in Table 2. Fusion enthalpies for these materials are also available in the literature. These data are also provided for comparison in Table 2.<sup>13–16</sup> Agreement of this work with the literature for the most part is very good. The last column of the Table 3 reports the average values used in subsequent calculations.

**Table 3.** A Comparison of Fusion Enthalpies from the Literature with this Work

	$\Delta H_{\text{fus}}(T_{\text{fus}})$	$T_{\text{onset}}/\text{K}$	Sample/mg	$\Delta H_{\text{fus}}(T_{\text{fus}})$	$T_{\text{fus}}/\text{K}$	$\Delta H_{\text{fus}}(T_{\text{fus}})_{\text{lit}}$	$T_{\text{fus}}/\text{K}_{\text{lit}}$	$\Delta H_{\text{fus}}(T_{\text{fus}})$ Avg.
Methyl paraben	26.3	398.6	13.03			24.31 <sup>a</sup>	398.5	
	26.3	398.5	10.88	$26.3 \pm 0.1$	398.6	$25.3 \pm 0.7^b$	399.2	$25.3 \pm 1.0^e$
	26.2	398.7	12.65					
	26.4	388.5	11.85			27.9 <sup>c</sup>	389.2	
Ethyl paraben	26.5	388.4	10.92	$26.5 \pm 0.1$	388.5	$26.4 \pm 0.8^b$	389.0	$26.5 \pm 0.5^f$
	26.4	388.4	11.91			32.5 <sup>d</sup>	388.9	
	27.2	368.8	10.49			28.0 <sup>a</sup>	369.2	
Propyl paraben	27.3	368.8	13.69	$27.3 \pm 0.1$	368.8	$27.2 \pm 0.8^b$	369.3	$27.5 \pm 0.4^e$
	27.3	368.8	13.3					
	26.0	340.7	13.68					
Butyl paraben	25.7	340.6	14.17	$25.9 \pm 0.3$	340.7	$26.6 \pm 0.8^b$	341.8	$26.3 \pm 0.5^e$
	26.1	340.7	15.56					

<sup>a</sup>From Ref. 13.<sup>b</sup>From Ref. 14.<sup>c</sup>From Ref. 15.<sup>d</sup>From Ref. 16.<sup>e</sup>Average of all data.<sup>f</sup>Average of  $26.5 \pm 0.1$  and  $26.4 \pm 0.8$  kJ·mol<sup>-1</sup>.

### Sublimation Enthalpies

The sublimation enthalpies of four parabens have been measured. The sublimation enthalpies are reported in the second column of Table 3,<sup>1,4</sup> and the corresponding mean temperatures are reported in column 3 of the table. As noted above, the mean temperature of measurement was evaluated by plotting the vapor pressure data as a function of temperature,  $\ln(p)$  versus  $1/T$  provided in the article. This reproduced the sublimation enthalpies reported as  $\Delta H_{\text{sub}}(298 \text{ K})$ . Adjustments of the sublimation enthalpies to  $T = 298.15 \text{ K}$  were accomplished using Eq. 2.<sup>17</sup> Also included in this table are the mean fusion enthalpies from Table 2, the fusion temperatures, the fusion enthalpies adjusted to  $T = 298.15 \text{ K}$ , and the vaporization enthalpies at  $T = 298.15 \text{ K}$ . Adjustments of the fusion enthalpies from the fusion temperature,  $T_{\text{fus}}$ , to  $T = 298.15 \text{ K}$  as reported in column 8 of Table 3 was achieved by using Eq. 3.<sup>18</sup> The  $C_p(\text{cr})$  and  $C_p(\text{l})$  terms refer to heat capacities of the solid and liquid, respectively. Heat capacities were estimated by group additivity<sup>19</sup> and are reported in column 4 of Table 3. Equations 2 and 3 have been previously shown to provide reasonable temperature adjustments of sublimation and fusion enthalpies to  $T = 298.15 \text{ K}$ .<sup>20</sup> The un-

certainty associated with both these adjustments has been assumed to be equivalent to 30% of the total. The vaporization enthalpies at  $T = 298.15 \text{ K}$  reported in the last column of Table 3 were calculated from the thermodynamic equality, Eq. 4.

$$\begin{aligned} \Delta H_{\text{sub}}(298.15 \text{ K})/(\text{kJ} \cdot \text{mol}^{-1}) \\ = \Delta H_{\text{sub}}(T_{\text{m}}) + [0.75 + 0.15 C_p(\text{cr})]/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \\ [T_{\text{m}}/\text{K} - 298.15 \text{ K}]/1000 \end{aligned} \quad (2)$$

$$\begin{aligned} \Delta H_{\text{fus}}(298.15 \text{ K})/(\text{kJ} \cdot \text{mol}^{-1}) \\ = \Delta H_{\text{fus}}(T_{\text{fus}}) \\ + [(0.15 C_p(\text{cr}) - 0.26 C_p(\text{l}))]/(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \\ - 9.83][T_{\text{fus}}/\text{K} - 298.15]/1000 \end{aligned} \quad (3)$$

$$\begin{aligned} \Delta H_{\text{vap}}(298.15 \text{ K}) \\ = \Delta H_{\text{sub}}(298.15 \text{ K}) - \Delta H_{\text{fus}}(298.15 \text{ K}) \end{aligned} \quad (4)$$

Also included in Table 3 are similar thermochemical properties for phenyl salicylate, one of the

**Table 4.** Temperature Adjustments of Sublimation and Fusion Enthalpies to  $T = 298.15 \text{ K}$ 

	$\Delta H_{\text{sub}}(T_{\text{m}})^a$ [kJ·mol <sup>-1</sup> ]	$T_{\text{m}}/\text{K}$	$C_p(\text{l})/C_p(\text{cr})$ [J·mol <sup>-1</sup> ·K <sup>-1</sup> ]	$\Delta H_{\text{sub}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> ]	$\Delta H_{\text{fus}}(T_{\text{fus}})$ [kJ·mol <sup>-1</sup> ]	$T_{\text{fus}}/\text{K}$	$\Delta H_{\text{fus}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> ]	$\Delta H_{\text{vap}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> ]
Methyl paraben	$98.8 \pm 0.8$	315.2	269/187.4	$99.3 \pm 0.8$	$25.3 \pm 1.0$	398.6	$20.1 \pm 1.9$	$79.2 \pm 2.1$
Ethyl paraben	$100.8 \pm 0.7$	319.7	300.9/214.2	$101.5 \pm 0.7$	$26.5 \pm 0.5$	388.5	$21.4 \pm 1.6$	$80.1 \pm 1.8$
Propyl paraben	$123.6 \pm 0.6$	326.2	332.8/241.2	$124.7 \pm 0.7$	$27.5 \pm 0.4$	368.8	$23.2 \pm 1.4$	$101.4 \pm 1.5$
Butyl paraben	$108.3 \pm 0.8$	326.7	364.7/268.1	$109.5 \pm 0.9$	$26.3 \pm 0.5$	340.7	$23.5 \pm 1.0$	$86.0 \pm 1.3$
Phenyl salicylate	109.1 <sup>b</sup>	294	358.4/246.8	$108.9 \pm 0.3$	$19.1 \pm 0.1^c$	315	$18.0 \pm 0.4$	$91.0 \pm 0.5^d$

<sup>a</sup>Data from Ref. 1 unless noted otherwise.<sup>b</sup>From Ref. 4.<sup>c</sup>Average of (19.2,<sup>22</sup> 19.16,<sup>23</sup> and 18.98<sup>24</sup>) kJ·mol<sup>-1</sup>.<sup>d</sup>Uncertainty associated with the temperature adjustment only.

materials used as a standard for the correlation gas chromatography experiments.

### Vaporization Enthalpies

The vaporization enthalpies of the parabens reported by Chatterjee et al.<sup>2</sup> and others were calculated from the Antoine Constants reported in the article using Eq. 5. The Antoine Constants and resulting vaporization enthalpies are listed in part A of Table 4 along with the values for phenyl salicylate, one of the compounds used as standards. The vaporization enthalpy of ethyl salicylate was calculated from a polynomial-relating vapor pressure and temperature over the temperature range cited in the table.<sup>21</sup> The constants used in this calculation are reported in part B of Table 4. The vapor pressure–temperature relationship used to calculate the vaporization enthalpy is reported as Eq. 6. The vaporization enthalpy was calculated as the negative product of the slope of the line and the gas constant obtained by plotting  $\ln(p/\text{mm})$  versus  $1/T$ .

$$\begin{aligned} \Delta H_{\text{vap}}(T_m) &= 2.303RB[T_m/(T_m + C)]^2 \text{ where } \log_{10}(p) \\ &= A - B/(C + T) \end{aligned} \quad (5)$$

$$\log(p/\text{mm}) = A'T^n + B' \log T + C' \quad (6)$$

Adjustments of these vaporization enthalpies from the mean temperature of measurement to  $T = 298.15$  K was accomplished using Eq. 7 and the results are summarized in Table 5.<sup>17</sup> An uncertainty of  $16 \text{ J mol}^{-1} \text{ K}^{-1}$  was used for the uncertainty in  $C_p(l)$ . Three of the four values reported for methyl salicylate were used in calculating the mean.

$$\begin{aligned} \Delta H_{\text{vap}}(298.15 \text{ K})/(\text{kJ} \cdot \text{mol}^{-1}) &= \Delta H_{\text{vap}}(T_m) + [(10.58 + 0.26 * C_p(l)/ \\ &(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}))(T_m/\text{K} - 298.15 \text{ K})]/1000 \end{aligned} \quad (7)$$

**Table 5.** Equations Used for the Evaluation of Vapor Pressures and Vaporization Enthalpies

	A	B	C	<i>T</i> /K Range	<i>T<sub>m</sub></i> /K	$\Delta H_{\text{vap}}(T_m)$ [kJ·mol <sup>-1</sup> ]	Ref.	
Antoine Constants Used to Calculate Vaporization Enthalpies								
Methyl paraben	5.23662	1159.34	-220.03	446–517	461	81.2	4	
Ethyl paraben	7.32	794.37	-260.86	448–505	477	74.1	2	
Propyl paraben	8.66	1491.58	-190.66	448–510	479	78.8	2	
Butyl paraben	6.32	357.58	-363.96	498–542	520	76.0	2	
Phenyl salicylate	6.09869	1829.98	-139.08	423–587	505	66.7	4	
	A'	B'	C'	<i>n</i>	<i>T</i> /K range	<i>T<sub>m</sub></i> /K	$\Delta H_{\text{vap}}(T_m)$ [kJ·mol <sup>-1</sup> ]	Ref.
Parameters of the Polynomial Used to Calculate Vaporization Enthalpy of Ethyl Salicylate								
Ethyl salicylate	-777390	707727	-15.12134	-2.16	431–461	446	66.7	21

### Retention Times

The experimental retention times for four runs are reported in Table 6. Since the enthalpies of transfer of two of the standards are quite similar, another compound benzyl salicylate, evaluated as an unknown in runs 1 and 2, was used as a standard in runs 3 and 4.

### RESULTS

The results of the correlations between  $\ln(t_o/t_a)$  versus  $1/T$  are provided in Table 7, runs 1–4. Equations 8–11 given below each run in Table 7 define the equation of the line obtained by correlating the vaporization enthalpies of the standards at  $T = 298.15$  K with their corresponding enthalpies of transfer measured at  $T = 448$  K. The results of the four correlations are summarized in Table 8. Also reported in this table are the fusion enthalpies and resulting sublimation enthalpies.

The results of this work are compared with literature values in Table 9 and Figure 2. Figure 2 illustrates how the literature values compare with values obtained by correlation gas chromatography using the enthalpies of transfer of run 4 as an example. Table 9 compares the vaporization and sublimation enthalpies evaluated in this work with the corresponding literature values. Assuming an uncertainty of  $4 \text{ kJ} \cdot \text{mol}^{-1}$  in the vaporization enthalpies of the compounds used as standards as noted above, two of three values for methyl paraben are within experimental error. For ethyl paraben, only the results reported by Perlovich et al.<sup>1</sup> are within experimental error. For propyl and butyl parabens, only the results reported by Chatterjee et al.<sup>2</sup> fall within experimental error of this work. Data reported by Chatterjee et al.<sup>2</sup> were obtained by Langmuir evaporation over the temperature range  $T = 473$ – $548$  K, using the Antoine Constants reported for methyl paraben by Stephenson and Malanowski<sup>4</sup> as a calibration standard. Of some concern is that the vaporization enthalpy calculated from these constants, the third entry in Table 5

**Table 6.** Results of the Correlations Between Enthalpies of Transfer and Vaporization Enthalpies

Run 1	Slope (T/K)	Intercept	$\Delta H_{\text{trn}}(448 \text{ K})$ [kJ·mol <sup>-1</sup> ]	$\Delta H_{\text{vap}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> (lit)]	$\Delta H_{\text{vap}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> (calc)]
Ethyl 3-hydroxyhexanoate	-4798.2	10.943	39.891	61.9	61.8 ± 0.4
Methyl salicylate	-4815.8	10.518	40.036	62.0	62.1 ± 0.4
Ethyl salicylate	-5141.4	10.928	42.744	66.5	66.5 ± 0.4
Methyl paraben	-6091.6	12.316	50.643		79.7 ± 0.4
Ethyl paraben	-6405.1	12.718	53.25		84.0 ± 0.4
Propyl paraben	-6818.5	13.203	56.686		89.7 ± 0.4
Butyl paraben	-7259.1	13.741	60.35		95.8 ± 0.4
Phenyl salicylate	-6810.3	12.624	56.618	89.6	89.6 ± 0.4
Benzyl salicylate	-7342.0	13.292	61.038		96.9 ± 0.4
$\Delta H_{\text{vap}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.661 \pm 0.006)\Delta H_{\text{trn}}(448 \text{ K}) - (4.441 \pm 0.27)$				$r^2 = 0.9999$	Eq. 8
Run 2	slope (T/K)	Intercept	$\Delta H_{\text{trn}}(448 \text{ K})$ [kJ·mol <sup>-1</sup> ]	$\Delta H_{\text{vap}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> (lit)]	$\Delta H_{\text{vap}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> (calc)]
Ethyl 3-hydroxyhexanoate	-4960.8	11.316	41.24	61.9	61.9 ± 0.5
Methyl salicylate	-4965.9	10.862	41.28	62.0	62.0 ± 0.5
Ethyl salicylate	-5290.5	11.27	43.98	66.5	66.5 ± 0.5
Methyl paraben	-6249.8	12.678	51.96		79.7 ± 0.6
Ethyl paraben	-6570.1	13.096	54.62		84.1 ± 0.6
Propyl paraben	-6983.1	13.58	58.05		89.8 ± 0.6
Butyl paraben	-7421.1	14.112	61.7		95.8 ± 0.6
Phenyl salicylate	-6970.1	12.989	57.95	89.6	89.6 ± 0.6
Benzyl salicylate	-7486.2	13.622	62.24		96.7 ± 0.6
$\Delta H_{\text{vap}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.743 \pm 0.008)\Delta H_{\text{trn}}(448 \text{ K}) - (10.04 \pm 0.38)$				$r^2 = 0.9999$	Eq. 9
Run 3	slope (T/K)	Intercept	$\Delta H_{\text{trn}}(448 \text{ K})$ [kJ·mol <sup>-1</sup> ]	$\Delta H_{\text{vap}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> (lit)]	$\Delta H_{\text{vap}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> (calc)]
Methyl salicylate	-4920.7	10.762	40.91	62.0	62.0 ± 0.8
Ethyl salicylate	-5249	11.178	43.64	66.5	66.5 ± 0.8
Methyl paraben	-6177.2	12.521	51.35		79.2 ± 0.9
Ethyl paraben	-6525.7	12.995	54.25		84.0 ± 0.9
Propyl paraben	-6945.2	13.493	57.74		89.7 ± 0.9
Butyl paraben	-7383.1	14.025	61.38		95.7 ± 1.0
Phenyl salicylate	-6920.8	12.879	57.54	89.6	89.4 ± 0.9
Benzyl salicylate	-7383.1	14.025	61.38	96.8	97.0 ± 1.0
$\Delta H_{\text{vap}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.643 \pm 0.012)\Delta H_{\text{trn}}(448 \text{ K}) - (5.18 \pm 0.63)$				$r^2 = 0.9999$	Eq. 10
Run 4	slope (T/K)	Intercept	$H_{\text{trn}}(448 \text{ K})$ [kJ·mol <sup>-1</sup> ]	$\Delta H_{\text{vap}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> (lit)]	$\Delta H_{\text{vap}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> (calc)]
Methyl salicylate	-4884.6	10.679	40.61	62.0	62.0 ± 0.3
Ethyl salicylate	-5213.1	11.095	43.34	66.5	66.5 ± 0.3
Methyl paraben	-6154.8	12.469	51.17		79.4 ± 0.3
Ethyl paraben	-6489.8	12.913	53.95		84.0 ± 0.3
Propyl paraben	-6905.8	13.404	57.41		89.7 ± 0.4
Butyl paraben	-7345.2	13.939	61.07		95.7 ± 0.4
Phenyl salicylate	-6890.7	12.81	57.29	91.0	89.5 ± 0.4
Benzyl salicylate	-7426.9	13.492	61.74	96.8	96.9 ± 0.4
$\Delta H_{\text{vap}}(298.15 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.649 \pm 0.004)\Delta H_{\text{trn}}(448 \text{ K}) - (4.96 \pm 0.22)$				$r^2 = 0.9999$	Eq. 11

**Table 7.** A Summary of the Vaporization and Sublimation Enthalpies

	$\Delta H_{\text{vap}}(298 \text{ K}) \text{ kJ}\cdot\text{mol}^{-1}$				Avg	$\Delta H_{\text{fus}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> ]	$\Delta H_{\text{sub}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> ]
	Run 1	Run 2	Run 3	Run 4			
Methyl paraben	79.7 ± 0.4	79.7 ± 0.6	79.2 ± 0.9	79.4 ± 0.2	79.5 ± 0.5	20.1 ± 1.9	99.6 ± 2.0
Ethyl paraben	84.0 ± 0.4	84.1 ± 0.6	84.0 ± 0.9	84.0 ± 0.2	84.0 ± 0.5	21.4 ± 1.6	105.4 ± 1.7
Propyl paraben	89.7 ± 0.4	89.8 ± 0.6	89.7 ± 0.9	89.7 ± 0.3	89.7 ± 0.6	23.2 ± 1.4	112.9 ± 1.5
Butyl paraben	95.8 ± 0.4	95.8 ± 0.6	95.7 ± 1.0	95.7 ± 0.3	95.8 ± 0.6	23.5 ± 1.0	119.3 ± 1.2
Benzyl salicylate	96.9 ± 0.4	96.7 ± 0.6			96.8 ± 0.5		

**Table 8.** Comparison of Vaporization and Sublimation Enthalpies Obtained by this Work with Literature Values

	$\Delta H_{\text{vap}} (298 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$		$\Delta H_{\text{sub}} (298 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$		Ref.
	This work	Literature	This work	Literature <sup>2</sup>	
Methyl paraben	79.5 ± 0.5	79.2 ± 2.1 94.3 ± 2.6 83.1 ± 0.6	99.6 ± 2.0	99.3 ± 0.8	1 4 5
Ethyl paraben	84.0 ± 0.5	80.1 ± 1.8 89.9 ± 2.9	105.4 ± 1.7	101.5 ± 0.7	1 2
Propyl paraben	89.7 ± 0.6	101.4 ± 1.5 96.4 ± 2.9	112.9 ± 1.5	124.7 ± 0.7	1 2
Butyl paraben	95.8 ± 0.6	86.0 ± 1.3 99.4 ± 3.5	119.3 ± 1.2	109.5 ± 0.9	1 2

**Table 9.** Adjustments of the Vaporization Enthalpies of the Parabens and Standards to  $T = 298.15 \text{ K}$ 

	$\Delta H_{\text{vap}}(T_m)$ [kJ mol <sup>-1</sup> ]	$T/K$ Range	$T_m$ (K)	$C_p(l)$ [J·mol <sup>-1</sup> ·K <sup>-1</sup> ]	$\Delta H_{\text{vap}}(298 \text{ K})^a$ [kJ·mol <sup>-1</sup> ] <sup>a</sup>	$\Delta H_{\text{vap}}(298 \text{ K})$ [kJ·mol <sup>-1</sup> ] Mean value	Ref.
Methyl paraben					79.2 ± 1.9		1
Methyl paraben					83.1 ± 0.6		5
Methyl paraben	81.2	446–476	461	269	94.3 ± 2.6		4
Ethyl paraben	74.1	448–505	477	300.9	89.9 ± 2.9		2
Ethyl paraben					80.1 ± 1.8		1
Propyl paraben	78.8	448–510	479	332.8	96.4 ± 2.9		2
Butyl paraben	76.0	498–542	520	364.7	99.4 ± 3.5		2
Methyl salicylate	59.9	327–357	342	269	63.4 ± 0.7		4
Methyl salicylate	58.7	329–359	344		62.4 ± 0.7		4
Methyl salicylate	56.9	288–318	303		57.3 ± 0.1 <sup>b</sup>		4
Methyl salicylate	55.8	327–383	355		60.3 ± 0.9	62.0 ± 1.8	25
Ethyl	61.9		298		61.9 ± 0.6	61.9 ± 0.6	6
3-hydroxyhexanoate							
Ethyl salicylate	53.4	431–461	446	300.9	66.5 ± 2.4	66.5 ± 2.4	21
Phenyl salicylate	66.7	423–587	505	358.4	88.2 ± 3.3		4
Phenyl salicylate					91.0 ± 0.5	89.6 ± 1.9	4

<sup>a</sup>Uncertainties associated with the temperature adjustment only.<sup>b</sup>Not used in calculating the mean.

does not agree well with this work and other literature values.

In summary, the results obtained for both vaporization and sublimation enthalpies by correlation gas chromatography do not support the reversal in magnitude observed for propyl and butyl paraben. They do agree with a portion of the data in the literature.

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