

Measurement of the Vaporization Enthalpy of Complex Mixtures by Correlation-Gas Chromatography. The Vaporization Enthalpy of RJ-4, a High-Energy-Density Rocket Fuel at $T = 298.15$ K

James S. Chickos,* Anna E. Wentz,[†] and Dorothea Hillesheim-Cox

Department of Chemistry, University of Missouri—St. Louis, St. Louis, Missouri 63121

Michael J. Zehe

NASA John Glenn Research Center, Lewis Field, Cleveland, Ohio 44135

The use of correlation-gas chromatography to measure the vaporization enthalpy $\{\Delta_1^g H_m(298.15 \text{ K})\}$ of complex mixtures is demonstrated using RJ-4, a high-energy-density rocket fuel, as a test sample. RJ-4 consists of a complex mixture of *exo*- and *endo*-dimethyltetrahydrodicyclopentadienes. A value of $55.3 \pm 0.9 \text{ kJ}\cdot\text{mol}^{-1}$ has been obtained for the mixture. Correlation-gas chromatography is applicable in obtaining the vaporization enthalpy of any complex mixture of materials that will pass through a gas chromatograph and for which vaporization enthalpies of suitable standards are available. Once the temperature dependence of each component is established, the results can be used to determine the vaporization enthalpy at any composition.

Introduction

The compositions of many industrially important materials are complex mixtures, often isomeric in nature. The physical properties of these mixtures can vary depending on the composition. Information on these properties is important in the design of equipment to handle them and in monitoring quality control. The vaporization enthalpy is one important physical property, particularly if the mixture is handled in the gas phase. Presently, the vaporization enthalpy of a mixture can only be measured by a vaporization calorimeter such as a Calvet calorimeter. We would like to report a much simpler technique, referred to as correlation-gas chromatography, that requires more routine analytical equipment and simultaneously provides both quality control and thermochemical information. This technique is illustrated by determining the vaporization enthalpy of RJ-4, a high-energy-density rocket fuel, consisting of a complex mixture of *exo*- and *endo*-dimethyltetrahydrodicyclopentadienes.¹

Correlation-gas chromatography has been frequently used to measure the vaporization enthalpy of pure compounds.² The technique consists of recording the retention time of an analyte as a function of temperature. The retention time, corrected for the dead volume of the column, measures the amount of time the analyte spends on the column and is inversely proportional to the analyte's vapor pressure on the column. A typical $\ln(1/t_c)$ versus $(1/T)/\text{K}$ plot results in a straight line with a slope equal to $-\Delta_{\text{sln}}^g H_m(T_m)$. The enthalpy term, $\Delta_{\text{sln}}^g H_m(T_m)$, is simply the enthalpy of transfer of the analyte from the column to the vapor at the mean temperature of measurement. Because the analyte is dissolved in the stationary phase of the column, it does not matter whether the analyte is a solid or a liquid.³

When the vaporization enthalpies of a mixture of analytes with known vaporization enthalpies, $\Delta_1^g H_m(T)$, are correlated with their respective enthalpies of transfer, $\Delta_{\text{sln}}^g H_m(T_m)$, a linear correlation is obtained. If the prepared mixture also contains several structurally related components with unknown vaporization enthalpies, the linear relationship observed between $\Delta_1^g H_m(T)$ and $\Delta_{\text{sln}}^g H_m(T_m)$ can be used to obtain the vaporization enthalpies that are unknown. Although this technique has been used primarily to obtain vaporization enthalpies at $T = 298.15$ K, in principle, it can be used to obtain vaporization enthalpies at any temperature, T , provided the vaporization enthalpies of all of the standards are referenced to the same temperature, T .

Application of this technique to a complex mixture follows directly from the temperature dependence of the retention time. Consider a mixture of i structurally related components. For each component detected by the gas chromatograph, either individually or as a multiple-component peak, the following relationship applies:

$$\begin{aligned} \ln(1/t_{1c}) &= \ln(A_1) - \Delta_{\text{sln}}^g H_m(T_m)_{(1)}/RT \\ \ln(1/t_{2c}) &= \ln(A_2) - \Delta_{\text{sln}}^g H_m(T_m)_{(2)}/RT \\ &\dots \\ \ln(1/t_{ic}) &= \ln(A_i) - \Delta_{\text{sln}}^g H_m(T_m)_{(i)}/RT \end{aligned} \quad (1)$$

Multiplying each component by its mole fraction and summing over all i components result in the following equation:

$$\sum_i n_i \ln(1/t_{ic}) = \sum_i n_i \ln(A_i) - \sum_i n_i \Delta_{\text{sln}}^g H_m(T_m)_{(i)}/RT \quad (2)$$

The enthalpy term on the extreme right, $n_i \Delta_{\text{sln}}^g H_m(T_m)_{(i)}$, is the enthalpy of transfer from solution to vapor of the entire mixture, $\Delta_{\text{sln}}^g H_m(T_m)_{(\text{mix})}$. A plot of

* To whom correspondence should be addressed. Tel.: 314 516 5377. Fax: 314 516 5342. E-mail: jsc@umsl.edu.

[†] Kirkwood High School, NSF-Solutia STARS Summer 2002 participant.

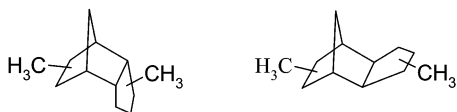


Figure 1. Structural formulas for the isomers of RJ-4.

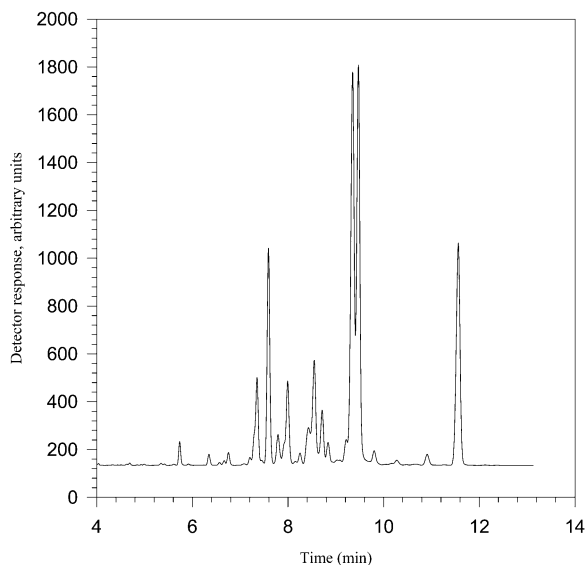


Figure 2. Gas chromatographic trace of RJ-4 at $T = 394.8$ K on a 30 m SPB-5 capillary column. The retention time of the solvent, CH_2Cl_2 , is not shown.

the sum of $n_i \ln(1/t_{ic})$ versus $1/T$ should result in a straight line with a slope of $-\Delta_{\text{sln}}^{\text{g}} H_m(T_m)_{(\text{mix})}$. If, in addition to the mixture of i components, several structurally related standards are also included in the mixture, a plot of $\ln(1/t_c)$ versus $1/T$ for each standard should also result in a linear plot. The $\Delta_{\text{sln}}^{\text{g}} H_m(T_m)$ term for each standard can be correlated to its respective vaporization enthalpy as described above. From the correlation equation and $\Delta_{\text{sln}}^{\text{g}} H_m$ of the mixture, the vaporization enthalpy of the ensemble, $\Delta_{\text{sln}}^{\text{g}} H_m(T_m)_{(\text{mix})}$, can be determined.

The rocket fuel RJ-4 is a complex mixture of *exo*- and *endo*-dimethyltetrahydrodicyclopentadienes.¹ The carbon skeleton of RJ-4 is given in Figure 1, and a gas chromatographic trace of this fuel is given in Figure 2. At 394.8 K, 20 peaks can be resolved by a 30 m SPB-5 column having a mole fraction greater than 0.003. A number of these peaks may contain multiple components. However, because these components are isomeric in nature and are not resolved by the column, the detector response sent to the integrator should still be proportional to the total amount these components contribute to the overall mixture. Two of the components with retention times of 5.76 and 6.38 min are indistinguishable from *exo*- and *endo*-tetrahydrodicyclopentadiene (THDCPD) and are likely contaminants from cyclopentadiene, a component presumably used in the production of methylcyclopentadiene, the monomeric precursor of RJ-4. *exo*-THDCPD and *endo*-THDCPD are the major components in JP-10, another high-energy-density rocket fuel.¹

Experimental Section

The following compounds were used as vaporization enthalpy standards: decane, *exo*- and *endo*-THDCPD, and tetradecane. Both *endo*- and *exo*-THDCPD were

obtained as commercial samples from Koch Specialty Chemical Co. and were used without further purification. The vaporization enthalpies of these two materials have recently been reported.⁴ Each was analyzed by gas chromatography, and its isomer was found to be present as the largest impurity. Samples of *n*-decane and *n*-tetradecane were obtained from Aldrich Chemical Co. The vaporization enthalpies of these materials have been determined numerous times and are well-known.⁵ Correlation-gas chromatography experiments were performed on an HP 5890A series II gas chromatograph equipped with a split/splitless capillary injection port and a flame ionization detector run at a split ratio of 100:1. Retention times were recorded to three significant figures following the decimal point on a HP 3989A integrator. The instrument was run isothermally using a 30 m SPB-5 capillary column. Helium was used as the carrier gas. At the temperatures of the experiments, the retention time of the solvent, CH_2Cl_2 , increased with increasing temperature. This is a consequence of the increase in viscosity of the carrier gas with temperature; it is the criterion used to confirm that the solvent is not being retained on the column. The retention times of the solvent were used to determine the dead volume of the column. Corrected retention times t_c were calculated by subtracting the measured retention time of each analyte from the retention time of the solvent as a function of temperature over a 30 K range. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke 51 K/J thermometer. The temperature was maintained constant to ± 0.1 K. The purities of the other standards were high (0.99 mole fraction). None had components with retention times similar to those of RJ-4. The standards and RJ-4 were analyzed as a mixture. RJ-4 was also analyzed by gas chromatography–mass spectrometry. All major components of RJ-4 exhibited a parent ion at m/z 164, confirming that the components are all isomeric. On this basis it has been assumed that the detector response to each component is proportional to the amount present. Integrator intensities have been used directly without any corrections to calculate the mole fraction of each component of RJ-4 separated by the column.

Small amounts of *exo*- and *endo*-THDCPD were present in the mixture. Their structural similarities to the components of RJ-4 also make them excellent standards. Because the vaporization enthalpy of the entire RJ-4 mixture is being evaluated, their contribution to the vaporization enthalpy, although extremely small, has been included. In the tables that follow, because both *exo*- and *endo*-THDCPD have been used as standards, the composition of RJ-4 has been adjusted to include the composition of these two isomers. The mole fractions of *exo*- and *endo*-THDCPD in RJ-4 were determined as 0.008 and 0.005, respectively. These compositions were maintained in experiments containing mixtures of the standards and RJ-4, even though additional *exo*- and *endo*-THDCPD had been added.

Results

Experimental retention times, t , for a mixture of standards and RJ-4 are given in Tables 1 and 2. For RJ-4, the mole fraction of each component, n_i , is also given in the table. A typical $\ln(1/t_c)$ versus $(1/T)/\text{K}$ plot for each of the standards results in good linear plots characterized by the equations and correlation coef-

Table 1. Retention Times of the Standards as a Function of Temperature

standard	<i>t</i> /min						
	394.75 K	399.85 K	404.95 K	410.05 K	415.05 K	420.05 K	425.05 K
CH ₂ Cl ₂	2.791	2.819	2.83	2.849	2.866	2.888	2.9
<i>n</i> -decane	4.516	4.304	4.114	3.962	3.84	3.741	3.65
<i>exo</i> -THDCPD	5.733	5.367	5.048	4.786	4.57	4.39	4.231
<i>endo</i> -THDCPD	6.345	5.887	5.492	5.167	4.899	4.675	4.479
<i>n</i> -tetradecane	20.895	17.53	14.868	12.76	11.103	9.766	8.679

Table 2. Retention Times, *t*, and Mole Fractions, *n_i*, of the Components of RJ-4 as a Function of Temperature^a

394.75 K		399.85 K		404.95 K		410.05 K		415.05 K		420.05 K		425.05 K	
<i>t</i> /min	10 ³ <i>n_i</i>	<i>t</i> /min	10 ³ <i>n_i</i>	<i>t</i> /min	10 ³ <i>n_i</i>	<i>t</i> /min	10 ³ <i>n_i</i>	<i>t</i> /min	10 ³ <i>n_i</i>	<i>t</i> /min	10 ³ <i>n_i</i>	<i>t</i> /min	10 ³ <i>n_i</i>
5.733	8.2	5.367	8.2	5.048	8.2	4.786	8.2	4.57	8.2	4.39	8.2	4.231	8.2
6.345	5	5.887	5	5.492	5	5.167	5	4.899	5	4.675	5	4.479	5
6.755	5.3	6.23	5.1	5.78	5	5.407	5	5.105	5.1	4.85	4.9	4.629	4.6
		6.607	3.8										
7.352	48.9	6.724	49.5	6.189	52.6	5.751	56.2	5.39	51.4	5.091	53.6	4.833	52
7.59	100.3	6.923	101.4	6.358	101.4	5.895	106.3	5.514	100.5	5.197	102.4	4.924	101
7.793	15.5	7.099	15.7	6.51	16.4	6.027	17.6	5.629	16.3	5.299	16.8	5.05	30.5
7.994	49.2	7.274	49.2	6.665	50.4	6.165	53.1	5.691	12.3	5.407	37.7	5.11	37
8.254	5.5	7.476	6.3	6.821	7.4								
8.43	23.1	7.615	30.9	6.939	34.2	6.385	37	5.751	37.8	5.519	39.6	5.188	31.5
8.55	62.7	7.736	55	7.048	54.3			5.912	40.7				
8.715	28.4	7.86	27.9	7.141	28.7	6.485	58.3	6.021	94.4	5.637	97.4	5.306	103.5
8.841	10	7.965	10.3	7.5	14.6	6.86	15.9	6.334	15.1	5.897	15.4	5.524	15.4
9.218	10.7	8.284	11.9	7.615	236.3	6.977	467	6.439	439.8	5.99	443.8	5.606	438.1
9.343	235.2	8.4	233.4	7.663	214.7								
9.462	218.5	8.485	216.6										
9.806	6.6	8.776	6.2	7.913	9.8	7.28	3.4	6.619	9.6	6.14	9.6	5.706	9.6
10.341	3.5	9.17	3.5	8.26	3.4	7.827	6.6	6.889	6.6	6.37	6.6	5.906	6.6
10.92	7.1	9.71	6.8	8.701	6.7	7.877	6.7	7.2	6.5	6.639	7	6.16	7.4
11.562	156.2	10.247	153.2	9.153	151	8.257	153.8	7.525	150.5	6.916	152.1	6.4	149.5

^a Note that the retention times of *exo*- and *endo*-THDCPD appear in both Tables 1 and 2 even though the retention times reported are for a single mixture of the standards and RJ-4. The mole fractions of *exo*- and *endo*-THDCPD in RJ-4 were determined separately.

Table 3. Equations Resulting from a Linear Regression of ln(1/*t_c*) versus (1/*T*)/K of the Standards and Correlation Coefficient, *r*², Describing the Quality of the Fit (Enthalpies in J·mol⁻¹)

standard	ln(1/ <i>t_c</i>) = -Δ _{sln} ^v <i>H_i</i> /RT + ln(<i>A_i</i>)	
<i>n</i> -decane	ln(1/ <i>t_c</i>) = (-38332 ± 90.0)/RT + (11.136 ± 0.0009),	<i>r</i> ² = 0.9999 (3)
<i>exo</i> -THDCPD	ln(1/ <i>t_c</i>) = (-36521 ± 127)/RT + (10.051 ± 0.0012),	<i>r</i> ² = 0.9999 (4)
<i>endo</i> -THDCPD	ln(1/ <i>t_c</i>) = (-37352 ± 126)/RT + (10.115 ± 0.0012),	<i>r</i> ² = 0.9999 (5)
<i>n</i> -tetradecane	ln(1/ <i>t_c</i>) = (-52567 ± 231)/RT + (13.124 ± 0.0022),	<i>r</i> ² = 0.9999 (6)

Table 4. Value of Σ*in_i* ln(1/*t_c*) for a 60:40 Mixture of *n*-Decane and *n*-Tetradecane and for RJ-4 (*r*², Correlation Coefficient)**

(1/ <i>T</i>)/K	Σ <i>i</i> <i>n_i</i> ln(1/ <i>t_c</i>)	
	60:40 <i>n</i> -decane/ <i>n</i> -tetradecane	RJ-4
0.002 352	-0.529	-0.947
0.002 380	-0.676	-1.084
0.002 409	-0.828	-1.223
0.002 439	-0.982	-1.367
0.002 469	-1.145	-1.519
0.002 501	-1.313	-1.675
0.002 533	-1.486	-1.838

$$\ln(1/t_{c})_{\text{hc}} = (-44026 \pm 135)/RT + (11.9312 \pm 0.0013), \quad r^2 = 0.9999 \quad (7)$$

$$\ln(1/t_{c})_{\text{RJ-4}} = (-40990 \pm 225)/RT + (10.655 \pm 0.00213), \quad r^2 = 0.9999 \quad (8)$$

ficients provided in Table 3. As an illustration of the application of eq 2 to a mixture, consider a 60:40 mixture of *n*-decane and *n*-tetradecane. The ideal enthalpy of transfer from solution to vapor of this mixture can immediately be evaluated from the data in Table 3 as the sum of the contributions of both components, 44.026 kJ mol⁻¹ [(0.6)(38332) + (0.4)(52567)]. Alternatively, consider a hypothetical compound having ln(1/

Table 5. Correlations of Enthalpies of Transfer from Solution to the Gas Phase with Vaporization Enthalpies from the Literature (*r*², Correlation Coefficient; Enthalpies in kJ·mol⁻¹)^a

compound	Δ _{sln} ^g <i>H_m</i> (<i>T_m</i>)	Δ ₁ ^g <i>H_m</i> (298.15 K)	
		lit.	calcd
<i>n</i> -decane	38.33	51.4 ⁵	51.55 ± 0.79
<i>exo</i> -THDCPD	36.52	49.1 ⁴	48.99 ± 0.75
<i>endo</i> -THDCPD	37.35	50.2 ⁴	50.17 ± 0.77
<i>n</i> -tetradecane	52.57	71.7 ⁵	71.68 ± 1.08
RJ-4	40.99		55.3 ± 0.84

$$\Delta_1^g H_m(298.15 \text{ K}) = (1.414 \pm 0.01)\Delta_{\text{sln}}^g H_m(T_m) - (2.654 \pm 0.136), \quad r^2 = 0.9999 \quad (9)$$

^a Uncertainties were calculated from the standard error in the slope (±2σ).

t_c)_{hc} equal to 0.6[ln(1/*t_c*)_{decane}] + 0.4[ln(1/*t_c*)_{tetradecane}]. Table 4 lists the values of ln(1/*t_c*)_{hc} for such a hypothetical compound along with the equation derived from a least-squares treatment of ln(1/*t_c*)_{hc} versus 1/*T* (eq 7). Note that both treatments give identical results for Δ_{sln}^g*H_m*(*T_m*). When the data in Table 2 are treated in a similar fashion, the left-hand side of eq 2 yields the values listed in the third column of Table 4. A linear regression analysis results in eq 8 given at the bottom of Table 4. Table 5 summarizes the values of Δ_{sln}^g*H_m*(*T_m*)

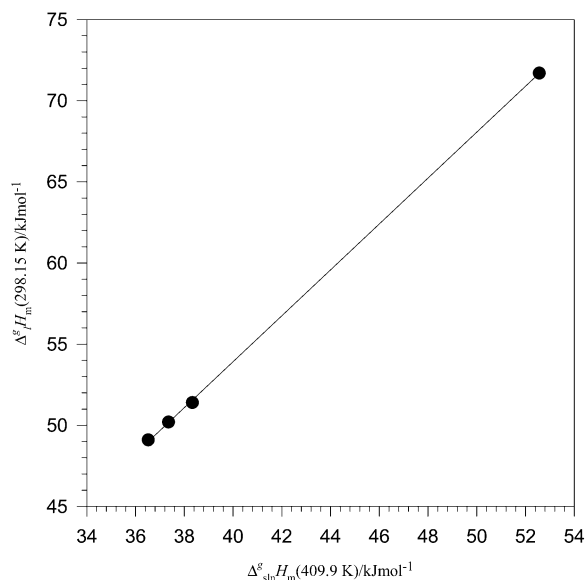


Figure 3. Correlation of $\Delta_1^{\text{g}}H_m(298.15 \text{ K})$ with $\Delta_{\text{sln}}^{\text{g}}H_m(T_m)$ of the standards measured at the mean temperature of the gas chromatographic measurements, $T_m = 409.9 \text{ K}$. The line represents the best fit to the data calculated by a linear regression analysis (eq 9).

Table 6. Symbols and Abbreviations

t	retention time (min)
t_c	corrected retention time obtained by subtracting the retention time of the solvent, CH_2Cl_2 , from the retention time of each analyte
$\Delta_{\text{sln}}^{\text{g}}H_m(T_m)$	enthalpy of transfer from solution to the gas phase at the mean temperature of measurement
$\Delta_1^{\text{g}}H_m(T)$	enthalpy of vaporization at temperature T
RJ-4	complex mixture of <i>exo</i> - and <i>endo</i> -dimethyltetrahydrodicyclopentadienes
<i>exo</i> -THDCPD	<i>exo</i> -tetrahydrodicyclopentadiene
<i>endo</i> -THDCPD	<i>endo</i> -tetrahydrodicyclopentadiene

measured in this work along with the vaporization enthalpies of the standards at $T = 298.15 \text{ K}$. Symbols and abbreviations are given in Table 6.

Correlation of $\Delta_1^{\text{g}}H_m(298.15 \text{ K})$ with $\Delta_{\text{sln}}^{\text{g}}H_m(409.9 \text{ K})$ results in Figure 3. The equation correlating the enthalpies of vaporization at $T = 298.15 \text{ K}$ with $\Delta_{\text{sln}}^{\text{g}}H_m(409.9 \text{ K})$ is given at the bottom of Table 5 (eq 9). Using this equation and $\Delta_{\text{sln}}^{\text{g}}H_m(T_m)$ of RJ-4 results in a vaporization enthalpy of $55.3 \pm 0.8 \text{ kJ mol}^{-1}$ at $T = 298.15 \text{ K}$.

Once the temperature dependence of all of the components in RJ-4 or in any mixture of isomers has been established, $\Delta_{\text{sln}}^{\text{g}}H_m(T_m)$ of different batches of the mix differing only in the composition of these components can immediately be evaluated. Substitution of the appropriate mole fractions in the left-hand term of eq 2 results in the sum of $n_i \ln(1/t_{ic})$ at each temperature. A plot of $\ln(1/t_c)$ versus $1/T$ should result in a linear plot with a slope equal to $-\Delta_{\text{sln}}^{\text{g}}H_m(T_m)$. The vaporization enthalpy can then be evaluated as before. The detector response of the gas chromatograph for each component would have to be determined independently for mixtures where the components are not isomers. Once this and the temperature dependence of the components have been established, the vaporization enthalpy would depend only on the relative composition of the components.

Discussion

One of the approximations inherent in the procedure described above is that the enthalpy of mixing is small in relation to the vaporization enthalpy and can be ignored. This is probably a good approximation for hydrocarbons but may be inappropriate for some mixtures. One of the characteristics of correlation gas chromatography is that if the vaporization enthalpies of pure materials are used as standards in the correlation, then the results obtained for mixtures will be for ideal solutions. However, this need not be the case. If the vaporization enthalpies of real mixtures are used as standards instead, then the results obtained will also reflect enthalpy of mixing terms as well. As long as the standards used are closely related to the compounds under investigation, good results should be obtained. Alternatively, the enthalpy of mixing could be determined independently if each of the pure components is available.

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