

Enthalpy of Vaporization of Toluene by Gas Chromatography

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Introduction

The enthalpy of vaporization can be measured calorimetrically, a laborious process, and spectrophotometrically, but is usually found by employing the Clausius-Clapeyron equation with measurements of the vapor pressure of the liquid at various temperatures. The procedure described below can be used with extremely small amounts of material and can work with impure samples, or even with mixtures.

On a practical level ΔH_{vap}^0 tells us how much heat will be required to convert a liquid into a vapor, an important consideration in a host of industrial operations. For so-called normal liquids, those free of molecular association in either the liquid or gaseous state, the ratio of the heat of vaporization to the normal boiling temperature is very nearly a constant $\sim 85 \text{ J K}^{-1} \text{ mol}^{-1}$ (Trouton's rule). Thus measurement of ΔH_{vap}^0 enables one to estimate the normal boiling point of the liquid. On a theoretical level the enthalpy of vaporization provides information about the size and nature of intermolecular forces in liquids. Clearly the stronger these forces are the larger will be the value of the enthalpy of vaporization.

Theory

Gas chromatography is based on a solute in a mixture partitioning itself between the mobile phase (He, usual carrier gas) and a stationary phase (a liquid coated on some type of support or on the walls of a capillary column). The *partition ratio* or *capacity factor*, k' , is the ratio of the moles of an analyte in the stationary phase, n_S , to the moles in the mobile phase, n_M :

$$k' = \frac{n_S}{n_M} = \frac{n_S}{C_M V_M} \quad (1)$$

where C_M is the concentration of the analyte in the mobile phase, and V_M is the volume of the mobile phase. The capacity factor basically is a measure of the time an analyte spends in the stationary phase relative to the time spent in the mobile phase and is given by:

$$k' = \frac{t_R - t_M}{t_M} \quad (2)$$

Here t_R , is the *retention time*, the time the analyte spends in the column from the point of injection to the point of detection, and t_M is the time it takes for the mobile phase to pass through the column; typically it is the retention time of air, a non-retained species. Now C_M is given by the ideal gas law as:

$$C_M = \frac{P_M}{RT} \quad (3)$$

where P_M is the pressure of the analyte in the nearly ideal gas phase, R is the gas constant, and T is the absolute temperature of the column. Using a standard state based on Raoult's law we may write:

$$P_M = a_S P_M^o = \gamma_S X_S P_M^o \quad (4)$$

Here a_S is the activity of the analyte in the stationary phase, P_M^o represents the vapor pressure of the pure volatile analyte, γ_S is the activity coefficient of the analyte in the stationary solvent, and X_S is the mole fraction of the analyte in the stationary phase. Since n_S is so much smaller than n_M we get:

$$X_S = \frac{n_S}{n_M + n_S} = \frac{n_S}{n_M} \quad (5)$$

Substituting eqs 3, 4 and 5 into eq 1 yields:

$$k' = \frac{RTn_M}{\gamma_S P_M^o V_M} \quad (6)$$

This equation represents a relatively easy way to measure activity coefficients of solutes in nonvolatile solvents. To examine the temperature dependence of k' , let us divide eq 6 by T and then take the natural logarithms:

$$\ln\left(\frac{k'}{T}\right) = \ln\left(\frac{Rn_M}{\gamma_S V_M}\right) - \ln(P_M^o) \quad (7)$$

Differentiating with respect to temperature and assuming that all the quantities in the first term on the right are constants if the temperature range is not too large, results in:

$$\frac{d(\ln(k'/T))}{dT} = 0 - \frac{d(\ln(P_M^o))}{dT} \quad (8)$$

This assumption is based on the fact that n_M and V_M are fixed by the column and activity coefficients of non-electrolytes vary little with temperature. Now the Clausius-Clapeyron equation gives us an expression for the term on the right side of this equation, i.e.,

$$\frac{d(\ln P_M^o)}{dT} = \frac{\Delta H_{vap}^0}{RT^2} \quad (9)$$

Substituting this into eq 8 and then integrating gives us:

$$\ln(k'/T) = + \frac{\Delta H_{vap}^0}{RT} + C \quad (10)$$

where ΔH_{vap}^0 is the standard enthalpy (heat) of vaporization of the analyte (assumed not to be a function of temperature) and C is the integration constant. Hence the value of ΔH_{vap}^0 is found by plotting $\ln(k'/T)$ versus $1/T$ and measuring the slope. Then ΔH_{vap}^0 is simply equal to R times the slope.

Procedure

GC System:

column - 30-m x 0.32mm capillary with 0.25 μm coating of poly(14% cyanopropylphenyl/86% dimethyl) siloxane (Supelco Equity 1701).

injection port and detector (FID) temperature - 200°C, isothermal column temperature 70 - 105°C in 5°C increments

injection volume - 1 μL .

All samples are run as dilute solutions in methylene chloride. Place one drop of toluene in 15 mL of methylene chloride. Even smaller concentrations will also produce good peaks. The exact concentration of the sample is unimportant for this experiment. Shake the resulting solution well to ensure that it is saturated with air, if using a GC/MS instrument in the MS detection mode.

Obtain retention times of toluene between 70 - 105°C interval, in 5°C increments for an organic compound (toluene). Also find the retention time of the solvent front, He flow rate (mL/min), He mobile phase linear velocity (cm/min)

(they are read off the method file for each temperature). The signal size under the conditions is $\sim 10^6$ cps look for signal of such a magnitude.

Treatment of Data and Results

Tabulate your results in Excel to analyze your data. Enter temperatures ($^{\circ}\text{C}$), and retention times of un-retained peak and analyte, and calculate k' , $1/T$, and $\ln(k'/T)$.

Column	Flow Speed	Retention Times (s)					
Temperature ($^{\circ}\text{C}$)	(cm/min)	Analyte	Solvent	'air'	k'	$1/T$ (K^{-1})	$\ln(k'/T)$

Prepare a plot of $\ln(k'/T)$ vs. $1/T$ and determine the regression equation for the data.

Use eq. 10 and the least squares slope to calculate the value of $\Delta H_{\text{vap}}^{\circ}$ (in kJ/mole) for your sample.

Calculate a literature value of $\Delta H_{\text{vap}}^{\circ}$ for your sample by using vapor pressure/ temperature data found in the Handbook of Chemistry and Physics and the integrated form of the Clausius-Clapeyron equation (eq. 9). Alternatively, data may be found in the NIST Chemistry Web Book (<http://webbook.nist.gov/chemistry/>). Use three or four data points such that the average temperature is approximately the same as your experimental average temperature. Compare your experimental value with this literature value.

In deriving eq. 10 it was necessary to assume that all of the values in the first term on the right side of eq. 7 are constants. Comment on this assumption and discuss what might happen to your experimental $\Delta H_{\text{vap}}^{\circ}$ if this is not strictly correct. Might it be possible to measure $\Delta H_{\text{vap}}^{\circ}$ of two or more compounds at the same time with our system?