**UNDERSTANDING INTERMOLECULAR FORCES USING A GAS CHROMATOGRAPH: ENTHALPY OF VAPORIZATION**

From *Organic Chemistry with Vernier*

# EXPERIMENT 10 INTRODUCTION

**Westminster College**

One well-known application of gas chromatography is its analytical capability used to obtain purely physiochemical data such as activity coefficients of solutes in various solvents, heats of solution, and enthalpies of vaporization of volatile compounds. It can also be used to demonstrate colligative properties. Here, we introduce the determination of the enthalpy of vaporization using retention times measured with a gas chromatograph (GC).

The enthalpy of vaporization, *ΔHvap,* is typically calculated by employing the Clausius- Clapeyron equation with measurements of the vapor pressure of the liquid at various temperatures. The enthalpy of vaporization provides information about the size and nature of intermolecular forces in liquids. Typically, the stronger these forces are, the larger the enthalpy of vaporization.

Gas chromatography is based on a solute in a mixture partitioning itself between the mobile phase and the stationary phase. With the Vernier Mini GC, the mobile phase is air and the stationary phase is a nonpolar phase capillary column. The amount of time a given chemical spends in the stationary phase relative to the amount of time it spends in the mobile phase is a very important quantity in elution chromatography; it is called the capacity factor, *k′*, and is given by:

*k*' *tR* *tM*

*tM*

where *tR* is the retention time of the compound; that is, the amount of time the chemical spends in the column from the point of injection to the point of detection. The time it takes for the mobile phase to pass through the column is referred to as *tM*; it is typically the retention time of a non-retained species. In this experiment, the non-retained compound you will be using is acetone and it functions as a very important standard to help normalize the amount of time it takes a species to run though the column, enabling calculation of *k*′. As part of this calculation, we are assuming that the retention time of the non-retained species (acetone) is independent of temperature.

To relate the capacity factor to the enthalpy of vaporization, the following equation is used1:

1 Ellison, H.R., Enthalpy of Vaporization by Gas Chromatography. A Physical Chemistry Experiment. Journal of Chemical Education, 2005. 82(7): p. 1086–1088.

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*k* 

*Hvap*  

ln' 

1

 C

*T* 

R *T* 

where *ΔHvap* is the standard enthalpy (heat) of vaporization of the compound. This value is assumed to be independent of temperature. *T* is the temperature in Kelvin, R is the gas constant in appropriate units, and C is a constant. The equation is written in the slope- intercept form where the value of *ΔHvap* is determined by plotting *ln(k*′*/T) vs. 1/T*.

# OBJECTIVES

In this experiment you will

* Collect and analyze GC data from various samples.
* Calculate the enthalpy of vaporization of various compounds from GC temperature dependent data.
* Identify an unknown sample based on its enthalpy of vaporization using values calculated from known standards.

# MATERIALS

|  |  |
| --- | --- |
| LabQuest or computer | Ethyl acetate |
| LabQuest App or Logger *Pro* | 2-butanone |
| Vernier Mini GC | 4-methyl-2-pentanone |
| 1 µL glass syringe | An unknown solution containing acetone and |
| Kimwipes® or paper towel | one of the following: 2-butanone, butyl |
| Acetone | acetate, propyl acetate |

**PROCEDURE**

1. Obtain and wear goggles. Protect your arms and hands by wearing a long-sleeve lab coat and gloves. Conduct this reaction in a fume hood.
2. Prepare or obtain three known solutions, each using acetone as the standard that will pass quickly through the column. Prepare each solution to a total volume of 1 mL in a 1:1 (v/v) mixture. Also obtain a solution of acetone for syringe cleaning.

Solution 1 contains acetone and ethyl acetate. Solution 2 contains acetone and 2-butanone.

Solution 3 contains acetone and 4-methyl-2-pentanone.

1. Prepare the Vernier Mini GC for data collection. Set the Temperature-Pressure values to:

|  |
| --- |
| Run 1 |
| Start temperature | 110℃ |
| Hold time | 10.0 min |
| Ramp rate | 0℃/min |
| Final temperature | 110℃ |
| Hold time | 0 min |
| Total length | 10.0 min |
| Pressure | 4.0 kPa |

1. Collect a 0.1 L volume of Solution 1 for injection. Once the Mini GC has reached the correct start temperature and pressure, the LED should turn green. Insert the needle into the injection port. Simultaneously, depress the syringe plunger and start data collection. Pull the needle out of the injection port immediately.
2. Data collection will end after ten minutes or you can choose to stop early if you are satisfied that your species has eluted completely. Analyze your chromatogram using Peak Integration.
3. Select another sample. Change the temperature profile for the next run. Continue to do isothermal runs in decreasing increments of 10°C until you reach 80°C (see data table).
4. Repeat Step 6 until you have completed all four temperature runs for all three solutions.
5. Obtain an unknown sample from your instructor and repeat Steps 3–6 with your unknown.
6. When you have completed your final data-collection run, turn off the Mini GC.

# DATA TABLE

## Solution 1: Acetone and ethyl acetate (1:1)

|  |  |  |
| --- | --- | --- |
| Temperature (℃) | Retention time for standard compound (min) | Retention time for test compound (min) |
| 110 |  |  |
| 100 |  |  |
| 90 |  |  |
| 80 |  |  |

**Solution 2: Acetone and 2-butanone (1:1)**

|  |  |  |
| --- | --- | --- |
| Temperature (℃) | Retention time for standard compound (min) | Retention time for test compound (min) |
| 110 |  |  |
| 100 |  |  |
| 90 |  |  |
| 80 |  |  |

**Solution 3: Acetone and 4-methyl-2-pentanone (1:1)**

|  |  |  |
| --- | --- | --- |
| Temperature (℃) | Retention time for standard compound (min) | Retention time for test compound (min) |
| 110 |  |  |
| 100 |  |  |
| 90 |  |  |
| 80 |  |  |

**Unknown Solution**

|  |  |  |
| --- | --- | --- |
| Temperature (℃) | Retention time for standard compound (min) | Retention time for test compound (min) |
| 110 |  |  |
| 100 |  |  |
| 90 |  |  |
| 80 |  |  |

**DATA ANALYSIS**

1. Enter your raw data (Temp (ºC), *tM* (min), *tR* (min)) into Logger *Pro* software or LabQuest App:
	1. With no sensor connected, choose New from the File menu.

In LabQuest App, tap the Table tab to display the data table. In Logger *Pro*, the data table is displayed to the left of the graph.

In addition to the default X and Y columns, you will need to insert a third (Manual) column. To do this, choose New Manual Column from the Data menu of Logger *Pro* or from the Table menu in LabQuest App.

In the data table, double-click (in Logger *Pro*) or tap (in LabQuest App) the X column heading. Name the column Temperature, with units of ºC. In the same manner, assign the Y column heading as Time M (min), and the manual column as Time R (min). Time M and Time R represent *tM* and *tR*, respectively.

Now enter your data. Select the first cell in the Temperature (ºC) column. Type in the temperature value, then press or tap Enter.

The cursor will now be in the Time M (min) column. Enter the corresponding Time M value. In the same way, enter the Time R value in the third column.

Continue in this manner to enter all of your data.

Do not worry about the graph that is automatically generated until you finish making all of the calculated columns in Step 2.

1. Using the experimental data you collected, calculate the following variables: Temp (K), *k′*, 1/T (1/K), ln(*k′*/T). Here is a brief summary of how to create new calculated columns using the example of converting Temperature (°C) into units of Kelvin.
	1. Choose New Calculated Column from the Data menu.
	2. Logger *Pro*
		* Enter **Temperature K** as the Name, **Temp K** as the Short Name, and **K** as the Units.
		* Enter the correct formula for the column (Temperature+273) into the Equation edit box. To do this, select “Temperature” from the Variables list, then enter

**+273**. In the Equation edit box, you should now see displayed: “Temperature”+273.

LabQuest App

* + - Enter **Temperature K** as the Name and **K** as the Units. Select the equation, X+A. Use Temperature(°C) as the Column for X. Enter **273** as the value for A.
		- Select OK.
	1. Repeat this process to create calculated columns for the remaining variables (*k′*, 1/T (1/K), ln(*k′*/T)) using the appropriate formulas found in the introduction.
1. Plot ln(*k′*/*T*) *vs.* 1/*T* (1/K). From the slope, the enthalpy of vaporization can be calculated using the equation in the introduction.
2. Find a literature value for Δ*Hvap* for each pure compound. Calculate the percent difference between your experimental value and the literature value.
3. Identify your unknown compound based on your calculations of the Δ*Hvap* for the possible unknowns. Calculate the percent error between your experimental value and the literature value.