**INVESTIGATING THERMODYNAMIC RELATIONSHIPS OF SUBSTITUTED HYDROCARBONS**

From *Organic Chemistry with Vernier*

# EXPERIMENT 11 INTRODUCTION

**Westminster College**

There are multiple ways to measure the change in thermodynamic parameters (i.e., Gibb’s free energy, Δ*G*; enthalpy, Δ*H;* and entropy, Δ*S*) during a chemical reaction. Gas chromatography provides one methodology for determining these values because the retention times reported are a result of a reaction between the mobile phase running through the column and the stationary phase that resides on the column. Here, you will measure the equilibrium constant experienced between the mobile and stationary phases which will allow you to isolate the Δ*G*, Δ*H*, and Δ*S* of the reaction.

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*; and 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.

The *k′* can also be described as the ratio of the mass of analyte in the stationary phase to the mass of analyte in the mobile phase at any given instant.1 This statement can be represented with the following equilibrium schematic.



1 Snow, N.H., Determination of free-energy relationships using gas chromatography*.* Journal of Chemical Education, 1996. 73(6): p. 592 597.

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The equilibrium constant that describes this reaction is referred to as the distribution coefficient, *K*c, and it can be expressed in terms of the capacity factor

*K*c = *k′β*

where *β* is the column phase ratio, a quantity typically given by the manufacturer. The Vernier Mini GC has a column phase ratio value of approximately 200.

Once the equilibrium constant (or distribution coefficient) is known, it is possible to determine various thermodynamic quantities. The standard Gibb’s free energy change involved in the mobile phase-stationary phase transition is calculated by:

Δ*G°*= –R*T* ln(*K*c)

By analyzing the retention time at more than one temperature, the enthalpy and entropy changes involved in the process can also be found.

Δ*G°*=Δ*H°*–*T*Δ*S°*

# OBJECTIVES

In this experiment you will

* Collect and analyze GC data from various samples.
* Calculate the equilibrium constant between the various compounds and the GC column.
* Use the equilibrium constant to identify the change in free energy of solution.
* From the temperature dependent data, calculate the change in enthalpy and entropy of the solution.
* Observe the changes in Gibb’s free energy with the number of carbon atoms in the samples studied.

# MATERIALS

|  |  |
| --- | --- |
| LabQuest or computer | Acetone |
| LabQuest App or Logger *Pro* | 2-butanone |
| Vernier Mini GC | Propyl acetate |
| 1 µL glass syringe | 4-methyl-2-pentanone |
| Kimwipes® or paper towel |

**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 2-butanone. Solution 2 contains acetone and propyl acetate.

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 | 115℃ |
| Hold time | 10.0 min |
| Ramp rate | 0℃/min |
| Final temperature | 115℃ |
| 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 syringe 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. 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 15°C until you reach 40°C (see the data table). Remember to rinse the syringe with a small amount of your next sample before starting a run.
4. Repeat Step 6 until you have completed all six temperature runs for all three solutions.
5. When you have completed your final data-collection run, turn off the Mini GC and clean up your lab area as directed.

# DATA TABLE

## Solution 1: Acetone and 2-butanone

|  |  |  |
| --- | --- | --- |
| Temperature (℃) | Retention time for standard compound (min) | Retention time for test compound (min) |
| 115 |  |  |
| 100 |  |  |
| 85 |  |  |
| 70 |  |  |
| 55 |  |  |
| 40 |  |  |

**Solution 2: Acetone and propyl acetate**

|  |  |  |
| --- | --- | --- |
| Temperature (℃) | Retention time for standard compound (min) | Retention time for test compound (min) |
| 115 |  |  |
| 100 |  |  |
| 85 |  |  |
| 70 |  |  |
| 55 |  |  |
| 40 |  |  |

**Solution 3: Acetone and 4-methyl-2-pentanone**

|  |  |  |
| --- | --- | --- |
| Temperature (℃) | Retention time for standard compound (min) | Retention time for test compound (min) |
| 115 |  |  |
| 100 |  |  |
| 85 |  |  |
| 70 |  |  |
| 55 |  |  |
| 40 |  |  |

**DATA ANALYSIS**

1. Enter your raw data (Temp (ºC), *tM* (min), *tR* (min)) into Logger *Pro* or LabQuest App:
	1. With no sensor connected, choose New from the File menu.
	2. 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.
	3. 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.
	4. 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.
	5. Now enter your data. Select the first cell in the Temperature (ºC) column. Type in the temperature value, then press or tap Enter.
	6. 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.
	7. Continue in this manner to enter all of your data.
	8. Do not worry about the graph that is automatically generated until you finish making all of the calculated columns in Step 2.
2. Using the experimental data you collected, calculate the following variables: Temp (K), *k′*, *K*c, –*T* (K), Δ*G* (kJ/mol). 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 for the remaining variables using the appropriate formulas.
1. Plot a graph of Δ*G* (kJ/mol) *vs.* –Temperature (K) for each test compound. Evaluate the slope and y-intercept to obtain the Δ*S*° and Δ*H*° from the appropriate equation presented in the introduction.
2. Using the information acquired in the above question, calculate Δ*G*° at 25°C for each test compound.
3. Of the three test substances investigated, rank them according to increasing number of carbon atoms. Generate a plot of Δ*G*° (kJ/mol) at 25°C *vs.* Number of Carbon Atoms.
4. Discuss how the sign of the thermodynamic values is consistent with the experiment you ran.