

Physical Chemistry Laboratory I
CHEM 445
DAS
Data Analysis, Vapor Pressure
 (Revised, 1/12/18)

The vapor pressure of a pure liquid is an intensive property of the compound. That is, the vapor pressure of a liquid is independent of the amounts of the two phases as long as both phases are present. This phenomenon is shown in many physical chemistry textbooks in plots of PV isotherms at temperatures below the critical temperature. The horizontal part of the P {vertical} vs. V {horizontal} isotherm corresponds to the constant vapor pressure of the liquid at that temperature, independent of the volume of each phase. The vapor pressure of every liquid is a strongly increasing function of temperature {much more than a linear increase} and a very slightly increasing function of applied pressure.

Eq. (1) for the variation of vapor pressure of a liquid with temperature is derived in many texts and is often called the Clausius-Clapeyron equation. Reasonable approximations: {V {gas} >> V {Liq} and PV = nRT} have been made to achieve this equation.

$$\left(\frac{1}{P}\right)\left(\frac{dP}{dT}\right) = \frac{d\{\ln P\}}{dT} = \frac{\overline{\Delta H_{\text{vap}}}}{RT^2} \quad (1)$$

In Eq. (1), P is the vapor pressure of the liquid {any unit OK}, T is the temperature in K, R is the gas constant, and $\overline{\Delta H_{\text{vap}}}$ is the molar heat of vaporization of the liquid. {As you know, it is not “legitimate” to take the logarithm of a number with units. Consequently, the pressure is always compared with reference to a standard state – 1 atm, 760 mm Hg, kPa, etc. However, this value only changes the intercept of the equation and not the slope.} The vapor pressure of a pure liquid is often represented by Eq. (2), the integrated form of Eq. (1), with the additional assumption that the heat of vaporization is independent of temperature.

$$\ln\{P\} = A - \frac{\overline{\Delta H_{\text{vap}}}}{RT} \quad \text{or} \quad \log\{P\} = A' - \frac{\overline{\Delta H_{\text{vap}}}}{2.3025RT} \quad (2)$$

The values of A and A' in Eq. (2) depend on the units used for pressure. The units for heat of vaporization depend on the units of R.

Although the heat of vaporization of a liquid is actually a temperature dependent function, Eq. (2) gives a good fit to vapor pressure data over a wide range of temperatures, as long as the temperature is well below the critical temperature and gives an average heat of vaporization over the temperature range. There are compensating errors in the approximations.

Many other equations have been proposed for the variation of vapor pressure of a liquid with temperature. Another equation that is often used to describe vapor pressure is the Antoine equation,

$$\log P = A - \frac{B}{t + C} \quad (3)$$

In this equation, A, B, and C are empirical constants obtained from a fit to the data; t is the temperature in °C. There is no physical significance for any of the constants.

The determination of vapor pressure of a liquid was an experiment in CHEM 445 for several years. The attached data were reported for this experiment in a previous semester. You will analyze these data in a report.

This “dry” lab will consist of two reports. The first report will include just the data table from Question 1 and the first two plots from Questions 2 and 3 **{75 points}** please submit into Canvas into the **Data Analysis Part I (DAS)**. The second report will include a **Summary** of what you consider to be the important conclusions **from the data of the experiment {25 points}**, and a **Results and Discussion section {100 points}**– all in the specified form. Because you did not do the experiment, **no Procedure section** is required. No **Introduction** is needed, either. Please submit into Canvas into the **Data Analysis Part II (DAS)**. Extensive discussions about writing lab reports are given on the Canvas site.

1. The data at the end of this experiment are not in the proper form for a technical report. They reflect the way data would be recorded in the notebook. Present the data in **Table 1**: temperature, both °C and K; as well as $1/T$, K^{-1} ; P ; and $\log\{P\}$ and $\ln\{P\}$ for each experiment. **Each table is numbered and has a brief descriptive heading above the table.** Columns are appropriately labeled, with units. Use standard abbreviations. Pay attention to headings and digits in the tables. Your choice of digits should reflect the presumed precision of the measurements. Gridlines help the presentation of the data. You control the width of the columns.

2. Plot these data in **Figure 1** as **vapor pressure (dependent variable, vertical axis, Torr = mm Hg, the values obtained from the meter) vs. temperature (independent variable, horizontal axis, t , °C, obtained in the experiment)**. The shape of the curve is independent of the units of pressure; so don't convert to SI unit. There are two sets of data that should be identified as two experiments on the plot. Add the necessary items to the Excel chart (you will refer to it as a figure in all reports) so that the graph looks reasonable. {Remember graph paper.}

All of the data plotted in Figure 1 should be given in a previous table – a rule for all PCHEM lab reports. You need not have a separate table for each line.

You must adjust the Excel Chart format to give a satisfactory figure each time. Label axes and use a reasonable number of digits for values on each axis. **Do not use a title within the figure.** (Ignore Microsoft) Vertical gridlines are essential to each figure.


A Trendline looks good in the figure, but **don't put an equation in the figure. Don't use a “connect a dot” plot.** When you write a report, **NEVER USE X AND Y AS VARIABLES** in any CHEM 445 lab report (and probably not in any other report, in spite Excel); give appropriate symbols.

Put a **brief descriptive title {caption} below the figure in the text of your report.** The descriptive title is not a sentence or part of the subsequent discussion. In addition to the figure caption, you must give a brief discussion about in the figure in the text below the figure.

This is the simplest plot to show whether or not the data are reproducible. The parameters from the trend line have no physical significance.

3. Plot the data (Excel Trendline, OK) in **Figure 2** in the more common form as **$\log\{P\}$ vs. $1/T$** , according to Eq. (2). {In this case, T is in K; it makes a difference. $\log\{P\}$ refers to base 10 logs.} Use different shapes or colors for the points for the two experiments. The traditional form is that the dependent variable, **$\log\{P\}$** , is on the vertical axis and the independent variable, **$1/T$** , is on the horizontal axis. Trendline gives a value for the slope. The intercept is not experimentally significant.

4. Question 4 uses the results from question 3. Trendline gives values for the parameters, but does not give an estimate of the uncertainty in these values.

Obtain values for the two constants in this equation and their uncertainties using  Regression or LINEST in Excel. Give the equation with values for the coefficients and **uncertainties** in the text. **{Repeat warning: do not use X and Y as variables.}** Each equation is written on a separate line and equations are numbered sequentially on line. Use Equation Editor or better (not standard typing) to make the equation easily readable.

Calculate the average heat of vaporization in kJ/mole (standard unit) for each set of data of **log{P} vs. 1/T plot**, with the uncertainty {using Regression or LINEST}.

Give a “reasonable” number of digits for the heat of vaporization and the uncertainty (standard error). The programs give a ridiculous number of digits in the answers. The value and the uncertainty should have the same number of decimals. Purists say that one should give an uncertainty with only one digit: $XX.XX \pm 0.0Y$. However, many report their data a little better than they should as $XX.XX \pm 0.YY$. Three or more digits in the uncertainty are wrong.

The integrated equation, Eq. (2), gives a single value for the heat of vaporization over this temperature range for each experiment. Are the values for **the two experiments in agreement?**

5. However, the heat of vaporization may not be temperature independent. Plot your data as **ln{P} vs. T** in **Figure 3**. This plot is not linear and is not the Clausius-Clapeyron equation. Fit your data with Excel – a second order plot will work. You need to choose the number of digits that you retain in the values of constants from your data. For example, a single digit like 0.02 is not a good choice because the value can be anywhere from 0.015 to 0.024.

Use the equation that fits your data and Eq. {1} to calculate the heat of vaporization at each temperature. **Are the values “relatively constant”? Is there a trend in the values?** Tabulate these data in **Table 2** and **compare the average value for the heat of vaporization from this table with the value you obtained with the integrated Clausius-Clapeyron equation, Eq. {2}.**

6. A better fit to vapor pressure data can be generally obtained by using the Antoine equation, Eq. (3) than with the Clausius-Clapeyron equation. Three constants will generally give a better fit than two. Obtaining the three coefficients for the Antoine equation is more difficult than obtaining two coefficients for the Clausius-Clapeyron equation, Eq. (2). The Antoine equation is not a linear function of temperature or reciprocal of temperature. However, data have been fitted to the Antoine equation for many years; so you should be able to obtain the coefficients using a computer.

a. Following Wilhoite and Zwolinski² (names you should associate with thermodynamic properties of pure compounds), one can rearrange Eq. (3) to the following:

$$t \cdot \log P = (AC - B) + A \cdot t - C \cdot \log P \quad (4)$$

The **t*logP** term is treated as the dependent variable: a linear function of two independent variables, **t** and **logP** – sometimes called Multiple Linear Regression. Analyze these data using LINEST or Regression to obtain the coefficients and their uncertainties. {Pay attention to the order of columns and the signs; they are confusing – or were to me.} Base 10 logs and temperature in °C.

Give the coefficients of the Antoine equation, **A**, **B**, and **C** and their uncertainties in the text.

b. Use **Solver**⁴ to calculate A, B, and C from the data and **Eq. (3), not Eq. (4)**. The values for the coefficients may be different from the values that you obtained using Eq. (4).

c. Check the fit of these equations to the experimental data with a plot, **Fig. 4**, of the fractional error, $\{P_{\text{Exp}} - P_{\text{calc}}\}/P_{\text{Exp}}$, vs. P_{Exp} for the values for P that you calculate at each temperature from the parameters in the **integrated form of the Clausius-Clapeyron equation** from the **Antoine equation using the parameters obtained from Multiple Linear Regression** using Eq. (4), and **from the Antoine equation using the parameters obtained from Solver**.

7. Use your constants from the **integrated Clausius-Clapeyron equation** to calculate the normal boiling point of 2-propanol and its uncertainty.

Calculating the uncertainty in the boiling point is tricky because the slope and intercept are not independent of each other. Rearrange the Clausius-Clapeyron equation to calculate T from P .

$$\log P = b + \frac{m}{T} \Rightarrow T = \frac{m}{\log P - b} \quad (5)$$

a. Use the **standard propagation of error analysis** (to calculate the uncertainty in the normal boiling point from the uncertainties in m and b (slope and intercept) that you obtained from Regression or LINEST. If the two variables, in this case, m and b , are independent of each other, then

$$U\{T\} = \sqrt{\left(\left(\frac{\partial T}{\partial b}\right)^2 * s_b^2 + \left(\frac{\partial T}{\partial m}\right)^2 * s_m^2\right)} \quad (6)$$

In Eq (6), $U\{T\}$ is the calculated uncertainty in the normal boiling point; $\frac{\partial T}{\partial b}$ is the partial derivative of (5) with respect to b ; $\frac{\partial T}{\partial m}$ is the partial derivative of (5) with respect to m and s_b^2 and s_m^2 are the squares of the uncertainties (variances) of the intercept and slope from your statistical analysis of the data. When you do this calculation, you may obtain a disconcertingly large uncertainty from a set of measurements that have only small uncertainties.³

b. This estimate of the uncertainty in the normal boiling point is calculated incorrectly because the slope and intercept in Eq. (6) are not independent variables. They are correlated. From your plot, you can easily see that a change in slope causes a change in intercept (and *vice versa*). There is a new term that is needed in the statistical analysis: the covariance.

From Harris {8th Ed or 9th Ed, Appendix B}, the uncertainty in T , including covariance, is calculated according to the equation,

$$U\{T\} = \sqrt{\left(\left(\frac{\partial T}{\partial b}\right)^2 * s_b^2 + \left(\frac{\partial T}{\partial m}\right)^2 * s_m^2 + 2\left(\frac{\partial T}{\partial m}\right)\left(\frac{\partial T}{\partial b}\right)s_{mb}\right)} \quad (7)$$

The first terms are the same as in Eq (6) and are necessarily positive. The third term may be positive or negative and s_{mb} is not immediately available from Regression or LINEST. However,

$$s_m^2 = \frac{s_y^2 n}{D} \quad s_b^2 = \frac{s_y^2 \sum (x_i^2)}{D} \quad s_{mb} = \frac{-s_y^2 \sum (x_i)}{D} \quad (8)$$

In these equations, s_y^2 is the average of the squares of the y deviations; n is the number of measurements, D is a messy determinant, and the other terms are the sum of squares of x_i values and sum of x_i values. In the case of the Clausius-Clapeyron equation, Eq (2) or Eq (5), you plot $\log P$ vs. $1/T$; consequently, $x_i = 1/T_i$. The values of s_m and s_b are given by Regression or LINEST.

Rearrange these equations to get an expression for s_y^2 in terms of s_m^2 and another expression for s_y^2 in terms of s_b^2 . Substitute these equations into the equation for s_{mb} and you will obtain two equations for s_{mb} , which will (should) give the same numerical value:

$$s_{mb} = (-s_b^2) \left(\frac{\sum(x_i)}{\sum(x_i^2)} \right) \quad \text{and} \quad s_{mb} = (-s_m^2) \left(\frac{\sum(x_i)}{n} \right) \quad (9)$$

Calculate s_{mb} from either equation in (9) and then calculate the uncertainty in the normal boiling point using Eq (7). Including covariance gives a more reasonable estimate in the uncertainty of the normal boiling point.

Data for this experiment are below.

References

1. Glasstone, S., *Textbook of Physical Chemistry*, 2nd Ed., D. van Nostrand Co., New York, 1946.
2. Wilhoite, R. C. and Zwolinski, B. J, *J. Phys. Chem. Ref. Data*, 2, Suppl. 1, 1973, App. B.
3. Meyer, E. F, *J. Chem. Educ.* **1997**, 74, 1339.
4. **Solver** is available as an add-in to Excel. Examples of the use of Solver for chemical calculations are given in Harris, *Quantitative Chemical Analysis* - any recent edition. A copy is available in PCHEM Lab. An early article on the use of Solver for chemical problems is D. C. Harris, *J. Chem. Educ.* **1998**, 75, 119. Most of the Internet sites that I found gave business examples.

Learning goals for this experiment: Vapor pressure as function of temperature; Clausius-Clapeyron and Antoine equations; data analysis and plotting with Excel; use of Solver; statistical analysis with covariance; writing technical reports.

Data Table: Vapor Pressure			
First Experiment		Second Experiment	
t, °C	P, Torr	t, °C	P, Torr
25.0	44.4	25.0	44.3
26.7	48.9	27.2	50.1
27.3	50.7	28.7	55.1
30.3	60.1	30.8	62.1
34.6	76.2	35.7	82.4
37.5	91.3	39.8	103.5
40.9	109.8	46.6	147.7
45.5	138.1	50.8	182.4
50.7	182.6	55.3	232.2
54.5	222.8	60.4	292.9
59.7	284.9	65.4	369.0
65.7	373.1	69.2	439.1
70.4	461.6	74.6	551.4
74.5	553.7	79.4	671.2
79.4	675.3	81.6	736.8
82.5	750.3	82.0	746.4