Worksheet: Determine Antoine constants for saturation pressure

Name(s) ____

This experiment measures the saturation pressure (vapor pressure) of a single component over a range of temperatures by injecting sufficient liquid into an evacuated tank at constant temperature to obtain vapor-liquid equilibrium. The constants in the Antoine equation are determined from a series of temperature/pressure measurements. The heat of vaporization is obtained from the Clausius-Clapeyron equation.

Student learning objectives

1. Be able to describe how saturation pressure changes with temperature.
2. Be aware of how saturation pressure can be measured.
3. Know how to fit data to a model to determine parameters.

Equipment

- A spherical tank in a constant-temperature bath. The tank has a port through which liquid is injected. The pressure gauge on the tank reads absolute pressure. Assume that the maximum operating pressure of the tank is greater than the saturation pressure of the liquid at high temperatures, and a pressure relief valve to prevents pressures above the tank rating.
- A vacuum pump (represented with a reset button in the digital experiment) evacuates the tank.
- A heater and temperature controller (represented by a temperature slider in the digital experiment) adjust the temperature of the tank.
- A beaker of the liquid (not shown) and a liquid syringe.

Questions to answer before starting the experiment

This experiment measures saturation pressures by injecting liquid into an evacuated tank. Would more or less liquid need to be injected at higher temperatures to determine saturation pressure? Why?

Suppose sufficient liquid were injected at 50°C to measure saturation pressure. What happens if more liquid is injected?

Given a limited temperature range for experiments because of the pressure rating of the tank, and given that you want to obtain the heat of vaporization from the Clausius-Clapeyron equation

$$\ln\left(\frac{P_1^{sat}}{P_2^{sat}}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where the temperatures are absolute temperatures (K), how should the temperatures chosen for measurements be distributed in the range? That is, should the temperatures be equally spaced in the temperature range or in the inverse temperature range? Explain why.

Before starting

Evacuate the tank (with the reset button) so that the pressure gauge reads zero absolute pressure.

Select a molecule (A, B, C, D, E) to inject from the dropdown menu. Note that the Antoine constants are only good over a temperature range, as indicated by the range of the Temperature slider.

Molecule selected ________________

Temperature range ______________________

Measure saturation pressures.

Select the amount of liquid to inject: ________ mL.

Pick the first temperature to make measurements.

Inject liquid with the syringe, allow the tank to equilibrate, and read pressure from the pressure gauge. How can you determine if you are at vapor-liquid equilibrium (VLE)?

Pick another temperature (keeping in mind how the measurements should be spaced in the temperature range) and repeat measurements until sufficient data are obtained to yield accurate Antoine constants. Record the data in the table below.

Temperature (°C)	Pressure (bar)

Determine Antoine constants.

The Antoine equation (in log base 10) is:

$$log\ \mathrm{P}^{\mathrm{sat}} = A - \frac{B}{T + C}$$

Although Excel Solver could be used to determine the Antoine parameters, it can have difficulty obtaining the best fit. A better approach is to use the LINEST function in Excel to apply multivariable linear regression to fit the saturation pressure (P^{sat}, bar) vs. temperature (T, °C) data in the table to a linearized form of the Antoine equation.

$$log\ P^{sat} = A + (\ AC - B\ )\left(\frac{1}{T}\right) + (\ -C\ )\ \frac{\log P^{sat}}{T}$$

In this equation, the two independent variables (from your measurements) are $\left(\frac{1}{T}\right)$ and $\frac{log\ P^{sat}}{T}$ and the dependent variable is $log\ P^{sat}$ on the left side of the equation. This is calculated from the right side of the equation.

Values of the Antoine parameters (A, B, C) with their units obtained from a multivariable linear regression:

A = _______________

B = _______________

C = _______________

Plot ln P^{sat} versus inverse <u>absolute temperature</u> and use the Clausius-Clapeyron equation to estimate the heat of vaporization (ΔH_{vap}, kJ/mol) of the molecule.

$$\ln\left(\frac{\mathrm{P}_1^{sat}}{P_2^{sat}}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where R is the ideal gas constant, P_1^{sat} is the saturation pressure at temperature T_1, and P_2^{sat} is the saturation pressure at absolute temperature T_2.

ΔH_{vap} = ___________ +/- _________

Questions to answer

1. Are the measurements valid if the tank is at high pressure (or low temperature) so that the gas phase is not ideal? Explain.

2. What are sources of error in the measurements?

3. Using literature data and your measurements of the heat of vaporization and the Antoine constants, which of these molecules is your molecule?
   benzene, toluene, methanol, ethanol, n-octane, n-heptane, water, iso-octane, cyclohexane

4. What safety measures would you employ if making this measurement in the laboratory?