Experiment 13: Vapor Pressure of a Pure Liquid

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Objective

- Measure the variation in vapor pressure with temperature and calculate the molar heat of vaporization of a liquid

- Construct a plot of ln(p) vs 1/T, and use the slope to calculate the heat of vaporization

Theory: Vapor Pressure

- Vapor Pressure: The pressure exerted by a vapor that is in thermodynamic equilibrium with it's condensed phases (solid and liquid) at a given temperature (T) in a closed system.

- Equilibrium Vapor Pressure: Vapor Pressure that is independent of the quantity of the liquid or vapor.

Theory: Clapeyron Equation

- Today, we are concerned with the equilibrium between the gas and liquid phase:

$$X\,(l) \leftrightarrow X\,(g) \qquad (P,T) \qquad (1)$$

- Through Thermodynamics, a definite relationship between P and T at equilibrium exists:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \qquad (2)$$

- Where ΔS and ΔV refer to the change in S and V when one phase transforms to another at constant T and P

Theory: Clapeyron Equation

- Since the change in state is Isothermal, ΔG equals 0 so that:

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V_m} \qquad (3)$$

- Eq 2 or 3 is known as the Clapeyron Equation, which is the exact expression that may be applied to phase equilibria of all kinds, but is currently presented here to be the one-component liquid-vapor case.

Theory: Heat of Vaporization (ΔH_v)

- For vapor pressures less than 1 atm, we can assume $V_{l,m}$ is negligible compared to $V_{g,m}$, so that $\Delta V_m = V_{g,m}$ so that:

$$\frac{dP}{dT} = \frac{\Delta H_v}{TV_{g,m}} \qquad (4)$$
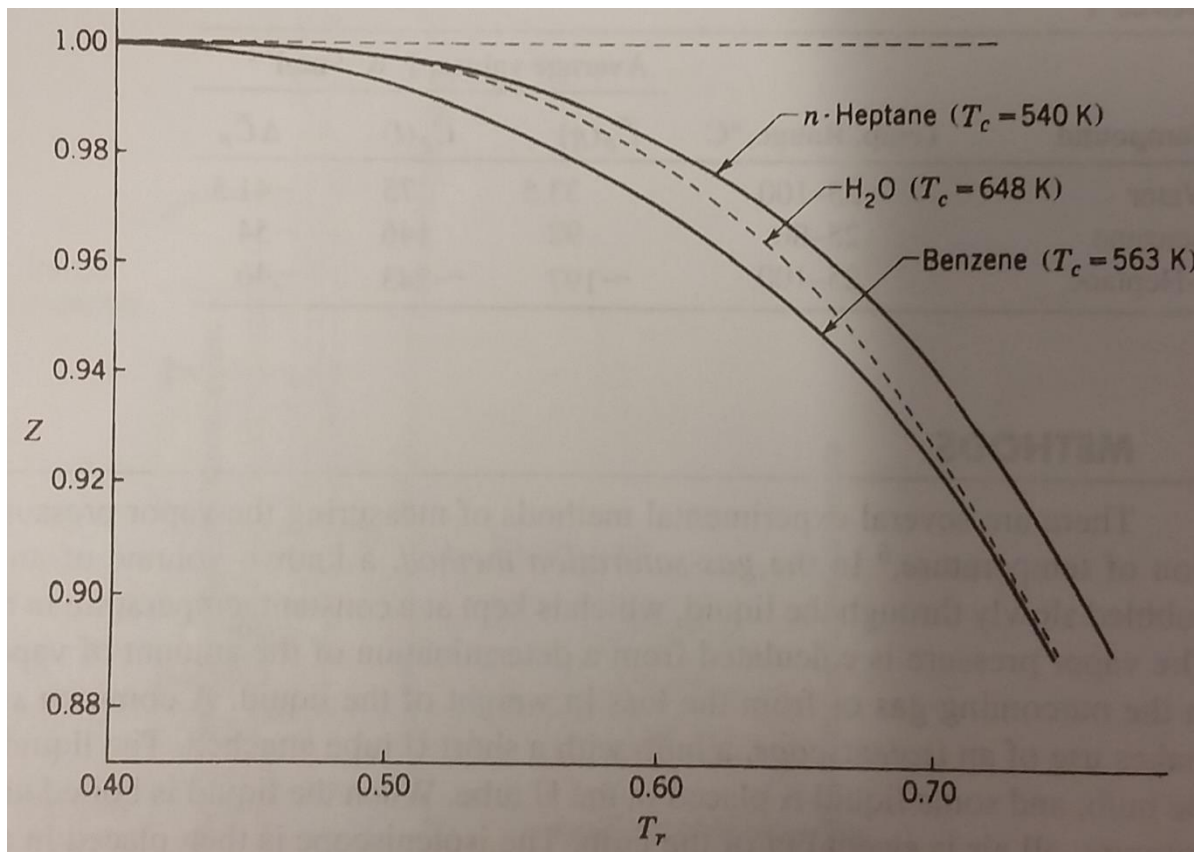
Theory: Compressibility factor (Z)

- Since d ln (P) = dP/P and d (1/T) = -dT/T^2 Eq 4 can be re-written:

$$\frac{d\ln(P)}{d(^1/_T)} = -\frac{\Delta H_v}{R}\frac{RT}{PV_{g,m}} = -\frac{\Delta H_v}{RZ} \qquad (5)$$

- Where the Compressibility Factor (Z) is defined as:

$$Z = \frac{PV_{g,m}}{RT} \qquad (6)$$

- Z is a correction factor to describe the deviation of a real gas from an ideal gas behavior

- Figure 1 shows the compressibility factor, Z as a function of reduced Temperature, Tr (Tr = T/Tc)

Theory: ΔH$_V$ as it varies with T

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p \ dT + \int_{P_1}^{P_2} (\frac{\delta \Delta H}{\delta p})_T \ dP \qquad (7)$$

- Where ΔC$_P$ is Heat capacity at constant P
- For a perfect gas, $(\frac{\delta \Delta H}{\delta p})_T$ is zero and for most real gases $(\frac{\delta \Delta H}{\delta p})_T$ is fairly small so that:

$$\Delta H_{T_2} \approx \Delta H_{T_1} + \overline{\Delta C_P}(T_2 - T_1) \qquad (8)$$

Boiling Point Method

Boiling Point Method

1.) fill the round bottom flask 1/3 with distilled water and boiling chips

2) Correctly position the thermometer such that the bulb is even with the top of the round bottom flask

3) Turn on the water for the condenser, make sure it is draining into the sink

4) Close the stopcock on the trap. Using the vacuum, evacuate the system until a steady reading is reached (about -840 mbar)

Boiling Point Method

5) Check for leaks by turning off the vacuum and checking the pressure for ~5min. If the pressure changes by ~10mbar, release the pressure using the stopcock and check connections

6) Once leak free, heat liquid to a steady boil (~60-80 variastat, then ~30)

7) Record the Barometer Pressure (BR Reading [mbar])

8) Allow pressure and temperature to equilibrate, take measurements every 30 seconds until +/- 0.1 ˚C and +/- 5 mbar

Boiling Point Method

9) Take 10 readings starting with the Ascending cycle first, then 10 readings with the Descending cycle

Pressure Ascending (MR Reading): 850, 700, 550, 400, 250, 100 mbar

Pressure Descending (MR Reading):175, 325, 475, 625, 775 mbar

10) Repeat process 1 additional time

11) For the highest and lowest pressures, record the pressure and temperature every 30 seconds 10 times, for each other pressure, record the temperature and pressure every 30 seconds until within 0.1 ˚C and 2 mbar

Method Notes

- Wear goggles at all times, the evacuated glassware can implode!

- Always have the hood glass lowered

- Be careful when adjusting pressure, do not touch the round bottom flask

Calculations (p 91)

1) Estimate Z for the saturated vapor at the appropriate temperature using Figure 1

2) Calculate the average pressure and temperature for the highest/lowest pressures recorded

Calculations (p 91)

3) Convert all Celsius temperatures to Kelvin and plot ln (p) versus 1/T [P = BR-MR in mbar, and T in Kelvin].

If no significant curvature: draw a straight line through the points.

If there is: draw a smooth curve through the points, and also draw a straight line tangent to the curve's midpoint.

4) Calculate the slope from your plot to obtain $\Delta H_v/RZ$, and calculate ΔH_v in J mol^{-1}

Error Propagation

1) Estimate error bars for only the first and last points of graph to determine the enthalpy of vaporization

2) Estimate the error in the straight line/tangent line slope using the "limiting slope method"

3) Estimate the error in Z by visual inspection

4) Propagate the errors to obtain the error in ΔH_V

Lab Report

1) **Cover Page:** Title of Experiment, Your Name, Your Partner's Name, Group Letter

2) **Abstract:** Single paragraph summarizing the experiment with your experimental heat of vaporization with error

3) **Introduction:** Discussion of the purpose of the lab

4) **Procedure:** Completed and Signed before class

5) **Data:** Signed before leaving the lab

6) **Graphical Analysis:** Plot of ln (P) vs 1/T with error bars where it's necessary

Lab Report Continued

7) Calculations: #1-4 from the presentation (Note: for the questions concerning the plot, have answers in Graphical Analysis)

8) Error Analysis: #1-4 (Note: for the questions concerning the plot, have answers in Graphical Analysis)

9) Discussion & Conclusion: Compare your results with literature values. Use your experimentally determined ΔH_v to calculate ΔS_v and compare the results to Trouton's Rule, explain any differences. **(Note: Cite your sources)**