Vapor Pressure of a Pure Liquid

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Abstract

In this investigation we will examine the relationship between vapor pressure and temperature by considering the properties of benzene, water, and n-heptane at various temperatures and within a vacuum apparatus.

Related Readings

1. Shoemaker, D. P., Garland, C. W., Nibler, J. W. "Experiments in Physcial Chemistry: Experiment 13: Vapor Pressure of a Pure Liquid." McGraw-Hill Companies, Inc: NY. Pp. 199-207. [6th edition in Nobel 107; 5th edition on reserve at library – both editions are equivalent for this experiment]
2. McQuarrie, D.A., Simon, J.D., "Physical Chemistry: A Molecular Approach." University Science Books: Sausalito, CA. Chapter sections 23-3 and 23-4 (pp 935-944).

Background

When a pure liquid is placed in an evacuated bulb, molecules will leave the liquid phase and enter the gas phase until the pressure of the vapor in the bulb reaches a definite value which is determined by the nature of the liquid and its temperature. This is called the vapor pressure of the liquid. In this experiment, the variation of vapor pressure with temperature will be measured and used to determine the molar heat of vaporization, $\Delta\overline{H}_{vap}$.

We are considering the equilibrium between the liquid and gas states. Under these conditions, the relationship between pressure and temperature is given by the Clapeyron equation (see McQuarrie and Simon, pp 938):

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \qquad (1)$$

Since the change in state is isothermal and ΔG is zero (because the system is at equilibrium), ΔS may be replaced by ΔH/T:

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} \qquad (2)$$

For the case of vapor-liquid equilibria in the range of vapor pressures less than 1 atm, one may assume that the molar volume of the liquid is negligible in comparison of the molar volume of the gas. In this case, the Clapeyron equation can be re-written as:

$$\frac{d\ln p}{d(1/T)} = \frac{-\Delta\overline{H}_{vap}}{RZ} \qquad (3)$$

where Z is the compressibility factor:

$$Z = \frac{p\overline{V}_g}{RT} \qquad (4)$$

Equation (3), along with p and T data, can be used to determine $\Delta\overline{H}_{vap}$. (Note: if you plot ln p vs. 1/T, the slope obtained should be $-\Delta H_{vap}/RZ$.) To do so, one needs to know the value of Z. Figure 1 (from Shoemaker, et al.) can be used to determine Z for n-heptane, water, and benzene at a given T_R. McQuarrie and Simon or the NIST webbook can be used to find T_c.

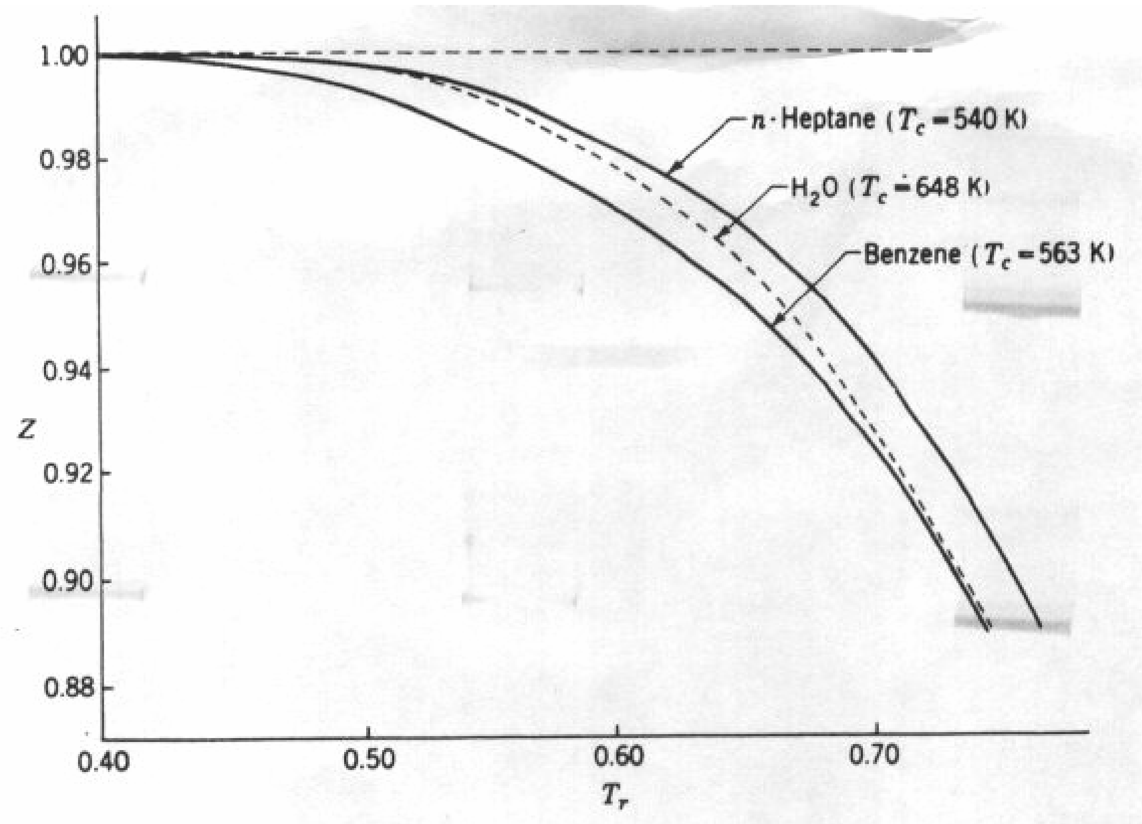

Figure 1: Z vs T_R for n-Heptane, H_2O and Benzene.

Pre-Lab Exercises

Read McQuarrie and Simon, Ch 23-3 and 23-4, and Experiment 13 of Shoemaker et al. (available in Nobel 107 or library). Visit Nobel 107 and examine the vapor pressure apparatus. Make a sketch in your notebook and prepare a procedure for the experiment. Note that our system is slightly different than that described in Shoemaker et al. Make the appropriate adjustments in your plan. **At the start of lab, or before lab, discuss your plan with the TA/lab instructor.**

Procedure
This section gives an overview of the procedure for this lab. You will use the detailed procedure developed by you for the pre-lab (once checked with the lab instructor/TA).

1. Check the apparatus to verify that everything is connected correctly (including the thermometer and manometer).
2. Fill the appropriate flask about ~1/3 full with one of the three liquids of interest; you'll need to repeat the experiment for all three liquids.
3. Collect readings of temperature and pressure (in your detailed procedure, be sure to note how you'll adjust the temperature and pressure). Hint: Read the manometer and thermometer nearly simultaneously once both have equilibrated (note: vapor should be condensing on and dripping off the thermometer to ensure equilibrium).

Report/Analysis
Write your lab report in the style of a communication. Use the following suggestions as starting points for your report…

- Include a sketch of the apparatus in the report (you can attach a hard copy at the end or save room in the experimental section to add a drawing).
- Determine $\Delta\overline{H}_{vap}$ for all three liquids (use Z from Figure 1 for the appropriate temperatures).
- Report an R^2 value and discuss any error in your data.
- Consider the differences in ΔH_{vap} between the compounds and why some compounds are higher then others.
- At the end of your report (i.e., separate from the report), add any comments on how to make this experiment better and logistically smoother.

References

1. Shoemaker, D. P., Garland, C. W., and Nibler, J. W. "*Experiments in Physical Chemistry*: Experiment 13: Vapor Pressure of a Pure Liquid", McGraw-Hill Co, Inc. New York. pp. 199-207.
2. McQuarrie, D.A., Simon, J.D., "Physical Chemistry: A Molecular Approach." University Science Books: Sausalito, CA. Chapter sections 23-3 and 23-4 (pp 935-944).