Liquid-Vapor Equilibrium

Purpose

The purposes of this experiment are to measure the vapor pressure of a pure liquid as a function of temperature and to use that relationship to calculate the heat of vaporization.

Discussion

For any two phases in equilibrium, the free energies must be equal

$$G_\alpha = G_\beta \qquad (8\text{-}1)$$

A small change in free energy in one phase must be balanced by a corresponding change in the other phase.

$$dG_\alpha = dG_\beta \qquad (8\text{-}2)$$

but $dG = VdP - SdT$; so

$$V\alpha dP - S\alpha dT = V\beta dP - S\beta dT \qquad (8\text{-}3)$$

This may be rearranged to give

$$\frac{dP}{dT} = \frac{S_\beta S_\alpha}{V_\beta V_\alpha} = \frac{\Delta S}{\Delta V} \qquad (8\text{-}4)$$

According to the Second Law of Thermodynamics

$$\Delta S = \frac{-\Delta H}{T} \qquad (8\text{-}5)$$

Substituting into equation 8-4,

$$\frac{dp}{dt} = \frac{\Delta H}{T\Delta V} \qquad (8\text{-}6)$$

Now let us consider the liquid-vapor equilibrium. Since the volume of a gas is much larger than that of the same mass of liquid, we may assume that $\Delta V = V_g - V_l \approx V_g$.

Let us also assume that the vapor behaves as an ideal gas; that is, $V_g = RT/P$. Thus

equation 8-6 becomes

$$\frac{dP}{dT} = \frac{P\Delta H}{RT^2} \qquad (8\text{-}7)$$

ΔH is now the enthalpy of vaporization. From calculus, we know that
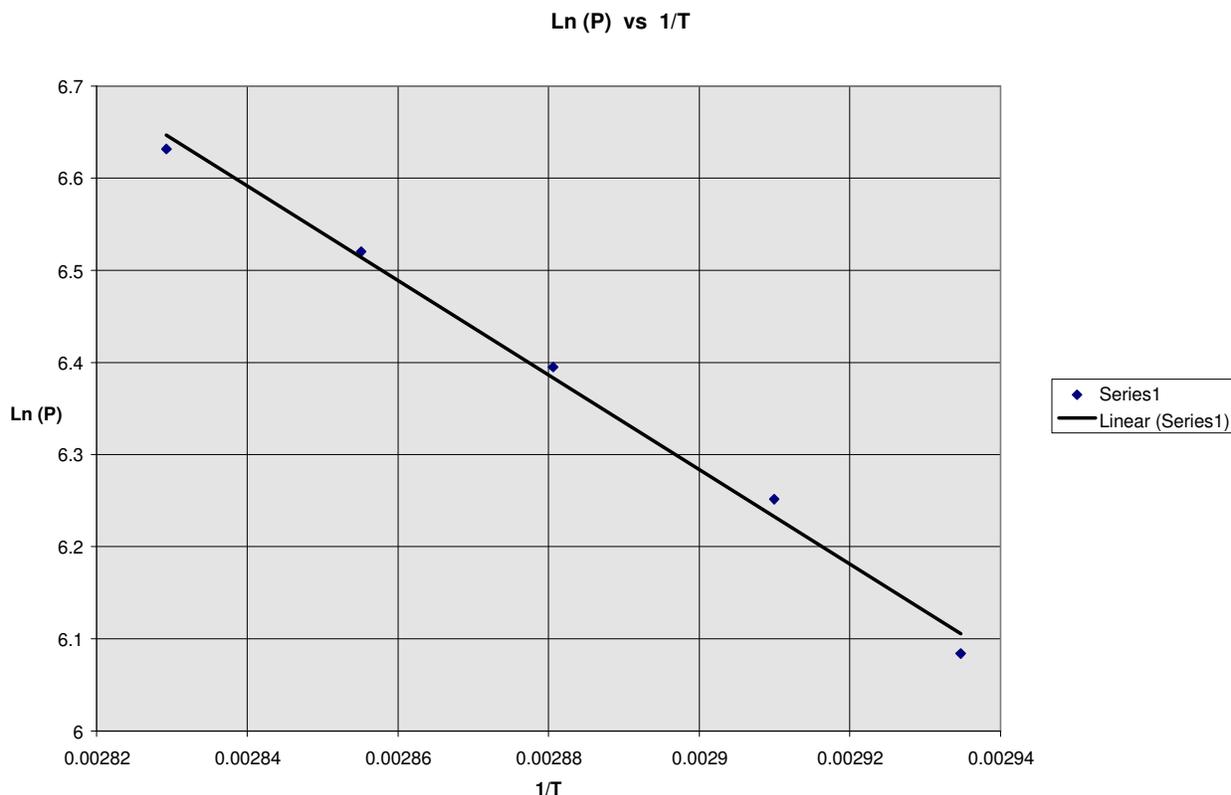
$$\frac{dP}{P} = d\left(\ln P\right) \qquad (8\text{-}8)$$

and

$$\frac{dT}{T^2} = -d\left(\frac{1}{T}\right) \qquad (8\text{-}9)$$

So, we can rewrite equation 8-7,

$$\frac{d\left(\ln P\right)}{d\left(\dfrac{1}{T}\right)} = -\frac{\Delta H}{R} \qquad (8\text{-}10)$$

When we plot $y = f(x)$ vs. x, dy/dx is the slope of the curve. If we plot $\ln P$ versus $1/T$, the slope will be $-\Delta H/R$.

Ln (P) vs 1/T

Thus the heat of vaporization can be calculated from Pressure-Temperature data.

In this experiment you will measure the boiling point at various pressures.

Equipment and Chemicals

Cottrell-Ramsay-Young boiling point apparatus, mercury, manometer, ballast bottle, and aspirator or cacuum pupm, microburner, barometer, hexane, cyclohexane, ethanol, or other volatile liquid.

Procedure

The apparatus should be assembled as shown in Figure 8-1. Care should be taken to see that the system is air-tight.

Place some liquid in the boiling apparatus. Boiling chips may be used to prevent bumping. Evacuate the system to the desired pressure. Carefully heat the liquid to

boiling. Avoid superheating and see that the boiling liquid percolates over the thermometer bulb. Determine the boiling pint at that given pressure. The pressure inside the system is the atmospheric pressure minus the difference in height of the two mercury columns in the manometer.

Add air to increase the pressure approximately four cm. Again determine the boiling point. Repeat at other pressures to get a wide range of pressures and temperatures.

Repeat with other samples of the same liquid.

CALCULATIONS

Plot a graph of $\ln P$ versus $\frac{1}{T}$. Determine the slope and use equation 8-10 to calculate the heat of vaporization. Also, use computer programs (LNREG1) to find slope.
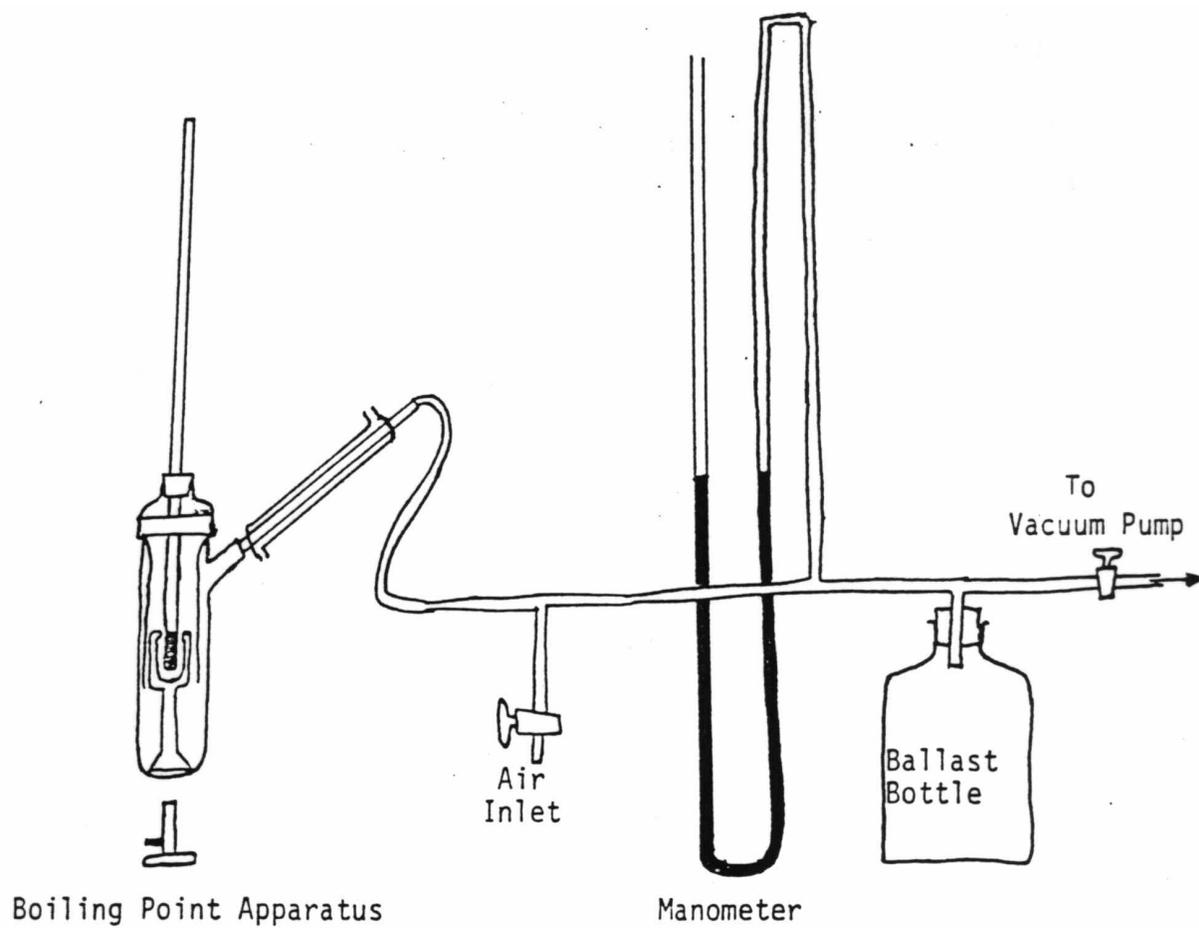
Figure 8-1. Cotttrell,Ramsay-Young Vapor Pressure Apparatus

SAMPLE CALCULATIONS

Experiment: Enthalpy of Vaporization

Sample Data:

Pressure (mmHg)	Boiling Pt. (°C)	Boiling Pt. (K)	ln P	1/T (x 10^{-3} K^{-1})
754.4	80.1	353.1	6.626	2.832
714.4	78.2	351.2	6.571	2.847
674.4	76.5	349.5	6.514	2.861
634.4	74.45	347.45	6.453	2.878
594.1	72.5	345.5	6.387	2.894

Calculations: Performing a linear regression gives the slope and y-intercept for the line of best fit through the data. For the above data, the slope is -3844.75 K. Thus, the value for the Heat of Vaporization (ΔH_{vap}) of cyclohexane is determined to be:

ΔH_{vap} = - (slope) x R = -(-3844.75 K) x 8.314 J/K mol
=-31965.25 J/mol