

# Experiment 3

## Vapor Pressure of a Pure Liquid : Boiling Point Method

### **Purpose :**

In this experiment the variation of vapor pressure with temperature will be measured and used to determine the molar heat of vaporization.

### **Principle :**

The change of vapor pressure with temperature is given by the differential form of the **Clausius-Clapeyron** equation, namely

$$\frac{d \log P}{dT} = \frac{\Delta \bar{H}_{vap}}{2.303RT^2} \quad \text{or} \quad \frac{d \log P}{d(1/T)} = -\frac{\Delta \bar{H}_{vap}}{2.303R} \quad (1)$$

The equation is more useful when integrated either as an indefinite integral or between specified limits. It is generally used in the following forms:

$$\log \frac{P_2}{P_1} = -\frac{\Delta \bar{H}_{vap}}{2.303R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2)$$

The validity of the **Clausius-Clapeyron** equation depends upon several assumptions

- (1) The heat of vaporization is independent of temperature.
- (2) The specific volume of liquid is small compared to that of the vapor.
- (3) The vapor obeys the simple equation of state for gases.

For many non-polar liquid the molar entropy of vaporization at the standard boiling point is constant.

$$\Delta \bar{S}_{vap, nbp} = \frac{\Delta \bar{H}_{vap, nbp}}{T_{nbp}} \approx 21 \text{ cal/deg} \cdot \text{mol} \approx 87 \text{ J/deg} \cdot \text{mol} \quad (3)$$

This equation is known as **Trouton's** rule and is useful to estimate the molar heat of vaporization of a liquid of known boiling point.

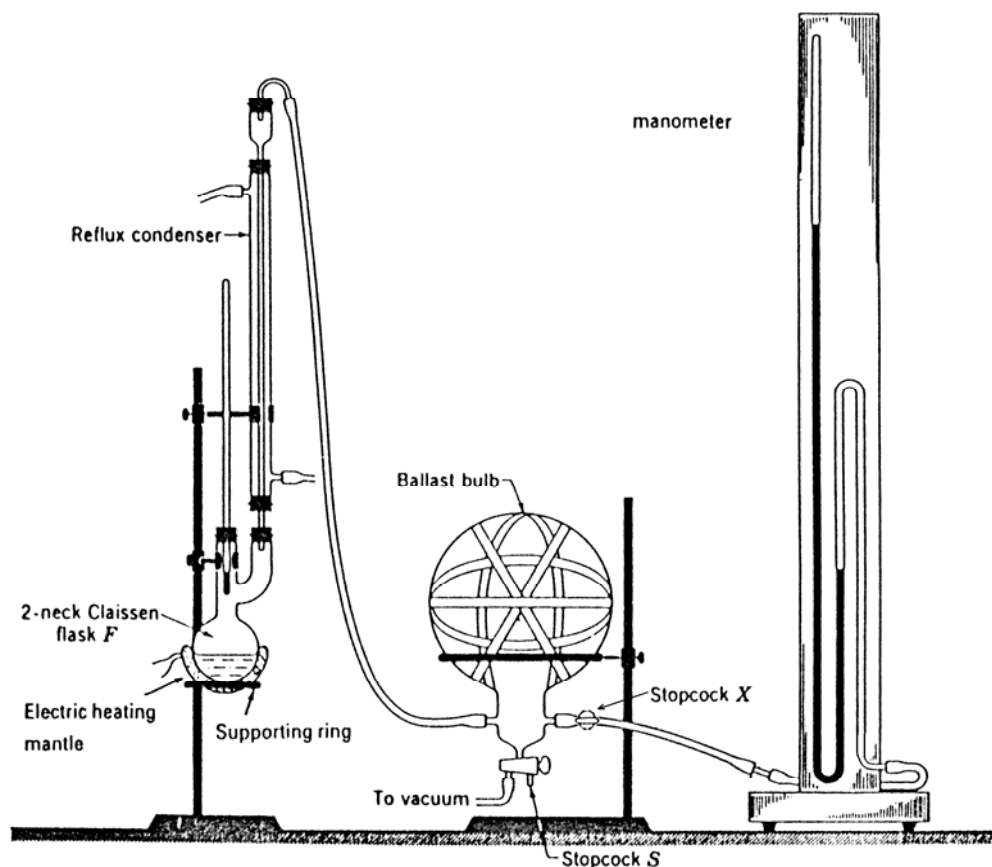
### **Apparatus and Chemicals :**

Two 250-ml round-bottomed flasks; reflux condenser; Claisen adapter; 100°C thermometer with one-hole rubber stopper; funnel; 100-ml graduated cylinder; magnetic stirring bar, ballast bulb; open-tube manometer; vacuum pump; magnetic stirrer; heating mantle, transformer; water pump.

Distilled water; n-heptane.

### **Procedures :**

- (1) Assemble the apparatus as **Fig. 3**. Pour about 75 ml of distilled water to be studied into the flask and add a few boiling chips to reduce "bumping".



**Figure 3. Boiling-point apparatus**

- (2) Close the stopcock *X* and don't heat the solvent. Draw out the air from the ballast bulb by using vacuum pump and adjust the pressure difference ( $\Delta h$ ) of the manometer to about *60 cm*. Use the manometer with the greatest care.
- (3) Open the stopcock *X* slowly and carefully and adjust the heating mantle so as to attain steady boiling of the liquid, but avoid heating too strongly. Begin to watch the manometer and the thermometer when the boiling condition is steady. When manometer and thermometer appear to be as steady as they can be maintained, read them as nearly simultaneously as possible.
- (4) Vapor should be condensing on and dripping from the thermometer bulb to ensure that the equilibrium temperature is obtained. Record the temperature and the readings of the manometer. The thermometer scale should be read to the nearest  $0.1^{\circ}\text{C}$ . In reading the manometer, record the position of each meniscus ( $h_R$ , and  $h_L$ ) and estimate your readings to the nearest *1 mm*.
- (5) Change the pressure in the system between measurements. After a short time admit some air or remove some air by opening stopcock *S* for a few seconds. Repeat as often as necessary to attain the desired pressure. Repeat **steps (3)-(4)** to get other data.

(6) Take readings at approximately the following pressure differences:

$$\Delta h = 60, 55, 50, 45, 40, 30, 20, 10, 0 \text{ cmHg.}$$

(7) Repeat **steps (1)-(6)** by using the n-heptane as a investigated reagent.

### **Calculations :**

(1) Correct all manometer pressure readings by  $\Delta h_{corr.} = (h_R - h_L)(1 - 1.8 \times 10^{-4} t)$ , where  $t$  is the Celsius temperature of the manometer.

(2) Plot  $\log P$  vs.  $1/T$  and calculate  $\Delta \bar{H}_{vap}$ .

(3) Extrapolate the  $\log P - 1/T$  curve to find the temperature at which  $P = 760$  mmHg. Compare this value with the accepted boiling point.

(4) Check the results with the **Trouton's** rule.

### **References :**

(1) **P. W. Atkins and J. de Paula**, "Physical Chemistry," 9th ed., pp. 105-107, 148-149, Oxford University Press, U.S.A (2010).

(2) **I. N. Levine**, "Physical Chemistry," 6th ed., pp. 213, 214-217, McGraw-Hill, U.S.A. (2009).

(3) **D. P. Shoemaker, C. W. Garland, and J. W. Nibler**, "Experiments in Physical Chemistry," 5th ed., pp. 219-229, McGraw-Hill, Singapore (1989).

(4) **O. F. Steinbach and C. V. King**, "Experiments in Physical Chemistry," pp. 83-89, American book company, U.S.A. (1950).