Name_____ Section_____

Partner _____ Date _____

Experiment 12B

MOLAR HEAT OF VAPORIZATION, ΔH_{VAP}

MATERIALS:

Isoteniscope, cyclohexane, water aspirator, barometer.

DISCUSSION:

As is the case for a sample of gas molecules, all the individual molecules of a liquid do not have the same energy. At any given temperature the molecular energies of a liquid may also be described by a Boltzmann distribution function. The molecules at the surface of a liquid are attracted toward the interior of the liquid by attractive intermolecular forces and in order for a liquid molecule to escape into the vapor it must have an energy at least equal to these attractive forces. Thus, the rate at which the molecules leave the surface of the liquid, R (or the rate of evaporation) should be proportional to the fraction of molecules having an energy equal to, or greater than, the escape energy, E. This fraction is given by the Boltzmann factor $e^{-E/kT}$ where k is the Boltzmann constant and T is the absolute temperature. Thus, $R = A_1e^{-E/kT}$ where A_1 is a constant of proportionality. Once in the vapor phase, the molecules also have a Boltzmann distribution of energies. These vapor molecules will constantly be bombarding the surface of the liquid and a certain fraction will have so little kinetic energy or will have it so dissipated upon collision with the surface that they will be captured. The number of molecules having this energy at a given temperature will depend upon the concentration of vapor molecules, which in turn depends upon the pressure, P, of the vapor. Then the rate of condensation, R_c, is given as $R_c = A_2P$ where A_2 is a constant of proportionality.

Since the vapor pressure above a liquid is a constant at constant temperature, the equilibrium rate of evaporation, R_e, is equal to the rate of condensation into the liquid, i.e. $R_e = R_c$.

(At this point, a dynamic equilibrium exists and there is a continuous interchange of molecules between the liquid and vapor phases even though the macroscopic properties of the system are remaining constant.)

$$A_1e^{-E/kT} = A_2P \quad \text{and} \quad P = \frac{A_1e^{-E/kT}}{A_2}$$

Taking the natural log of both sides yields

$$\ln P = \ln\left(\frac{A_1}{A_2}\right) - \left(\frac{E}{kT}\right)$$

or

$$\ln P = -\frac{E}{kT} + A_3$$

Multiplying both E and k by Avogadro's number yields

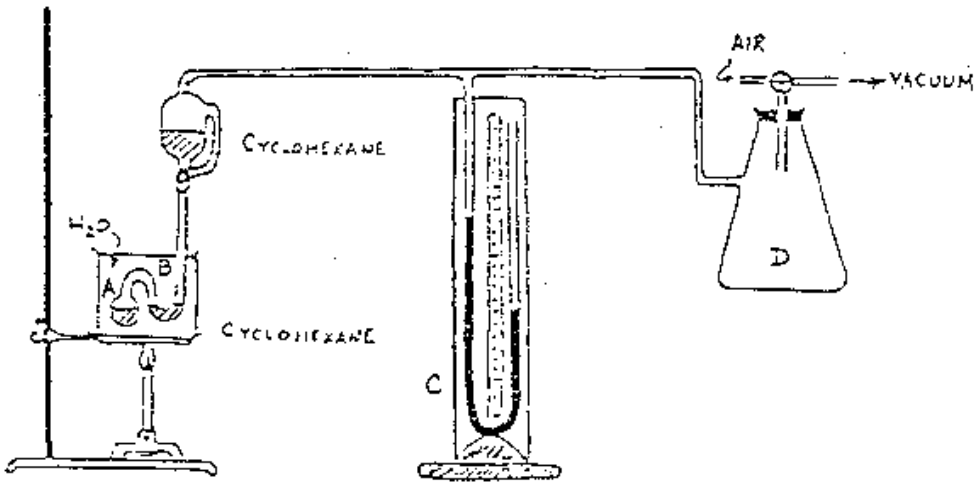
$$\ln P = \frac{-\Delta H_{vap}}{RT} + A_3$$

where ΔH_{vap} is the molar heat of vaporization and R is the gas constant.

MOLAR HEAT OF VAPORIZATION OF CYCLOHEXANE

PROCEDURE (group demonstration)

There are three methods generally used for measuring vapor pressure of liquids: static, dynamic, and gas saturation. We will use the most simple, and perhaps the most accurate, static method. This employs the use of an isoteniscope. A bulb **A** is half filled with cyclohexane as is the attached U tube, **B** (see diagram). The bulb **A** is connected to a mercury manometer **C** and to a large vessel **D** which serves as a ballast tank to smooth out minor pressure fluctuations. The isoteniscope **A-B** is placed in the water bath and the apparatus evacuated until the liquid boils and the air in **A** has been removed. (This usually takes about five minutes.) The pressure is now adjusted by admitting air into **D** until the levels in the U tube are the same. The pressure above the cyclohexane, which is the vapor pressure, is now equal to the pressure above **B** which may be determined by means of the manometer.



Starting from a temperature of about 15°C, record both temperature and pressure at intervals of approximately 7°C. With this data make a plot of 1n P vs 1/T. The slope of this straight (?) line (Was Boltzmann correct?) times (-)R should yield ΔH_{vap}. Data manipulation, graphing, and regression analysis (including linear regression) can be easily accomplished using a computer spreadsheet such as QUATTRO.

LAB REPORT:

In your lab report for this experiment include:

1. All data and calculations.

2. A plot of 1n P vs 1/T

3. The percentage deviation of your ΔH_{vap} for cyclohexane from the literature value. (Give reference.)

4. The value of A_3.