KNUDSEN EFFUSION

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- ABSTRACT:

  The Knudsen effusion method is used to determine the vapor pressure of naphthalene at several temperatures.

- TEXT REFERENCE:


- OTHER REFERENCES:

- GENERAL DESCRIPTION AND THEORY:

  Gases which are in a vessel at very low pressures will collide with the wall. If there is an opening in the wall the gas molecule colliding with the area of the hole will leave the container. By determining the loss of material from the container over a period of time, both the rate of effusion and the vapor pressure of the material may be determined.

- EQUIPMENT:

  The equipment required is a vacuum system with provision for a Knudsen cell which is connected to the vacuum system and which can be placed in a temperature bath. A diagram of the system is given below.

- CHEMICALS:

  Naphthalene.
• DIAGRAMS:

Knudsen Cell

Figure 1

Figure 2
**LABORATORY PROCEDURE:**

Two determinations will be done per run. First perform a determination at the ice temperature and room temperature and then a determination at above 30°C. About 1.5 hours will be required for the first run and about one hour for the second run. The hole diameter is 1.588 mm and the length of the hole is 1.184 mm. (The l/r ratio is 1.49, giving a Clausing factor of 0.5806).

The Knudsen cell used in this experiment is a copper tube which can be inserted into an Ultra-Torr vacuum connection. Weigh the naphthalene into this cell and attach it to the vacuum system by means of the ultra-torr connector. Then start the vacuum system with the side valve closed (see figure 1). The main switch is on the side of the frame with the AC receptacle box (see figure 2). Next turn on the vacuum pump. Set up an ice water mixture to cover the bottom of the Knudsen cell. Use temperature control on the inside Knudsen cell. The thermocouple gage is on the front panel and it will be on at this time. Now the valve can be opened (the line on the knob will be vertical when open and horizontal when closed) and the experiment started. Make sure that water is flowing through the diffusion pump and the trap. When the pressure has dropped below 100 microns, the diffusion pump can be turned on by using the switch on the main panel. (The vacuum system will probably be running before the lab starts so that opening the side valve will evacuate the upper system.) Allow the system to run for about one and a half hours. Remember to record the time. Turn the valve to pumps off and open the side valve slowly. Air will gradually leak in and the cell can be removed when the pressure increases to over 2000 microns. Weigh the cell and start again for a run at room temperature.

**CALCULATIONS:**

The net rate of effusion through the hole is given by:

\[
\frac{dn_{\text{eff}}}{dt} = \frac{A(P - P')}{\sqrt{2\pi MRT}}
\]

where \(P\) and \(P'\) are the pressures on either side of the hole, \(A\) is the hole area, \(M\) is the molecular weight of the gas, \(T\) is the temperature and \(R\) is the ideal gas constant. Assuming that the hole has negligible thickness and that the pressure on the vacuum side of the hole is negligible, the effusion rate expressed in terms of weight loss per unit area per unit time (\(Z'\)) is given by:

\[
Z' = \frac{mN^*u}{4} = \frac{m}{4} \left( \frac{N_A P}{RT} \right) \left( \frac{8RT}{\pi M} \right)^{\frac{1}{2}}.
\]
where $m$ is the mass of a single molecule, $N^*$ is the number density, and $N_A$ is Avogadro’s number. This may be integrated over time and solved for pressure to give:

$$P = \left( \frac{g}{At} \right) \left( \frac{2\pi RT}{M} \right)^{\frac{1}{2}},$$

where $g$ is the mass loss. Be sure to keep track of the units for this calculation. Since the hole is not infinitely thin, we must take into account the likelihood that some of the molecules will collide with the edge and return to the inside of the cell. Clausing (Ann. Physik. 1932, 12, 961) derived a factor ($K$) to account for this effect ($P_{\text{true}} = P_{\text{measured}}/K$).

If we assume that $\Delta C_p$ for the vaporization process is negligible, we may obtain $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$ for the vaporization from a plot of $\ln P$(in atmospheres) versus $1/T$:

$$\ln P = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}.$$

Compare the thermodynamic values and vapor pressures with those found in the literature.

- **LITERATURE VALUES:**