

## VAPOR PRESSURE OF A PURE LIQUID

**OBJECTIVE:** To measure the temperature dependence of the vapor pressure of a pure liquid and to use this data to determine the molar heat of vaporization of this pure liquid using the Clausius-Clapeyron equation.

**THEORY:** We are concerned with the equilibrium between a pure liquid and its vapor:



It can be shown thermodynamically that a definite relationship exists between the values of  $P$  and  $T$  at equilibrium as given by

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad (2)$$

In Eq.(2)  $dP$  and  $dT$  refer to infinitesimal changes in  $P$  and  $T$  for an equilibrium system composed of a pure substance with both phases always present;  $\Delta S$  and  $\Delta V$  refer to the change in  $S$  and  $V$  when one phase transforms to the other at constant  $P$  and  $T$ . Because the change in state (1) is isothermal and  $\Delta G = 0$ ,  $\Delta S$  can be replaced by  $\Delta H/T$ . The result is

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \quad (3)$$

Equation (2) or (3) is known as the Clapeyron equation. It is an exact expression which may be applied to phase equilibria of all kinds although it has been presented here in terms of the one-component liquid-vapor case. Since the heat of vaporization,  $\Delta H_v$  is positive and  $\Delta V$  is positive for vaporization, it is then obvious that the vapor pressure must increase with increasing temperature.

For the case of vapor-liquid equilibria in the range of vapor pressures less than one atm, one may assume that the molal volume of the liquid  $V_l$  is negligible in comparison with that of the gas  $V_g$  so that  $\Delta V \cong V_g$ . This assumption is very good in the low pressure region, since  $V_l$  is usually a few tenths of a percent of  $V_g$ .

$$\frac{dP}{dT} = \frac{\Delta H_v}{TV_g} \quad (4)$$

Since  $d(\ln P) = dP/P$  and  $d(1/T) = -dT/T^2$ , we can rewrite Eq.(4) in the form,

$$\frac{d(\ln P)}{d(1/T)} = \frac{-\Delta H_v}{R} \quad \frac{RT}{PV_g} = - \frac{\Delta H_v}{zR} \quad (5)$$

where we have introduced the compressibility factor ( $z$ ) for the vapor:

$$z = \frac{PV_g}{RT} \quad (6)$$

Eq.(5) is a convenient form of the Claperyon equation. We can see that if the vapor were a perfect gas ( $z = 1$ ) and  $\Delta H_v$  were independent of temperature, then a plot of  $\ln P$  vs.  $1/T$  would be a straight line with a slope having the value of  $\Delta H_v/R$ . Indeed, for many liquids  $\ln P$  is almost a linear function of  $1/T$ , which implies at least that  $\Delta H_v/z$  is almost constant.

Let us now consider the behavior of  $z$  as a function of temperature for the saturated vapor. It is difficult to carry out  $P$ - $V$ - $T$  measurements on gases close to condensation and such data are scarce, but data are available for water, and theoretical extrapolations have been made for the vapor of "normal" liquids based on data obtained at higher temperatures. Figure 1 shows the variation of the compressibility factor  $z$  for a saturated vapor as a function of temperature in the case of water and two normal liquids, benzene and n-heptane. For the temperature axis, a "reduced" temperature  $T_r$  is used;  $T_r = T/T_c$ , where  $T_c$  is the critical temperature. This has the effect of almost superimposing the curves of many different substances; indeed by the law of corresponding states such curves would be exactly superimposed. In general, it is clear that  $z$  decreases as the temperature increases.

*Figure 1.* The compressibility factor  $z$  of saturated vapor as function of reduced temperature  $T_r$  for water, benzene, and *n*-heptane.

Water, due to its high critical temperature, is a reasonably ideal gas even at 100°C where  $z = 0.986$ . But *n*-heptane at its one atm boiling point of 98°C has a value of  $z = 0.95$  and is relatively nonideal. For many substances, sizable gas imperfections are present even at pressures below one atmosphere.

The next thing to consider is the variation of  $\Delta H_v$  with temperature. For a change in state such as Eq.(1),

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p dT + \int_{P_1}^{P_2} \left( \frac{\partial H}{\partial P} \right) dP \quad (7)$$

Since the last term is zero for an ideal gas and small for most real gases, Eq.(7) can be approximated by

$$\Delta H_{T_2} \cong \Delta H_{T_1} + \Delta C_p(T_2 - T_1) \quad (8)$$

where the average value over the temperature interval,  $\Delta C_p$ , is used. In order for  $\Delta H_v$  to be temperature independent,  $\Delta C_p$  must be very close to zero, which is generally not the case. Heat capacities for water, benzene and n-heptane are given in the Table below. Values for other organic compounds can be found in the "Handbook of Chemistry and Physics", 58th Ed. (1977-1978) pp. D160-161.

Compound	Temp. Range (°C)	Average Values (J deg <sup>-1</sup> mol <sup>-1</sup> )		
		$C_p(g)$	$C_p(l)$	$\Delta C_p$
Water	25-100	34	75	-41
Methanol	25-65	44	82	-38
n-Heptane	25-100	166	225	-59

For n-heptane, the specific heat of both gas and liquid changes rapidly with temperature; use of average values will give only an order of magnitude result. In general, the value of  $\Delta H_v$  will decrease as the temperature increases. Since both  $\Delta H_v$  and  $z$  decrease with increasing temperature, it is possible to see why  $\Delta H_v/z$  might be almost constant and give a nearly linear plot of  $\ln P$  vs.  $1/T$ .

There are several experimental methods of measuring the vapor pressure as a function of temperature. In the gas-saturation method a known volume of an inert gas is bubbled slowly through the liquid, which is kept at constant temperature in a thermostat. The vapor pressure is calculated from a determination of the amount of vapor contained in the outgoing gas or from the loss in weight of the liquid. A common static method makes use of an isoteniscope, a bulb with a short U tube attached. The liquid is placed in the bulb and some liquid is placed in the U tube. When the liquid is boiled under reduced pressure, all air is swept out of the bulb. The isoteniscope is then placed in a thermostat. At a given temperature the external pressure is adjusted so that both arms of the U tube are at the same height. At this setting, the external pressure, which is equal to the pressure of the vapor in the isoteniscope, is measured with a mercury manometer. A common dynamic method is one in which the variation of the boiling point with external applied pressure is measured (see Fig. 2). The total pressure above the liquid can be varied and maintained at a given value by use of a large volume ballast bulb; this pressure is then measured with a mercury manometer. The liquid to be studied is heated until boiling occurs, and the temperature of the refluxing vapor is measured in order to avoid any effects of superheating. **The experimental procedure which you will follow is that for the isoteniscope method.**

**PROCEDURE:** In this technique much of the equipment shown in Fig. 2 is used, but the distilling flask and reflux condenser are replaced by an isoteniscope mounted in a glass thermostat as shown in Fig. 3.

*Figure 2. Boiling-point apparatus.*

The heater-stirrer unit is to ensure thermal equilibrium. The liquid to be studied is placed in the isoteniscope so that the bulb is about one-half full and there is about 3 cm of liquid in each arm of the U tube. Then the isoteniscope is placed in the thermostat (which should be at room temperature) and is connected to the ballast bulb and manometer (which are assembled and connected as in Fig.2).

Air is swept out of the bulb by cautiously reducing the pressure in the ballast bulb until air bubbles through the U-tube liquid at a reasonable rate; avoid evaporating too much of the liquid in the U-tube. After 2 or 3 minutes carefully admit air through stopcock **S** until the liquid levels in both arms of the U tube are equal; then read the temperature and the pressure on the mercury manometer.

The thermometer scale should be read to the nearest 0.1°C. In reading the manometer, record the position of each meniscus ( $h_1$  and  $h_2$ ); keeping your line of sight level with the meniscus to avoid parallax error. Estimate your readings to the nearest 0.5 mm.

To ensure removal of all the air, repeat the procedure above until successive vapor-pressure readings are in good agreement. If the amount of liquid in the U-tube becomes inadequate, tilt the isoteniscope so that some liquid from the bulb is transferred over into the U-tube.

Once the air is removed and a good pressure reading at room temperature is obtained, heat the thermostat bath to a new temperature about 3°C above room temperature. Keep the liquid levels in the U-tube approximately equal at all times. When the bath temperature is steady at its new value, adjust the pressure in the ballast bulb until the levels in the U-tube are equal and record both temperature and pressure.

Take readings at approximately 3°C intervals until the bath is at about 50°C. Take several readings at approximately 0°C using an ice-water bath to attain this temperature.

*Figure 3.* Isoteniscope. This is connected to the ballast bulb and manometer in Figure 2.

**CALCULATIONS:** Correct all manometer pressure readings ( $h_2 - h_1$ ) for the fact that the mercury is not at 0°C by multiplying by  $(1 - 0.00018T)$  where  $T$  is the Celsius temperature of the manometer. If  $T$  has been reasonably constant during the experiment, use an average value and apply the same correction factor to all pressures.

Convert all Celsius temperatures to absolute temperatures and plot  $\ln P$  vs.  $1/T$ . If there is no systematic curvature draw the best straight-line through the points. If there is noticeable curvature, draw a smooth curve through the points and also draw a straight line tangent to the curve about the mid-point.

Determine the slope of the straight line or tangent. From Eq.(5) it follows that this slope is  $\Delta H_v/Rz$ . Estimate the value of  $z$  for the saturated vapor at the appropriate temperature from Fig.1 or by using the Berthelot equation, which may be written

$$z = 1 + \frac{9PT_c}{128P_cT} \left( 1 - 6 \frac{T_c^2}{T^2} \right) \quad (9)$$

where  $P_c$  and  $T_c$  are the critical constants for the substance in question. Calculate  $\Delta H_v$  in Joules per mole. Report the value of the heat of vaporization and of the vapor pressure for the liquid together with the applicable temperature (corresponding to the mid-point of the range studied.)

Discuss possible systematic sources of error.

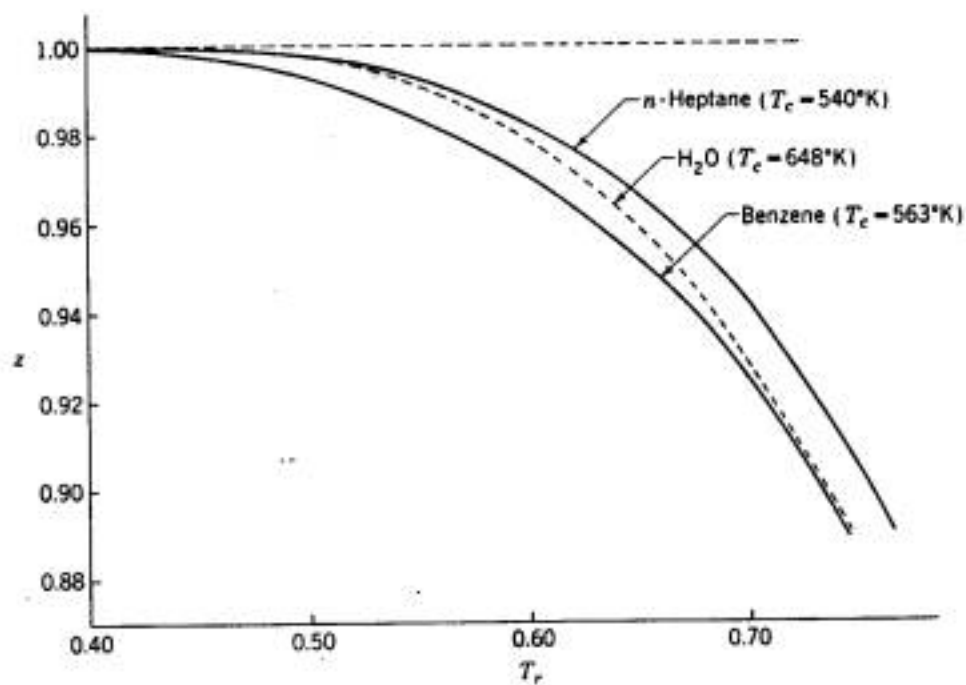


Figure 1. The compressibility factor  $z$  of saturated vapor as function of reduced temperature  $T_r$  for water, benzene, and  $n$ -heptane.

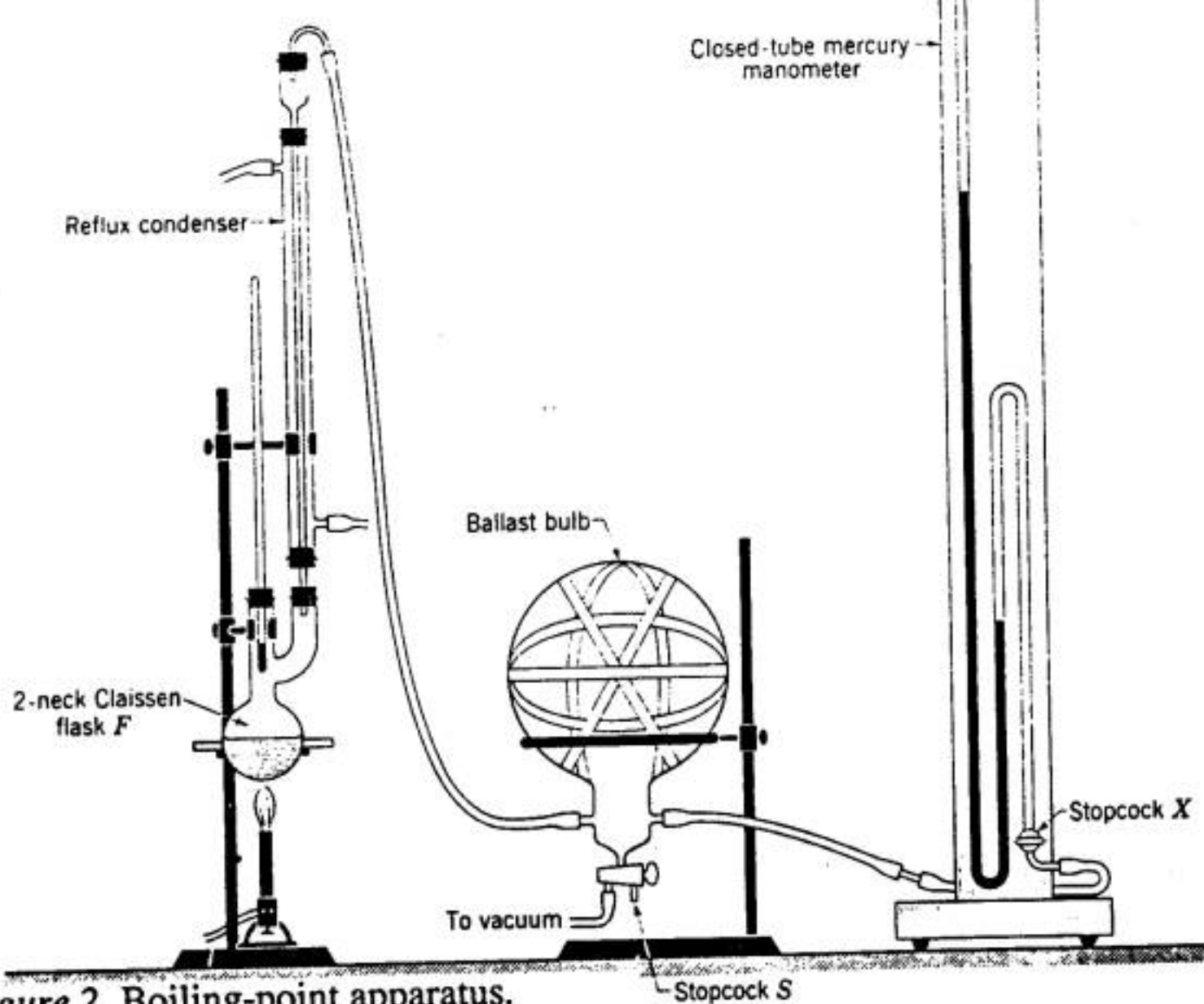
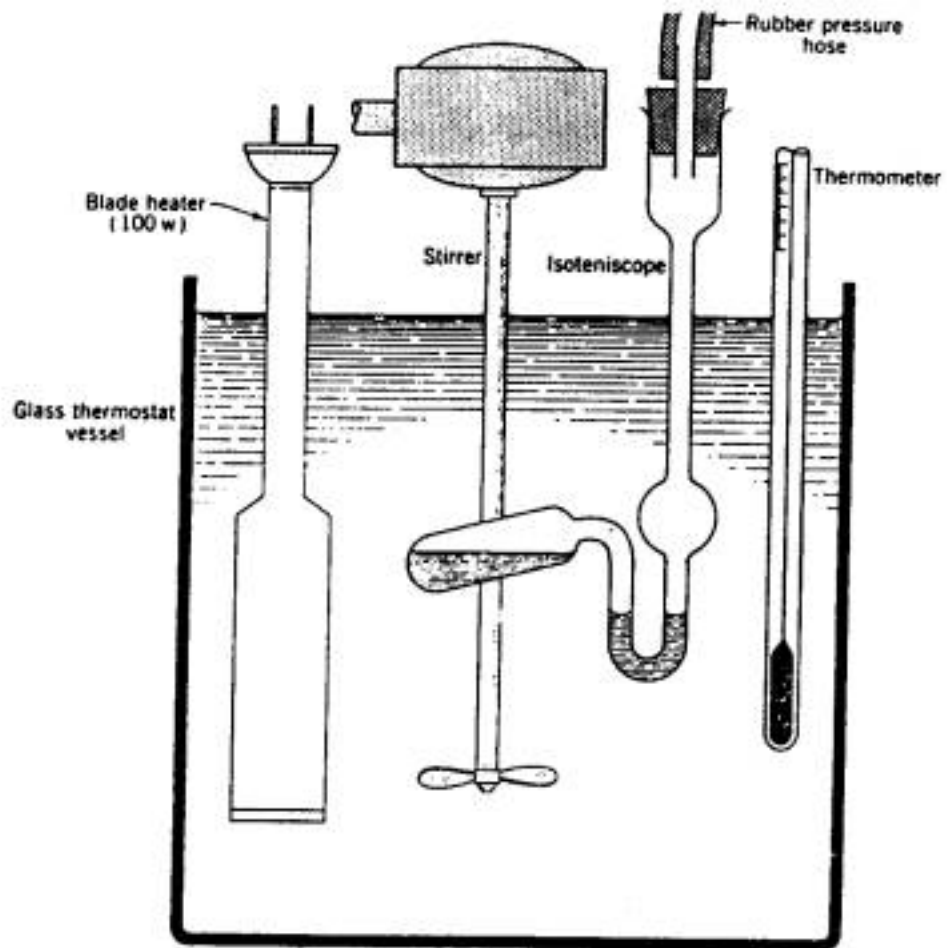


Figure 2. Boiling-point apparatus.



*Figure 3.* Isotenoscope. This is connected to the ballast bulb and manometer in Figure 2.