Physics 360/371 Intermediate Laboratory

Experiment #11 Critical Point and Thermal Equation of State

References: Heat and Thermodynamics, Zemansky and Dittman (6th Ed.) pp. 28-30, pp. 245-248, pp. 253-259

The isothermal behaviour of a certain gas is to be studied and its critical point (P_c,V_c,T_c) determined. The gas is contained in a variable volume capillary which can be maintained at constant temperatures. Thus the pressure - volume relationships at various temperatures will allow a determination of the critical point. This experiment will involve the study of gas with a critical temperature in the range 0-55C and a critical pressure below 5MPa.

The apparatus will be used to obtain vapour pressure curves, observe phase transitions between the gas and liquid phases, determine the critical point, and evaluate the latent heat of evaporation using the Clausius-Clapeyron relationship.

The apparatus consists of a graduated measurement capillary surrounded by a circulating water bath which allows for adjustment of the gas temperature. The volume in the capillary can be adjusted by a variable mercury column which is controlled by a rotating handwheel. (see Fig. 1) The gas under study is introduced to the capillary via a system of valves. A vacuum pump connected to the device is first used to evacuate the capillary of any contaminants.

Notes:

1. Do not subject the measurement capillary to any thermal shock. Temperature changes should be gradual. If any mechanical defects are observed do not apply any pressure to the capillary until you have notified a demonstrator.

2. Do not operate at temperatures outside the range of 0°C to 55°C or at pressures in excess of 5MPa.

3. Do not apply excessive force to the handwheel when lowering the mercury column. The lower stop can be clearly felt; applying force past this point will damage the apparatus.

4. Never open both the filling and evacuation valves simultaneously. A single valve handle is employed to ensure this does not occur.

5. Follow all instructions with respect to handling the high pressure gas cylinders.

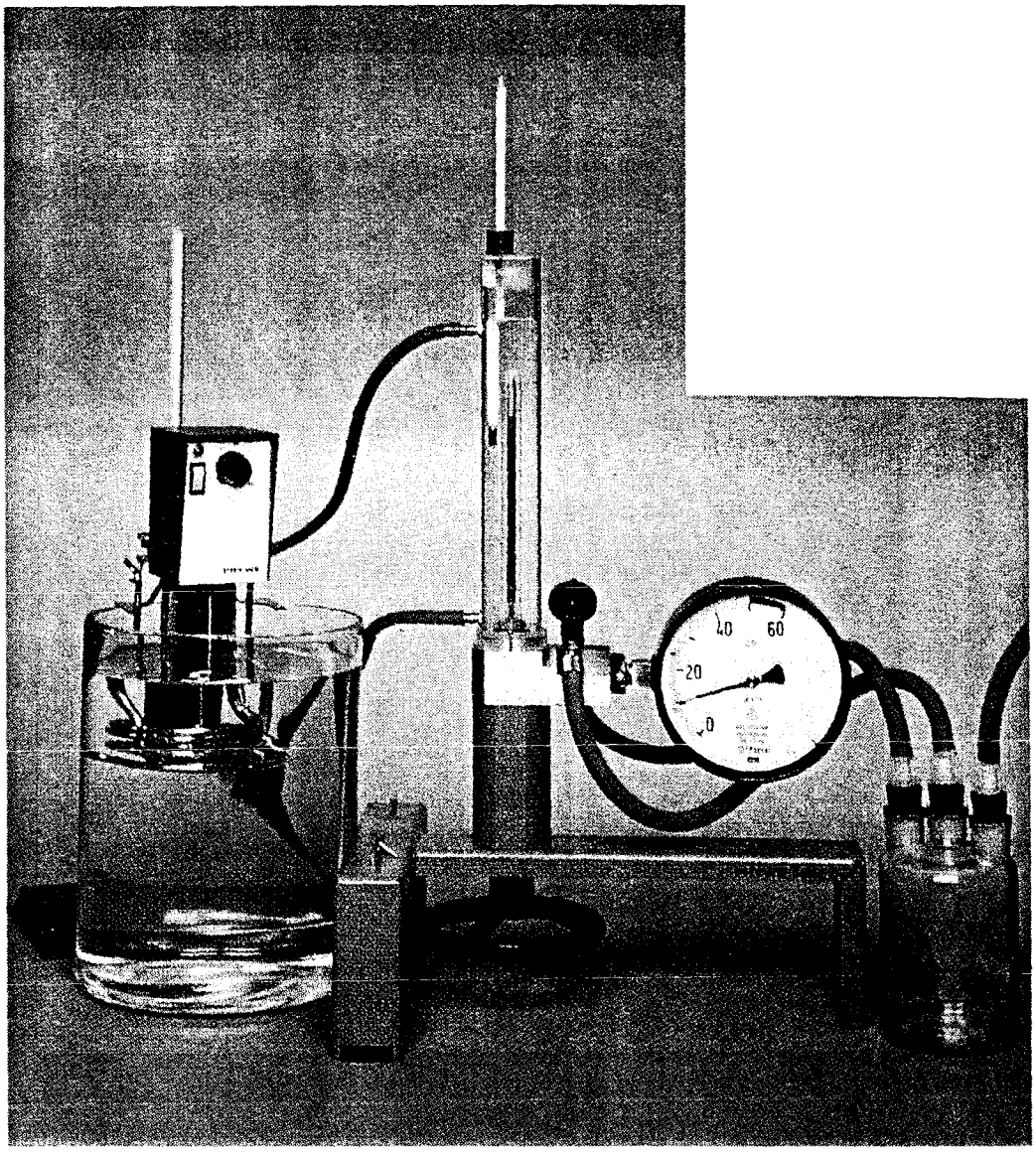

Figure 1

6. Mercury vapour is poisonous. To avoid removing liquid mercury from the apparatus when evacuating, ensure the mercury column is fully lowered. (i.e. handwheel at lower stop.) Check also that the vacuum pump exhaust is vented to the outside.

Procedure:

The measurement capillary must first be evacuated before introducing the gas to be studied. An ordinary rotary vacuum pump will be used. First, ensure the mercury column is fully lowered to its lower stop. Using the removable valve handle check that the gas inlet (rear valve) is fully closed. Now start the rotary pump and transfer the handle to the evacuation valve.. Open the evacuation valve and observe the pressure decrease on the gauge. It is advisable to pump on the system for 20 - 30 minutes in order to completely evacuate the capillary of air (or previous gases). Attach the gas cylinder to the filling connection at the rear of the apparatus. Note that this cylinder has an internal valve which is opened as the cylinder is screwed onto the inlet valve. Do not tilt the cylinder as you attach it; doing so may damage the internal valve. Thread the cylinder snugly onto the inlet but don't overtighten it. To ensure no residual air remains between the gas cylinder and the inlet valve, proceed as follows: first close the evacuation valve, then transfer the handle to the inlet valve and slowly open it to admit a small amount of sample gas. Keep the chamber pressure below 1MPa. Close the inlet valve, transfer the handle, and once again open the evacuation valve. Pump on the chamber for 1 to 2 minutes to remove any residuals then close the evacuation valve. Now transfer the handle and admit some sample gas, to obtain a pressure of approximately .5 MPa.

The apparatus is now ready for measurements. Add the icewater mixture to the large beaker, and switch on the circulating bath. There is a switch on the rear of the motor which disables the heater; switch it off first. Adjust the tubing clamp on the supply hose of the circulation system so that there is a uniform bath surrounding the capillary without causing water to spill from the top of the jacket. (This will happen quite quickly once the pump is started if the tubing clamp is not properly adjusted.) Allow a minute or so for the capillary to come to thermal equilibrium, monitoring with the thermometer provided. You are now ready to take P,V, measurements. Rotate the handwheel to raise the mercury column into the capillary area. Record pressure and volume measurements for volumes down from 4.0 mL in .1 mL increments. You should wait a few seconds after each increment to allow the pressure and temperature to stabilize. When you reach maximum pressure, (i.e. volume can no longer be reduced, and all gas is liquified) lower the mercury column. Make sure to monitor the final temperature of the bath. Switch on the heater, set the thermostat to a chosen value, and allow the bath to once again come to equilibrium at the new temperature. Repeat P,V measurements. This process should be repeated for 6 or 7 different temperatures over the range of 0-50C.

Shut-Down Procedure:

Switch off the circulation bath and open the tubing clamp to allow the water in the jacket to drain out, then switch on the rotary pump, open the evacuation valve **[Make sure mercury column is fully lowered.]** and pump out the sample gas for 1-2 min. Close the valve and switch off the pump. Unscrew the gas cylinder from the apparatus quickly to avoid excessive release of the gas.

Analysis:

From your sheaf of P,V isotherm curves determine the critical temperature and pressure. (The horizontal portions of these curves represent the isobaric isothermal liquefaction with decrease in volume from vapour to liquid. As T is increased, the horizontal portion decreases and at the critical point, reduces to a point of inflexion. Above the critical temperature, the vapour cannot be condensed, no matter how high the applied pressure.

Obtain values of P and T for each of the condensation curves. The Clausius-Clapeyron eqn. relates these values of P and T (for which vapour and liquid co-exist) to the molar latent heat of vaporization, L:

$$\frac{dP}{dT} = L/T(V_g - V_f)$$

where V_g and V_f are the molar volumes of the gaseous and liquid phases, respectively. If $V_f << V_g$ and the vapour is considered to approximate an ideal gas, $V_g \approx \frac{RT}{P}$ and $\frac{dP}{dT} \approx \frac{LP}{RT^2}$

Integration gives $\ln(P) = -\frac{L}{RT} + C$

From a log-linear plot of P vs 1/T, determine the value of the latent heat of evaporation.

Check whether Trouton's rule is obeyed for this substance:
$L/RT_B \approx 9$ (where the normal boiling point, $T_B \approx 0.6T_C$)

Apparatus:

-Critical Point Apparatus
-Rotary Vacuum Pump
-Circulating Pump and Thermostat
-Thermometer
-Tubing, Connectors, and Hose Clamp
-Cylinder of Sample Gas (Ethane C_2H_6 or Sulphur Hexafluoride SF_6)