

# PURE LIQUID-VAPOUR EQUILIBRIUM

## OBJECTIVE

Determine the vapour pressure of a liquid as a function of temperature by the isoteniscope method, and calculate the enthalpy of vapourisation of the liquid.

## INTRODUCTION

If the pressure on a gas/vapour is increased at constant temperature its volume will decrease (isotherm  $T_3$  in Fig.1). At temperatures below  $T_c$  e.g.  $T_1$ , when the pressure reaches a definite value the volume is observed to decrease markedly for an infinitesimal increase in pressure (A-B in Fig. 1). The marked decrease in volume is due to the formation of increasing amounts of liquid, commencing at A, until at point B the gas/vapour is completely converted to liquid. The line A-B represents equilibrium between the pure liquid and its vapour.

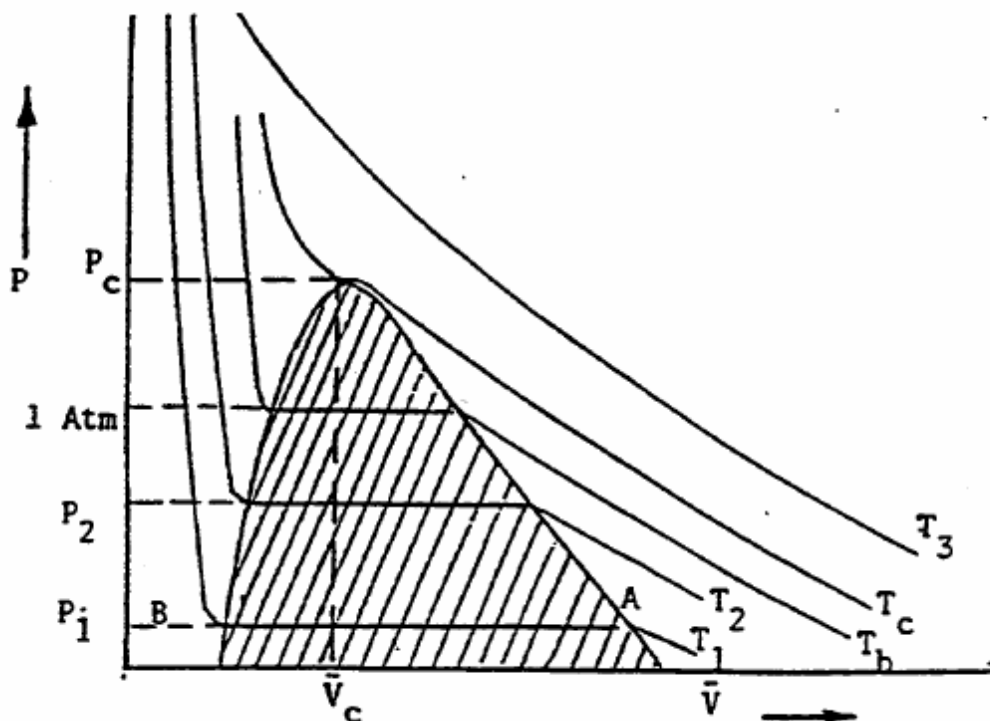


Fig.1. Isotherms in the region of liquid vapour equilibrium.

The constant pressure  $P_1$  is the equilibrium vapour pressure of the liquid at temperature  $T_1$ . As the temperature is increased, the vapour pressure of the liquid increases also. The temperature  $T_b$  for which the liquid has a vapour pressure exactly equal to 1 atmosphere is called the normal boiling point of the liquid. At higher temperatures such as  $T_2$  the horizontal portions of the isotherms become shorter. For example the length C - D is shorter than A - B. This is because the pressure  $P_2 > P_1$  and the molar volumes of the vapour become smaller.

The temperature at which the horizontal portion just vanishes is called the **CRITICAL TEMPERATURE**,  $T_c$ , and the corresponding (vapour) pressure is called the **CRITICAL PRESSURE**,  $P_c$ . The shaded area in Fig.1 includes all states of the system which correspond to the existence of two phases, liquid and vapour.

Part of the shaded area, up to the normal boiling point,  $T_b$ , of the liquid, is the subject of this experiment in which the vapour pressure dependence on temperature will be investigated. This dependence can be related to the enthalpy of vapourisation  $\Delta H_{vap}$  in the following way. For equilibrium between the liquid and vapour at constant temperature and pressure, the liquid and vapour must be at the same chemical potential.

$$\mu_l(T, P) = \mu_v(T, P) \quad [1]$$

where for a one-component system  $\mu = \bar{G}$ , the molar Gibbs free energy.

If this relationship is to be satisfied over the whole temperature range for which liquid and vapour can co-exist it must follow that T and P are not independent variables. For an infinitesimal change in temperature, if equilibrium is to be maintained

$$d\mu_l = d\mu_v \quad [2]$$

Since

$$d\mu = d\bar{G} = \bar{V}dP - \bar{S}dT \quad [3]$$

we can write

$$\bar{V}_l dP - \bar{S}_l dT = \bar{V}_v dP - \bar{S}_v dT \quad [4]$$

and

$$\frac{dP}{dT} = \frac{(\bar{S}_v - \bar{S}_l)}{(\bar{V}_v - \bar{V}_l)} = \frac{\Delta \bar{S}_{vap}}{\Delta \bar{V}_{vap}} \quad [5]$$

where  $\Delta \bar{S}_{vap}$  and  $\Delta \bar{V}_{vap}$  are the entropy and volume changes accompanying the transfer of one mole of liquid to the vapour state at constant P and T. At equilibrium,

$$\mu_v - \mu_l = \Delta \bar{G}_{vap} = \Delta \bar{H}_{vap} - T \Delta \bar{S}_{vap} = 0 \quad \Leftrightarrow \quad \Delta \bar{S}_{vap} = \frac{\Delta \bar{H}_{vap}}{T} \quad [6]$$

and [5] becomes

$$\frac{dP}{dT} = \frac{\Delta \bar{H}_{vap}}{T \Delta \bar{V}_{vap}} \quad [7]$$

This relationship [7] is known as the **CLAPEYRON EQUATION**. It may be simplified by making the approximation  $\Delta \bar{V}_{vap} = V_v$ . The molar volume of the liquid can be neglected compared to that of the vapour. Defining the compressibility factor of the vapour as

$$z \equiv \frac{P\bar{V}_v}{RT} \quad [8]$$

we can write

$$\frac{(dP/P)}{(dT/T^2)} = \frac{\Delta \bar{H}_{vap}}{zR} \quad \text{or} \quad \frac{d \ln P}{d(1/T)} = - \frac{\Delta \bar{H}_{vap}}{zR} \quad [9]$$

For an ideal gas  $z = 1$  and we obtain the **Clausius-Clapeyron** equation

$$\frac{d \ln P}{d(1/T)} = - \frac{\Delta \bar{H}_{vap}}{R} \quad [10]$$

Thus if the vapour were indeed an ideal gas and  $\Delta \bar{H}_{vap}$  independent of temperature then, within the limits of the approximation  $\Delta \bar{V}_{vap} = V_v$ , a plot of  $\ln P$  against  $1/T$  would be a straight line of slope  $-\bar{H}_{vap}/R$ . Since the plot is quite linear for most liquids we can deduce that, at least,  $\Delta \bar{H}_{vap}/z$  is fairly constant. Note that  $\Delta \bar{H}_{vap}$  and  $z$  are both temperature dependent parameters.

$$\Delta \bar{H}_{vap}(T_2) = \Delta \bar{H}_{vap}(T_1) + \Delta \bar{C}_p(T_2 - T_1) \quad [11]$$

where  $\Delta \bar{C}_p = \bar{C}_p(\text{vapour}) - \bar{C}_p(\text{liquid})$ .  $z$  can be estimated from the universal charts based on the law of corresponding states or by use of an equation of state such as the Berthelot equation.

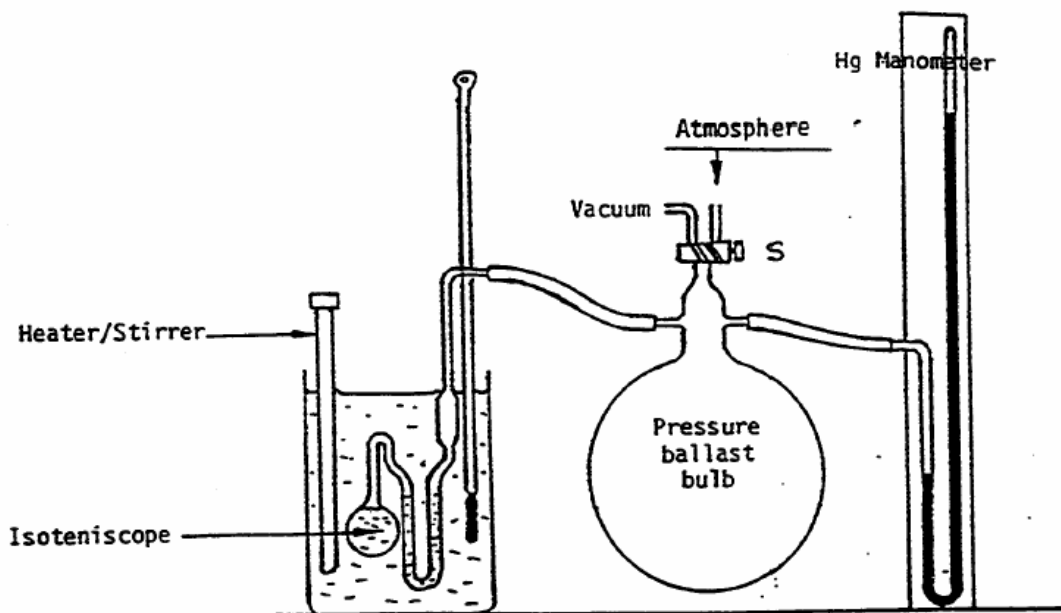
$$z = 1 + \frac{9}{128} \frac{P_r}{T_r} (1 - 6T_r^2) \quad [12]$$

where  $P_r$  and  $T_r$  are the reduced pressure and temperature.

[NB.  $P_r = P/P_c$  and  $T_r = T/T_c$  where  $P_c$  and  $T_c$  are the critical pressure and temperature.]

### PROCEDURE

The isoteniscopic method will be used to complete this lab. A diagram of the apparatus is shown in Figure 2 below. The principle of the method is that when the liquid levels inside the U-tube of the *isoteniscope* are equal, the vapour pressure of the liquid in the bulb acting on the one side of the U-tube is equal to the external pressure acting on the other side of the U-tube. The latter is measured with the closed-end mercury *manometer*. Do not forget to record the room temperature and pressure located at the last fume hood in room ABB 107.



**Fig. 2. Vapour-Pressure Apparatus – The Isoteniscope Method**

1. Assemble the apparatus as shown in Fig.2 but do not connect the *isoteniscope*.
2. Prepare enough half-and-half slurry of crushed ice and water to fill the water bath. Set the temperature control on the heater/stirrer unit for stirring only.
3. Fill the isoteniscope bulb approximately 3/4 full with the liquid under investigation and fill the U-tube with the same liquid to about half-way up the enlarged section of the isoteniscope.
  - a. This may be a little trying, be sure to ask your TA for help if you need it.
4. Connect the isoteniscope to the remainder of the apparatus.
5. Start the stirrer and turn the stopcock S to the vacuum pump and evacuate air trapped between the isoteniscope bulb and the U-tube. It is worthwhile checking the first point against a published value for the vapour pressure [2] to ensure that all the air has been removed. Otherwise the partial pressure of the residual air may make your subsequent work useless.
6. Equalize the levels of the liquid in the U-tube taking great care not to re-admit air into the isoteniscope bulb. Should this happen, then you must remove it before proceeding further.
7. Allow time for the liquid to assume the temperature of the bath, note its temperature and read the mercury manometer.
8. Raise the temperature of the bath by about 5 °C and repeat the measurements of temperature and pressure.
9. Continue raising the temperature of the bath by 5 °C until no further measurement of pressure is possible.

### CALCULATIONS

Record room temperature and correct the measured mercury columns to equivalent ones at 0 °C using the relation

$$P_a = P_m(1 - 1.8 \cdot 10^{-4} t) \quad [13]$$

where  $P_m$  is the measured pressure and  $P_a$  is the corrected total pressure to be used in computations and  $t$  is room temperature in °C. Plot the logarithm of the vapour pressure against the reciprocal of the absolute temperature. Determine the slope,  $A$ , and intercept,  $B$ , of this plot by two methods.

$$\ln P = \frac{A}{T} + B \quad [14]$$

1. Draw the best straight line through the points by eye and determine the values of  $A$  and  $B$  from this line.
2. Review the theory of Least-Squares Analysis to calculate  $A$  and  $B$  for this line. You are required to perform this analysis with any spreadsheet. Calculate  $\Delta H_{\text{vap}}$  from the visually estimated and least-squares determined slopes using [10].

This value for the  $\bar{H}_{\text{vap}}$  is inaccurate because of the assumptions made in deriving the Clausius-Clapeyron equation. Determine the compressibility factor for a particular point, say 25 °C, on the  $\ln P$  vs  $1/T$  curve and use it together with the slope of the curve at that point to calculate the corrected  $\bar{H}_{\text{vap}}$ . Deduce from the graph the normal boiling point of the liquid and compare it with the accepted value.

### DISCUSSION

Discuss critically the experimental procedure paying attention to accuracy. Compare  $\bar{H}_{\text{vap}}$  values obtained from the visual slope, the least-squares analysis and the literature. For most liquids the plots of  $\ln P$  versus  $(1/T)$  and equation (10) predicts the decrease of  $\bar{H}_{\text{vap}}$  with increase in temperature. Account for this apparent paradox. Could the liquid used be classified as "normal" according to Trouton's Rule?

### REFERENCES

1. Shoemaker, Garland, Steinfeld and Nibler, "Experiments in Physical Chemistry", 4th edition, McGraw-Hill, pp. 197 ff.
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4. R.G. Mortimer "Physical Chemistry", Benjamin/Cummings, Redwood City, Calif., 1993, 176-183.