

in ethanol = 1.7323 g. Then the upthrust of the sinker in water = 4.7654×10^{-3} kg. See Table 2.2.1 for specimen results at 20 °C.

Table 2.2.1. Specimen results at 20 °C

Approximate volume ethanol/cm ³	3
Mass empty bottle/g	43.9462
Mass bottle + ethanol/g	46.3347
Mass bottle + ethanol + water/g	100.0786
Mass of sinker in solution/g	0.7858
Upthrust of sinker in solution/kg	4.7227×10^{-3}
Mass of ethanol W_e /kg	2.3885×10^{-3}
Mass of water W_w /kg	5.3744×10^{-2}
Mass of ethanol in solution containing 1 kg of water W_e'/kg	4.4442×10^{-2}
Molality m_e /mol kg ⁻¹	0.965
Density of solution ρ /kg m ⁻³	989.3
Excess volume V^E/m^3	-5.570×10^{-6}

Accuracy

Errors can arise if the sinker touches the walls of the bottle, or if air bubbles become attached to the sinker. Consequently one or two points may have to be ignored when drawing the curve of excess volume against molality. Despite such errors and the fact that excess volume is calculated from the small difference between large numbers, this experiment produces results of good accuracy, and values within a few per cent of published data^[3] can be obtained with care.

Comment

An understanding of partial molar volume is clearly important in explaining the relations between the scales which can be used to describe the composition of a mixture. The effects we have studied also give some hint as to the role of intermolecular forces in the structure of liquids, examined in detail in Expt 7.2.

Technical notes

Apparatus

Sinker—see Apparatus section;†† chemical balance with bridge and wire to take sinker,‡† twelve sample bottles, in the form of glass cylinders 3.5 cm diameter by about 10 cm long, marked at the 60 cm³ level;† thermostat tank set at 20 °C; ethanol in dispenser set to 1 cm³.

References

- [1] *Physical chemistry*. P. W. Atkins. Oxford University Press, Oxford, 3rd edn (1985), Sect. 8.1.

- [2] *Liquids and liquid mixtures*. J. S. Rowlinson and F. L. Swinton, Butterworths, London, 3rd edn (1982), ch. 4.
 [3] *Density of ethyl alcohol and of its mixtures with water*. N. S. Osborne. *Bull. Bur. Stand.* 9, 424, (1913).

2.3 Vapour pressures of liquids

This experiment involves the measurement of the vapour pressures of ethanol and cyclohexane over a range of temperatures.

The method used in this experiment is a very simple one.^[1] A narrow tube, closed at its top end, is dropped into a vessel containing a thermometer and some of the sample liquid, Fig. 2.3.1. The liquid is boiled so that its vapour displaces any air in the narrow tube. Then pressure is applied to equalize the liquid levels inside and outside the tube, whereupon the applied pressure as measured with a mercury manometer, is equal to the vapour pressure.

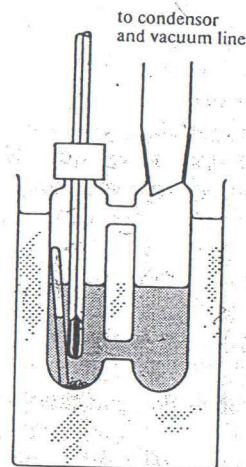


Fig. 2.3.1. Arrangement of the sample vessel

The variation of vapour pressure with temperature yields both the enthalpy of vaporization ΔH_{vap} and the entropy of vaporization ΔS_{vap} . From the magnitude of ΔS_{vap} it may be deduced whether or not the liquid or vapour is associated.

Theory

From the definition of free energy, G , we may derive the relation

$$dG = V dp - S dT. \quad (2.3.1)$$

Consider a system comprising a liquid and its vapour at equilibrium which undergoes a very small reversible change. Equating the changes in free energy in the liquid and gaseous phases

$$V(l) dp - S(l) dT = V(g) dp - S(g) dT \quad (2.3.2)$$

Therefore

$$\frac{dp}{dT} = \frac{S(g) - S(l)}{V(g) - V(l)} = \frac{\Delta S_{\text{vap}}}{\Delta V_{\text{vap}}} \quad (2.3.3)$$

Since the two phases are in equilibrium

$$\Delta G_{\text{vap}} = \Delta H_{\text{vap}} - T\Delta S_{\text{vap}} = 0, \quad (2.3.4)$$

where T is the temperature of the equilibrium, i.e. the boiling point at the pressure under consideration. So

$$\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T, \quad (2.3.5)$$

and we obtain the *Clapeyron equation* which is exact for systems at equilibrium:

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vap}}}{T \Delta V_{\text{vap}}} \quad (2.3.6)$$

To a good approximation, the term $\Delta V_{\text{vap}} = V(g) - V(l)$ may be replaced by $V(g)$ since the volume of the gas is so much greater than the volume of the liquid. If the vapour is assumed to obey the perfect gas equation, then for one mole

$$pV(g) = RT. \quad (2.3.7)$$

Therefore from eqn (2.3.6)

$$\frac{dp}{dT} = \Delta H_{\text{vap}} p / RT^2, \quad (2.3.8)$$

from which is obtained the *Clausius–Clapeyron equation*

$$\frac{d(\ln p)}{dT} = \Delta H_{\text{vap}} / RT^2. \quad (2.3.9)$$

Assuming ΔH_{vap} is independent of temperature, the equation may be integrated to give

$$\ln p = -\Delta H_{\text{vap}} / RT + \text{const.} \quad (2.3.10)$$

The entropy of vaporization at the boiling point under 1 atm has been found to be approximately the same for all substances not associated in their liquid or vapour phases. For such substances ΔS_{vap} lies in the range $85\text{--}90 \text{ J K}^{-1} \text{ mol}^{-1}$. This observation is known as *Trouton's rule*.

Is ΔH_{vap} independent of temperature? What must the value of ΔH_{vap} be at the critical point?^[2]

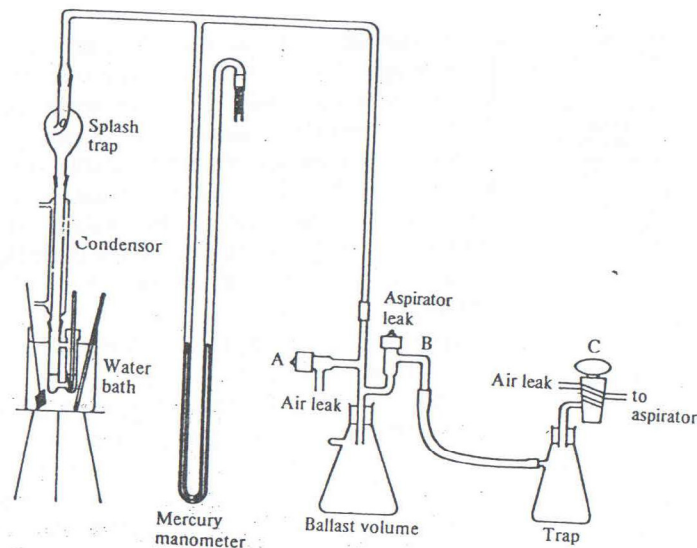


Fig. 2.3.2. The vacuum line

Apparatus

The apparatus is shown in Figs. 2.3.1 and 2.3.2. The sample vessel, enclosing the narrow tube, thermometer, and sample liquid, is immersed in a large beaker of water. Into the beaker dips a thermometer and stirrer, and under it is a bunsen burner. The boiling tube is attached via a reflux condenser and splash trap to a ballast volume, adjustable leaks, an aspirator with trap, and mercury manometer.

Procedure

Measure the ambient atmospheric pressure p_{atm} with a barometer.

Place one of the narrow tubes supplied for the experiment in the sample vessel, half fill the vessel with the sample liquid, add some anti-bumping granules, and arrange the thermometer, as shown in Fig. 2.3.1. Close the adjustable air leak and aspirator leak (taps A and B).

Turn on the aspirator. Heat the water in the water bath to about 30°C and stir it.

By fractionally opening the tap between the aspirator and the vacuum line, reduce the pressure in the line until the liquid boils gently, thus removing air from the narrow tube. Using the adjustable air leak, increase the pressure in the line slowly until the liquid level in the narrow tube rises to the level of the liquid outside it. Maintain the pressure near this equilibrium value for at least 5 min before taking readings. Do not allow the liquid to

A consideration of the relative densities of mercury and the test liquids shows that in practice, sufficient precision will be obtained in this experiment simply by obtaining a stable level of liquid somewhere in the body of the vapour pressure tube.

rise to the top of the narrow tube, as it is difficult to make it descend again. If this does happen a fresh tube may have to be dropped into the liquid. Note the temperature of the stirred water, and read the manometer. Repeat the procedure described in this paragraph until constant results are obtained, showing that there is no air in the narrow tube.

Repeat the observations at intervals of about 6 K up to the boiling point of the liquid. Boiling cools the liquid, so make sure it is at the temperature of the water bath when a measurement is made.

Repeat the entire experiment with the other sample liquid (cyclohexane or ethanol).

At the end of the experiment, turn off the aspirator and immediately open it to the air through tap C.

Calculation

The vapour pressure of water varies in a similar manner; at 500 mmHg, the atmospheric pressure at the summit of Mont Blanc, water boils at 89 °C.

Calculate the vapour pressure at each temperature for the two liquids, and plot the results in such a way that you obtain the enthalpies of vaporization. *Why do the units of pressure not matter?* Calculate the entropies of vaporization of these liquids at their boiling points under a pressure of 760 mmHg (1 atm), which are 78.3 °C and 80.7 °C respectively.

Compare the entropies of vaporization with the value from Trouton's rule. By considering the effect of association of a liquid or vapour on its entropy and hence the entropy change on vaporization, deduce whether ethanol and cyclohexane are associated, and if so in which phase.

Results

Accuracy

The assumptions employed in the theory of this experiment are far from accurate (p. xix), but the errors which they create tend to cancel under conditions far removed from the critical point of the liquid.^[2] The apparatus itself is capable of results to ± 2 per cent, but errors of 20 per cent may arise if observations are not made carefully.

Comment

There are many other ways of measuring vapour pressure. The boiling point of a liquid under a known applied pressure may be found, or an *isotenoscope* may be used, which incorporates a narrow U-tube on which the balance point between the vapour pressure and applied pressure can be accurately determined.

Technical notes

Apparatus

Narrow tubes[†] (3 cm \times ≥ 2 mm i.d.) sealed at one end;[†] sample vessel (Fig. 2.3.1);[†] vacuum line (Fig. 2.3.2);[†] accurate barometer.[‡] Ethanol, cyclohexane, anti-bumping granules.

Other liquids

The apparatus is not suitable for water.

References

- [1] A simple isotenoscope and an improved method of vapor pressure measurement M. W. Lindauer. *J. Chem. Educ.* **37**, 532 (1960).
- [2] Putting Clapeyron's equation into practical use with no help from Clausius S. Waldenstrom, K. Stegavik, and K. R. Naqvi. *J. Chem. Educ.* **59**, 30 (1982).

2.4 Distillation of ideal and azeotropic liquid mixtures

This experiment illustrates the effect of temperature on the liquid-vapour phase equilibria of binary mixtures, and is in two parts. In Part A, a mixture of benzene and tetrachloromethane (carbon tetrachloride) is distilled, and the degree of separation of the liquids used to determine the efficiency of a distillation column. In Part B, the characteristics of the *n*-propanol/water system are investigated with the aid of a simple still. Two types of graph are used to analyse the results, and the phase rule (p. 22) confirms that at constant pressure they both describe the systems completely. The first is a plot of liquid composition against vapour composition, and the second a graph of both against temperature.

Theory

A(i) Ideal mixtures

Benzene and tetrachloromethane form an almost *ideal mixture*, because the forces between the molecules of both components of the mixture are almost identical. The vapour pressure of the mixture obeys *Raoult's Law*, changing linearly with mole fraction from that of pure benzene to that of pure tetrachloromethane. Not only do these liquids form a near ideal mixture, but also their boiling points are very similar. They are therefore very difficult to separate by distillation, and can be used as a sensitive test of the efficiency of a distillation column.

A(ii) Distillation columns^[1]

Let us consider a bubble-plate fractionating column, Fig. 2.4.1, as used in oil refineries. The more bubble plates a column has and the better the equilibrium between the descending liquid and ascending vapour, the better the separation achieved between the components of a mixture. The vapour rising from a