
PHYSICAL CHEMISTRY

FIFTH EDITION

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The cover as illustrated by Ian Worpole, is based on Peter Atkins' representation of the amplitude of the antibonding orbital formed from the overlap of two H1s orbitals.

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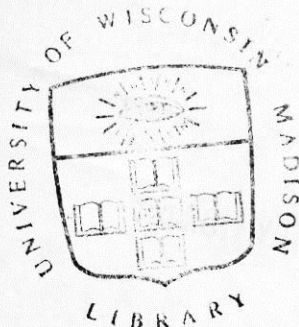
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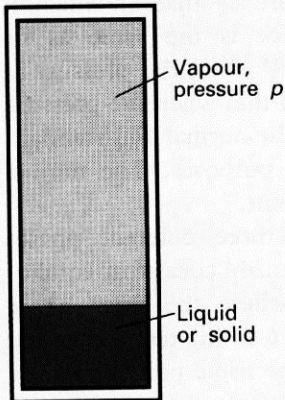
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6.3 The vapour pressure of a liquid or solid is the pressure exerted by the vapour in equilibrium with the condensed phase.

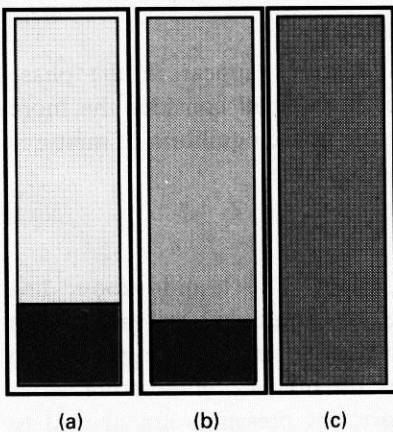
6.1 Phase boundaries

Consider a sample of a pure substance in a closed vessel of constant volume. The pressure of a vapour in equilibrium with its condensed phase at a specified temperature is called the **vapour pressure** of the substance at that temperature (Fig. 6.3). Hence, as anticipated above, the phase boundaries between the liquid and the vapour and between the solid and the vapour show how the vapour pressures of the two condensed phases vary with temperature. The vapour pressure of a substance increases with temperature because, at higher temperatures, the molecules can escape more readily from the attractive interactions that bind them to their neighbours in the condensed phase.

Critical points and boiling points

The behaviour of a liquid heated in an open vessel differs from that of a liquid in a sealed vessel. In an open vessel, the liquid vaporizes from its surface as it is heated. At the temperature at which its vapour pressure would be equal to the external pressure, vaporization can occur throughout the bulk of the liquid and the vapour can expand freely into the surroundings. The condition of free vaporization throughout the liquid is called **boiling**. The temperature at which the vapour pressure of a liquid is equal to the external pressure is called the **boiling temperature** at that pressure. Note that a liquid does not suddenly start to form a vapour at its boiling temperature, for even at lower temperatures there is an equilibrium between the liquid and its vapour: at the boiling point the vapour pressure is great enough to drive back the atmosphere and vaporization can occur freely. For the special case of an external pressure of 1 atm, the boiling temperature is called the **normal boiling point** T_b . With the replacement of 1 atm by 1 bar as standard pressure, there is some advantage in modifying the definition so that the transition temperature refers to that pressure; the term **standard boiling point** is then used. Because 1 bar is slightly less than 1 atm (1.00 bar = 0.987 atm), the standard boiling point of a liquid is slightly lower than its normal boiling point. The normal boiling point of water is 100.0°C; its standard boiling point is 99.6°C.

When a liquid is heated in a sealed vessel, boiling does not occur. Instead, the temperature, vapour pressure, and the density of the vapour rise continuously (Fig. 6.4). At the same time, the density of the liquid decreases as a result of its expansion. There comes a stage at which the density of the vapour is equal to that of the remaining liquid and the surface between the two phases disappears. The temperature at which the surface disappears is the **critical temperature** T_c (which we first encountered in Section 1.4). The corresponding vapour pressure is the **critical pressure** p_c . At and above this temperature a single uniform phase fills the container and an interface no longer exists. That is, above the critical temperature the liquid phase of the substance does not exist.



6.4 (a) A liquid in equilibrium with its vapour. (b) When a liquid is heated in a sealed container, the density of the vapour phase increases and that of the liquid decreases slightly. (The decrease in quantity of liquid is a result of vaporization.) (c) There comes a stage at which the two densities are equal and the interface between the fluids disappears. This occurs at the critical temperature. The container needs to be strong: the

Melting points and triple points