to CO_2, and the amount of gas evolved calculated from the increase in pressure.

1.3 LIQUIDS

The properties of liquids have not been systematized to nearly so great an extent as have those of gases, and the theoretical explanation of liquid properties is relatively even less far advanced. The most important basis of liquid nature is the attractive force between individual molecules, which is much more significant than in a gas, because in the liquid the molecules are so very much closer to one another. Along with this influence go the effects of molecular size and shape, and all these factors are quite specific to the particular liquid substance concerned.

For the most part, liquids may be grouped into two categories, with the line of demarcation based upon the order of magnitude of intermolecular forces. To the class of *normal* liquids belong those such as benzene, carbon tetrachloride, and the lower paraffin hydrocarbons, which are *nonpolar*, that is, have no permanent dipoles or only very small ones. The *associated* liquids, of which water and alcohols are excellent examples, have fairly large dipoles, and indeed behave as if the attractive forces are so great that several individual molecules may combine to form polymers, which have a definite, if transient, existence.

In studying liquids, then, it is well to keep in mind the manner in which their properties may be influenced by the presence or absence of molecular association; in view of the great biological and practical importance of water, the nature of associated liquids is of special interest.

Vapor pressure

A liquid placed in a closed container with a volume larger than the liquid volume evaporates into the free space and eventually comes into equilibrium with its vapor. This is not to say that the transfer of molecules from the liquid surface to the vapor space ceases, but rather that the molecular concentration in the vapor becomes great enough so that the rate of condensation of vapor molecules is equal to the rate of volatilization of liquid molecules. The pressure of the vapor when equilibrium has thus been attained is a function of the liquid substance and of the temperature, and is termed the *vapor pressure* of the liquid.

Vapor pressure is a measure of the volatility of a liquid, of the ease with which it can be converted into a gas. It measures the *escaping tendency* of molecules from the liquid phase. Of course, the greater the mass of the individual molecule, the more energy must be supplied to give it sufficient velocity so that it can fly off from the liquid surface; nevertheless, molecular mass and other circumstances being equal, the magnitude of vapor pressure is an inverse indication of the forces between molecules in the liquid.

The vapor pressure of a liquid may be considered in relation to the phase diagram of the substance. It is the one pressure for a given temperature at which liquid and gas can coexist, and on the phase diagram, as that of water discussed earlier, the curve which divides the gas region from the liquid region is exactly the vapor pressure-temperature curve for the liquid.

The higher the temperature, the greater is the average kinetic energy of the molecules of a liquid, and the larger is the fraction of the molecules which possess sufficient energy to overcome the attraction exerted by neighboring molecules. Thus as the temperature increases, the tendency of molecules to fly off from the liquid as vapor increases and the vapor pressure increases. The *boiling point* of a liquid is the temperature at which visible evolution of bubbles of vapor occurs at a particular value of the external pressure. The requirement for bubble formation is that the vapor pressure of the liquid equal the imposed external pressure and therefore the boiling point varies widely with variation of external pressure. The *normal* boiling point, which is commonly cited as the boiling point of a liquid, is the temperature at which ebullition occurs under an external pressure of one atmosphere.

It is found that the mathematical form of the equation relating vapor pressure p and absolute temperature T is the same for liquids generally:

$$\log p = -\frac{C_1}{T} + C \tag{1.16}$$

C_1 and C are constants for a particular liquid. It is further found that C_1 is related to the heat of vaporization of the liquid, represented by ΔH_v:

$$C_1 = \frac{\Delta H_v}{2.303R} \tag{1.17}$$

The heat of vaporization is the change in energy of one mole of the substance as it goes from the liquid state to the vapor state; it is thus also the excess energy which a mole of the substance has as vapor over that which it has in the liquid phase. The symbol Δ, delta, is frequently used, as it is here, to indicate a change or difference in some property associated with a physical or chemical change. ΔH in general is the amount of energy H which the products of change possess less the amount possessed by the reactants, and in this case the change is the process of vaporization. In equation (1.17), R is the gas constant, and it must be expressed, of course, in the same units of energy and for the same amount of material as is the heat of vaporization.

Substitution of the value of C_1 in equation (1.16) leads to:

$$\log p = -\frac{\Delta H_v}{2.303RT} + C \tag{1.18}$$

If this equation is applied to a given liquid at two temperatures, T_2 and T_1, at which the vapor pressures are p_2 and p_1, respectively, there are obtained two equations:

$$\log p_2 = -\left(\frac{\Delta H_v}{2.303R}\right)\left(\frac{1}{T_2}\right) + C$$

and

$$\log p_1 = -\left(\frac{\Delta H_v}{2.303R}\right)\left(\frac{1}{T_1}\right) + C$$

Subtracting the second equation from the first yields:

$$\log \frac{p_2}{p_1} = -\left(\frac{\Delta H_v}{2.303R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

or

$$\log \frac{p_2}{p_1} = \left(\frac{\Delta H_v}{2.303R}\right)\left(\frac{T_2 - T_1}{T_2 T_1}\right) \tag{1.19}$$

This is the *Clausius-Clapeyron* equation, useful for predicting the vapor pressure at any temperature not too far removed from a temperature for which the vapor pressure is known, given also the heat of vaporization, or for calculating the heat of vaporization from any two vapor pressure measurements at different temperatures.

Example: The heat of vaporization of water is 540 calories per gram. Predict the vapor pressure in mm. of Hg at 95.0° C. *Solution:* The molar heat of vaporization is 540 cal./g. multiplied by the molecular weight, 18.0 grams. The vapor pressure at the boiling point, 100° C., is 760 mm. Then:

$$\log \frac{760}{p_{95}} = \frac{(540)(18.0)}{(2.303)(1.987)}\frac{(100.0 - 95.0)}{(373.2)(368.2)} = 0.0773$$

$$p_{95} = (760)/(1.195) = 636 \text{ mm.}$$

The value obtained by experiment is 634 mm.

In Figure 1.11 are shown vapor pressure plots for several typical liquids. If equation (1.18) is obeyed, the plot of $\log p$ against the reciprocal of the absolute temperature is a straight line. This is evident upon comparison of the equation with the type equation of a straight line: $y = ax + b$, where a is the slope of the line or rise per unit distance on the scale of abscissas, and b is the intercept or value of the ordinate y when x is equal to zero. Thus for the present equation, the slope of a $\log p$ versus $1/T$ plot will be equal to $-\Delta H_v/2.303R$. The advantages of a straight-line plot are twofold: the graph provides a rapid means of taking into account the results of a series of measurements at different temperatures when the heat of vaporization is desired, and a straight line permits much more accurate interpolation or extrapolation of data to obtain values for temperatures at which measurements have not been made than does a curved line.
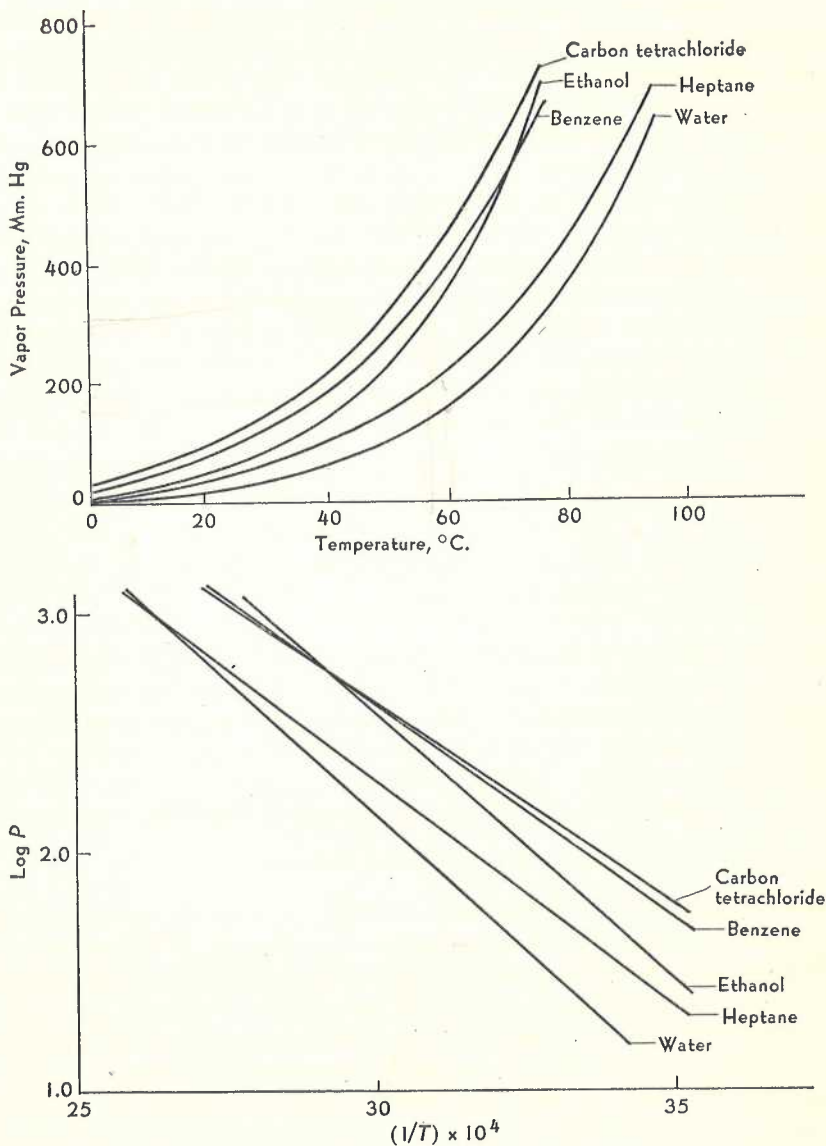
FIG. 1.11 Vapor pressures of liquids.

There are several different methods of vapor pressure measurement which may be employed. In the first, a small amount of liquid is introduced into the space above the mercury surface in a closed-end manometer or barometer. The increase in pressure within the tube, which is indicated by the fall in mercury level, is equal to the vapor pressure. The variation

of temperature which is usually desired is not, however, conveniently accomplished with this equipment.

A second method involves the determination of the temperature at which the liquid boils under various external pressures. The sample is placed in a vessel and subjected to a fixed external pressure; if the pressure is to be less than atmospheric it is established with the aid of an aspirator or vacuum pump. The temperature of the vessel is raised until boiling is observed. As evaporation proceeds, the liquid is cooled because energy equivalent to the heat of vaporization is absorbed. Care must be exercised to strike a balance between the rate at which heat is supplied and the rate at which it is consumed by evaporation, so that a true equilibrium temperature is maintained and superheating is avoided. One arrangement directed to this end allows the liquid to flow from a separatory funnel through a fine tube leading into the vaporizing flask and thence onto the thermometer, keeping moist a wick surrounding the thermometer bulb.

In yet another method, a stream of inert gas is bubbled through the volatile liquid at a rate sufficiently slow so that the gas is saturated with vapor of the liquid. The partial pressure of vapor in the gas mixture leaving the bubbler or saturator is then equal to the vapor pressure of the liquid. From the change in weight of the liquid, the number of moles of vapor formed may be computed. If the volume of inert gas passing is large compared to the volume of vapor formed, which happens when the vapor pressure is small compared to atmospheric pressure, the total volume leaving is practically equal to the volume of inert gas V, and the ideal gas equation may be applied in the form:

$$p_i = \frac{n_i R T}{V}$$

If the vapor pressure is larger than a few millimeters, the method is still applicable, but the calculations must take into account the volume change resulting from the addition of the vapor volume to the inert gas volume.

Example: At 60° C., 10.0 liters of N_2 are bubbled through aniline ($C_6H_5NH_2$, M. W. 93.12). The inert gas is at one atmosphere pressure. 0.256 gram of liquid is evaporated. Calculate the vapor pressure of aniline at 60°. *Solution:*

$$p = \frac{\frac{0.256}{93.1}(0.0821)(333°)}{10} \text{ atm.} \times 760 \frac{\text{mm.}}{\text{atm.}}$$

$$= 5.7 \text{ mm.}$$

Surface tension

A droplet of liquid, such as a raindrop or a globule of mercury, tends to assume a spherical shape; this is a manifestation of the general tendency