chapter twelve

Changes of State. Vapours

SOLID TO LIQUID: FUSION

The Solid State

Substances exist in the solid, liquid or gaseous state. In the *solid state*, a body has a regular, geometrical structure. Sometimes this structure gives the body a regular outward form, as in a crystal of alum; sometimes, as in a strand of wool, it does not. But X-rays can reveal to us the arrangement of the individual atoms or molecules in a solid; and whether the solid is wool or alum, we find that its atoms or molecules are arranged in a regular pattern. This pattern we call a *space-lattice*; its form may be simple, as in metals, or complicated, as in wool, proteins, and other chemically complex substances.

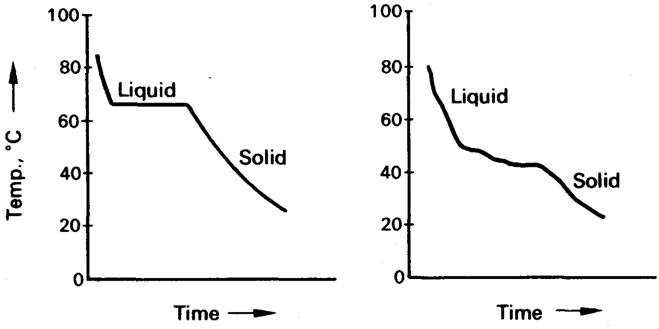
We consider that the atoms or molecules of a solid are vibrating about their mean positions in its space-lattice. And we consider that the kinetic energy of their vibrations increases with the temperature of the solid: its increase is the heat energy supplied to cause the rise in temperature. When the temperature reaches the melting-point, the solid liquefies. Lindemann has suggested that, at the melting-point, the atoms or molecules vibrate so violently that they collide with one another. The attractive forces between them can then no longer hold them in their pattern, the space-lattice collapses, and the solid melts. The work necessary to overcome the forces between the atoms or molecules of the solid, that is, to break-up the space-lattice, is the latent heat of melting or fusion.

The Liquid State

In the liquid state, a body has no form, but a fixed volume. It adapts itself to the shape of its vessel, but does not expand to fill it. We consider that its molecules still dart about at random, as in the gaseous state, and we consider that their average kinetic energy rises with the liquid's temperature. But we think that they are now close enough together to attract one another—by forces of a more-or-less gravitational nature. Any molecule approaching the surface of the liquid experiences a resultant force opposing its escape (see p. 128, Surface Tension) Nevertheless, some molecules do escape, as is shown by the fact that the liquid evaporates: even in cold weather, a pool of water does not last for ever. The molecules which escape are the fastest, for they have the greatest kinetic energy, and therefore the greatest chance of overcoming the attraction of the others. Since the fastest escape, the slower, which remain, begin to predominate: the average kinetic energy of the molecules falls, and the liquid cools. The faster a liquid evaporates, the colder it feels on the hand—petrol feels colder than water, water feels colder than paraffin. To keep a liquid at constant temperature as it evaporates, heat must be supplied to it; the heat required is the latent heat of evaporation.

Melting and Freezing

When a solid changes to a liquid, we say it undergoes a *change of state* or *phase*. Pure crystalline solids melt and freeze sharply. If, for example, paradichlorbenzene is warmed in a test tube until it melts, and then allowed to cool, its temperature falls as shown in Fig. 12.1 (a).



(a) Paradichlorbenzene (b) Paraffin wax

FIG. 12.1. Cooling curves, showing freezing.

A well-defined plateau in the cooling curve indicates the freezing (or melting) point. While the substance is freezing, it is evolving its latent heat of fusion, which compensates for the heat lost by cooling, and its temperature does not fall. An impure substance such as paraffin wax, on the other hand, has no definite plateau on its cooling curve; it is a mixture of several waxes, which freeze out from the liquid at slightly different temperatures (Fig. 12.1 (b)).

Supercooling

If we try to find the melting-point of hypo from its cooling curve, we generally fail; the liquid goes on cooling down to room temperature. But if we drop a crystal of solid hypo into the liquid the temperature rises to the melting-point of hypo, and the hypo starts to freeze. While the hypo is freezing, its temperature stays constant at the melting-point; when all the hypo has frozen, ite temperature starts to fall again (Fig. 12.2).

The cooling of a liquid below its freezing-point is called *supercooling*; the

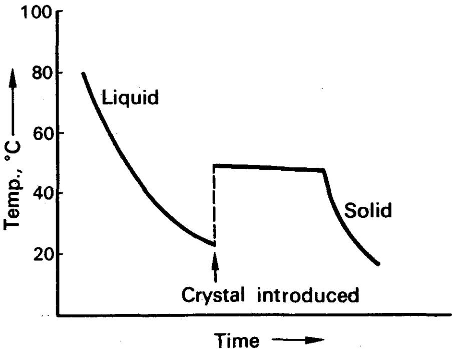


FIG. 12.2. Cooling curve of hypo.

molecules of the liquid lose their kinetic energy as it cools, but do not take up the rigid geometric pattern of the solid. Shaking or stirring the liquid, or dropping grit or dust into it, may cause it to solidify; but dropping in a crystal of its own solid is more likely to make it solidify. As soon as the substance begins to solidify, it returns to its melting (or freezing) point. *The melting-point is the only temperature at which solid and liquid can be in equilibrium.*

No one has succeeded in warming a solid above its melting-point—or, if he has, he has failed to report his success. We may therefore suppose that to superheat a solid is not possible; and we need not be surprised. For the melting-point of a solid is the temperature at which its atoms or molecules have enough kinetic energy to break up its crystal lattice: as soon as the molecules are moving fast enough, they burst from their pattern. On the other hand, when a liquid cools to its melting-point, there is no particular reason why its molecules should spontaneously arrange themselves. They may readily do so, however, around a crystal in which their characteristic pattern is already set up.

Pressure and Melting

The melting-point of a solid is affected by increase of pressure. If we run a copper wire over a block of ice, and hang a heavy weight from it, as in Fig. 12.3, we find that the wire slowly works through the block. It does not cut its way through, for the ice freezes up behind it; the pressure of the wire makes the ice under it melt, and above the wire, where the pressure is released, the ice freezes again. The freezing again after melting by pressure is called *regelation*.

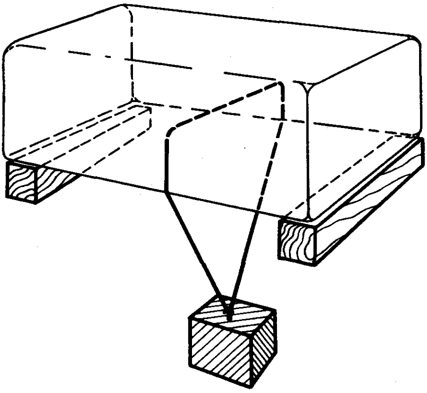


FIG. 12.3. Melting of ice under pressure.

This experiment shows that increasing the pressure on ice makes it melt more readily; that is to say, *it lowers the melting-point* of the ice. We can understand this effect when we remember that ice shrinks when it melts (see p. 209); pressure encourages shrinking, and therefore melting.

The fall in the melting-point of ice with increase in pressure is small: 0·0072°C per atmosphere. It is interesting, because it explains the slipperiness of ice; skates for example, are hollow ground, so that the pressure on the line of contact is very high, and gives rise to a lubricating film of water. Ice which is much colder than 0°C is not slippery, because to bring its melting-point down to its actual temperature would require a greater pressure than can be realized. Most substances swell on melting; an increase of pressure opposes the melting of such substances, and raises their melting-point.

Freezing of Solutions

Water containing a dissolved substance freezes below 0°C. The depression of the freezing-point increases at first with the concentration, but eventually reaches a maximum. The lowest freezing-point of common salt solution is -22°C, when the solution contains about one-quarter of its weight of salt. When a solution does freeze, pure ice separates out; an easy way of preparing pure water is therefore to freeze it, remove the ice, and then melt the ice. The water which is mixed with the ice in determining the ice-point of a thermometer must be pure, or its temperature will not be 0°C.

When ice and salt are mixed, the mixture cools below 0°C, but remains liquid. As the proportion of salt is increased, the temperature of the mixture falls, until it reaches a minimum at -22°C. A mixture of ice and salt provides a simple means of reaching temperatures below 0°C, and is called a 'freezing mixture'.

The phenomena of the freezing of solutions are important in chemistry, and particularly in metallurgy. We shall give a brief explanation of them later in this chapter.

LIQUID TO GAS: EVAPORATION

Evaporation differs from melting in that it takes place at all temperatures; as long as the weather is dry, a puddle will always clear up. In cold weather the puddle lasts longer than in warm, as the rate of evaporation falls rapidly with the temperature.

Solids as well as liquids evaporate. Tungsten evaporates from the filament of an electric lamp, and blackens its bulb; the blackening can be particularly well seen on the headlamp bulb of a bicycle dynamo set, if it has been frequently over-run through riding down-hill. The rate of evaporation of a solid is negligible at temperatures well below its melting-point, as we may see from the fact that bars of metal do not gradually disappear.

Saturated and Unsaturated Vapours

Fig. 12.4 (*a*) shows an apparatus with which we can study vapours and their pressures. A is a glass tube, about a metre long, dipping in a mercury trough and backed by a scale S. Its upper end carries a bulb B, which is fitted with three taps T, of which T_1 and T_2 should be as close together as possible. Above T_1 is a funnel F. With T_1 closed but T_2 open, we evacuate the bulb and tube through T_3, with a rotary pump. If the apparatus is clean, the mercury in A rises to the barometer height H. Meanwhile we put some ether in the funnel F. When the apparatus is evacuated, we close T_3 and T_2. We now open and close T_1, so that a little ether flows into the space C. Lastly, we open T_2, so that the ether evaporates into the bulb B. As it does so, the mercury in A falls, showing that the ether-vapour is exerting a pressure (Fig. 12.4 (*b*)). If h is the new height of the mercury in A, then the pressure of the vapour in mm of mercury is equal to $H-h$.

By closing T_1, opening and closing T_2, and then opening T_1 again,

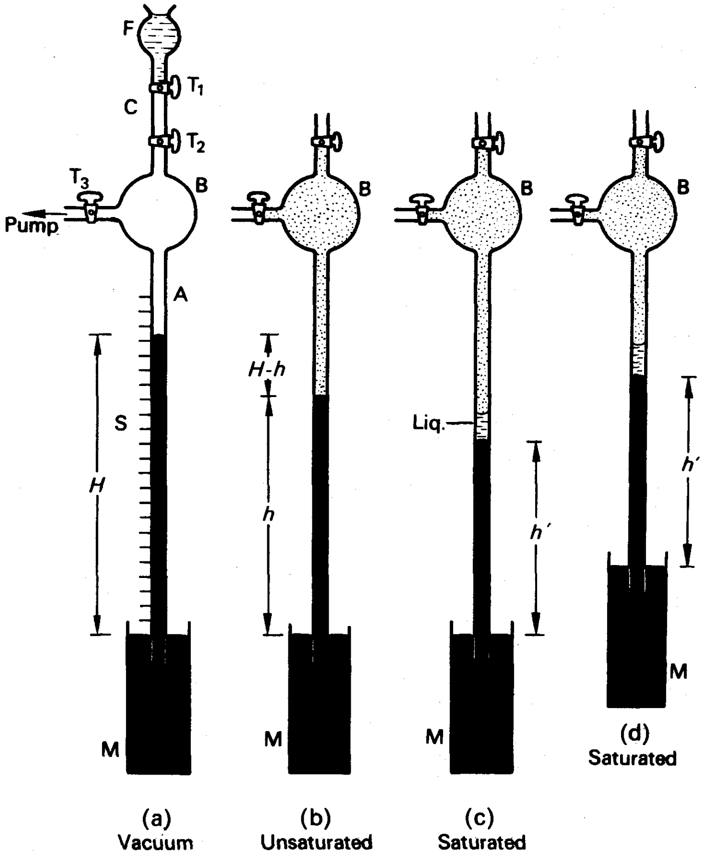


FIG. 12.4. Apparatus for studying vapours.

we can introduce more ether into the space B. At first, we find that, with each introduction, the pressure of the vapour, $H-h$, increases. But we reach a point at which the introduction of more ether does not increase the pressure, the height of the mercury column remains constant at h'. At this point we notice that liquid ether appears above the mercury in A (Fig. 12.4 (*c*)). We say that the vapour in B is now *saturated*; *a saturated vapour* is one that is in contact with its own liquid.

Before the liquid appeared in the above experiment, the pressure of the vapour could be increased by introducing more ether, and we say that the vapour in B was then *unsaturated.*

Behaviour of Saturated Vapour

To find out more about the saturated vapour, we may try to expand or compress it. We can try to compress it by raising the mercury reservoir M. But when we do, we find that the height h' does not change: the pressure of the vapour, $H-h'$, is therefore constant (Fig. 12.4 (*d*)). The only change we notice is an increase in the volume of liquid above the mercury. We conclude, therefore, that reducing the volume of a saturated vapour does not increase its pressure, but merely makes some of it condense to liquid.

Similarly, if we lower the reservoir M, to increase the volume of the vapour, we do not decrease its pressure. Its pressure stays constant, but the volume of liquid above the mercury now decreases; liquid evaporates, and keeps the vapour saturated. If we increase the volume of the vapour until all the liquid has evaporated, then the pressure of the vapour begins to fall, because it becomes unsaturated (see Fig. 12.5 (*a*)).

Effect of Temperature: Validity of Gas-laws for Vapours

We cannot heat the apparatus of Fig. 12.4 through any great rise of temperature. But we can warm it with our hands, or by pointing an electric fire at it. If we do warm it, we find that the ether above the mercury evaporates further, and the pressure of the vapour increases. Experiments which we shall describe later show that the pressure of a saturated vapour rises, with the temperature, at a rate much greater than that given by Charles's law. Its rise is roughly exponential.

To Boyle's law, saturated vapours are indifferent: *their pressure is independent of their volume.* Unsaturated vapours obey Boyle's law roughly, as they also obey roughly Charles's law. Fig. 12.5 (*a*). Vapours, saturated and unsaturated, are gases in that they spread throughout their vessels; but we find it convenient to distinguish them by name from gases such as air, which obey Charles's and Boyle's laws closely. We shall elaborate this distinction later.

PROPERTIES OF SATURATED VAPOURS

Temperature °C	Water Pressure, mm mercury	Mercury	Ethyl Ether
		Pressure, mm mercury	Pressure, mm mercury
−20	0·784 (ice)		
−10	1·96 (ice)		112
0	4·56	0·00016	185
10	9·20	0·00043	291
20	17·5	0·0011	440
30	31·7	0·0026	
34·6			760
40	55·1	0·0057	921
50	92·3	0·0122	
60	149	0·0246	1734
70	234		
80	355	0·0885	2974
90	526		
100	760	0·276	4855
150	3569	2·88	
200	11647	17·8	
250	29770	75·8	
300	67620	249	
356·7		760	

Fig. 12.5 (*b*) shows the effect of heating a saturated vapour. More and more of the liquid evaporates, and the pressure rises very rapidly. As soon as all the liquid has evaporated, however, the vapour becomes unsaturated, and its pressure rises more sedately.

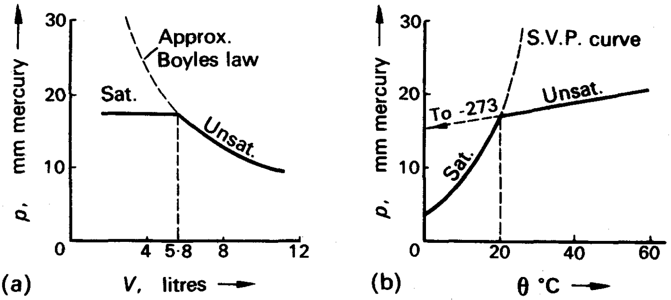


FIG. 12.5. Effect of volume and temperature on pressure of water vapour.

Fig. 12.6 (*a*) shows isothermals for a given mass of liquid and vapour at two temperatures, $\theta_1 = 10°\text{C}$, and $\theta_2 = 21°\text{C}$. The temperatures are chosen so that the saturated vapour pressure at θ_2 is double that at θ_1. The absolute temperatures are $T_1 = 273+\theta_1 = 283$ K, and $T_2 = 273+\theta_2 = 294$ K. Because the saturated vapour pressure rises so rapidly with temperature, the absolute temperature T_2 is not nearly double the absolute temperature T_1. Consequently the isothermals for the unsaturated vapour are fairly close together, as shown; and the transition from saturated to unsaturated vapour occurs at a smaller volume at the higher temperature.

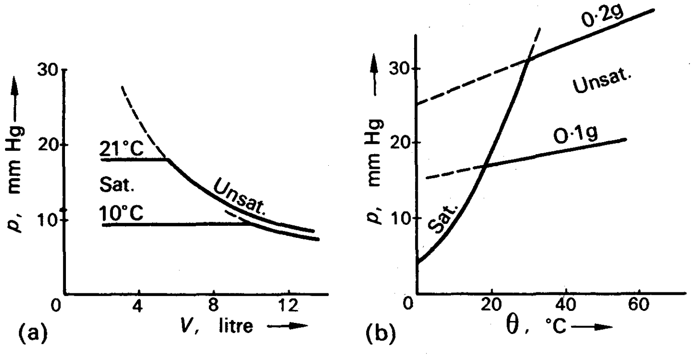


FIG. 12.6. Relationship between pressure, temperature, total mass, and volume, for water-vapour and liquid.

Fig. 12.6 (*b*) shows pressure-temperature curves for a vapour, initially in contact with different amounts of liquid, in equal total volumes. The more liquid present, the greater is the density of the vapour when it becomes unsaturated, and therefore the higher the pressure and temperature at which it does so.

Kinetic Theory of Saturation

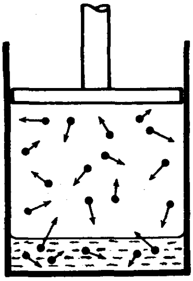


FIG. 12.7. Dynamic equilibrium.

Let us consider a vapour in contact with its liquid, in an otherwise empty vessel which is closed by a piston (Fig. 12.7). The molecules of the vapour, we suppose, are rushing randomly about, like the molecules of a gas, with kinetic energies whose average value is determined by the temperature of the vapour. They bombard the walls of the vessel, giving rise to the pressure of the vapour, and they also bombard the surface of the liquid.

The molecules of the liquid, we further suppose, are also rushing about with kinetic energies determined by the temperature of the liquid. The fastest of them escape from the surface of the liquid. At the surface, therefore, there are molecules leaving the liquid, and molecules arriving from the vapour. To complete our picture of the conditions at the surface, we suppose that the vapour molecules bombarding it are not reflected— as they are at the walls of the vessel—but are absorbed into the liquid. We may expect them to be, because we consider that molecules near the surface of a liquid are attracted towards the body of the liquid.

We shall assume that the liquid and vapour have the same temperature. Then the proportions of liquid and vapour will not change, if the temperature and the total volume are kept constant. Therefore, at the surface of the liquid, molecules must be arriving and departing at the same rate, and hence evaporation from the liquid is balanced by condensation from the vapour. This state of affairs is called a *dynamic equilibrium*. In terms of it, we can explain the behaviour of a saturated vapour.

The rate at which molecules leave unit area of the liquid depends simply on their average kinetic energy, and therefore on the temperature. The rate at which molecules strike unit area of the liquid, from the vapour, likewise depends on the temperature; but it also depends on the concentration of the molecules in the vapour, that is to say, on the density of the vapour. The density and temperature of the vapour also determine its pressure; the rate of bombardment therefore depends on the pressure of the vapour.

Now let us suppose that we decrease the volume of the vessel in Fig. 12.7 by pushing in the piston. Then we momentarily increase the density of the vapour, and hence the number of its molecules striking the liquid surface per second. The rate of condensation thus becomes greater than the rate of evaporation, and the liquid grows at the expense of the vapour. As the vapour condenses its density falls, and so does the rate of condensation. The dynamic equilibrium is restored when the rate of condensation, and the density of the vapour, have returned to their original values. The pressure of the vapour will then also have returned to its original value. *Thus the pressure of a saturated vapour is independent of its volume.* The proportion of liquid to vapour, however, increases as the volume decreases.

Let us now suppose that we warm the vessel in Fig. 12.7, but keep the piston fixed. Then we increase the rate of evaporation from the liquid, and increase the proportion of vapour in the mixture. Since the volume is constant, the pressure of the vapour rises, and increases the rate at which molecules bombard the liquid. Thus the dynamic equilibrium is restored, at a higher pressure of vapour. The increase of pressure with temperature is rapid, because the rate of evaporation of the liquid increases rapidly—almost exponentially—with the temperature. A small rise in temperature causes a large increase in the proportion of molecules in the liquid moving fast enough to escape from it.

Boiling

A liquid boils when its saturated vapour pressure is equal to the atmospheric pressure. To see that this is true, we take a closed J-shaped tube, with water trapped in its closed limb (Fig. 12.8 (*a*)). We heat the tube in a beaker of water, and watch the water in the J-tube. It remains trapped as at (*a*) until the water in the beaker is boiling. Then the water in the J-tube comes to the same level in each limb, showing that the pressure of the vapour in the closed limb is equal to the pressure of the air outside (Fig. 12.8 (*b*)).

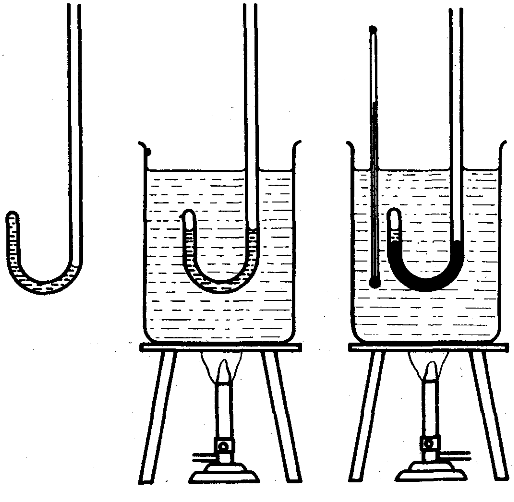


FIG. 12.8. Use of J-tube for boiling-point.

The J-tube gives a simple means of measuring the boiling-point of a liquid which is inflammable, or which has a poisonous vapour, or of which only a small quantity can be had. A few drops of the liquid are imprisoned by mercury in the closed limb of the tube, all entrapped air having been shaken out (Fig. 12.8 (*c*)). The tube is then heated in a bath, and the temperature observed at which the mercury comes to the same level in both limbs. The bath is warmed a little further, and then a second observation made as the bath cools; the mean of the two observations is taken as the boiling-point of the liquid.

Boiling differs from evaporation in that a liquid evaporates from its surface alone, but it boils throughout its volume. If we ignore the small hydrostatic pressure of the liquid itself, we may say that the pressure throughout a vessel of liquid is the atmospheric pressure. Therefore, when the saturated vapour pressure is equal to the atmospheric pressure, a bubble of vapour can form anywhere in the liquid.

Generally the bottom of the liquid is the hottest part of it, and bubbles form there and rise through the liquid to the surface. Just before the liquid boils, its bottom part may be at the boiling-point, and its upper part below. Bubbles of vapour then form at the bottom, rise in to the colder liquid, and then collapse. The collapsing gives rise to the singing of a kettle about to boil.

Further Consideration of Boiling

The account of boiling which we have just given is crude because in it we ignored the effect of surface-tension. Because of surface tension, a bubble can exist in a liquid only if there is an excess pressure inside it. If γ is the surface-tension of the liquid, and r the radius of the bubble, the excess pressure is $2\gamma/r$. If the bubble is formed at a depth h below the surface of the liquid, as in Fig. 12.9, the external pressure acting on it is

$$P = P_a + h\rho g,$$

where P_a = atmospheric pressure, ρ = density of liquid, g = acceleration of gravity.

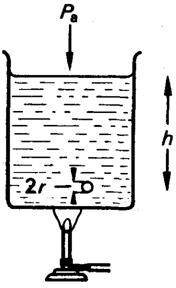


FIG. 12.9. Boiling.

Therefore a bubble, of radius r, can form at a depth h only if its vapour pressure, p, satisfies the equation

$$\begin{aligned} p &= P + \frac{2\gamma}{r} \\ &= P_a + h\rho g + \frac{2\gamma}{r}. \end{aligned}$$

If the radius r is small, the term $2\gamma/r$ is great, and the bubble cannot form unless the vapour pressure is considerably above atmospheric. In fact the equation shows that a bubble can never start from zero radius, because it would require an infinite vapour pressure to do so. Bubbles actually form on roughnesses in the vessel, or specks of solid suspended in the liquid. Very clean water in a very smooth beaker may not boil until it is well above 100°C; its bubbles then grow violently, and the liquid 'bumps' in the beaker. A piece of broken pipe-clay prevents bumping, by presenting fine points for the bubbles to form on.

Thus the temperature of a boiling liquid is not definite—it depends on the conditions of boiling. But the temperature of the vapour is definite. The vapour escaping is in equilibrium with the liquid at the surface, and is at atmospheric pressure. Its temperature, therefore, is the temperature at which the saturated vapour pressure is equal to the atmospheric pressure. This idea is important in defining the upper fixed point of the temperature scale (p. 190). We say that the upper fixed point is the temperature of the steam from water boiling under a pressure of 760 mm mercury. We must not refer to the temperature of the water, and we must specify the atmospheric pressure because as we have just seen, it determines the temperature of the steam.

TEMPERATURE OF SATURATED STEAM AT PRESSURES
NEAR NORMAL ATMOSPHERIC

Barometer height, H, mm	680	690	700	710	720	730	740	750	751
Temperature, θ, °C	96·910	97·312	·709	98·102	·490	·874	99·254	·629	·666
Barometer height, H, mm	752	753	754	755	756	757	758	759	760	761
Temperature, θ, °C	·704	·741	·778	·815	·852	·889	·926	·963	100·000	·037
Barometer height, H, mm	762	763	764	765	766	767	768	769	770	780
Temperature, θ, °C	·074	·110	·147	·184	·220	·257	·294	·330	·367	·729

In general, around $H = 760$ mm, the temperature is given by

$$\theta = 100 + 0{\cdot}036\,(H-760) - 2{\cdot}3\times10^{-5}\,(H-760)^2.$$

Variation of Saturated Vapour Pressure with Temperature

We can now see how the relationship between the pressure of a saturated vapour and its temperature can be measured. We must apply various known air pressures to the liquid, heat the liquid, and measure the temperature of its vapour. Fig. 12.10 shows a suitable apparatus, due to Regnault. The flask F contains the liquid, water in a laboratory experiment, and the flask R is an air reservoir. The pressure of the air in R is shown by the mercury manometer M; if its height is h, the pressure in mm mercury is

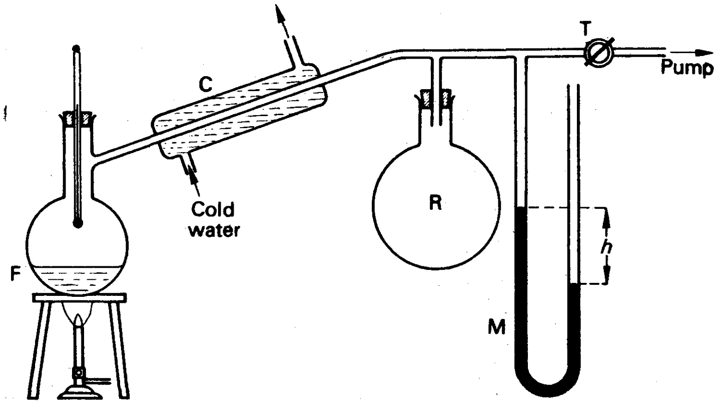


FIG. 12.10. Apparatus for variation of S.V.P. with temperature.

$$p = H - h,$$

where H is the barometer height.

We first withdraw some air from R through the tap T, with a filter pump, until p is about 700 mm. We then close T and heat the water gently. The water vapour condenses in the condenser, and runs back to the flask. After a few minutes the water boils steadily. The temperature of the vapour, θ, and the pressure, p, become constant and we record their values. We next remove the flame from the flask F, and let the apparatus cool for a minute or two. Then we withdraw some more air from R, close T again, and repeat the observations.

If we wish to find the saturated vapour pressure when it is above atmospheric, that is to say, when the temperature is above the normal boiling-point of the liquid, air is pumped into the reservoir R—with a bicycle pump—instead of drawing it out. The manometer M then shows the excess pressure, and

$$p = H+h.$$

With simple glass apparatus we cannot go far in this direction.

Boiling Point of a Solution

At a given pressure, the boiling-point of water containing a dissolved substance is higher than that of pure water. The temperature of the steam evolved from the solution, however, is the temperature of saturated steam at the prevailing pressure. Traces of dissolved substances in the water therefore do not affect the steam point in thermometry.

Since a liquid boils when its saturated vapour pressure is equal to the atmospheric pressure, we must conclude that dissolving a substance in water lowers its saturated vapour pressure, at a given temperature (Fig. 12.11). We may explain this by supposing that the molecules of the dissolved substance, which do not evaporate, hinder the escape of the molecules of the water.

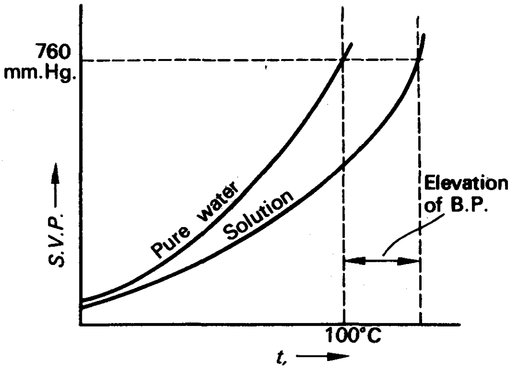


FIG. 12.11. Effect of solute on saturated vapour pressure.

The lowering of the vapour pressure of water by a dissolved solid gives striking support to the kinetic theory of evaporation. For measurements of the vapour pressure show that reduction does not depend on the nature of the solute; it depends only on the number of dissolved particles in the solution expressed as a fraction of the total number of particles (solute plus water molecules). In fact, if there are n solute particles to every $100-n$ water molecules, then

$$\frac{\Delta p}{p} = \frac{n}{100},$$

where p is the saturated vapour pressure of water, and Δp is the lowering by solution. Thus the lowering simply depends on the number of particles hindering evaporation.

Effect of Altitude on Boiling Point

The pressure of the atmosphere decreases with increasing height above the earth's surface, because the thickness, and therefore the weight, of the belt of air above the observer decreases. The rate of fall in pressure is almost uniform over fairly small heights—about 85 mm mercury per km. But at great altitudes the rate of fall diminishes. At the height of Everest, 9000 m, the atmospheric pressure is about 280 mm of mercury. On account of the fall in atmospheric pressure, the boiling point of water falls with increasing height. Cooking-pots for use in high mountainous districts, such as the Andes, are therefore fitted with clamped lids. As the water boils, the steam accumulates in the pot, and its pressure rises above atmospheric. At about 760 mm mercury a safety valve opens, so that the pressure does not rise above that value, and the cooking is done at 100°C.

The fall in the boiling-point with atmospheric pressure gives a simple way of determining one's height above sea-level. One observes the steam point with a thermometer and hypsometer (p. 190). Knowing how the steam point falls with pressure, and how atmospheric pressure falls with increasing height, one can then find one's altitude. The hypsometer was, in fact, devised for this purpose, and takes its name from it; *hypsos* is Greek for height. Hypsometers have been carried up Himalayan peaks; and one was found by Scott and his companions in Amundsen's abandoned tent at the South Pole.

Variation of Latent Heat with Temperature

When we speak of the latent heat of evaporation of a liquid, we usually mean the heat required to vaporize unit mass of it at its normal boiling-point, that is to say, under normal atmospheric pressure. But since evaporation takes place at all temperatures, the latent heat has a value for every temperature. Regnault measured the latent heat of steam over a range of temperatures, by boiling water at controlled pressures, as in measuring its saturated vapour pressure. His apparatus was in principle similar to Berthelot's (Fig. 9.10); but he connected the outlet tube to an air reservoir, manometer, and pump, as in Fig. 12.10. Modern measurements give, approximately,

$$l = 2520 - 2{\cdot}5\theta$$

where l is the specific latent heat in kJ kg^{-1} at θ°C.

Internal and External Latent Heats

The volume of 1 g of steam at 100°C is 1672 cm^3. Therefore when 1 g of water turns into steam, it expands by 1671 cm^3; in doing so, it does work against the atmospheric pressure. The heat equivalent of this work is that part of the latent heat which must be supplied to the water to make it overcome atmospheric pressure as it evaporates; it is called the 'external latent heat'. The rest of the specific latent heat—the internal part—is the equivalent of the work done in separating the molecules, against their mutual attractions.

The work done, W, in the expansion of 1 g from water to steam is the product of the atmospheric pressure p and the increase in volume ΔV:

$$W = p.\Delta V.$$

Normal atmospheric pressure corresponds to a barometer height H 760 mm. Hence, as on p. 228,

$$\begin{aligned} p = g\rho H &= 9{\cdot}81 \times 13600 \times 0{\cdot}76 \\ &= 1{\cdot}013 \times 10^5 \text{ N m}^{-2} \end{aligned}$$

and $$W = p.\Delta V = 1{\cdot}013 \times 10^5 \times 1671 \times 10^{-6} \text{ joule.}$$

The external specific latent heat in joules is therefore

$$\begin{aligned} l_{ex} &= 1{\cdot}013 \times 10^5 \times 1671 \times 10^{-6} \\ &= 170 \text{ J g}^{-1} = 170 \text{ kJ kg}^{-1}. \end{aligned}$$

This result shows that the external part of the specific latent heat is much less than the internal part. Since the total specific latent heat l is 2270 joule g^{-1}, the internal part is

$$\begin{aligned} l_{in} = l - l_{ex} &= 2270 - 170 \\ &= 2100 \text{ J g}^{-1} = 2100 \text{ kJ kg}^{-1}. \end{aligned}$$

Density of a Saturated Vapour

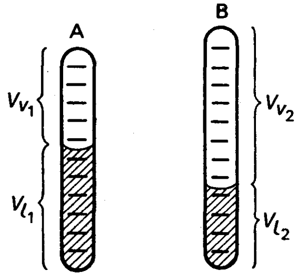


FIG. 12.12. Determination of density of a saturated vapour.

In any experiment to measure the density of a saturated vapour, the vessel containing the vapour must also contain some liquid, to ensure that the vapour is saturated. The problem is therefore to find how much of the total mass is vapour, and how much is liquid. Fig. 12.12 shows one method of solving this problem, due to Cailletet and Mathias.

A, B are two glass tubes, which have been calibrated with volume scales, and then evacuated. Known masses m_1, m_2 of liquid are introduced into the tubes, which are then sealed off. The tubes are warmed to the same temperature in a bath, and the volumes of liquid V_{l_1}, V_{l_2} and of vapour V_{v_1} V_{v_2} are observed. Then if ρ_l and ρ_v are the densities of liquid and vapour respectively:

$$m_1 = \rho_l V_{l_1} + \rho_v V_{v_1}$$

$$m_2 = \rho_l V_{l_2} + \rho_v V_{v_2}.$$

From these equations ρ_l can be eliminated, and ρ_v found. The equations can also, of course, be made to give ρ_l; this method is useful for finding the density of a liquid 'gas'—e.g. liquid oxygen (p. 324).

Density of an Unsaturated Vapour

We have seen that the molecular weight of a gas, μ, is given very nearly by $\mu = 2\Delta$, where Δ is the density of the gas relative to that of hydrogen (p. 230).

The proof that $\mu = 2\Delta$ depends on Avogadro's principle, which says that equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules. This principle is true only of those gases which we normally call 'perfect'—which obey Boyle's and Charles's laws accurately (p. 225). It is not true of saturated vapours, but it is roughly true of vapours which are far from saturation. To find the molecular weight of a substance which is liquid at room temperature, therefore, we must vaporize it, and measure the density of its vapour when it is as far from saturation as we can conveniently get it.

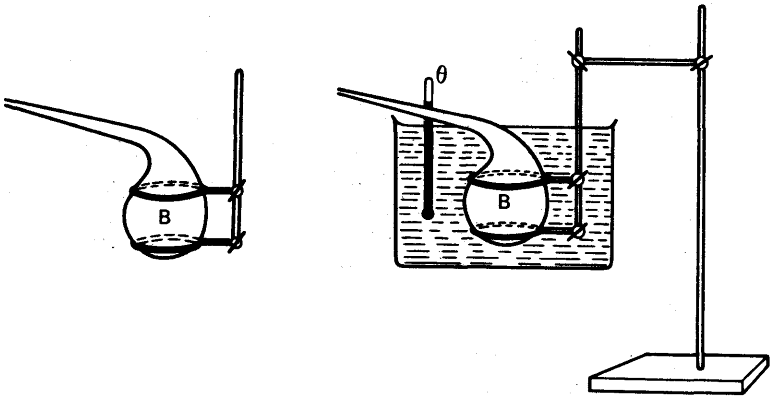


FIG. 12.13. Determination of density of an unsaturated vapour.

Several methods have been devised for doing this, one of which, Dumas's of 1827, is illustrated in Fig. 12.13. A glass bulb B, with a long thin stem, is weighed and then partly filled with liquid by warming and dipping. The amount of liquid introduced must be great enough to ensure that all the air in the bulb will be driven out by vapour when the liquid evaporates. The liquid is made to evaporate by plunging the bulb into a bath at a temperature θ about 40°C above its boiling-point. It then evaporates rapidly, and its vapour sweeps the air out of the bulb. When vapour has stopped coming out, the stem is sealed with a flame: the bulb now contains nothing but the vapour, at the temperature θ and under atmospheric pressure.

The bulb is removed, allowed to cool, dried, and weighed. The stem is then broken at the tip under water; since nearly all the vapour has condensed, at the room temperature, water rushes in and fills the bulb.

Let m_1 = mass of bulb full of air, at room temperature.
m_2 = mass of bulb full of vapour.
m_3 = mass of bulb full of water.

Since the mass of air in the bulb is negligible compared with that of water, we have, *numerically*,

$$\text{Volume of bulb in cm}^3,\ V_1, = m_3 - m_1 \text{ in g.}$$

The mass of air in the bulb at room temperature is

$$m_a = V\rho_a,$$

where ρ_a is the density of air at room temperature and atmospheric pressure. The mass of the bulb itself is

$$m_b = m_1 - m_a,$$

and the mass of vapour which filled it when hot is

$$m_v = m_2 - m_b.$$

This mass of vapour occupied the volume V_1 at the temperature θ; its density was therefore

$$\rho_v = \frac{m_v}{V_1}.$$

Since the temperature was well above the boiling-point, the vapour was far from saturated; Boyle's and Charles's laws can therefore be used to reduce its density to s.t.p., for comparison with that of hydrogen.

WATER-VAPOUR IN THE ATMOSPHERE: HYGROMETRY

The water vapour in the atmosphere is important because it affects our comfort. Except in cold weather, we sweat continuously: the water in the sweat evaporates, draws its latent heat of evaporation from the skin, and so keeps us cool. Beads of sweat appear only when the water cannot evaporate as fast as it reaches the surface of the skin; we then feel uncomfortably hot.

On the other hand, if water evaporates from the skin too rapidly, the skin feels parched and hard; around the mucous membranes—at the mouth and nose—it tends to crack.

The rate at which water evaporates, from the skin or anywhere else, depends on the pressure of the water vapour surrounding it. If the water vapour above the skin is far from saturated, evaporation is swift. If the vapour is already saturated, water reaching the skin comes immediately into dynamic equilibrium with it; individual molecules are exchanged between liquid and vapour, but no mass of liquid is lost, and water accumulates.

The Partial Pressure of Atmospheric Water

The atmosphere contains other gases besides water-vapour, such as oxygen and nitrogen. In speaking of the water-vapour, therefore, we must refer to its 'partial pressure', as explained on p. 222.

Water-vapour in the atmosphere is also important because it affects the weather. Let us suppose that the atmosphere has a temperature of 20°C—a warm day—and that the water vapour in it has a partial pressure of 12 mm mercury. It will have a density of about 12 mg per litre. The density of *saturated* water vapour at 20°C is 17·3 mg per litre, and its pressure 17·5 mm mercury. The water vapour in the atmosphere is therefore not saturated.

Now let us suppose that the atmosphere cools to 14°C, without changing its composition. The 6°C fall in temperature will hardly affect the density of the water vapour, but it will bring the atmosphere to saturation. For the pressure of saturated water vapour at 14°C is 12 mm mercury, and its density about 12 mg per litre. If the atmosphere cools any further, water vapour will condense out of it, forming drops of liquid water—that is, of fog or cloud.

Relative Humidity

The dampness of the atmosphere, besides affecting the weather and our comfort, is important also in storage and manufacture of many substances—tobacco and cotton, for example. From what we have said already, we can see that the important factor is not the actual proportion of water vapour in the atmosphere, but its nearness to saturation. In the above example, the density of the vapour remained almost constant, but we would have felt the atmosphere becoming much damper as it cooled from 20°C to 14°C.

The dampness of the atmosphere is expressed by its *relative humidity, R.H.*, which is defined as follows:

$$R.H. = \frac{\text{mass of water-vapour in a given volume of atmosphere}}{\text{mass of an equal volume of saturated water-vapour at the same temperature}} \quad (1)$$

In other words,

$$R.H. = \frac{\text{density of water-vapour in atmosphere}}{\text{density of saturated water-vapour at the same temperature}}$$

Because an unsaturated vapour roughly obeys Boyle's law, its density is roughly proportional to its pressure; the relative humidity as defined above is therefore roughly given by

$$R.H. = \frac{\text{partial pressure of water-vapour present}}{\text{S.V.P. at temperature of atmosphere}}$$

where S.V.P. stands for 'saturated vapour pressure'.

Before describing the methods of measurement, we must warn the reader against thinking that the atmosphere 'takes up' water vapour. The atmosphere is not a sponge. Water-vapour exists in it in its own right; and our knowledge of vapours makes us feel sure that, if we could live in an atmosphere of water-vapour alone, we would have just the same experiences of humidity as we now have in our happily richer surroundings.

Dew-point

In the evening, the earth cools more rapidly, by radiation, than the air above it. Then, on smooth surfaces such as metals, we often find a thin film of moisture. The surface has cooled to such a temperature that the water vapour in contact with it has become saturated, and has begun to condense. No fog has formed because the atmosphere in general is warmer than the cold solid, and the vapour in it is not saturated. The temperature of a cold surface on which dew just appears is called the *dew-point*: it is *the temperature at which the saturated vapour-pressure of water is equal to the partial pressure of the water-vapour present in the atmosphere.*

If we know the dew-point, we can find the corresponding pressure of saturated water-vapour, p_1, from tables. From the same tables we can find the pressure of saturated water-vapour at the temperature of the atmosphere. If this is p_2, then, from p. 310, the relative humidity, *R.H.*, is given by

$$R.H. = \frac{p_1}{p_2} \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

Dew-point Hygrometers

Hygrometery is the measurement of relative humidity, and a *hygrometer* is an instrument for measuring it. Many forms of dew-point hygrometer have been devised; we shall describe only the one due, like so much apparatus in Heat, to Regnault. It consists of two glass tubes, A, B, with silver-plated thimbles C, D cemented on to their lower ends. C contains ether, into which dips a thermometer T and a glass tube R (Fig. 12.14). To use the hygrometer, we first place a sheet of glass between it and ourselves, to prevent our breath from adding to the humidity of the air around it. We then gently blow air through the ether, by means of a scent-spray bulb connected through a rubber tube to R. (Alternatively, we may pass in a gentle stream of coal-gas, and burn it at the end of a long tube connected to the outlet S.) The gas or air passing through the ether carries away its vapour, and makes it evaporate continuously. In doing so it cools, since it must provide its latent heat of evaporation from its own heat content. When the ether has cooled to the dew-point, a film of mist appears on the thimble C; the thimble D enables us to notice this more sharply, by contrast. At the moment when the dew appears, the thermometer T is read. The flow of air or gas through the ether is stopped, and the ether allowed to warm up. The temperature at which the dew vanishes is noted, and the mean of this and the temperature at which it appeared is taken as the dew-point, θ_1 say. By so doing we correct reasonably well for any difference of temperature between the ether and the outer surface of the tube. Lastly, we take the temperature of the room, θ_2, often from a thermometer (not shown) in B, and look up the saturation pressures at θ_1, θ_2 respectively. These are given in the following table. Then

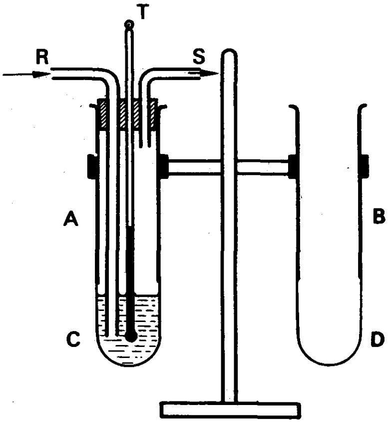


FIG. 12.14. Regnault's hygrometer.

$$\text{relative humidity} = \frac{\text{S.V.P. at } \theta_1}{\text{S.V.P. at } \theta_2} \times 100 \text{ per cent.}$$

PRESSURE AND DENSITY OF SATURATED WATER VAPOUR

θ°C	0	2	4	6	8	10	12	14	16	18	20
p, mm mercury	4·58	5·29	6·10	7·01	8·04	9·21	10·5	12·0	13·6	15·5	17·5
ρ, mg/litre (or g m^{-3})	4·84	5·54	6·33	7·22	8·21	9·33	10·6	12·0	13·5	15·2	17·1
θ°C	22	24	26	28	30	32	34	36	38	40	
p, mm mercury	19·8	22·3	25·1	28·3	31·7	35·5	39·8	44·4	49·5	55·1	
ρ, mg/litre (or g m^{-3})	19·2	21·5	24·1	26·9	30·0	33·5	37·2	41·3	45·8	51·1	

The Wet-and-dry-bulb Hygrometer

A piece of wet cloth feels cold, because the moisture evaporating from it takes latent heat, and cools the remaining liquid. This effect is used in the *wet-and-dry-bulb hygrometer*. A piece of muslin is tied round the bulb of a thermometer, and allowed to dip into a small jar of water. It is mounted, with a second, dry-bulb, thermometer, in a louvred draught-shield (Fig. 12.15). The rate at which water evaporates from the muslin increases as the relative humidity of the atmosphere falls; the cooling of the wet bulb therefore also increases. The greater the difference in reading of the two thermometers, the less is the relative humidity. By calibration against a chemical hygrometer, tables and charts have been prepared which give the relative humidity in terms of the thermometer readings.

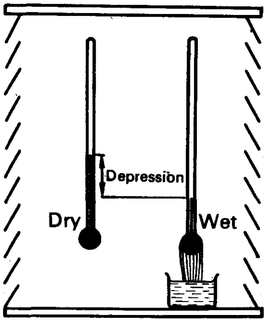


FIG. 12.15. Wet-and-dry bulb hygrometer.

WET-AND-DRY-BULB HYGROMETER TABLE
(Percentage relative humidity)

Dry-bulb reading °C	Difference (depression of wet-bulb), °C									
	1	2	3	4	5	6	8	10	12	14
0	82	65	48	31%						
5	85	72	58	45	32%					
10	88	76	65	54	44	34%				
15	90	80	71	61	52	44	27	12%		
20	91	83	74	66	59	51	37	24	12%	
25	92	84	77	70	63	57	44	33	22	12%
30		86	79	73	67	61	50	39	30	21%

The wet-and-dry-bulb hygrometer is not very reliable when used in a simple screen. It is more accurate if a steady stream of air is driven past it by a fan, or by whirling the thermometers around in a frame like a football-fan's rattle. The hygrometer is then said to be ventilated.

The Hair Hygrometer

Human hair expands in length in damp air. A hair hygrometer is one consisting of a bundle of hairs fixed to a spring at one end, and wrapped round a spindle at the other. The expansion of the hair turns the spindle and moves a pointer over a scale, which is directly calibrated in relative humidities. Such instruments need to be recalibrated frequently, because the hair shows elastic fatigue.

THE BEHAVIOUR OF REAL GASES; CRITICAL PHENOMENA

A perfect, or ideal, gas is one which obeys Boyle's and Charles's law exactly, and whose internal energy is independent of its volume. No such gas exists, but at room temperature, and under moderate pressures, many gases approach the ideal closely enough for most purposes.

We shall consider now the departures of gases from perfection; in doing so we shall come to appreciate better the relationship between liquid, vapour, and gas, and we shall see how gases such as air can be liquefied.

Departures from Boyle's Law

In 1847 Regnault measured the volumes of various gases at pressures of several atmospheres. Using the apparatus of Fig. 12.16, he found that, to halve the volume of the gas, he did not have quite to double the pressure on it. The product pV, therefore, instead of being constant, decreased slightly with the pressure. He found one exception to this rule: hydrogen. By compressing the gases further, Regnault found the variation of pV with p at constant temperature, and obtained results which are represented by the early parts of the curves in Fig. 12.17.

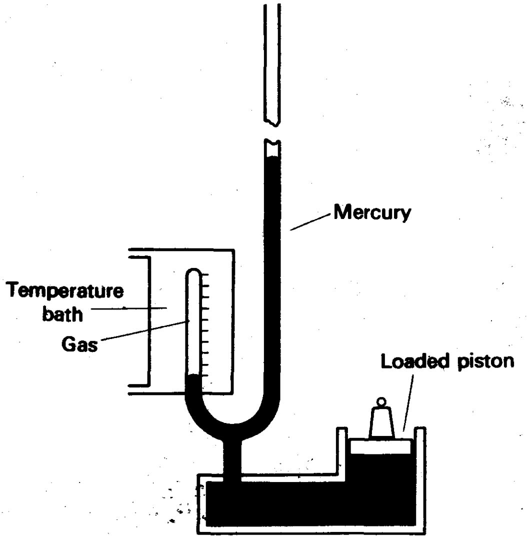


FIG. 12.16. Regnault's apparatus for isothermals at high pressure.

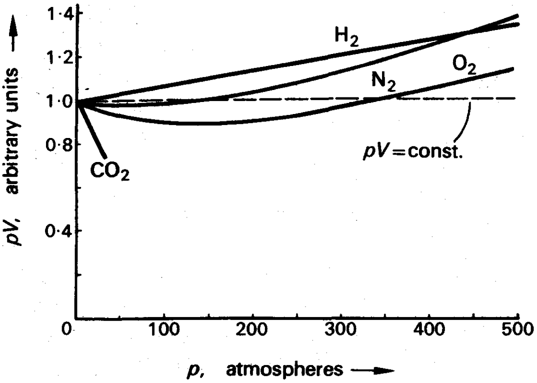


FIG. 12.17. Isothermals for various gases, at room temperature and high pressure.

The complete curves in the figure show some of the results obtained by Amagat in 1892. Amagat's apparatus for nitrogen is shown in Fig. 12.18. To get high pressures, he put the apparatus at the bottom of a coal-mine, and made the manometer tube out of rifle barrels, screwed together and standing up the shaft. He reached a pressure of 3000 atmospheres.

Having found the volume-pressure relationship for nitrogen, Amagat used it to measure high pressures in the laboratory, without having to resort to the mine. His method was similar to that of Andrews, which we are about to describe; by means of it he found the pressure-volume relationships for other gases.

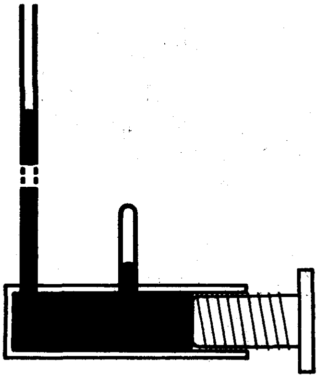


FIG. 12.18. Amagat's apparatus for isothermals at high pressure.

Andrews' Work on Carbon Dioxide

In 1863 Andrews made experiments on carbon dioxide which have become classics. Fig. 12.19 shows his apparatus. In the glass tube A he trapped carbon dioxide above the pellet of mercury X. To do this, he started with the tube open at both ends and passed the gas through it for a long time. Then he sealed the end of the capillary. He introduced the mercury pellet by warming the tube, and allowing it to cool with the open end dipping into mercury. Similarly, he trapped nitrogen in the tube B.

Andrews then fitted the tubes into the copper casing C, which contained water. By turning the screws S, he forced water into the lower parts of the tubes A and B, and drove the mercury upwards. The wide parts of the tubes were under the same pressure inside and out, and so were under no stress. The capillary extensions were strong enough to

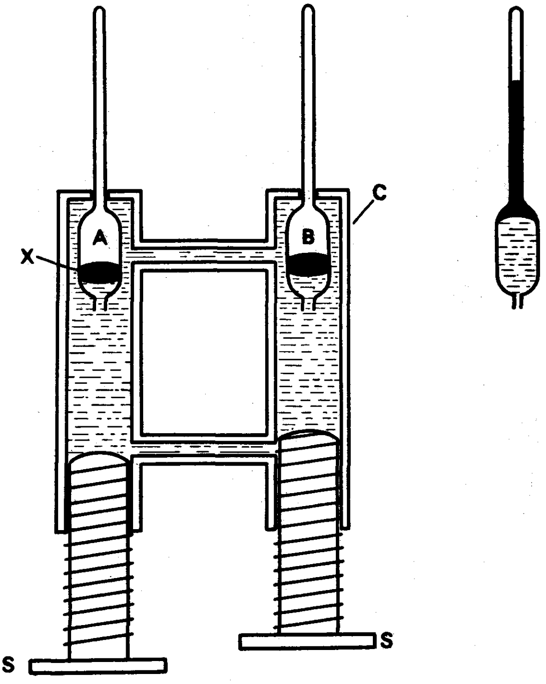


FIG. 12.19. Andrews's apparatus for isothermals of CO_2 at high pressures.

withstand hundreds of atmospheres. Andrews actually reached 108 atmospheres.

When the screws S were turned far into the casing, the gases were forced into the capillaries, as shown on the right of the figure, and greatly compressed. From the known volumes of the wide parts of the tubes, and the calibrations of the capillaries, Andrews determined the

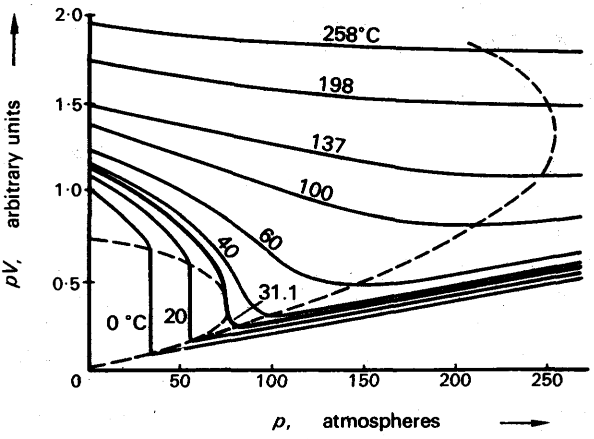


FIG. 12.20. Isothermals for CO_2, as pV/p curves, at various temperatures. The small dotted loop passes through the ends of the vertical parts; the large dotted loop is the locus of the minima of pV.

volumes of the gases. He estimated the pressure from the compression of the nitrogen, assuming that it obeyed Boyle's law.

For work above and below room temperature, Andrews surrounded the capillary part of A with a water bath, which he maintained at a constant temperature between about 10°C and 50°C.

Fig. 12.20 shows some of Andrews's results, corrected for the departure of nitrogen from Boyle's law; it also shows the results of similar experiments over a wider range of temperature, by Amagat in 1893.

Critical Temperature

Before we can interpret Andrews's results for carbon dioxide, we must describe a simple experiment, made by Cagniard de la Tour in 1822. De la Tour made a tube of strong glass, as shown in Fig. 12.21. In the bulb he had water, round the bend mercury, and at the top—where the tube was sealed off—air. He heated the tube in a bath to over 300°C. The expansion of the liquids was taken up by the compression of the air, from which de la Tour estimated the pressure; it went beyond 100 atmospheres. Above about 100°C he observed what we would expect; that a meniscus formed in bulb, showing that steam was present as well as water. But above about 300°C he noticed that the meniscus vanished: that there was no observable distinction between liquid and vapour. The temperature at which the meniscus vanished he called the *critical temperature.*

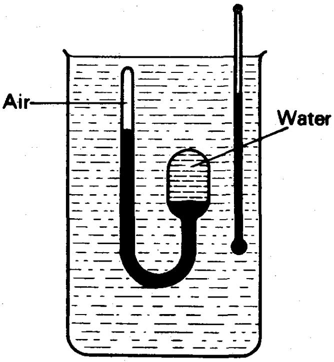


FIG. 12.21. Cagniard de la Tour's experiment.

If we consider the nature of a saturated vapour, the phenomenon of the critical temperature need not surprise us. For as its temperature rises a saturated vapour becomes denser, whereas a liquid becomes less dense. The critical temperature is, we may suppose, the temperature at which liquid and saturated vapour have the same density. Fig. 12.22 supports this view: it shows the results of measurements made on liquid oxygen by the method of Cailletet and Mathias (p. 307).

Behaviour of Carbon Dioxide near the Critical Point

Now let us turn to Andrews' isothermals for carbon dioxide. These are shown again, this time as a simple pressure-volume diagram, in Fig. 12.23. Let us consider the one for 21·5°C, ABCD. Andrews noticed that, when the pressure reached the value corresponding to B, a meniscus appeared above the mercury in the capillary containing the carbon dioxide. He concluded that the liquid had begun to form. From B to C, he found no change in pressure as the screws were turned, but simply a decrease in the volume of the carbon dioxide. At the same time the meniscus moved upwards, suggesting that the proportion of liquid was increasing. At C the meniscus disappeared at the top of the tube, suggesting that the carbon dioxide had become wholly liquid. Beyond C the pressure rose very rapidly; this confirmed the idea that the carbon dioxide was wholly liquid, since liquids are almost incompressible.

Thus the part CBA of the isothermal for 21·5°C is a curve of volume against pressure for a liquid and vapour, showing saturation at B; it is like the isothermal for water given in Fig. 12.5 (*a*), p. 300. And the curve GFE is another such isothermal, for the lower temperature 13·1°C; the two curves are like the two in Fig. 12.6 (*a*), p. 300.

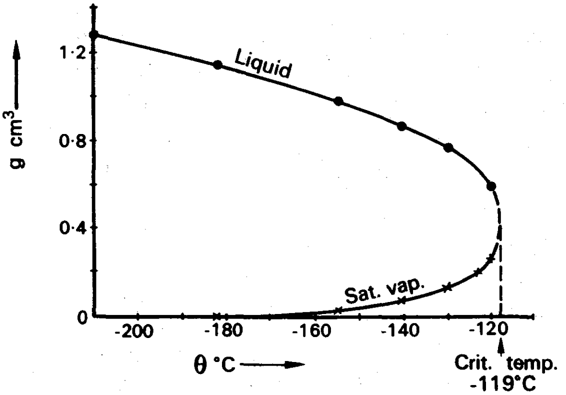


FIG. 12.22. Densities of liquid oxygen, and its saturated vapour.

The isothermal for 31·1°C has no extended plateau; it merely shows a point of inflection at X. At that temperature, Andrews observed no meniscus; he concluded that it was the critical temperature. The isothermals for temperature above 31·1°C never become horizontal, and show no breaks such as B or F. At temperatures above the critical, no transition from gas to liquid can be observed.

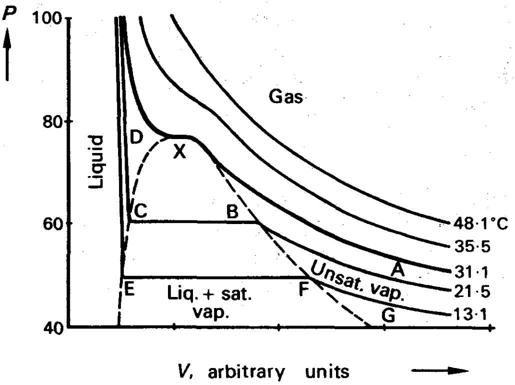


FIG. 12.23. Andrews's isothermals for CO_2.

The isothermal for 48·1°C conforms fairly well to Boyle's law; even when the gas is highly compressed its behaviour is not far from ideal.

The point X in Fig. 12.23 is called the critical point. The pressure and volume (of unit mass) corresponding to it are called the *critical pressure* and *volume*; the reciprocal of the critical volume is the critical density.

CRITICAL CONSTANTS OF GASES AND BOILING POINTS
(At atmospheric pressure)

Substance	Critical			Boiling-point °C
	Temperature °C	Pressure, atmospheres	Density kg m^{-3}	
Argon	−122	48	0·53 × 10^3	−186
Neon	−229	27	0·48	−246
Helium	−268	2·26	0·069	−269
Chlorine	146	76	0·57	− 34
Hydrogen	−240	12·8	0·031	−253
Nitrogen	−146	33	0·31	−196
Oxygen	−118	50	0·43	−183
Air	−140	39	0·35	
Ammonia	130	115	0·24	− 33·5
Carbon dioxide	31·1	73	0·46	− 78·2
Ethylene	10	52	0·22	−102·7
Freon, CCl_2F_2	112	40	0·56	
Sulphur dioxide	155	79	0·52	− 10·8
Water	374	219	0·4	100

The above account of the phenomena near the critical point is over-simple, and may create the impression that these phenomena are fully understood. They are not; but this is not the place to say much about the matter. We may just point out that, even at temperature well above the critical, and when no meniscus can be seen, considerable differences of density can be found in a so-called gas. They have been shown by including, in a sealed tube of liquid and vapour, a number of small glass balls of different densities. When the tube was heated above the critical temperature, each ball floated at a point where the substance had a density equal to that of the ball.

Gases and Vapours

A gas above its critical temperature cannot be liquefied. Early attempts to liquefy gases such as air, by compression without cooling, failed; and the gases were wrongly called 'permanent' gases. We still, for convenience, refer to a gas as a vapour when it is below its critical temperature, and as a gas when it is above it. But the distinction is not the same as that between an ideal gas and one which is far from ideal. For a gas which is near its critical point, though it may be a little above its critical temperature, does not obey Boyle's law, as Fig. 12.23 shows. On the other hand, a vapour which is far from saturation obeys Boyle's law fairly well.

Refrigeration

The action of a refrigerator depends on the absorption of its latent heat by a liquid—the working substance—in evaporating. The working substance must be one whose vapour has a critical temperature above normal atmospheric temperatures, so that it can be liquefied by compression alone. Common working substances are ammonia, carbon dioxide, sulphur dioxide, and specially developed compounds such as the two varieties of Freon: CCl_2F_2, and $C_2Cl_2F_4$. The working substance is compressed by a pump, P, in Fig. 12.24, and passed through a metal pipe C; there the heat of compression is carried away by circulating water, and the substance liquefies. The liquid passes to a reservoir R. From the reservoir, liquid escapes through a throttle valve V into the coil D, which is connected to the low pressure side of the pump. The coil D lies round the walls of the space to be cooled (not shown).

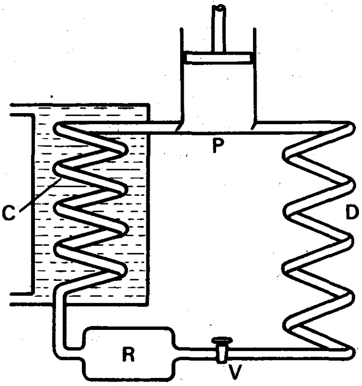


FIG. 12.24. Refrigeration.

When the liquid escapes from the reservoir, it starts to evaporate, because of the low pressure. It draws its latent heat from its own heat content, and cools. Not all of the liquid evaporates as it emerges, and the mixture of cool liquid and vapour passes round the metal coil D. If the atmosphere in the chamber containing D is warmer than the liquid, the liquid evaporates further. The latent heat which it requires is furnished by the surroundings of D, which are therefore cooled.

THE EQUILIBRIUM OF SOLID, LIQUID, VAPOUR

We have pointed out that solids as well as liquids evaporate (p. 297). A solid thus has saturated vapour over it, just as a liquid has, and the pressure of the saturated vapour depends on the temperature. The table on p. 299 shows the pressure of saturated water vapour over ice, at −10°C and −20°C.

The Triple Point

In Fig. 12.25, the curve AP relates the saturated vapour pressure of ice to its temperature; at any point on the curve, ice and water-vapour are in equilibrium. BP is the saturated-vapour-pressure curve of water; at any point on it, water and water-vapour are in equilibrium. CP is the curve relating the melting-point of ice with the pressure: at any point on it, ice and water are in equilibrium. The three curves meet at the point P, whose co-ordinates are $p = 4{\cdot}6$ mm mercury, $\theta = 0{\cdot}01$°C. These are the only conditions in which ice, water, and water-vapour can exist together: if either the temperature or pressure is altered, at least one phase vanishes. If, when the pressure and temperature are altered, their new values happen to lie on one of the curves, then the two corresponding phases survive, liquid and solid along PC, for example. But if the new conditions lie in one of the three sectors of the diagram—say in PAC—then the only phase which survives is the one corresponding to that sector: solid, in PAC. The point P is called the *triple point*.

The curve AP, which gives the saturated vapour pressure of ice, is steeper at P than the curve BP for water. It is steeper because a solid evaporates less readily than a liquid—molecules escape from it less easily. Therefore the saturated-vapour-pressure of the solid falls more rapidly with the temperature.

Fig. 12.26 shows the triple point for carbon dioxide. Its co-ordinates are $p = 3800$ mm mercury, $\theta = -56{\cdot}6$°C. At atmospheric pressure, 760 mm mercury, therefore, solid carbon dioxide (CO_2) can be in equilibrium with its vapour, but not with liquid CO_2. It is therefore dry, and in America it is called 'dry ice'; in England it is called 'carbon-dioxide snow'. At atmospheric pressure its temperature is $-78{\cdot}5$°C, and it is much used as a coolant—in ice-cream trucks, for example.

Solid carbon dioxide is prepared by simply opening the valve of a cylinder containing carbon dioxide at high pressure. The gas rushes out, and does work in acquiring kinetic energy of mass motion. Since the expansion is rapid, it is adiabatic, and the gas cools. As it does so, it goes over directly to the solid phase.

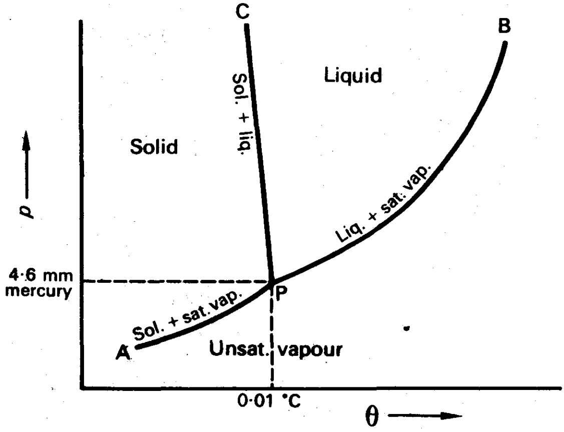


FIG. 12.25. Triple point for water (*not to scale*).

When solid carbon dioxide is warmed, it goes over directly into vapour. So, incidentally, do solid iodine and a few other substances, at atmospheric pressure. The change from solid to vapour is called sublimation. As the diagram shows, liquid CO_2 cannot exist at any temperature at all, if the pressure is below 3800 mm mercury (5·1 atmospheres).

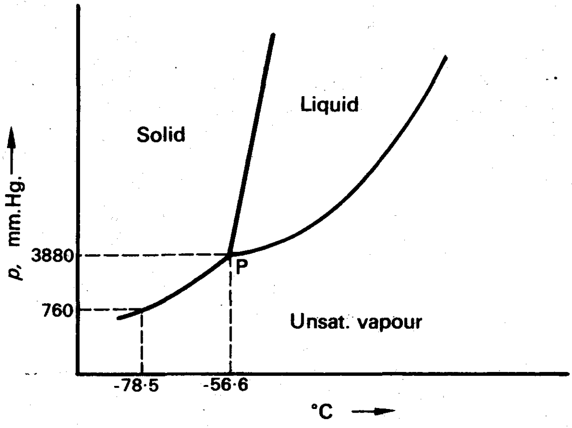


FIG. 12.26. Triple point for carbon dioxide (*not to scale*).

Freezing of Solutions

We have seen that dissolving a solid in water lowers its vapour pressure, and also its freezing-point (p. 297). To explain the lowering of the freezing-point, let us draw, as in Fig. 12.27, the curves of the saturated vapour pressures of ice, water and solution. We see that the curve for the solution cuts the ice curve at a point Q which corresponds to a temperature θ_1, below 0°C. This is the only temperature at which ice and solution can be in equilibrium. At a higher temperature, θ_2, ice has the higher vapour pressure: it therefore sublimes faster than water evaporates from the solution, and, on the whole, vapour from the ice condenses into the solution. At a lower temperature θ_3, the solution has the higher vapour pressure; water therefore evaporates from it faster than the ice sublimes, and, on the whole, water from the solution condenses on the ice. Thus the temperature θ_1 is the freezing-point of the solution. It is the temperature at which solution and ice exchange water molecules one for one, and neither grows at the expense of the other.

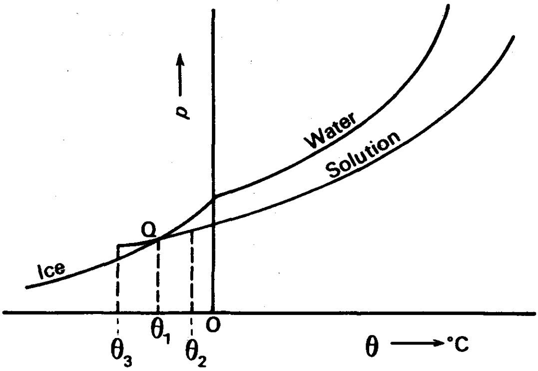


FIG. 12.27. Equilibrium between ice and a solution in water.

We can now see why ice and salt, for example, form a freezing mixture. When salt is mixed with ice, it dissolves in the water clinging to the ice, and forms a solution. Since this is above its melting-point, being at 0°C, it has a lower saturation vapour pressure than the ice (Fig. 12.27). Therefore the ice sublimes and condenses in the solution. In effect, the ice becomes water. And in doing so it abstracts its latent heat of fusion from its surroundings. Thus the mixture changes from solid ice and salt to a liquid solution of salt, and its temperature falls below 0°C.

LIQUEFACTION OF GASES

If one of the so-called permanent gases, hydrogen or nitrogen, is to be liquefied, it must first be cooled below its critical temperature. There are three principal ways of doing this: (i) the gas may be passed through a cold bath containing a more easily liquefied gas, which is boiling at a reduced pressure and therefore has a very low temperature; (ii) the gas may be allowed to expand adiabatically and do work, losing its heat-energy in the process; (iii) the gas may be cooled by a method depending on the fact that, for a real gas, the internal energy is not independent of the volume.

The third of these is the commonest nowadays, and the only one which we shall describe. First we must explain the phenomenon on which it depends.

The Joule-Kelvin Effect

We have already described, on p. 241, Joule's crude experiments on the expansion of a gas into a vacuum—a 'free expansion', as it is called. These experiments suggested that in such an expansion the gas lost no internal energy, and therefore did no work. We concluded that the molecules of a gas had negligible attraction for one another, since otherwise work would have had to be done against their attractions whenever the gas expanded.

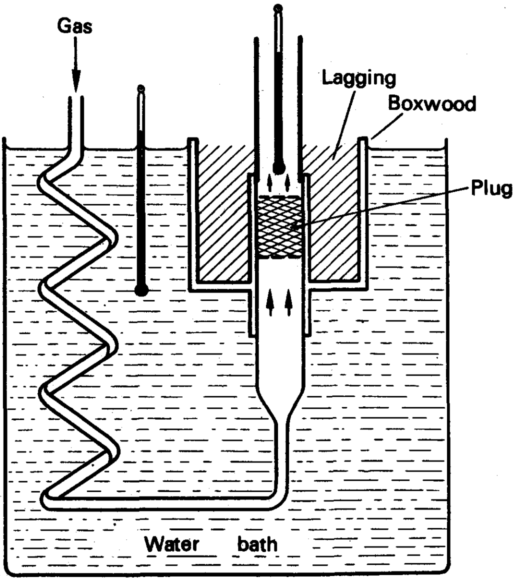


FIG. 12.28. Joule-Kelvin apparatus.

In 1852, Joule and Kelvin made more delicate experiments of essentially the same kind. They allowed a gas at high pressure to expand into a vacuum through a plug of cotton wool (Fig. 12.28). The plug prevented eddies from forming in the gas, so that the gas did not acquire any kinetic energy of motion in bulk. Neither did the gas do any external work, since it pushed back no piston. Nevertheless, Joule and Kelvin found that the gas was cooled slightly in its passage through the porous plug. Therefore work must have been done in separating its molecules; and this work must have been done at the expense of their kinetic energy, the heat-energy of the gas.

The magnitude of the cooling in the Joule-Kelvin effect depends on the temperature at which the gas enters the plug; for air at room temperature it has the order of 0·1°C per atmosphere pressure difference.

It is not essential for the gas to expand into a vacuum. Whenever a gas expands from high pressure to low, its volume increases, and some work is done against its inter-molecular attractions. If heat cannot enter the gas, the work is done at the expense of the gas's internal energy, and the gas cools. The cooling is analogous to that which takes place in an adiabatic expansion, but in a normal adiabatic expansion most of the work is done externally against a piston (compare p. 251). An ideal gas would cool in an adiabatic expansion with external work, but not in a free expansion—it would show no Joule-Kelvin effect.

The Linde Process

The cooling of a gas in a free expansion is small, but Linde devised an ingenious arrangement for making it cumulative, and so producing a great temperature fall. His apparatus is shown diagrammatically in Fig. 12.29. When air is to be liquefied, it must first be freed of carbon dioxide and water, which would solidify and choke the pipes; both are removed by solid caustic soda in a vessel not shown in the figure. The pure air is compressed to about 150 atmospheres by the pump P, and the heat of compression is removed in the water-cooled copper coil C. The air then passes down the copper coil D, which runs within another copper coil E. It emerges through the nozzle N whose opening can be adjusted from outside. The nozzle lies inside a Dewar vessel or thermos flask F. The air expands on emerging, and is cooled by the Joule-Kelvin effect. It then passes upwards through the outer coil E, and as it does so, cools the incoming gas. The incoming gas is thus cooled before making its expansion, and after its expansion becomes cooler still. On escaping through E it cools the following gas yet further. Thus the cooling of the escaping gas continuously helps the cooling of the arriving gas, and the cooling is said to be *regenerative*. Eventually the gas emerging from the nozzle cools below the critical temperature; and since the actual pressure, 150 atmospheres, is well

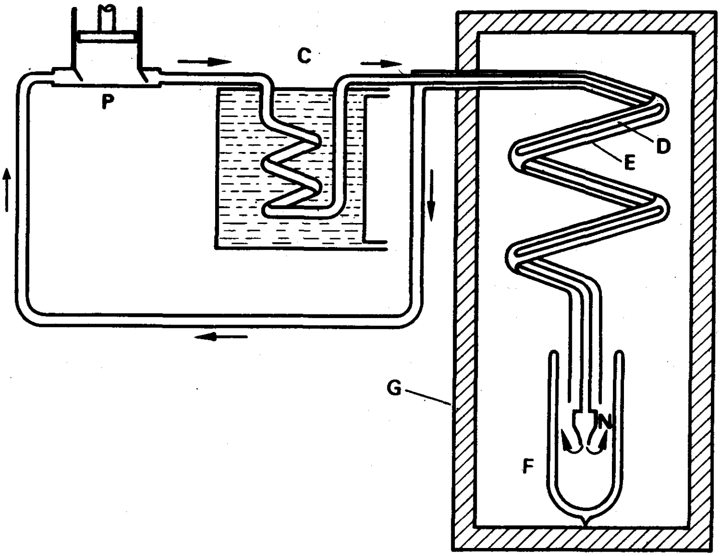


FIG. 12.29. Liquefaction of air.

above the critical pressure, 39 atmospheres, the gas liquefies and collects in the flask. The liquefier is heavily lagged with insulating material, G, to prevent heat coming in from the outside.

The reader should appreciate that the regenerative cooling takes place only in the double coil. At all stages in the process the air enters the inner coil at the temperature of the cooling water around C. But as time goes on it passes through ever-cooler gas coming up from the nozzle, until liquid begins to form and the system reaches equilibrium.

Liquid Nitrogen and Oxygen

As the table on p. 318 shows, the boiling-point of nitrogen, at atmospheric pressure, is $-196°C$, whereas that of oxygen is $-183°C$. When liquid air is exposed to the atmosphere, therefore, the nitrogen boils off faster and the proportion of liquid oxygen increases. The so-called liquid air sold commercially is mostly liquid oxygen. It is more dangerous than true liquid air, particularly if there is hydrogen about.

Hydrogen and Helium

At orinary temperatures, the Joule-Kelvin effect is reversed for helium and hydrogen, that is, a free expansion causes warming. We cannot go into the explanation of that here, but we may say that it is connected with the fact that the pV/p curves of hydrogen and helium rise with increasing pressure, instead of falling at first (Fig. 12.17, p. 314).

These gases show a Joule-Kelvin cooling, however, if they are sufficiently cooled before the expansion. Hydrogen must be cooled below $-83°C$ and helium below $-240°C$; these temperatures are called the *inversion temperatures* of the gases.

Hydrogen can be cooled below its inversion temperature by passing it through a coil in liquid air before it enters the double coil of the liquefier. Helium must be passed through a coil in liquid hydrogen, boiling under reduced pressure.

EXAMPLES

1. Describe an experiment which demonstrates that the pressure of a vapour in equilibrium with its liquid depends on the temperature.

A narrow tube of uniform bore, closed at one end, has some air entrapped by a small quantity of water. If the pressure of the atmosphere is 760 mm of mercury, the equilibrium vapour pressure of water at 12°C and at 35°C is 10·5 mm of mercury and 42·0 mm of mercury respectively, and the length of the air column at 12°C is 10 cm, calculate its length at 35°C. (*L.*)

First part. See text.

Second part. For the given mass of air,

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

$p_1 = 76-1{\cdot}05 = 74{\cdot}95$ cm, $V_1 = 10$, $T = 273+12 = 285$ K;

$p_2 = 76-4{\cdot}2 = 71{\cdot}8$ cm, $T_2 = 273+35 = 308$ K;

$$\therefore \frac{74{\cdot}95\times 10}{285} = \frac{71{\cdot}8\, V_2}{308}$$

$$\therefore V_2 = \frac{74{\cdot}95\times 10\times 308}{285\times 71{\cdot}8} = 11{\cdot}3.$$

2. State Dalton's law of partial pressures; how is it explained on the kinetic theory? A closed vessel contains air, saturated water-vapour, and an excess of water. The total pressure in the vessel is 760 mm of mercury when the temperature is 25°C; what will it be when the temperature has been raised to 100°C? (Saturation vapour pressure of water at 25°C is 24 mm of mercury.) (*C.*)

First part. See text.

Second part. From Dalton's law, the pressure of the air at 25°C = 760−24 = 736 mm of mercury. Suppose the pressure is p mm at 100°C. Then, since pressure is proportional to absolute temperature for a fixed mass of air, we have

$$\frac{p}{736} = \frac{373}{298},$$

from which $p = 921$ mm.

Now the saturation vapour pressure of water at 100°C = 760 mm.

$$\therefore \text{total pressure in vessel} = 921+760 = 1681 \text{ mm mercury.}$$

3. Define *relative humidity* and *dew-point.* Describe an instrument with which the dew-point can be determined. The relative humidity in a closed room at 15°C is 60 per cent. If the temperature rises to 20°C, what will the relative humidity become? On what assumptions is your calculation based? (Saturation vapour pressure of water-vapour at 15°C = 12·67 mm of mercury, at 20°C = 17·36 mm.) (*L.*)

First part. See text.

Second part. Suppose p is the actual water vapour pressure in mm mercury in the air at 15°C.

Then

$$\frac{p}{12{\cdot}67} = \text{relative humidity} = 60 \text{ per cent.}$$

$$\therefore p = \frac{60}{100}\times 12{\cdot}67 = 7{\cdot}60 \text{ mm.}$$

Assuming the pressure of the water-vapour is proportional to its absolute temperature, the pressure p_1 at 20°C is given by

$$\frac{p_1}{7{\cdot}60} = \frac{273+20}{273+15}.$$

$$\therefore p = \frac{7{\cdot}60\times 293}{288} = 7{\cdot}73 \text{ mm.}$$

$$\therefore \text{relative humidity at 20°C} = \frac{7{\cdot}734}{17{\cdot}36}\times 100 \text{ per cent} = 45 \text{ per cent.}$$

4. What is meant by *saturation pressure of water vapour, dew-point*? Describe *briefly* the principles underlying two *different* methods for the determination of the relative humidity in the laboratory.

A barometer tube dips into a mercury reservoir and encloses a mixture of air and saturated water vapour above the mercury column in the tube, the height of the column being 70 cm above the level in the reservoir. If the atmospheric pressure and the saturation pressure of water vapour are respectively 76 cm and 1 cm of mercury, determine the height of the column when the tube is depressed in the reservoir to reduce the air volume to half its initial value. (*L.*)

First part. The saturation pressure of water vapour is the pressure of water vapour in contact with water in a closed space. The dew-point is the temperature at which the air is just saturated with the water-vapour present. The different methods for measuring relative humidity concern the dew-point (Regnault) hygrometer and the wet-and-dry bulb hygrometer, discussed on pp. 311–2.

Second part. We apply the gas laws to the *air* only, as the mass of the air remains constant. From Dalton's law.

$$\begin{aligned}\text{pressure of air} &= \text{total pressure} - \text{pressure of water-vapour}\\ &= (76-70)-1 = 5 \text{ cm mercury.}\end{aligned}$$

The volume of the air changes from V, say, to $V/2$. Hence the new pressure, p, of the air is given, from Boyle's law, by

$$5 \times V = p \times \frac{V}{2}$$

$$\therefore p = 10 \text{ cm.}$$

$$\therefore \text{new total pressure of mixture of gases} = 10+1 = 11 \text{ cm.}$$

$$\therefore \text{new height of mercury column} = 76-11 = 65 \text{ cm.}$$

5. What is meant by the *relative humidity* of the air? Describe in detail a good method for finding it.

Air at 19·5°C has a relative humidity of 75 per cent. Calculate its dew-point and the mass of water vapour contained in 1 litre, being given that the boiling-points of water under pressure of 12 mm, 14 mm, 16 mm and 18 mm of mercury are 14°C, 16·45°C, 18·55°C and 20·45°C respectively. Assume that water vapour behaves as an ideal gas, that its density at s.t.p. is 0·00080 g per cm^3. (*N.*)

First part. The relative humidity of the air is the ratio of the mass of water-vapour in a given volume of the air to the mass of water-vapour required to saturate that volume. A good method for finding it is by the dew-point (Regnault) hygrometer, described on p. 311.

Second part.

$$\text{Relative humidity} = \frac{\text{s.v.p. of water at dew-point}}{\text{s.v.p. of water at 19·5°C}} \times 100 \text{ per cent.}$$

$$\therefore 75 = \frac{\text{s.v.p. at dew-point}}{\text{17 mm mercury}} \times 100$$

$$\therefore \text{s.v.p. at dew-point} = \tfrac{3}{4} \times 17 = 12·75 \text{ mm mercury.}$$

$$\begin{aligned}\therefore \text{dew-point} &= 14°\text{C} + \frac{0·75}{2} \times 2·45°\text{C}\\ &= 14·9°\text{C},\end{aligned}$$

as s.v.p. at 14°C = 12 mm, at 16·45°C = 14 mm.

To find the mass of water-vapour in 1 litre. The pressure of water-vapour =

s.v.p. at dew-point = 12·75 mm = 1·275 cm mercury; the absolute temperature = 273 + 19·5 = 292·5 K.

$$\therefore \text{vol. in cm}^3 \text{ at s.t.p.} = 1{,}000 \times \frac{1{\cdot}275}{76} \times \frac{273}{292{\cdot}5}$$

$$\therefore \text{mass of water-vapour} = 1{,}000 \times \frac{1{\cdot}275}{76} \times \frac{273}{292{\cdot}5} \times 0{\cdot}0008$$

$$= 0{\cdot}013 \text{ g.}$$

EXERCISES 12

1. Distinguish between a saturated and an unsaturated vapour. What is meant by *saturation vapour pressure*?

Describe an experiment to measure the saturation vapour pressure of water vapour for temperatures between 20°C and 100°C. Indicate graphically the results which would be obtained from such an experiment. (*L.*)

2. Explain concisely **four** of the following in terms of the simple kinetic theory of matter:

(*a*) energy must be supplied to a liquid to convert it to a vapour without change of temperature;

(*b*) when some water is introduced into an evacuated flask, some of the water at first evaporates, but subsequently, provided the temperature of the flask is kept constant, the volume of the water present remains unchanged;

(*c*) gases are generally poor conductors of heat compared with solids;

(*d*) when a gas, which is enclosed in a thermally insulated cylinder provided with a piston, is compressed by moving the piston, the temperature of the gas is raised;

(*e*) water can be heated by stirring. (*O. & C.*)

3. Distinguish between a *saturated* and an *unsaturated* vapour. Describe an experiment to investigate the effect of pressure on the boiling point of water and draw a sketch graph to show the general nature of the results to be expected.

A column of air was sealed into a horizontal uniform-bore capillary tube by a water index. When the atmospheric pressure was 762·5 torr (mm of Hg) and the temperature was 20°C, the air-column was 15·6 cm long; with the tube immersed in a water bath at 50°C, it was 19·1 cm long, the atmospheric pressure remaining the same. If the s.v.p. of water at 20°C is 17·5 torr, deduce its value at 50°C. (*O. & C.*)

4. What is meant by *saturation vapour pressure*? Describe an experiment to investigate the variation of the saturation pressure of water vapour with temperature.

Sketch the isothermal curve relating pressure and volume (*a*) for a mass of dry air at room temperature, (*b*) for water vapour at 100°C. (*L.*)

5. Explain the physical principles of a domestic refrigerator employing an evaporating liquid and give a labelled diagram showing its essential components. How may the temperature of the main storage compartment be regulated and what factors determine the lowest attainable temperature?

A certain refrigerator converts water at 0°C into ice at a maximum rate of 5 g per minute when the exterior temperature is 15°C. Assuming that the rate at which heat leaks into the refrigerator from its surroundings is proportional to the temperature difference between the exterior and interior and is 2·5 watt deg C^{-1}, what is the maximum exterior temperature at which this refrigerator could just maintain a temperature of 0°C in the interior? [Specific latent heat of fusion of ice = 330 kJ kg^{-1}.] (*O. & C.*)

6. Use the simple kinetic theory of matter to answer the following questions:
(*a*) How do gases conduct heat?
(*b*) Why does a liquid tend to cool when it evaporates?
(*c*) Why does the boiling point of a liquid depend upon the external pressure?
Show that the pressure p, the density ρ, and the mean square molecular velocity $\overline{c^2}$ of an ideal gas are related by $p = \frac{1}{3}\rho\overline{c^2}$, stating any assumptions at the points where they become necessary in the proof. (*O. & C.*)

7. State *Boyle's law* and *Dalton's law of partial pressures.*

The space above the mercury in a Boyle's law apparatus contains air together with alcohol vapour and a little liquid alcohol. Describe how the saturation vapour pressure of alcohol at room temperature may be determined with this apparatus.

A mixture of air and saturated alcohol vapour in the presence of liquid alcohol exerts a pressure of 12·8 cm of mercury at 20°C. When the mixture is heated at constant volume to the boiling point of alcohol at standard pressure (i.e. 78°C), the vapour remaining saturated, the pressure becomes 86·0 cm of mercury. Find the saturation vapour pressure of alcohol at 20°C. (*L.*)

8. The saturation pressure of water vapour is 1·2 cm of mercury at 14°C and 2·4 cm of mercury at 25°C. Describe and explain the experiment you would perform to verify these data.

Explain qualitatively in terms of the kinetic theory of matter (*a*) what is meant by saturation vapour pressure, (*b*) the relative magnitudes of the saturation vapour pressures quoted.

Sketch a graph showing how the saturation pressure of water vapour varies between 0°C and 110°C. (*N*.)

9. Draw p against v curves for temperatures above, at, and below the critical temperature, for a real gas. Explain the significance of critical temperature.

Sketch graphs of pv against p at the same temperatures for a real gas. What would be the form of the pv against p curves for an ideal gas?

Describe briefly experiments which provide the data on which these curves for a real gas are based. (*O. & C.*)

10. Compare the properties of saturated and unsaturated vapours. By means of diagrams show how the pressure of (*a*) a gas, and (*b*) a vapour, vary with change (i) of volume at constant temperature, and (ii) of temperature at constant volume.

The saturation vapour pressure of ether vapour at 0°C is 185 mm of mercury and at 20°C it is 440 mm. The bulb of a constant volume gas thermometer contains dry air and sufficient ether for saturation. If the observed pressure in the bulb is 1000 mm at 20°C, what will it be at 0°C? (*L.*)

11. Explain the terms *relative humidity, dew-point.* Describe in detail an experiment to determine the dew-point.

Find the mass of air and water-vapour in a room of 20 × 10 × 5 cubic metres capacity, the temperature being 20°C and the pressure 750 mm of mercury. Assume that the saturation pressure of water-vapour at the dew-point is 9·0 mm of mercury; that the density of dry air at s.t.p. is 1·30 kg m^{-3}; that the density of water vapour is $\frac{5}{8}$ that of air under the same conditions of pressure and temperature. (*L.*)

12. Define *pressure of a saturated vapour, critical temperature.* Give an account of the isothermal curves for carbon dioxide at temperatures above and below its critical temperature.

Some liquid ether is sealed in a thick-walled glass tube, leaving a space containing only the vapour. Describe what is observed as the temperature of the tube and its contents is raised above 197°C, which is the critical temperature for ether. (Assume that the vessel is strong enough to withstand the internal pressure.) (*L.*)

13. Define *dew-point* and explain what is meant by *relative humidity*. Describe how you would determine the dew-point of the atmosphere.

What is the relative humidity of an atmosphere whose temperature is 16·3°C if its dew-point is 12·5°C? The following table gives the saturation pressure, *p*, of water-vapour in mm of mercury at various temperature, *t*.

t°C	10	12	14	16	18	20
p mm	9·20	10·51	11·98	13·62	15·46	17·51

(*N.*)

14. Give briefly the principles of one method each for liquefying (*a*) chlorine, (*b*) hydrogen.

Describe a suitable container for liquid air. Point out carefully the physical principles involved. (*C.*)

15. Give an account of three methods used to obtain temperatures below 0°C. Describe a method for liquefying air. How must the procedure be modified in order to liquefy hydrogen? (*N.*)

16. Describe in detail the method you would use to find (*a*) the melting-point of lead, and (*b*) the boiling-point of brine.

An alloy of copper and silver is made with different percentage composition. For each mix the melting-point is measured, with the following results:—

M.P. deg C . .	960	810	760	740	760	790	900	1080
Per cent of copper in alloy . .	0	20	30	40	50	60	80	100

Plot a curve showing the relation between the melting-point in degrees Centigrade and the percentage of copper present. Comment on the curve. (*L.*)