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Physics, Chapter 17: The Phases of Matter

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17

The Phases of Matter

17-1 Phases of a Substance

A substance which has a definite chemical composition can exist in one or more *phases*, such as the vapor phase, the liquid phase, or the solid phase. When two or more such phases are in equilibrium at any given temperature and pressure, there are always surfaces of separation between the two phases.

In the solid phase a pure substance generally exhibits a well-defined crystal structure in which the atoms or molecules of the substance are arranged in a repetitive lattice. Many substances are known to exist in several different solid phases at different conditions of temperature and pressure. These solid phases differ in their crystal structure. Thus ice is known to have six different solid phases, while sulphur has four different solid phases.

A substance in the liquid phase is fluid; that is, it flows under the application of a shearing stress. Many substances normally classified as solids are really highly viscous fluids. Such substances (glass or pitch are examples), exhibit no well-defined melting point but soften and flow more readily as the viscosity decreases with increasing temperature. The common observation that fluids cannot withstand a shearing stress depends upon the fact that the viscosity of most fluids is small. A highly viscous fluid such as glass is capable of withstanding considerable shearing stress without apparent deformation. When the applied shearing stress is made to oscillate rapidly, even normal liquids display a shear modulus.

Based on information largely derived from x-ray scattering experiments similar to the experiments used to determine the crystal structure of solids (see Chapter 44), we know that the molecules of a liquid are not entirely independent of each other but are coordinated. The central molecule of a group of coordinated molecules is surrounded by a group of from about 3 to 11 other molecules in the first coordination shell, at a distance of about 1 molecular diameter from the central molecule. A smaller number of

molecules forms the second coordination shell, at a distance of about 2 molecular diameters from the central molecule. Thus there is considerable organization of the molecules of a liquid. The degree of organization of the liquid tends to increase as the temperature of the liquid approaches the freezing point, and, conversely, the degree of organization tends to decrease as the liquid approaches the boiling point.

Most liquids exhibit a single liquid phase. The most abundant isotope of helium, of atomic weight 4, is a notable exception. At atmospheric pressure helium liquefies at a temperature of 4.2° abs. Upon further cooling to 2.2° abs, the original liquid, known as helium I, changes to helium II which displays an abnormally low viscosity and a high thermal conductivity. Helium II flows through capillary tubes with great rapidity, and passes through tightly packed plugs of porous material as though they were sieves. The superfluidity of helium II is thought to be associated with the distribution of the energy levels of liquid helium near the absolute zero. It is interesting in this connection that the isotope of helium of atomic weight 3 displays no superfluidity.

All substances exhibit only one vapor phase. A vapor at low pressure is often termed a gas. As we have seen in the preceding chapter, the molecules of a gas are isolated from each other and interact with each other only rarely. As the pressure is increased, each gas molecule collides with other molecules more frequently, with a tendency for the molecules to form in clusters. The ideal gas law is correct only as long as no clusters are formed, for each cluster behaves like a complex molecule and tends to reduce the effective number of molecules per unit volume. The condensation of droplets from a vapor may be interpreted as the formation of giant clusters.

We have already considered two types of phase changes, solid to liquid and liquid to vapor (see Section 15-3). A third type of phase change, that from solid to vapor, is called *sublimation*. Heat must be added to produce this change of phase; the quantity of heat required to change a unit mass of a substance from solid to vapor at constant temperature is called the *heat of sublimation*. Conversely, when a substance is condensed directly from the vapor to the solid phase, heat must be removed from the substance.

In this chapter we shall consider some important phenomena associated with changes of phase.

17-2 Vaporization. Vapor Pressure

One method for studying the process of vaporization and the properties of a vapor is illustrated in Figure 17-1. A tube *A* about 1 m long is first filled with mercury and then inverted and put into a long reservoir *R* containing mercury. The level of the mercury in *A* will be at the barometric height

above the level in R . The space above the mercury in A contains mercury vapor at a very low pressure, which we shall neglect for the purpose of the present discussion. If a small quantity of liquid ether is put into the open end of tube A , the ether will rise to the top of the mercury column and vaporize into the space above it. Let us suppose that there is no trace of liquid ether above the mercury column; that is, the ether has completely evaporated. We shall observe that the level of the mercury in column A is much lower than before. If we push the tube A slowly into the reservoir R , we shall find that at some stage in this process a small layer of liquid ether will appear on top of the mercury column in A . As the tube is pushed down still farther, the thickness of the ether layer increases.

If we determine the pressure due to the ether vapor, that is, the difference between the barometric height and the height h of the column of mercury in tube A , we note that, as long as there is a film of liquid ether at the top of the mercury column, the pressure of ether vapor remains constant. A vapor which is in contact with its parent liquid is said to be a *saturated vapor*. The *pressure of a saturated vapor depends only upon its temperature*. If the apparatus is modified so that we can vary the temperature of the liquid ether and of its saturated vapor, it will be found that the pressure of the saturated vapor increases rapidly with increasing temperature. Under the conditions of the experiment, the liquid phase is in equilibrium with its saturated vapor. There is a continuous inter-

change of molecules between the liquid and the vapor phases such that the mass of the liquid phase and the mass of the vapor phase remain constant at a particular pressure, volume, and temperature.

When water, placed in an open dish, is heated by a flame, the water will show an increase in temperature until the boiling point is reached. While the water is boiling, the temperature remains constant. The heat supplied to the dish is used to convert the liquid water to the vapor phase. Since the dish is open to the atmosphere, the pressure of the water vapor just above the liquid surface must be equal to the pressure of the atmosphere. The *boiling point* is that temperature at which the pressure of the

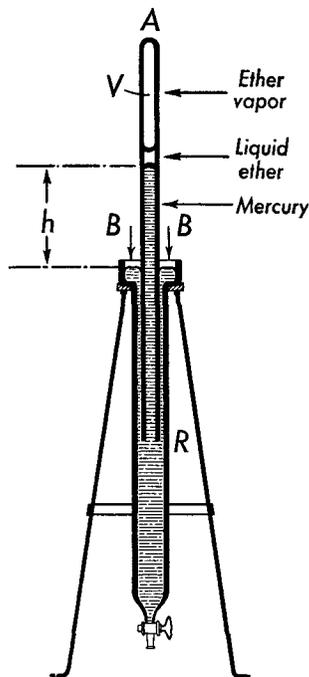


Fig. 17-1 Method of measuring the saturated vapor pressure of ether.

saturated vapor is equal to the atmospheric pressure. When the pressure on the liquid is 76 cm of mercury, the boiling point of water is, by definition, 100°C or 212°F . The boiling point of a liquid at this pressure is called its *normal boiling point*. The normal boiling points of several substances are shown in Table 17-1.

TABLE 17-1 NORMAL BOILING POINTS

Substance	Temperature in $^{\circ}\text{C}$
Sulphur*	444.6
Mercury	356.7
Water*	100.0
Alcohol (ethyl)	78.3
Ether	34.6
Oxygen*	-182.97
Nitrogen	-195.8
Hydrogen	-252.8
Helium	-269

* Fixed points of the International Temperature Scale of 1948.

The relationship between the temperature of water and the pressure of its saturated vapor can be investigated by placing the water in a boiler which has a thermometer and a pressure gauge fitted into it. The water is first boiled vigorously to drive off the air above it, and the boiler valve is then closed. In such a boiler the water is in equilibrium with its saturated

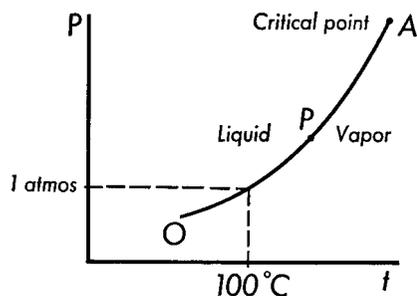


Fig. 17-2 Vaporization curve of water.

vapor, and the relationship between vapor pressure and temperature may be plotted, as in Figure 17-2. This curve is called the *vaporization curve of water*. From the preceding discussion we see that a point P along the vaporization curve OA of Figure 17-2 represents the temperature at which water boils at a particular pressure. If the temperature is greater than the boiling point at a particular pressure, the water

must all be in the vapor phase. If the temperature is less than the boiling point at that pressure, the water must all be in the liquid phase.

When a mass m of liquid is transformed from the liquid to the vapor phase at a temperature t , a quantity of heat mL must be supplied to the liquid, where L is the latent heat of vaporization at this temperature. This heat must supply the energy required to change the internal energy

of the substance and to perform the mechanical work associated with the change in volume of the substance. If U_v is the internal energy of a mass m of vapor at the temperature t , and U_l is the corresponding internal energy of the liquid, we have, from the first law of thermodynamics,

$$mL = U_v - U_l + P(V_v - V_l), \quad (17-1)$$

where P is the pressure at which the phase change takes place and V_v and V_l are the volumes of the vapor and liquid, respectively. Although Equation (17-1) has been written to describe the phase change from liquid to vapor, an analogous equation can obviously be written to describe any other phase change. In transformations involving the vapor phase, the $P \Delta V$ term may represent a significant part of the heat required to vaporize a substance, because of the large changes in volume associated with such transformations. It must be observed that the measurement of the latent heat of vaporization at a particular temperature is made under conditions of constant pressure, unless specifically noted to the contrary.

17-3 The Critical Point

The vaporization curve is not indefinite in extent; it has both an upper and a lower limit. The upper limit is known as the *critical point*, shown as point A in Figure 17-2. The temperature and pressure at the critical point are known as the *critical temperature* and *critical pressure*. If a glass vial containing a liquid and its saturated vapor is heated to the critical temperature, the meniscus dividing the liquid from the vapor phase disappears. At temperatures above the critical temperature the substance cannot exist as a liquid; that is, no matter how great the pressure, it cannot be put into the liquid phase. At the critical temperature the densities of the liquid and the vapor are equal, and the heat of vaporization is zero. This suggests that the molecules of a substance have sufficient kinetic energy to overcome the bonds of coordination through which molecules become coordinated in the liquid phase when the temperature is greater than the critical temperature. A distinction is sometimes made between the vapor states above and below the critical temperature: above the critical temperature a substance is usually called a gas; below the critical temperature a substance is usually called a vapor. The critical temperature of carbon dioxide is 31.1°C or 88°F , and its critical pressure is 73 atm. Tanks of carbon dioxide, used for carbonating soft drinks, are usually labeled "liquid carbonic gas," which is clearly a misnomer on a hot summer day.

The substances which are known as gases at ordinary temperatures have very low critical temperatures. They must first be cooled to low temperatures before they can be liquefied. In terms of our conception of a vapor as clusters of very few molecules, and a liquid droplet as a giant

cluster, we may infer that a substance which is chemically active, and therefore must be surrounded by a relatively intense attractive force field, should be more easily formed into clusters and liquefied than a substance which is chemically inactive. A second factor which must influence the formation of clusters of molecules in a gas is the length of time they spend in each other's neighborhood. According to the kinetic theory of gases, the average speed of the molecules of a gas at a given temperature depends only upon the molecular mass, with the more massive molecules having the lower speeds. The substance which should be hardest to liquefy is the lightest of the noble gases, that is, helium. This is indeed the case, for the critical temperature of helium is -268°C , or 5° abs, the lowest of all known substances. The critical temperature and pressure of some common substances are shown in Table 17-2.

TABLE 17-2 CRITICAL CONSTANTS

Substance	Critical Temperature in $^{\circ}\text{C}$	Critical Pressure in Atmospheres
Ammonia	132	112
Carbon dioxide	31.1	73
Ether	194	35.5
Helium	-268	2.3
Hydrogen	-240	13
Nitrogen	-147	34
Oxygen	-119	50
Water	374	218

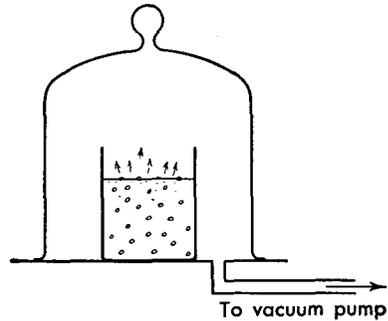
17-4 Evaporation

A liquid such as water or alcohol, when left open to the atmosphere, will evaporate; that is, the liquid will change to a vapor and go into the atmosphere. If the atmosphere above the liquid surface is set into motion, the rate of evaporation will be increased. The heat that is required to vaporize a liquid must come either from the external surroundings or from the remaining liquid. If the liquid is placed in a fairly well insulated container, or if the process of evaporation is so rapid that the liquid cannot get sufficient heat from the surrounding bodies, the temperature of the liquid will be lowered.

If a large jar is placed over the liquid container, some of the liquid will evaporate until equilibrium is established between the liquid and its vapor, that is, until the partial pressure of the vapor in the air is equal to the saturated vapor pressure at the temperature of the air. The air is then said to be *saturated* with vapor. If the jar over the liquid container is

removed and a fresh supply of unsaturated air is blown over the liquid, evaporation will start again and will continue as long as the vapor pressure in the air is less than the saturated vapor pressure. Substances such as ether, which have a large vapor pressure at atmospheric temperature, evaporate rapidly when exposed to a moving air stream. Substances with very low vapor pressure, such as octoil S , a vacuum-pump oil with a vapor pressure of about 10^{-7} mm Hg at room temperature, evaporate at an extremely slow rate.

Fig. 17-3 Rapid evaporation of water when the pressure above it is reduced causes it to cool very rapidly. If the evaporation is sufficiently rapid, the remaining water may freeze.



From the viewpoint of the kinetic theory of matter, we may conceive of the process of evaporation as one in which only the more rapidly moving molecules of the liquid have sufficient energy to overcome the forces of attraction at the liquid surface. The escape of the rapidly moving molecules from the liquid decreases the average energy of the molecules of the liquid and therefore lowers the internal energy and the temperature of the remaining liquid. If a small beaker of water is placed under a bell jar which is continuously evacuated by a vacuum pump, as shown in Figure 17-3, the water vapor is rapidly removed from the surface of the liquid. The selective removal of the most rapidly moving molecules from the liquid lowers the temperature of the liquid, and if the pumping action is sufficiently fast, the water may freeze. Thus it is possible to freeze water without first providing a low-temperature reservoir, that is, a body whose temperature is at or below the ice point.

17-5 Throttling Process

When a fluid goes from a region of high pressure to one of lower pressure, it undergoes a *throttling process*. Let us suppose that a gas is confined in a cylinder at a pressure P_1 , and that, by motion of a piston, the gas in the cylinder is forced through a narrow aperture in the base of the cylinder into a second cylinder, as shown in Figure 17-4. By means of a second piston in the second cylinder, the gas in that cylinder is maintained at a

lower pressure P_2 . Assume that both cylinders have insulating walls, so that the heat ΔQ passing into or out of the system is zero. We may calculate the work done in the throttling process by imagining that the piston at the left in Figure 17-4 is moved to the right by a force F_1 such that

$$F_1 = P_1A,$$

where A is the area of the piston. The piston moves a distance l_1 in sweeping the gas out of the left-hand cylinder, so that the work done on the gas is

$$F_1l_1 = P_1Al_1 = P_1V_1,$$

where V_1 is the original volume of the gas in the left-hand cylinder. In accordance with the sign convention adopted for the first law of thermo-

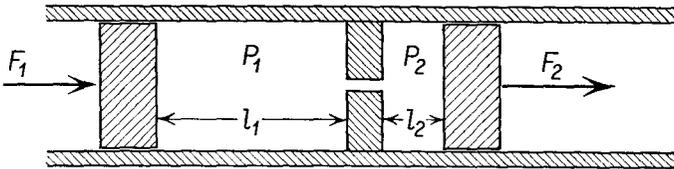


Fig. 17-4 Throttling process.

dynamics, as in Section 15-6, this is work done on the gas and is therefore negative work. Similarly, the work done by the gas in expanding into the second cylinder is $+P_2V_2$. Substituting these results into the first law of thermodynamics, as expressed in Equation (15-6), we find

$$0 = U_2 - U_1 - P_1V_1 + P_2V_2,$$

where U_1 and U_2 represent the internal energy of the gas in cylinder 1 and cylinder 2, respectively. On transposing, we find

$$U_1 + P_1V_1 = U_2 + P_2V_2,$$

or

$$U + PV = \text{constant.} \tag{17-2}$$

The quantity $U + PV$ is called the *enthalpy*. Thus the enthalpy of a fluid remains unchanged in a throttling process. The throttling process is the basis for mechanical refrigeration systems and for the liquefaction of gases.

In a refrigeration system a refrigerant is compressed to a high pressure by a pump, is cooled to room temperature by circulating air or water, and is permitted to expand through an expansion valve to a lower pressure. This process is a throttling process, in which the enthalpy of the refrigerant remains constant, according to Equation (17-2). The enthalpy is tabulated for many refrigerants as a function of the temperature, so that a knowledge of the initial and final pressures and the initial temperature in a throttling process enables one to find the final temperature by consulting an appropri-

ate enthalpy table. Liquids which evaporate as a result of a throttling process always drop in temperature and are therefore always used in refrigerating systems (see Section 19-6).

If a perfect gas should undergo a throttling process, the final temperature should be the same as the initial temperature, while for real gases the temperature change in a throttling process may be positive or negative, depending on the state of the gas. From the microscopic point of view, if the forces that molecules exert on each other are predominantly attractive, work will be done in the expansion, and the temperature will be lowered; if the forces between molecules are repulsive, the molecules will have greater kinetic energy when farther apart, and the temperature will be raised in the expansion. If the molecules exert no force on each other, as in a perfect gas, no work is done in the expansion, and there will be no change in kinetic energy and hence no change in temperature.

In one type of liquefaction process, the gas to be liquefied undergoes a throttling process. The initial state of the gas—that is, its pressure, volume, and temperature—and the pressure of the final state are so chosen, that the temperature of the gas will be lowered during this process. The cooler gas then circulates around the incoming gas so that its temperature is lowered still further. This recirculation process continues until some of the emergent fluid is partially liquefied; the liquid is collected in a thermos flask, and the cold vapor is recirculated.

17-6 Fusion

The temperature at which a solid melts depends upon the pressure. For most substances the temperature of the melting point increases with increasing pressure. In a few exceptional cases, such as ordinary ice, cast iron, and type metal, there is a decrease in volume on melting. This unusual behavior of type metal is of practical value in the casting of type; clear sharp type is produced as the solidifying metal expands against the mold. The expansion which takes place when water freezes has many important consequences. The specific gravity of ice is 0.92, so that the ice formed in a lake floats on top of the water. Since the ice is a poor conductor of heat, the water in the deeper portions of a lake may remain unfrozen throughout the winter so that aquatic life can continue beneath the surface. The curve *OB* in Figure 17-5 shows the variation of the melting point of ice with pressure. Each point on the curve represents a definite temperature and pressure at which ice and water are in equilibrium.

The fact that an increase in pressure results in a lowering of the melting point of ice leads to a series of interesting results. We make snowballs by compressing loose snowflakes. The ice beneath an ice skate is at higher pressure than the ice around it. This increase in pressure causes the ice

or snow to melt, even though the temperature is below 0°C . Upon release of the pressure, the water refreezes. This process of melting at a temperature below 0°C because of the increased pressure, and then refreezing when

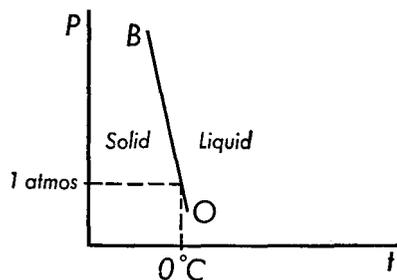


Fig. 17-5 Fusion curve of water.

the pressure is removed, is known as *regelation*. If a wire is looped over a block of ice and a heavy weight is hung from the wire, the wire will pass completely through the block of ice through the process of regelation. After the wire has passed through it, the block is still in one solid piece.

It can be shown on the basis of thermodynamic principles that the latent heat L , the temperature T , the change in volume of a unit mass of substance ΔV , and the pressure P associated with a phase change are related through the equation

$$\frac{dP}{dT} = \frac{L}{T \Delta V}. \quad (17-3)$$

This equation is known as *Clapeyron's equation*. The quantity dP/dT is the slope of curve on the PT diagram which describes the boundary between the two phases, such as the vaporization curve OA of Figure 17-2 or the fusion curve OB of Figure 17-5. In melting, a positive quantity of heat L is always delivered to a unit mass of the substance. The slope of the curve will depend upon the volumes of a unit mass of substance in the two phases. In the case of the transition from ice to water, the quantity $\Delta V = V_w - V_i$; that is, the change in volume is the volume of a unit mass of substance in the final state V_w minus the specific volume in the initial state V_i . Since here ΔV is a negative quantity, the slope of the fusion curve is negative. In most phase changes the final state is less dense than the initial state, and the slope of the curve is positive, as in Figure 17-2.

The melting points of several substances are shown in Table 17-3.

TABLE 17-3 MELTING POINTS AT ATMOSPHERIC PRESSURE

Substance	Temperature in $^{\circ}\text{C}$	Substance	Temperature in $^{\circ}\text{C}$
Aluminum	660	Platinum	1773.5
Copper	1083	Silver*	960.8
Gold*	1063.0	Sodium	97.5
Lead	327.4	Tungsten	3410
Mercury	-38.87	Water*	0
Nickel	1455	Zinc	419.5

* Fixed points of the International Temperature Scale of 1948.

17-7 Superheating and Supercooling

If a liquid is heated very slowly, it may remain in the liquid phase at temperatures above the boiling point. If a vapor is cooled very slowly, it may be cooled below the boiling point without the formation of droplets of liquid. Similarly, a liquid may be cooled below its freezing point without freezing setting in. These phenomena are called *superheating* and *supercooling*. When a substance is superheated or supercooled, mechanical agitation, or some other disturbance, may serve to initiate the phase transition. Under certain conditions dry-ice crystals or crystals of sodium iodide may be introduced into a cloud to start the formation of water droplets and cause rain. It is customary to introduce ceramic beads in boiling flasks in chemistry laboratories to prevent superheating and the consequent eruptive boiling, or bumping, which takes place under these circumstances.

Both of these phenomena have been exploited in nuclear physics as a means of visualizing the passage of charged particles through matter in two very important devices called the *cloud chamber* and the *bubble chamber*. When rapidly moving charged particles pass through matter, they leave behind an invisible trail of electrically charged molecules called ions. In a supercooled vapor these ions act as nuclei for droplet formation, and in a superheated liquid they act as nuclei for vapor formation. In a cloud chamber a trail of water droplets is used to mark the passage of a charged particle, and in a bubble chamber the trail is marked by vapor bubbles in an otherwise clear liquid. Photographs of tracks in a cloud chamber and in a bubble chamber are shown in Chapters 45 and 46.

At the present time there is no satisfactory theory which quantitatively accounts for phase transitions and for the phenomena of superheating and supercooling from the molecular viewpoint. This study is part of a branch of physics known as *statistical mechanics*.

17-8 Sublimation

The change from the solid directly into the vapor phase, although very common, is not usually observed directly because the more common vapors are usually colorless. A piece of solid carbon dioxide, which is white, goes directly into the vapor phase at atmospheric pressure. This substance, known as "dry ice," does not melt, because the liquid phase does not exist at ordinary temperatures at atmospheric pressure. Another common example is the sublimation of tungsten in an electric light bulb. When the filament is hot, some of the tungsten passes into the vapor phase and is subsequently deposited as a solid onto the cooler glass bulb, thereby blackening the bulb.

To focus our attention on the process of sublimation, let us consider a flask containing some ice, and let us suppose that the air has been completely removed from the flask. If we keep the ice at a temperature of -10°C , the ice will sublime, forming water vapor in the flask. This process will continue until the vapor pressure reaches a value of 1.97 mm of mercury. Thereafter the vapor pressure will remain the same as long as the temperature of the system is -10°C . In this state the ice and water vapor are in equilibrium. If the temperature is lowered, some of the vapor will condense, and the equilibrium vapor pressure will be lowered; if the temperature is raised, some of the ice will sublime, and the equilibrium vapor pressure will be raised. The curve OC in Figure 17-6 shows the relationship between the vapor pressure and the temperature of sublimation for ice. The equilibrium vapor pressure drops rapidly with decreasing temperature. In accordance with Equation (17-3), the sublimation curve has a positive slope.

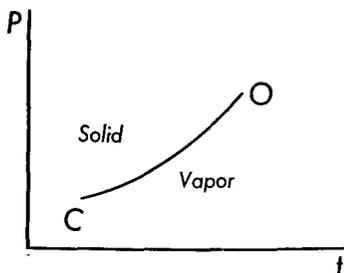


Fig. 17-6 Sublimation curve of water.

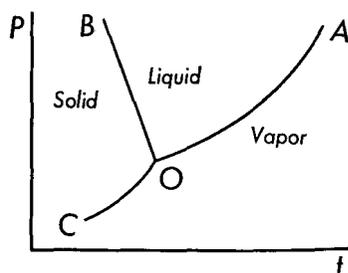


Fig. 17-7 Triple point of water.

17-9 Triple Point

The three curves for water—the vaporization curve, the fusion curve, and the sublimation curve—are plotted on a single graph in Figure 17-7. A point on a curve represents a state of equilibrium between two phases at a definite temperature and pressure. All three curves intersect at one point O , which is known as the *triple point*. At this point all three phases of water are in equilibrium. The temperature of the triple point is 0.01°C , and the pressure is 4.59 mm of mercury. As long as the temperature and pressure are maintained at these values, ice, water, and water vapor will coexist in the same flask and remain in equilibrium. If the temperature should be raised slightly, the ice will melt, and the state of the system will be represented by a point on the curve OA . If the conditions of temperature or pressure are changed in any way, one of the phases will disappear.

The temperatures at which specified phase changes occur under a standard pressure of 1,013,250 dynes/cm², that is, a standard atmosphere,

have provided the means of achieving a practical scale of temperature. The fundamental fixed points (the ice point and the steam point) and the primary fixed points, chosen by the Tenth International Conference of Weights and Measures in 1948, are shown in Table 17-4. In 1954 a pro-

TABLE 17-4 FUNDAMENTAL AND PRIMARY FIXED POINTS OF THE INTERNATIONAL TEMPERATURE SCALE UNDER THE STANDARD PRESSURE OF 1,013,250 DYNES/CM²

Fixed Point	Temperature
Boiling point of oxygen	-182.970°C
Melting point of ice*	0°C
Boiling point of water*	100°C
Boiling point of sulphur	444.600°C
Freezing point of silver	960.8°C
Freezing point of gold	1063.0°C

* Fundamental fixed points.

posal made earlier by Giauque was adopted, to the effect that the temperature scale be redefined on the basis of the absolute zero of temperature and the triple point of water. As shown in Section 14-3, the temperature assigned the triple point of water was 273.16° abs. At the present time it is impossible to distinguish between the temperature scale based upon the triple point of water and the temperature scale based upon the ice point and the steam point.

17-10 The P - V - T Surface

As we have seen, the phase of a substance is determined by a knowledge of its pressure, volume, and temperature. If the pressure, volume, and temperature of a unit mass of a substance are plotted on three perpendicular axes, a surface is generated which summarizes all the information which might be given in PT diagrams, in PV diagrams, and in tables of density. Such surfaces for a substance which expands on freezing and for a substance which contracts on freezing are shown in Figure 17-8. The condition of a unit mass of the substance is therefore determined by any two of the three variables P , V , and T , when the substance is in equilibrium. For example, when the conditions of pressure and temperature are such that the substance is in one or another of its phases, the pressure and temperature determine the volume of a unit mass of the substance and, therefore, its density. The triple point is a point only on the PT diagram. On the PVT surface the triple point is a line perpendicular to the PT plane. Thus the volume of a constant mass of a substance at the triple point may have a wide range of values. In fact, if this were not so it would be difficult, if not impossible,

to achieve a mixture of solid, liquid, and vapor in equilibrium within a closed container, for it would be necessary to introduce into the container a mass of substance precisely appropriate to the volume of the container.

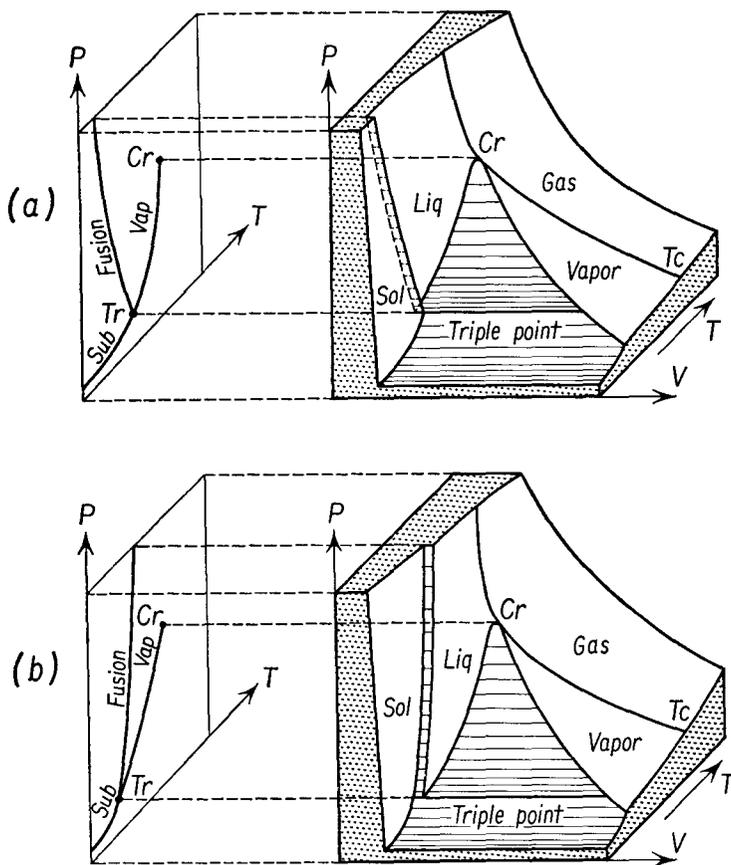


Fig. 17-8 (a) P - V - T surface for a substance which expands on freezing. (b) P - V - T surface for a substance which contracts on freezing. (By permission, from *Heat and Thermodynamics*, 4th ed., by Mark W. Zemansky. Copyright 1957. McGraw Hill Book Company, Inc.)

The PVT surface may be considered as a graph of an empirical *equation of state* of a particular substance, for it represents the functional relationship between the thermodynamic variables of pressure, volume, and temperature of the substance; in addition, the surface provides information about the state, or phase, of the substance. From the PVT surface we may note that if the pressure of a liquid is reduced, at constant temperature, the liquid passes into the vapor phase. In gasoline engines this

produces the phenomenon called “vaporlock,” for the pumping of liquids in pipes depends upon the fact that a liquid is essentially an incompressible fluid, while a vapor is very compressible. Similar problems arise in connection with ships’ propellers, where the reduced pressure generated by the rotation of the propeller causes *cavitation*, in which the generation and collapse of vapor bubbles not only reduces the efficiency of the propeller but causes considerable wear of the propeller blades.

17-11 Humidity of the Atmosphere

One of the most important constituents of the atmosphere is water vapor. The amount of water vapor in the air is a variable quantity. As we have seen, a mass of air is saturated when the pressure of the water vapor in that mass of air is equal to the saturated vapor pressure at the temperature of the air. Figure 17-9 is a curve showing the saturated vapor pressure as a function of the temperature of the air, while Table 17-5 gives the saturated vapor pressure at various temperatures. Usually, however, the actual vapor pressure is less than the saturated vapor pressure. The term *relative humidity* is defined as the ratio of the actual vapor pressure to the saturated vapor pressure at the temperature of the air. Thus if r is the relative humidity, p the actual vapor pressure, and P the saturated vapor pressure at the temperature of the air, then

$$r = \frac{p}{P} \quad (17-4)$$

and is usually expressed in percentages. For example, suppose that the actual vapor pressure is 3.0 mm of mercury when the temperature of the air is 50°F. Since the saturated vapor pressure at this temperature is 9.2 mm of mercury, the relative humidity is

$$r = \frac{3.0}{9.2} = 0.325 = 32.5 \text{ per cent.}$$

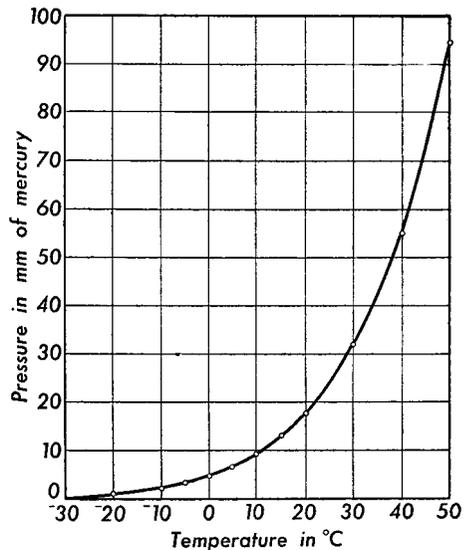


Fig. 17-9 Saturation vapor pressure curve.

At any given temperature, the mass of water vapor in the air is proportional to the pressure of the water vapor. Hence the relative humidity can also be defined as the ratio of the mass of water vapor in a given volume of air to the mass of water vapor required to saturate it. Table 17-5 gives the mass of water vapor in a cubic meter of saturated air at various temperatures.

TABLE 17-5 PROPERTIES OF SATURATED WATER VAPOR

Temperature in °C	Temperature in °F	Pressure in Milli- meters of Mercury	Grams of Water Vapor in a Cubic Meter of Air
-10	14	2.15	2.16
-5	23	3.16	3.26
0	32	4.58	4.85
5	41	6.54	6.80
10	50	9.21	9.40
15	59	12.79	12.83
20	68	17.54	17.30
30	86	31.82	30.37
40	104	55.32	51.12
50	122	92.51	
60	140	149.41	
70	158	233.7	
80	176	355.1	
90	194	525.8	
100	212	760.0	
120	248	1,489.1	
140	284	2,710.9	
160	320	4,636	
180	356	7,520	
200	392	11,659	

A simple instrument for measuring the relative humidity is the hair *hygrometer*. Human hair is used in its construction. The length of the hair increases as its cells absorb moisture from the air. The hair hygrometer consists of a bundle of human hairs exposed to the atmosphere; one end of the bundle is attached to an adjustable screw and the other end to a lever which moves a pointer over a scale. The apparatus is sketched in Figure 17-10. The scale is calibrated in terms of the relative humidity.

Another type of hygrometer consists of a combination of a wet-bulb thermometer and a dry-bulb thermometer. The two thermometers are identical except that a piece of wet muslin is wrapped around the bulb of one thermometer and kept moist by a wick dipping into a trough of water.

If the air is not saturated with water vapor, water will evaporate from the wet-bulb thermometer, producing a drop in temperature. The relative humidity is then determined from the difference in the readings obtained from the two thermometers and the tables or graphs of humidity.

17-12 Dew-Point Temperature

It is a common experience to observe moisture condensing on the outside surface of vessels containing cold beverages. This moisture is produced by the condensation of the water vapor from the air onto the cold surface. When the relative humidity is less than 100 per cent, the vapor pressure is less than the saturation pressure. The temperature to which the air must be lowered in order to become saturated with the mass of water vapor in it remaining constant is called the *dew-point temperature*. When the dew-point temperature is known, its location on the saturation pressure curve of Figure 17-9 will also give the actual vapor pressure in the air. Since the saturation vapor pressure at the temperature of the air is also known from this curve, the relative humidity is easily determined. Human comfort depends on relative humidity as well as upon temperature, and this fact must be taken into account in air-conditioning equipment. Unless the temperature and relative humidity fall within certain limits, sometimes called the comfort zone, most of us experience discomfort.

Illustrative Example. When the temperature of the air is 86°F, a dew-point determination shows that the dew-point temperature is 50°F. Determine the relative humidity of the atmosphere.

From Table 17-5, the saturated pressure P at 86°F is 31.8 mm. At the dew-point temperature, 50°F, the saturated vapor pressure p is 9.2 mm. The relative humidity r is therefore

$$r = \frac{p}{P} = \frac{9.2}{31.8} = 0.29 = 29 \text{ per cent.}$$

Problems

17-1. When 1 gm of water boils at 1 atm pressure, its volume changes from 1 cm³ in the liquid phase to 1,671 cm³ in the vapor phase. Apply the first law of thermodynamics to this process and calculate (a) the work done by the fluid in expanding against the external pressure, (b) the change in internal energy in this process, and (c) the fraction of the latent heat of vaporization which goes into internal energy.

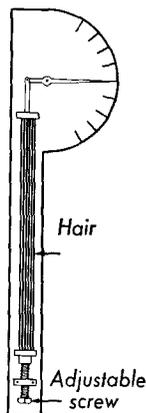


Fig. 17-10
Hair hygrometer.

17-2. A 1-ton air conditioner is rated as being capable of manufacturing 1 ton of ice at 0°C in a 24-hr day, from water at 0°C . What is the rate, in watts, at which a 1-ton air conditioner can remove heat from a room?

17-3. The latent heat of vaporization of water under standard conditions is 539.6 cal/gm. (a) What is the vapor pressure of water under these conditions? (b) Using the data of problem 17-1 and Clapeyron's equation, find the vapor pressure of water at a temperature of 101°C .

17-4. Water boils at a temperature of 417°F at a pressure of 300 lb/in². Under these conditions 1 lb of water has a volume of 0.0189 ft³ and 1 lb of steam has a volume of 1.5414 ft³. The heat of vaporization of water at this temperature is 740 Btu/lb. (a) Determine the work done by 1 lb of water in changing to steam. (b) Determine the change in internal energy of the system in this process.

17-5. Prove that the enthalpy of a perfect gas is a function of the temperature only.

17-6. (a) Calculate the slope of the fusion curve of water at 0°C if the specific gravity of ice is 0.92. (b) Determine the pressure necessary to lower the melting point to -1°C .

17-7. The air admitted to a room on a winter day when the outside temperature is 32°F has a dew point of 14°F . The air is heated electrically until its temperature is 68°F . (a) What is the relative humidity of the outside air? (b) What is the relative humidity of the heated air in the room?