two exactly similar thin metallic vessels are filled with two different substances, and after being heated to a common temperature are allowed to cool in air under the same conditions, the times which they occupy in falling to any other common temperature will be proportional to the quantities of heat which they emit, if we can assume that the contents of the vessels are at sensibly the same temperatures as their surfaces. We have thus a comparison of the thermal capacities of the two substances per unit volume.

In the case of solid substances, their differences in conducting power render the method worthless; but Regnault has found that it gives tolerably correct results in the case of liquids. In fact the extreme mobility of liquids, combined with their expansion when heated, prevents any considerable difference of temperature from existing in the same horizontal layer; so that the centre is sensibly at the same temperature as the circumference.

CHAPTER VII.

FUSION AND SOLIDIFICATION.

72. Fusion.—Many solid bodies, when raised to a sufficiently high temperature, become liquid. This change of state is called *melting* or *fusion*, and the temperature at which it occurs (called the melting-point, or temperature of fusion) is constant for each substance, with the exception of the variations—which in ordinary circumstances are insignificant—due to differences of pressure (§ 86). The melting-points of several substances are given in the following table:—

TABLE OF MELTING-POINTS, IN DEGREES CENTIGRADE.

Mercury,	−39	Tin,	230
Ice,	0	Bismuth,	262
Butter,	33	Lead,	326
Lard,	33	Zinc,	412
Spermaceti,	49	Antimony,	432
Stearine,	55	Aluminium,	600
Yellow Wax,	62	Bronze,	900
White Wax,	68	Pure Silver,	954
Stearic Acid,	70	Gold,	1045
Phosphorus,	44	Copper,	1054
Potassium,	63	Cast Iron,	1050 to 1250
Sodium,	95	Steel,	1300 to 1400
Iodine,	107	Wrought Iron,	1500 to 1600
Sulphur,	110	Platinum,	1775

Some bodies, such as charcoal, have hitherto resisted all attempts to reduce them to the liquid state; but this is to be attributed only to the insufficiency of the means which we are able to employ.

It is probable that, by proper variations of temperature and pressure, all simple substances, and all compound substances which would not be decomposed, could be compelled to assume the three forms, solid, liquid, and gaseous.

The passage from the solid to the liquid state is generally abrupt;

but this is not always the case. Glass, for instance, before reaching a state of perfect liquefaction, passes through a series of intermediate stages in which it is of a viscous consistency, and can be easily drawn out into exceedingly fine threads, or moulded into different shapes.

73. Definite Temperature.—When the solid and liquid forms of a substance are present in contact with each other in the same vessel, and time is allowed for uniformity of temperature to be established; the temperature will be that of the melting-point, and will be quite independent of the relative proportions of solid and liquid in the vessel. For example, water and ice, in any proportions, if brought to a uniform temperature, will be at 0° C.

It is sometimes stated that, if heat be applied to a vessel containing ice and water, the temperature of the contents will remain at 0° C. till all the ice is melted; but this statement is not strictly accurate. The portions of the water in contact with the sides and receiving heat from the sides, will be at a somewhat higher temperature than the portions in contact with the ice. If, however, the application of heat be stopped, and uniformity of temperature be established through the whole mass, by stirring or otherwise, the temperature of the whole will then be 0° C.

For each substance that passes, like ice, by a sudden transition, from the solid to the liquid state, without an intermediate pasty condition, there is one definite temperature at which the solid and the liquid forms can exist in contact under atmospheric pressure. This temperature is variously styled the *temperature of fusion*, the *melting-point*, and the *freezing-point*.

74. Latent Heat of Fusion.—Although the solid and liquid forms of a substance can exist together at the same temperature, the application of heat is requisite for reducing the solid to the liquid form. If ice at 0° C. be put into a vessel and placed on the fire, it will be gradually melted by the heat which it receives from the fire; but at any time during the operation, if we stop the application of heat, and stir the contents till uniformity of temperature is established, the temperature will be 0° C. as at first. The heat which has been received has left its effect in the shape of the melting of ice, not in the shape of rise of temperature. Heat thus spent is usually called *latent heat*, a name introduced by Black, who was the first to investigate this subject. A similar absorption of heat without rise of temperature occurs when a boiling liquid is converted into vapour. Hence it is necessary to distinguish between the *latent heat of fusion*

and the *latent heat of vaporization*. The former is often called the latent heat *of the liquid*, and the latter *of the vapour*. Thus we speak of the latent heat of water (which becomes latent in the melting of ice), and of the latent heat of steam (which becomes latent in the vaporization of water).

The same amount of heat which is absorbed in the conversion of the solid into the liquid, is given out when the liquid is converted into the solid; and a similar remark applies to the conversion of vapour into liquid.

75. Measurement of Heat of Fusion.—The heat required *to convert unit mass* of a substance from the solid to the liquid form is employed as the measure of the latent heat of liquefaction of that substance. Its amount for several substances is given in the last column of the following table:—

Substances.	Melting-point.	Specific Heats		Latent Heat of Fusion.
		In the Solid State.	In the Liquid State.	
Ice, ...	0°	·5040	1·0000	79·250
Phosphorus, . .	44·20	·2000	·2000	5·400
Sulphur, . . .	111	·2020	·2340	9·368
Bromine, . . .	− 7·32	·0840	·1670	16·185
Tin, ...	232	·0560	·0640	14·252
Bismuth, . . .	266	·0308	·0363	12·640
Lead, . . .	326	·0314	·0402	5·369
Mercury, . . .	− 39	·0319	·0333	2·820

The most accurate determinations of latent heat of fusion have been made by a method similar to the "method of mixtures" which is employed in the determination of specific heats.

Let i grammes of ice at 0° be mixed with w grammes of water at $t°$, and when all the ice is melted let the temperature of the whole be $\theta°$. Then if the specific heat of water at all temperatures between 0° and $t°$ can be taken as unity, we have $w(t-\theta)$ units of heat lost by the w grammes of water, and spent partly in melting the ice, and partly in raising the temperature of the water produced by the melting from 0° to $\theta°$. Hence if x denote the latent heat of liquefaction, we have

$$w(t-\theta)=i(x+\theta);$$

whence we find

$$x=\frac{wt}{i}-\frac{w+i}{i}\theta.$$

One gramme of water at between 79° and 80°, or between 79 and 80

grammes of water at 1°, will be just enough to melt one gramme of ice at 0°; and the final temperature of the whole will in each case be 0°.

For any other substance, let T° be the melting-point, s the specific heat of the substance in the liquid form, and x the latent heat of liquefaction. Then if i grammes of the solid at T° be mixed with w grammes of the liquid at t°, and θ° be the temperature of the whole when all the solid is melted, we have

$$s\,w\,(t-\theta) = i\,x + i\,(\theta-T);$$

whence

$$x = \frac{w}{i}\,s\,(t-\theta) - (\theta-T).$$

In these calculations we have tacitly assumed that no heat is gained or lost externally by the substance under examination. Practically, it is necessary (as in the determination of specific heats) to take account of the thermal capacity of the calorimeter (that is the vessel in which the substance is contained) and of the heat gained or lost by the calorimeter to surrounding bodies. For substances which have a high melting-point, a different method may be employed. The body in the molten state may be inclosed in a small thin metal box and immersed in the water of the calorimeter. Let m be the mass of the body, T′ its initial temperature, T its melting-point, $s′$ its specific heat in the liquid, and s in the solid state, θ the final temperature of the calorimeter, and x the latent heat of the substance, which is required; then the heat lost by the body is

$$m\,s′\,(T′-T) + m\,x + m\,s\,(T-\theta),$$

and this quantity, together with the heat lost by the envelope must be equated to the heat gained by the calorimeter and its original contents, subject to a correction for radiation which can be determined by the ordinary methods.

As regards the two specific heats which enter this equation, s the specific heat in the solid state may be regarded as known, and $s′$ the specific heat in the liquid state can be deduced by combining this equation with another of the same kind in which the initial temperature is very different. In the case of bodies which, like mercury and bromine, are liquid at ordinary temperatures, the specific heat in the solid state can be found by a similar but inverse process.

76. **Conservatism of Water.**—The table in § 75 shows that the

heat of fusion is much greater for ice than for any of the other substances mentioned. It is 14 times as great as for lead, and 28 times as great as for mercury. Ice is, in this sense, the most difficult to melt, and water the most difficult to freeze, of all substances; a fact which is of great importance in the economy of nature, as tending to retard the processes both of freezing and thawing. Even as it is, the effects of a sudden thaw are often disastrous; and yet, for every particle of ice melted, as much heat is required as would raise the water produced through 79° C. or 142° F.

77. **Solution.**—The reduction of a body from the solid to the liquid state may be effected by other means than by the direct action of heat; it may be produced by the action of a liquid. This is what occurs when, for instance, a grain of salt or of sugar is placed in water; the body is said to be *dissolved* in the water. Solution, like fusion, is accompanied by the disappearance of heat consequent on the change from the solid to the liquid state. For example, by rapidly dissolving nitrate of ammonia in water, a fall of from 20° to 25° C. can be obtained.

Unlike fusion, it is attached to no definite temperature, but occurs with more or less freedom over a wide range. Rise of temperature usually favours it; but there are some strongly marked exceptions.

78. **Freezing-mixtures.**—The absorption of heat which accompanies the liquefaction of solids is the basis of the action of freezing-mixtures. In all such mixtures there is at least one solid ingredient which, by the action of the rest, is reduced to the liquid state, thus occasioning a fall of temperature proportional to the latent heat of its liquefaction.

The mixture most commonly employed in the laboratory is one of snow and salt. There is a double absorption of heat caused by the simultaneous melting of the snow and dissolving of the salt. Professor Guthrie found that the proportions of the two ingredients and their initial temperatures may vary between very wide limits without affecting the temperature obtained. This definite temperature is the freezing-point of a definite compound of salt and water. When ordinary sea-water in a vessel is subjected to cold, the ice first formed is fresh; and the brine increases in strength by the freezing out of the water till it has attained the strength of the definite compound above mentioned. Then a change occurs, and the ice formed is no longer fresh, but of the same composition as the brine. From this point onward until all the brine is frozen the temperature of

the liquid is −22° C., which is, accordingly, the temperature obtained by mixing snow and salt.[1]

Fahrenheit intended that the temperature thus obtained should be the zero of his scale, the freezing-point of water being 32° and the boiling-point 212°; but the thermometers with which he worked were extremely rough, and if we define his scale by the two ordinary fixed points, the temperature −22° C. will not be 0° F., but −7·6° F.

79. The following mixtures are also sometimes employed.

	Proportions by Weight.	Fall of Temperature Produced.
Snow, ...	3	from 0° to −48°.
Crystallized Chloride of Calcium, . . .	4	
Nitrate of Ammonia, ...	1	from + 10° to −15°.
Water, ...	1	
Sal-ammoniac, ...	5	
Nitrate of Potash, ...	5	from + 10° to −15°.
Sulphate of Soda, ...	8	
Water, ...	16	
Sulphate of Soda, ...	8	from + 10° to −17°.
Hydrochloric Acid, ...	5	

Fig. 46 represents an apparatus intended for the artificial production of ice. The water to be frozen is inclosed in a mould formed of two concentric vessels—an arrangement which has the advantage
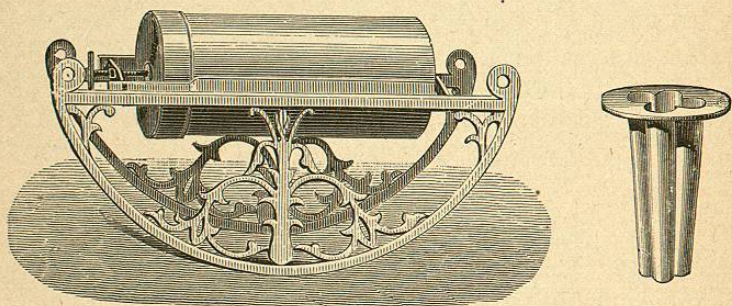

Fig. 46.—Freezing Rocker.

of giving a large surface of contact; and the mould is immersed in the freezing-mixture (hydrochloric acid and sulphate of soda) which is contained within a metal cylinder mounted on a cradle, the rocking of which greatly assists the operation.

80. Solidification or Congelation.—All liquids are probably capable of being solidified; though some of them, for example, alcohol and bisulphide of carbon, have never yet been seen in the solid state.

[1] *Proceedings of Physical Society of London*, January, 1875, p. 78.

The temperature of fusion is the highest temperature at which congelation can occur, and is frequently called the *temperature of congelation* (or the *freezing-point*); but it is possible to preserve substances in the liquid state at lower temperatures. Liquids thus cooled below their so-called freezing-points have, however, if we may so say, a *tendency to freeze, which is only kept in check by the difficulty of making a commencement.* If freezing once begins, or if ever so small a piece of the same substance in the frozen state be allowed to come in contact with the liquid, congelation will quickly extend until there is none of the liquid left at a temperature below that of fusion. The condition of a liquid cooled below its freezing-point has been aptly compared to that of a row of bricks set on end in such a manner that if the first be overturned, it will cause all the rest to fall, each one overturning its successor.

The contact of its own solid infallibly produces congelation in a liquid in this condition, and the same effect may often be produced by the contact of some other solid, especially of a crystal, or by giving a slight jar to the containing vessel.

Despretz has cooled water to −20° C. in fine capillary tubes, without freezing, and Dufour has obtained a similar result by suspending globules of water in a liquid of the same specific gravity with which it would not mix, this liquid being one which had a very low freezing-point.

81. Heat set free in Congelation.—At the moment when congelation takes place, the thermometer immediately rises to the temperature of the melting-point. This may be easily shown by experiment. A small glass vessel is taken, containing water, in which a mercurial thermometer is plunged. By means of a frigorific mixture the temperature is easily lowered to −10° or −12°, without the water freezing; a slight shock is then given to the glass, congelation takes place, and the mercury rises to 0°.

The quantity of ice that will be formed when congelation sets in, in water which has been cooled below the freezing-point, may be computed—very approximately at least—in the following way:—

Suppose we have unit mass of water at the temperature $-t°$, and when congelation sets in suppose that it yields a mass x of ice and a mass $1-x$ of water, both at 0°.

To melt this ice and bring the whole mass to the state of water at 0° would require the addition of $79·25\,x$ units of heat; but to bring the whole mass of water from $-t$ to 0° would require t units of heat.

These two quantities of heat must be the same, subject to a possible correction which will be discussed in the chapter on thermodynamics. Hence we may write

$$79 \cdot 25\, x = t; \qquad x = \frac{t}{79 \cdot 25}.$$

Whatever the original quantity of water may be, this value of x expresses the fraction of it which will be converted into ice.

82. Crystallization.—When the passage from the liquid to the solid state is a gradual one, it frequently happens that the molecules group themselves in such a manner as to present regular geometric forms. This process is called crystallization, and the regular bodies thus formed are called crystals. The particular crystalline form assumed depends upon the substance, and often affords a means of recognizing it. The forms, therefore, in which bodies crystallize are among their most important characteristics, and are to some extent analogous to the shapes of animals and plants in the organic world.

In order to make a body crystallize in solidifying, the following method is employed. Suppose the given body to be bismuth; the first step is to melt it, and then leave it to itself for a time. The metal begins to solidify first at the surface and at the sides, where it is most directly exposed to cooling influences from without; accordingly, when the outer layer of the metal is solidified, the interior is still in the liquid state. If the upper crust be now removed, and the liquid bismuth poured off, the sides of the vessel will be seen to be covered with a number of beautiful crystals.

If the metal were allowed to stand too long, the entire mass would become solid, the different crystals would unite, and no regularity of structure would be observable.

83. Flowers of Ice.—The tendency of ice to assume a crystalline form is seen in the fern-leaf patterns which appear on the windows in winter, caused by the congealing of moisture on them, and still more distinctly in the symmetrical forms of snow-flakes (see Chap. xi.). In a block of ice, however, this crystalline structure does not show itself, owing to the closeness with which the crystals fit into each other, so that a mass of this substance appears almost completely *amorphous*. Tyndall, however, in a very interesting experiment, succeeded in gradually *decrystallizing* ice, if we may use the expression, and thus exhibiting the crystalline elements of which it is composed. The experiment consists in causing a pencil of solar rays
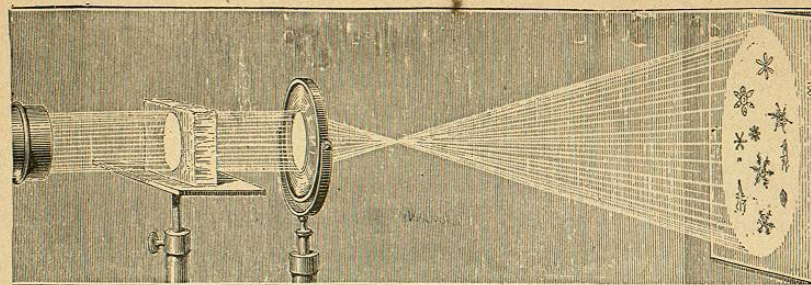
Fig. 47.—Flowers of Ice projected on a Screen.

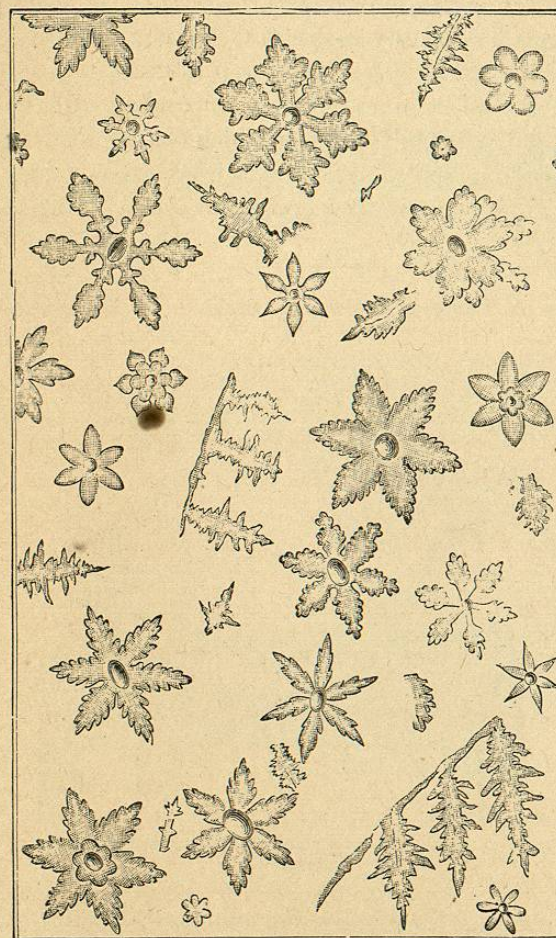to fall perpendicularly to the surfaces of congelation on a sheet of ice, such as is naturally formed upon the surface of water in winter. A lens placed behind the ice (Fig. 47) serves to project upon a screen the image of what is found in the interior of the block. The successive appearances observed upon the screen are shown in Fig. 48. A small luminous circle is first seen, from which branch out rays, resembling the petals of a flower whose pistil is the circle. Frequent changes also occur in the shape of the branches themselves, which are often cut so as to resemble fern-

Fig. 48.—Flowers of Ice.