MELTING POINT METHODS AT HIGH TEMPERATURES.

BY LEO I. DANA, B.S.,* AND PAUL D. FOOTE, PH.D.†

(Communicated to the TRANSACTIONS OF THE FARADAY SOCIETY.)

Introduction: The determination of a melting or freezing point, whether for a physical or physico-chemical purpose, resolves itself into the measurement of a temperature under particular conditions and with appropriate technique. The accuracy and ease with which melting points at high temperatures may be determined is due to the comparatively recent developments in pyrometry, electric furnace construction and refractory materials.

The general classes of substances considered are metals, alloys, salts, and refractory materials. For the temperature measurements, thermoelectric, resistance and optical pyrometers are employed, depending upon the temperature range and other controlling conditions.

The melting or freezing point of a· pure crystalline substance is defined as the temperature at which the solid phase can remain in equilibrium with the liquid phase at normal atmospheric pressure. The effect of pressure is ordinarily insignificant; it is only when the pressure reaches many atmospheres that any change in the melting or freezing point can be readily detected. At the melting point there is a discontinuous change of a number of the physical properties of a material, e.g., thermal conductivity, electrical resistivity, specific volume, etc. In general alloys, excepting eutectoids, mixtures of refractory oxides and materials with impurities do not have a definite melting point, but become liquid gradually; that is, they melt over a temperature interval and consequently are considered as having a "melting range."

1.—USE OF THERMOELECTRIC PYROMETERS.

Pure Materials.--General Discussion : The experimental arrangement of this method consists of a crucible containing the substance in which a thermocouple, either protected or unprotected, is centrally inserted. The crucible is placed in a uniformly heated portion of an electric furnace. On account of cleanliness, clarity of the atmosphere, and preciseness of control, electric resistance furnaces are preferable to gas or fuel fired furnaces for accurate melting point determination. When a melting or freezing point is to be observed, the temperature of the furnace is gradually raised or lowered, and the temperature as indicated by the thermocouple is noted at frequent and preferably uniform intervals of time. If all conditions were ideal the temperature of the charge would remain constant during melting or freezing. Thus the temperature-time curve would be characterised by a straight line exactly parallel to the axis of time and by a discontinuous change of slope at either end of the line marking the beginning and ending of the period of melting or

---

* Assistant Physicist.
† Physicist U.S. Bureau of Standards.

freezing. Actually, however, the change of state shown by the curve, even for pure materials, is not sudden, but more or less gradual. Only a part of the freezing curve will be flat, and the melting curve usually possesses greater obliquity than the freezing curve. For this reason freezing point determinations are usually more reliable, and are employed whenever possible, although the temperature thus obtained is frequently called the melting point, to which it is numerically equivalent.

The reasons for obliquity, and for its existence to a greater degree in the melting curves, have been discussed in detail by White.* On heating, the furnace walls are hotter than the crucible, and hence heat flows from the furnace to the crucible. When a layer of the charge near the wall of the crucible reaches the melting point the heat absorbed by the charge goes to supply that necessary for the latent heat of fusion, and the temperature of the outside layer tends to remain fairly constant. The thermocouple measures the temperature of the solid metal in the centre of the charge, and when thus surrounded by an isothermal layer the rate at which the inside temperature increases is greatly diminished, resulting in a rounding off of the temperature-time curve. As the isothermal layer progresses inward the temperature of the couple slowly rises until the material immediately surrounding it begins to melt, when a condition of stationary temperature is maintained for a short time, during which the thermocouple reading gives the true melting point. While the centre of the charge is melting, however, the temperature of the outer layer of material in the crucible rises very rapidly, and a large temperature gradient is established between the outside and centre. The resulting rapid flow of heat to the centre of the crucible accelerates the melting and, if the layer of remaining solid metal is unequally distributed about the couple, tends to increase the temperature readings and cause another rounding off of the temperature-time curve. The apparent degree of obliquity found near the beginning and end of the melting period depends considerably on the sensitivity of the temperature measurements and scale of plotting. Thus highly accurate data obtained with a precision potentiometer may be plotted on so large a temperature scale that the curve may appear quite oblique, while the same data replotted on a less extended scale appears fairly flat. Aside from this, however, the degree of obliquity varies according to the factors controlling the differences in temperature within the charge, such as dimensions and thermal properties, rate of heat supply, etc. If the solid metal could be stirred during a melting point determination the temperature gradients could be diminished, but even with powdered materials, where stirring is possible, it is not convenient, and does not appear to be very satisfactory. The larger the diameter of the charge the faster the rate of heating, the smaller the diffusivity, and the lesser the latent heat of fusion, the greater will be the tendency to obliquity. The obliquity may be decreased by slow heating and by using a charge of fairly small diameter. The protection tubes of the thermocouple should be small, of thin wall, and should be deeply immersed in the charge. With metals the obliquity is not so great as with salts, on account of their higher heat diffusivity and latent heat of fusion ; in fact, for most cases the obliquity is of negligible importance with pure metals. But with salts and certain refractory materials, unless special care is taken, the obliquity may be so great as to almost completely obscure the true melting phenomenon.

---

* White. Melting Point Determinations. Am. J. Sci., 28, 453, 1909.

188 MELTING POINT METHODS AT HIGH TEMPERA-

On cooling, the crucible is hotter than the furnace walls, and heat flows from the crucible to the furnace. The outer layer of the charge solidifies first, and, during freezing, acts as an isothermal layer, thus decreasing the temperature differences between the centre and outside of the charge. The rate at which the temperature of the couple falls decreases, causing a rounding off of the first part of the temperature-
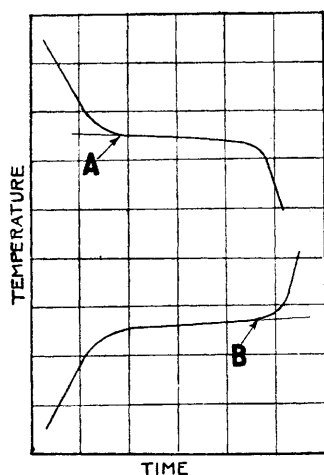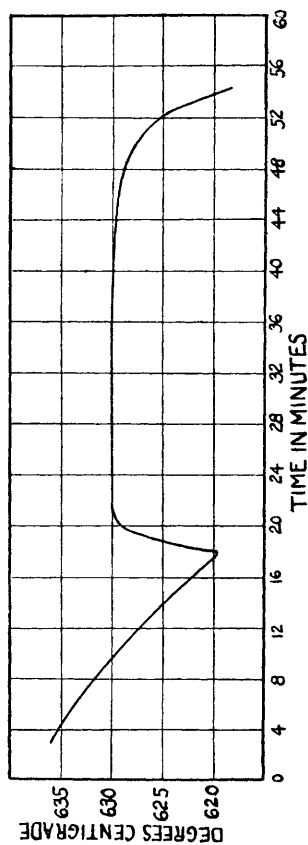

FIG. 1.

FIG. 2.

time curve. While the centre of the charge is freezing the outside is completely frozen and rapidly falls in temperature, increasing the temperature gradient and the outward flow of heat, and hence the latter part of the freezing is accelerated.

The first part of the approximately flat portion of the curve for freezing corresponds to the true freezing point, and the latter part of the approximately flat portion of the curve for melting corresponds to the true melting point. The same precautions of high narrow charges, narrow protecting

tubes, sufficient depth of immersion, and small thermocouple wires apply to both cases.

In general the freezing curves are more sharply defined than the melting curves. A liquid cooling and subject to convection currents is likely to possess a more uniform temperature distribution than a solid on heating. Furthermore, the freezing point is chosen at a time immediately following a period of small temperature gradients, while the melting point must be chosen near the end of the period of melting when there is possibility of temperature non-uniformity. A further factor of importance is the constancy of heat supply. On cooling with a furnace well insulated, the freeze may extend over a considerable time with all power supply shut off. The furnace thus acquires a uniform rate of cooling. In heating, however, the effect of slight variations in the power supply may alter the true character of the melting curve. Fig. 1 shows a freezing and a melting curve in which considerable obliquity is present. The true temperature for freezing is obtained by extrapolating the straight portion of the freezing curve and noting at what temperature A the continued straight line deviates from the observed curve. The melting point B is similarly obtained from the melting curve. The first part of the freezing curve and the last part of the melting curve determine these two temperatures as stated above.

It is impossible to obtain satisfactory freezing curves with certain materials, such as silicates, on account of extremely slow crystallisation, and the melting curves, even though frequently poorly defined, must be employed. The phenomenon of surfusion or supercooling is well illus-trated by water, which may be cooled to $-30°$ C. without freezing. Surfusion is due to conditions which do not favour the attainment of equilibrium between the solid and liquid phases at the true freezing point. The conditions tending to produce equilibrium and the elimination of surfusion are slow cooling, stirring of the liquid and the presence of nuclei which serve as centres of crystallisation. When a supercooled liquid freezes it crystallises very rapidly, and the temperature rises to the true freezing point provided the supercooling has not proceeded too far. The subsequent freezing takes place in a normal manner. Surfusion in most metals seldom exceeds 0.1 or 0.2° C., but in the case of antimony it is very marked, and may amount to 30°, depending upon the rate of cooling, as shown by Fig. 2. Supercooling also occurs in alloys, especially in eutectics. While the contrary phenomenon of superheating is negligible with pure metals, it may become of importance with alloys, particularly in allotropic transformation and with salts and silicates.

Precision Work with Pure Metals : The primary method for the standardisation of thermocouples consists in determining the emf developed by the couple at the freezing points of several very pure metals. The metals so employed are those the freezing points of which have been accepted as fixed points on the high temperature scale, e.g., tin, cadmium, zinc, antimony, aluminium, silver, gold, copper, etc. For this work and for the reverse problem of accurately determining the freezing points of metals and alloys, the greatest precautions against contamination of the couple and the metal are requisite. Precision work at high temperatures requires the use of homogeneous platinum—90 per cent. platinum, 10 per cent. rhodium couples. The diameter of the wire usually employed is 0.5 or 0.6 mm., but for certain special purposes wires of 0.1 mm. are useful.

Crucibles and Protecting Tubes : Of all crucible materials Acheson graphite has the greatest utility. It is very pure, can be machined into any desired shape, and is not attacked by most of the common metals. At high temperatures the gases formed from its oxidation provide the reducing atmosphere necessary for the protection of the metal. The following table illustrates sizes of graphite crucibles which have been used in various investigations. For resistance thermometry the largest size shown is necessary, but for general work the intermediate size is recommended. In this case a smaller protecting tube is desirable; for example, one with an outside diameter of 5 mm.

Some metals, such as nickel and iron, combine with graphite, and certain other metals also should not be heated under the reducing conditions present with graphite. Crucibles of magnesia, alumina, or

TABLE I.

Laboratory.	Crucible Dimensions, all in cm.				Charge Dimensions.		Protection tube Diameter.		Distance from bottom of charge to protection tubes.
	Inside.		Outside.						
	Diam.	Height	Diam.	Height	Diam.	Height	Outside.	Inside.	
B. of S. ...	7	15	8.5	16	7	11	1.0	0.8	1
Geophysical Laboratory	2.7	8	3.7	10	2.7	5	0.8	0.5	0.5
B. of S. ...	1.2	3	2	3.5	1.2	2	0.15	0.1	0.3

mixtures of the two are suitable for iron and nickel. Porcelain crucibles may be used for many of the metals, but there is always danger of these cracking when the metal melts or freezes.

Up to 500° C. protection tubes and insulating tubes for the couple, made of pyrex glass, are useful. From 500° to 1,100° C. lower grade porcelain glazed on the outside only or fused quartz are satisfactory. Above 1,100° C. tubes having a composition approximating that of sillimanite, Al_2O_3, SiO_2 are recommended.*

Porcelain tubes, or crucibles, or any material containing silica cannot be used in contact with aluminium, as the silica is readily attacked. Aluminium may be melted in a graphite crucible, and the porcelain protecting tube may be itself protected by a very thin sheath of graphite. Fig. 3 illustrates one convenient manner in which the sheath may be mounted in the crucible. The sheath is held down in the metal by the weight of the cover, and is allowed to remain in the crucible after the aluminium is frozen. The thermocouple protecting tube fits tightly inside the sheath. At present there is no satisfactory protecting tube for nickel. This material and its alloys can be best studied by optical methods.

---

* Such porcelain is made by Stupakoff Laboratories, Pittsburg under the trade name " Usalite," and by Charles Engelhard Co., New York, under the trade name " Impervite."

Table of Melting Points : The following table lists the more common metals, the melting points of which can be used for the standardisation of thermocouples by the crucible method:—

TABLE II.

Metal.			Melting Point °C.	Crucible Material.	Atmosphere.
Tin ...	...	...	231.9	Graphite, porcelain or pyrex glass	Reducing, Neutral or Air.
Bismuth	...	...	271	,,	Reducing or Neutral.
Cadmium	...	...	320.9	,,	,,
Lead	...	...	327.4	Graphite	,,
Zinc	...	...	419.4	,,	,,
Antimony	...	...	630.0	,, ͬ	Reducing, CO
Aluminium		...	658.7	,,	,,
Silver	...	...	960.5	,,	,,
Gold	...	...	1063.0	,,	Reducing, Neutral or Air.
Copper	...	...	1083.0	,,	Reducing, CO
Nickel	...	...	1452	MgO, Al_2O_3 or mixtures of the two	H_2, N_2, or vacuum.

The surface of the metal should be covered with a layer of powdered or flaked graphite, and the crucible should be provided with a cover having a hole through which the thermocouple tube is inserted. Under no circumstances should graphite be exposed to an air current above 500° C., as it readily oxidises and crumbles away. The furnace should be tightly closed at the bottom, and no larger openings exposed at the top than absolutely necessary. When fairly small graphite crucibles are employed, it is frequently desirable to use a larger outside crucible of porcelain and fill the space between the two crucibles with graphite powder, as shown in Fig. 4.

Construction of Furnace : Fig. 4 shows the construction of a furnace using crucibles of the intermediate size given in Table I. for operation up to 1,100° C. The graphite crucible H, containing the metal G, and the pyrometer tube A, rests in a porcelain crucible F, and is completely covered by powdered graphite E. The porcelain crucible is supported by the alundum tube D. The heater tube is of alundum, R. A. 98, length 25 cm., inside diameter 5 cm., and wall thickness 3 mm. This is preferably corrugated on the outside, and is wound with sixty to eighty turns of No. 14 " Chromel A " wire, C, to the ends of which are welded the lead in terminals K of No. 10 Chromel. The alundum tubes B and D rest on a good-conducting fire-brick about 5 × 8 × 8 cm. The shell M, 32 cm. high, is of sheet iron or monel metal painted with aluminium paint. The ends of the shell are closed by impregnated asbestos boards N, 1 cm. thick and 17 cm. in diameter. The annular space O is packed with silocel powder. The lead in wires are insulated from the metal shell by asbestos board or steatite bushings. The furnace in series with a rheostat for control may be operated on 110 volts, and consumes about 1 kw. at 1,100° C.

Larger furnaces are required for the large crucibles described in Table I. Such a furnace may be constructed from the following stock material:—Alundum tube R. A. 98, length 45 cm., inside diameter 8˙cm., wall thickness 6 mm. Chromel A winding No. 5 wire; sixty turns separated by asbestos cord and covered over with a layer of alundum cement. Diameter of shell 36 cm., height of shell 60 cm.; silocel powder insulation, general construction similar to Fig. 4. Power required for
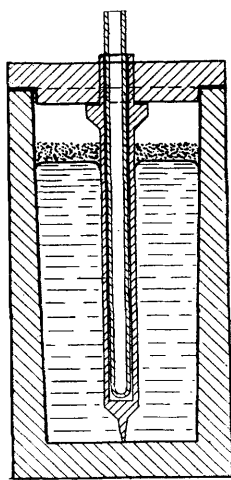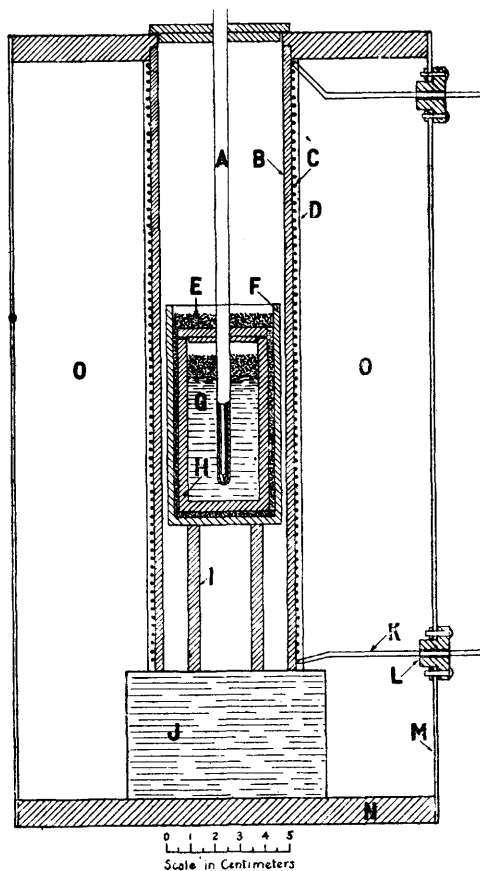

FIG. 3.

Scale in Centimeters

FIG. 4.

1,100° C., about 55 amperes at 60 volts. Using the large crucibles, a freeze of copper with all power off extends over a period of about twenty minutes.

General Precautions : In order to melt for the first time a metal which is in small pieces, the graphite crucible, filled with the material, fitted with a cover having a hole in which the thermocouple fits tightly, and surrounded by powdered graphite, is slowly heated. If convenient CO or N_2 may be passed into the furnace, but CO_2 should not be used. The surface of the metal should not be covered with graphite at first,

as it may filter into the interior and become imprisoned there. When the metal has been melted, however, the graphite layer on the surface is quite desirable. With the exception of antimony, which should be stirred just as the freezing point is reached to reduce supercooling, it is not advisable to stir the molten metals, as pockets of graphite are thereby formed.

If there is doubt concerning the proper depth of immersion several determinations should be made at different depths until a position is found where a slight variation does not affect the temperature measurement.

The pyrometer tube may be allowed to remain in the metal for a few degrees below the freezing point without breaking, and if it cannot be removed then, the metal should be immediately remelted.

ACTUAL FREEZING AND MELTING CURVES
OF PURE ZINC
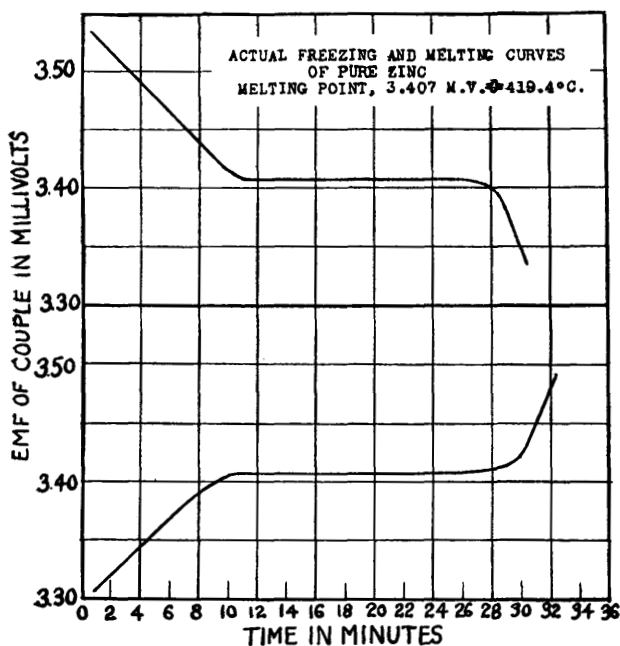MELTING POINT, 3.407 M.V.=419.4°C.

FIG. 5.

A uniform rate of cooling of about 2° C. per minute from 10° C. above the melting point is satisfactory for a freezing point determination. The values obtained from melting and freezing curves should agree to from 0.1 to 0.01° for pure metals, and the curves should have a flat portion extending over at least ten minutes. If the curve is not fairly flat the metal is likely impure, and hence possesses a melting range instead of a true melting point. Fig. 5 illustrates an observed freezing and melting curve for zinc. The freezing curve is constant to 0.05° C. for a period of fifteen minutes and the melting curve for ten minutes. The obliquity in the latter part of the melting curve amounts to 0.1° C. in six minutes.

194 MELTING POINT METHODS AT HIGH TEMPERA-

Metals with Impurities and Alloys : An impurity in a metal usually lowers the melting point and produces obliquity in the melting and freezing curves, the magnitude of both of these effects increasing, within limits, as the amount of impurity is increased. Assuming the amount of impurity is small and that an ideal solution with the metal in the liquid state is formed, the lowering of the freezing point Δt may be expressed appropriately by the Raoult-Van't Hoff equation : —

$$\Delta t = \frac{R\theta^2}{L} \frac{N_1}{N}$$

in which $R = 1.99$, $\theta =$ absolute temperature of the freezing point of the pure metal, $L =$ molar latent heat fusion of the pure metal, $N_1 =$ number of mols of impurity, and $N =$ number of mols of pure metal. In Fig. 6,
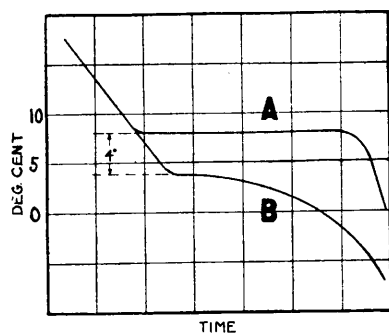

FIG. 6.

A represents the freezing curve of a pure substance, and B the curve obtained when an impurity is present. The lowering of the freezing point is $4°$ C., an amount readily caused by a few tenths of a percent of an impurity at about $800°$ C. In general, the above equation for freezing point lowering holds only for an impurity which forms the simplest type of eutectic alloy with the pure metal. Evidently it cannot be applicable to those impurities which are wholly or partially soluble in the metal in the solid state—that is, which form solid solutions—for in some of these cases the melting point is raised by the addition of the impurity, as, for example, nickel added to copper.

For most of the common metals the oxide is insoluble in the pure metal, but in the copper this is not the case, and special care must be taken, preferably by the maintenance of a strongly reducing atmosphere, to avoid the formations of cuprous oxide Cu_2O. This oxide forms a eutectic with copper saturating it at 3.45% of Cu_2O or 0.395% of oxygen by weight, and freezing at $1,063°$ C. As an example of the application of the above equation, the freezing point lowering of copper at the eutectic, considering the Cu_2O as the dissolved impurity, will be calculated : —

$$\Delta t = \frac{R\theta^2}{L} \frac{N_1}{N} = \frac{2 (1083 + 273)^2 (2.19)}{(63.6) (43.3) (143)}$$

$$\Delta t = 20.4°C$$

The lowering found experimentally is $20.0°$ C.

If the copper contains only a small amount of the oxide the first solidification begins slightly below the melting point of pure copper, and crystals of copper separate from the solution. The concentration

of the dissolved impurity Cu_2O accordingly increases, so that the freezing point of the remaining part of the solution is still lower.   The pure copper will continue to separate from the liquid at a gradually decreasing temperature until the solution becomes saturated with Cu_2O.   This results in rounding or obliquity of the cooling curve.   When the remaining solution is saturated both the Cu and the Cu_2O solidify together, at a constant temperature, as a eutectic mixture.   At this point a halt occurs in the cooling curve, the magnitude of which depends upon the amount of the eutectic present.   The effect of a small amount of Cu_2O will escape notice in an ordinary melting point determination, but if a considerable oxide is present the freezing curve shows the two retardations, one below 1,083° and the other at 1,063° C.   Observation continued through the latter point may serve as a rough criterion of the purity of copper suspected of contamination by its oxide.   The obliquity of the curve also may be an indication of impurity.   If a copper wire is slowly heated in air the melting usually begins at the eutectic point 1,063° instead of at 1,083° C.
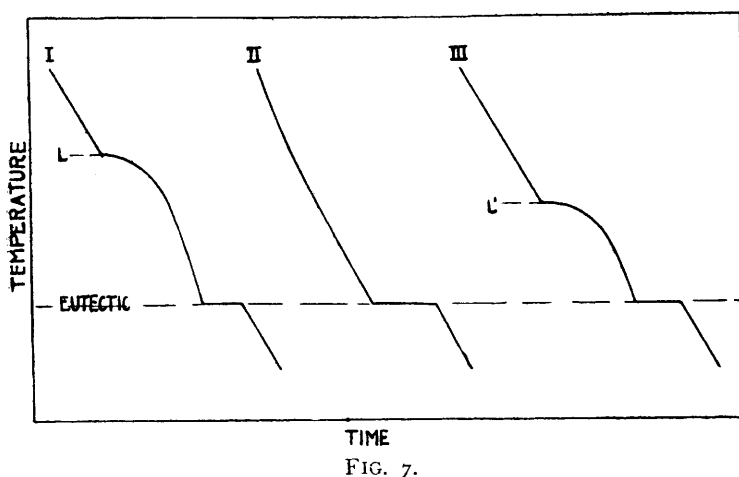

TIME

FIG. 7.

Oxygen dissolves in silver, and may lower the melting point as much as 5° C. if the silver is heated in air.

An alloy may be considered as a metal containing large proportions of one or more impurities.   Let us consider the simplest case of an alloy of two metals A and B, which are mutually soluble when liquid and insoluble when solid.   If A first begins to separate from the solution the remaining liquid becomes richer in B, and, as shown above, this part of the freezing curve gradually changes in slope, as illustrated by Fig. 7, Curve I, L.   As the temperature is lowered the solution finally becomes saturated with B, and A and B crystallise together as a eutectic, shown in Fig. 7, by the lower flat portion of the cooling curve.   The alloy accordingly has a melting or freezing range extending from the temperature at which separation of A first begins to the temperature at which the eutectic mixture solidifies.   If the original composition of the alloy is the eutectic mixture, there exists a true melting point as shown in Fig. 7, II, and not a melting range.

196 MELTING POINT METHODS AT HIGH TEMPERA-

The general form of the temperature-composition diagram of the simple, binary alloy described above is illustrated by Fig. 8. The curves I, II, and III, of Fig. 7 show the form of the cooling curves obtained with the alloys of compositions I., II., and III. of Fig. 8.

Often a binary alloy exhibits two halts in the melting and freezing curves, one oblique and one flat, or both oblique. Furthermore, other complications may arise, such as the formation of solid solutions, compounds and allotropic transformations accompanied by heat changes which require more sensitive methods of detection than by a simple cooling curve. In general, the larger the melting range in a binary alloy the
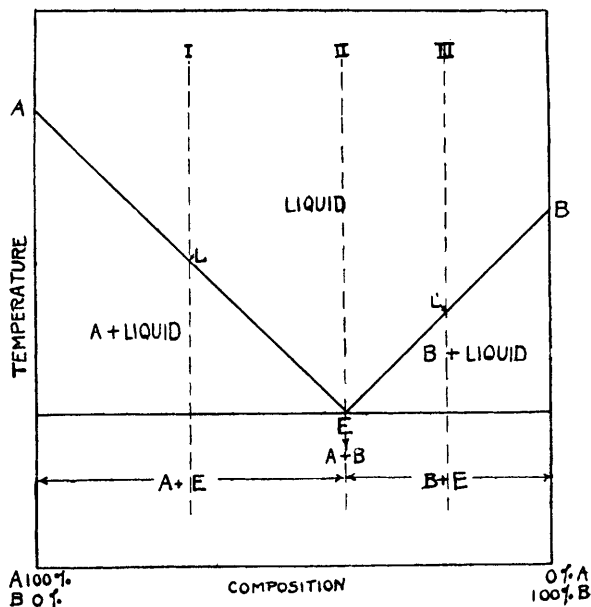

Fig. 8.

more difficult it becomes to locate the lower transformation point because of the small amount of crystallisation per degree drop in temperature and the resulting small heat effect. The same general details for melting point of pure metals apply to alloys. The eutectic alloy of silver and copper, 71.9% Ag, 28.1% Cu, melts at 779° C., and is useful as a standardisation temperature for thermocouples.

For alloys having a large melting range, accurate control of the rate of heating and cooling is essential. Automatic control of the rate may be obtained by a salt-water rheostat as applied by Burgess and Crowe,* or an automatic magnetic control system may be installed. Scott and Freeman† describe a modified Rosenhain furnace especially useful for critical point work. This consists of a vertical tube furnace, with a uniform temperature gradient, through which the material under investigation is automatically moved at a definite rate.

* Bur. Stds. Sci. P. No. 213.
† Bull. Am. Inst. Min. & Met. Eng., Aug., 1919.

If the ordinary temperature-time curve does not give evidence of a change of state at the beginning or end of a melting range or at a transformation point, the more sensitive means of detection, such as the inverse-rate method and differential method, may be employed.

The inverse-rate method consists in determining the time required for the specimen to fall a definite temperature interval—for example, 2° C.—and in plotting this time against the temperature. In effect it amounts to differentiating the temperature-time curve in respect to temperature. The experimental arrangements are the same as for the ordinary-time method, except that the time must be measured more accurately. Merica*has described a simple and effectual device consisting
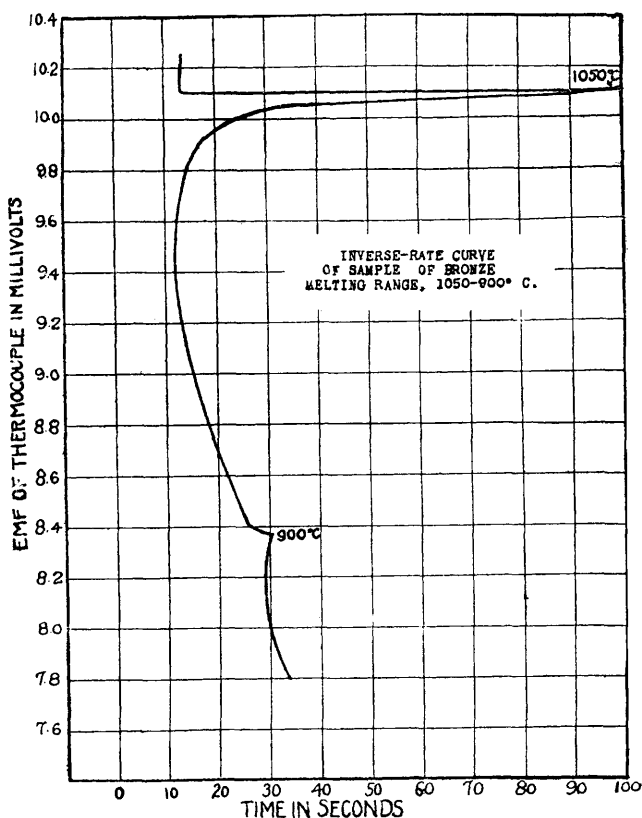

FIG. 9.

of two stop watches, one of which is stopped and started at the end of each time interval. Fig. 9 shows an inverse rate curve through the melting range of a bronze. The lower transformation at 900° C. could not be detected by the ordinary temperature-time method.

The differential method is still more sensitive to small thermal changes. This consists in measuring the temperature differences between the

*Bull. Am. Inst. Min. & Met. Eng., July, 1919.

material in which the transformation takes place and a neutral body having no transformation points in the same temperature interval, such as platinum or nickel, and plotting this difference against the temperature of the material. Two thermocouples are employed, as illustrated by Fig. 10, one a differential couple and the other an ordinary couple,
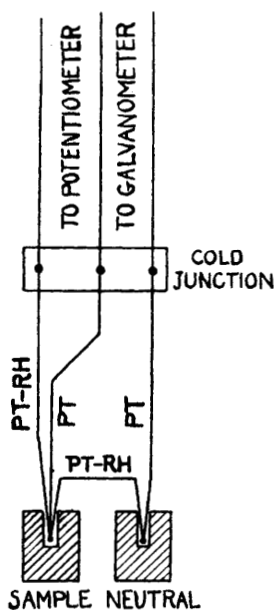

FIG. 10.

which measures the temperature of the sample under investigation. By use of a sensitive galvanometer with the differential couple, extremely minute thermal transformations may be easily detected. Since the material under test and the neutral body are placed in close proximity in the furnace, slight variations in the rate of heating produce no noticeable effect.

Another method of interpreting the data is by means of the derived differential curve, first suggested by Rosenhain.* This amounts to differentiating the differential curve in respect to the temperature and plotting the value so obtained against the temperature. The derived differential is accordingly related to the differential curve in the same manner that the inverse rate is related to the temperature-time curve. Thus, if θ is the temperature of the material being investigated and θ^1 the temperature of the neutral body, the derived differential is the graph

$$\frac{d(\theta - \theta^1)}{d\theta} \, vs\theta$$

The method consists in observing successive values of $(\theta - \theta^1)$ for equal increments of θ, say $2°$ C., and plotting successive differences in these values of $(\theta - \theta^1)$ against θ. The experimental arrangement is the same

---

* Burgess. Bur. Stds. Sci. P. 99.

TURES: L. I. DANA, B.S., AND P. D. FOOTE, Ph.D.   199

as that required for the differential method. Fig. 11 shows both differ-
ential and derived differential curves for the same sample of pure iron
at the transformation points A_2 and A_3.

Inorganic Salts and Silicates: On account of the low heat diffusivity
and latent heat of fusion of salts and silicates, considerable difficulty
is encountered because of the obliquity of the melting or freezing curves.
Consequently it is necessary to use tall, narrow charges and slow rates
of heating. Few salts can be heated in a reducing atmosphere, and hence
graphite crucibles are prohibited. Porcelain and fire clay are attacked
by most salts, so that metal crucibles must be employed. Of these
platinum, platinum alloys, and nickel have the widest utility. The
thermocouple protecting tube of porcelain must be itself protected by
a thin metal sheath. In many cases salts do not attack platinum per-
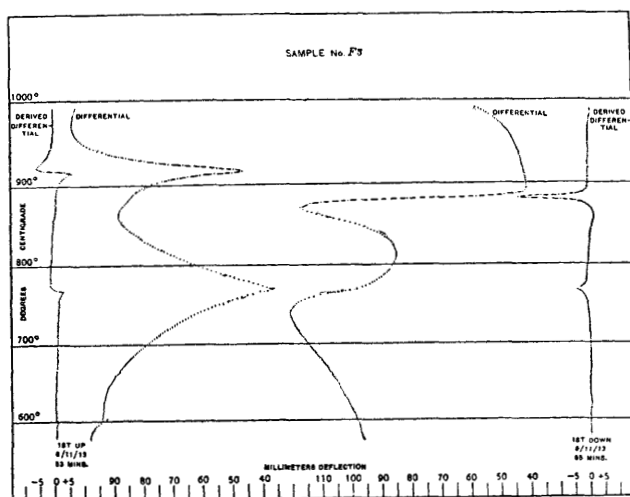ceptibly, so that the thermocouple may be immersed directly in the molten

FIG. 11.

salt. When this is done the crucible must be free from volatile metals,
such as iridium, especially for work at high temperatures; otherwise
the couple will become contaminated. If no protecting tube is employed
very small crucibles may be used, from 1 to 2 cm. in diameter and 2 to
4 cm. high. If the salt is quite volatile and the vapours distil into
the furnace, an additional protection tube for the furnace heater is
necessary. The melting or freezing points of the nitrates, chlorides,
and sulphates of the alkali and alkali earth metals may be determined
in the above described manner.

The melting points of silicates and other compounds of metallic
oxides are usually comparatively high, and their great viscosity when
liquid, slow melting, slow crystallisation, and under-cooling introduce
many difficulties in the melting point determination. Many crystalline
silicates which have a definite melting point do not show a definite freez-
ing point on account of the high viscosity of the liquid, thus preventing
the formation of crystal nuclei. The liquid supercools and the viscosity

may so increase that a glass is formed; thus borax may be melted but once, and, on cooling, a clear glass results, which, with reheating, shows no marked heat transformation at the melting point. Other materials acting in this manner to a lesser degree are diopside, $MgSiO_3$ $CaSiO_3$ melting at 1,391° C. and lithium metasilicate Li_2SiO_3 melting at 1,202° C. Consequently in silicate melting point determinations the melting curves are almost exclusively considered. Fig. 12 A represents about as good a curve as is usually obtained with a silicate.

In another class of silicates the melting requires a large time interval, probably on account of the high viscosity of the liquid, so that the material will easily superheat as well as supercool. Both the melting and freezing curves may be so oblique that no halt in the curves is perceptible. Fig. 12 C shows a heating curve for a slow melting silicate, which gives practically no information as to the true melting point. Silicates of this class may be differentiated by studying the melting curves obtained for different rates of heating. If the faint trace of a halt in the melting curve shifts with rate of heating it is fairly conclusive
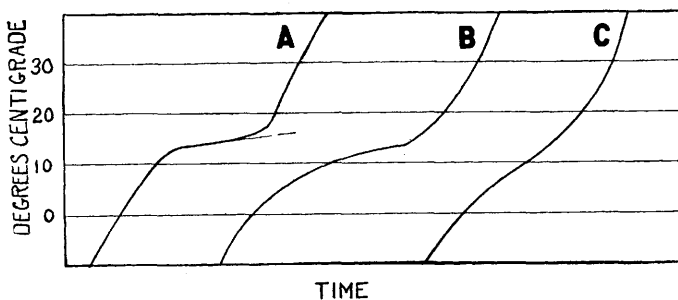

FIG. 12.

evidence that this method is not applicable. A method which has been employed for such materials by the Geophysical Laboratory is to heat the substance for a considerable time at various constant temperatures, and, after quenching in mercury, investigate the crystalline properties under a petrographic microscope. The crystalline structure is destroyed by the melting. Materials of this type are albite Na Al Si_3O_8 melting below 1,200° C., orthoclase K Al Si_3O_8, and quartz SiO_2 melting at 1,710° C.

The apparatus used by the Geophysical Laboratory for silicate work is shown in Fig. 13. The marquardt or sillimanite porcelain tube A is jointed to a platinum sleeve B, 5 × 1.2 cm., into which tightly fits the platinum crucible C containing the charge. The platinum thermocouple, carefully centred, is inserted with no protection. Great care must be taken to avoid the presence of impurities, such as chips of porcelain, from the tube A, etc., as the lowering of the freezing point by impurities is proportional to the square of the absolute temperature, and becomes very serious at high temperatures. Fig. 12 B shows a heating curve of a silicate containing an impurity.

White has found that, in general, the electrical leakage through the molten salt is not of serious importance. However, this must be considered for precision work at high temperatures, as well as the leakage from the furnace heating current to the couple. The latter may be

diminished by preventing any part of the heated couple or crucible from coming into contact with the furnace wall. Thermionic leakage to the couple may be minimised by electrostatic shielding Leakage may be usually detected by moving the couple and by reversing or cutting off temporarily the heating current.

The rate of heating should be from $2°$ to $8°$ C. per minute. On account of the tendency of the melting curves to obliquity, and on account of
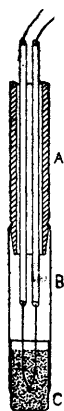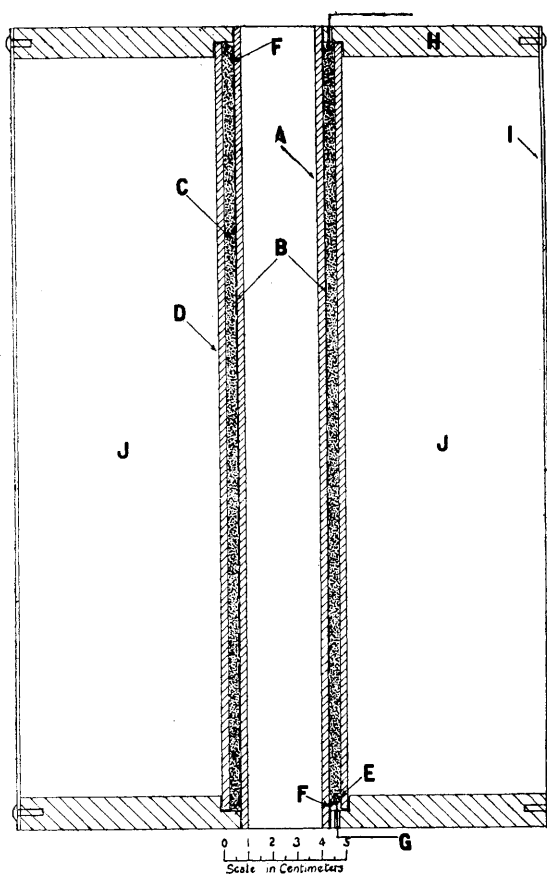

FIG. 13.

FIG. 14.

the small heat transformations involved, it is necessary to maintain a careful furnace control so that irregularities in heating will not appear on the melting curve. Even then it is possible that more sensitive methods of thermal analysis may be desirable, such as the inverse rate or the differential methods described elsewhere.*

* For further details on silicates see publications of the Geophysical Laboratory in the Am. J. Sci. and Jaeger, " Physico-chemical Measurements at High Temperatures," Walters, Groningen, Holland, 1913.

Since an oxidising atmosphere is necessary, the furnace employed for high melting point work with salts and silicates must be wound with platinum. Fig. 14 shows a furnace suitable for temperatures up to 1,550° C. The tube A of Norton alundum R.A.98, 33 cm. long, 3 cm. bore, and 3 mm. wall, is wound with platinum or platinum-rhodium ribbon B, 1 to 2 cm. wide and 0.01 or 0.02 cm. thick, with the turns about 3 mm. apart. The ends of the foil are bound with a turn of platinum wire F, to which are fused the heavy silver lead wires G. Around the tube A is a second tube D, and the space between the two tubes is packed with Norton R. R. alundum, 120 mesh, to prevent local heating of the ribbon. The space between the shell I and the tube D is filled with sintered magnesite.

Table of Melting Points : The following table gives the melting points of several salts and silicates determined at the Geophysical Laboratory: —

TABLE III.

MELTING POINTS OF SALTS, SILICATES, AND OTHER COMPOUNDS.

Substance.	Formula.	Melting Point. °C.
Sodium Molybdate	Na_2MoO_4	687
Borax	$Na_2B_4O_7$	741
Sodium Chloride	NaCl	801
Sodium Sulphate	Na_2So_4	884
Sodium Metasilicate	Na_2SiO_3	1088
Lithium Metasilicate	Li_2SiO_3	1202
Lithium orthosilicate	Li_4SiO_4	1255
Eutectic between diopside and calcium metasilicate	$MgSiO_3 . CaSiO_3 .60\%$ $CaSiO_3 40\%$	1357
Penta Calcium trialuminate ...	$5CaO.3Al_2 O_3$	1382
Diopside	$MgSiO_3. CaSiO_3$	1391
Eutectic between Calcium Metasilicate and cristobalite	$CaSiO_3 77\%$ $SiO_2 23\%$	1426
Calcium metasilicate	$CaSiO_3$	1540
Anorthite	$CaSiO_3 .Al_2SiO_5$	1551
Magnesium Metasilicate	$MgSiO_3$	1554
Calcium Aluminate	$CaO. Al_2O_3$	1592
Cristobalite	SiO_2	1710 Quenching method.

Technical Melting Point Determinations : For ordinary technical testing, in which an accuracy of 5° to 10° C. is sufficient, the general procedure is the same as that discussed for precision work, except that less care is required in experimental details. When large couples are used it is necessary to procure much larger crucibles, approximately in the same proportion illustrated by Table I. It is not a wise practice to immerse a bare base metal couple directly in a molten salt or metal The couple should be protected by a metal or ceramic tube, preferably of thin wall, in order to reduce heat conduction. For metals, Dixon graphite crucibles, which are less susceptible to oxidation than the

Acheson graphite, or pure fire clay (except for aluminium) are satis-
factory, while for salts, iron, calorised iron, nickel, nickel-chromium
alloys, or duriron are serviceable.   For the checking of thermocouples,
pots of commercial tin, lead, zinc, sodium chloride, and copper of a
fair degree of purity are sufficient.   The melting points of these materials
will rarely differ from those of the pure substances by 10° C., and if
close checks are required the melting points may be determined by means
of an accurately calibrated couple.   A gas furnace may be employed for
heating, but the flame should not be allowed to strike the crucible on
one side only.   If the burner is directed along a radius of the furnace
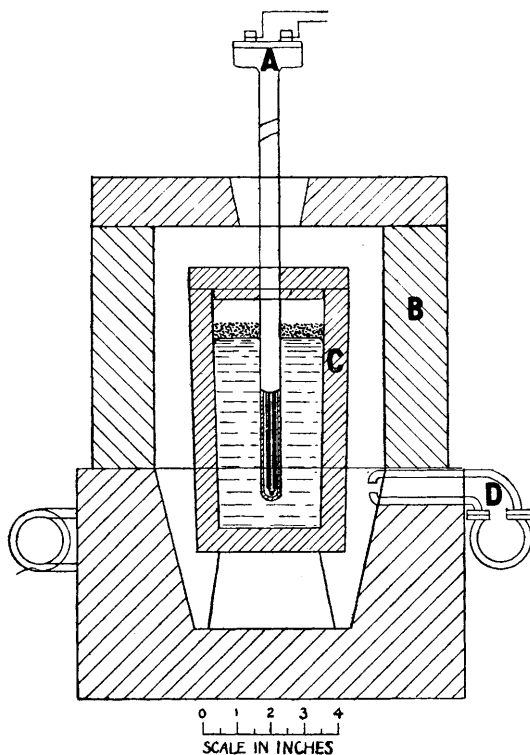

SCALE IN INCHES

Fig. 15.

Fig. 16.

instead of tangential to its surface, a baffle may be interposed before
the crucible or the crucible may be mounted on a pedestal above the
flame.   Under these circumstances it is desirable to protect the crucible
by an outer metal tube.   An excellent form of gas furnace is the melter's
furnace made by the American Gas Furnace Company and illustrated
by Fig. 15.   For ordinary laboratory work size No. 3 is suitable.   The
furnace is provided with three burners D, only one of which appears
in the drawing, mounted tangentially to the circumference in order to
produce a spiraling flame.   Excellent temperature uniformity is thus
obtained.

Wire Method : The wire method of determining melting points of metals consists in inserting at the hot junction of the couple a small length of wire drawn from the material to be investigated. Usually a rare metal couple is employed. The couple is cut apart at the hot junction, and the sample wire, preferably of about the same diameter as the wire of the couple and about 1 cm. or less in length, is fused (not soldered) in. The couple is then mounted in a narrow tube, which may be closed at the lower end, and inserted into a uniformly heated furnace as illustrated by Fig. 16. The temperature of the furnace is increased very slowly as the melting point is approached, and the emf of the couple is observed at the instant that the circuit is broken by the melting, evidence of which is shown by the galvanometer deflection of the potentiometer or of the simple indicator dropping to zero. The temperature corresponding to this emf on the calibration curve of the couple is the desired melting point. The introduction of the short piece of metal produces no effect on the thermoelectric circuit provided it is at a uniform temperature. The two metals most satisfactorily employed with this method are gold and palladium, although many other metals could be used with the proper atmosphere. The experimental manipulation for palladium is a little difficult. A platinum wound furnace similar to Fig. 14 must be used, and the two insulating tubes of the couple must not come into contact with each other or with the furnace walls, otherwise electrical leakage occurs. A leak between the wires of the couple produces a peculiar effect at the instant of melting of the palladium. Instead of the galvanometer showing zero deflection it will indicate the very large voltaic emf developed when the porcelain acts as an electrolyte, since the metallic shunt of low resistance across this emf is broken when the palladium melts. With proper care, results by this method are reproducible to 1° C. It is frequently convenient to sight a microscope of low power on the loop of wire and observe the melting. If the rate of heating is slow, sufficient time elapses from the incipient melting to secure several reliable potentiometric readings before the circuit is broken.

The wire method is occasionally employed for copper heated in air. The temperature so obtained, however, is not reliable. It may be any value from 1,063° to 1,083° C., depending upon the rate of heating and hence upon the amount of oxide formed.

II.—USE OF RESISTANCE THERMOMETERS.

The standard temperature scale as used and distributed by the Bureau of Standards is defined in the interval −40° to 450° C. by means of platinum resistance thermometers calibrated in ice, and steam and sulphur vapour (444.6° C.). Platinum of a high degree of purity is readily obtainable, and its purity is assured if the mean temperature coefficient of resistance of the thermometer between 0° and 100° C. is not less than 0.00388 and if the constant δ of the Callendar equation used for expressing the relation between temperature and resistance is not greater than 1.52. The temperature scale from 450° C. to 1,100 C. is defined by the melting points of pure antimony, silver, gold and copper, and interpolation between these points is based on the temperature scale defined by the rare metal couple (Pt, 90% Pt− 10% Rh) calibrated at two of these fixed points, antimony and copper and a third point, zinc, fixed by the resistance thermometer.

It has been found that the scale defined by the resistance thermometer calibrated as above agrees with the thermocouple scale as closely as this may be reproduced, even up to 800° C. Above this range the behaviour of a resistance thermometer is likely to be erratic. The calibration is subject to changes on account of volatisation of the platinum and strains introduced by the warping of the mica frame upon which the wire is wound. Reliable precise measurements can be obtained only by intercomparison of several thermometers. Below 800° C., however, the temperature scale defined by the resistance thermometer is probably more closely reproduced by different resistance thermometers than is the thermocouple scale reproduced by different thermocouples. Hence when very high precision is required, 0.1° C. or better, the resistance thermometer offers some advantages in the range 450° to 800° C. Below 450° C. the resistance thermometer is the most accurate means of temperature measurements, since its temperature scale is accepted as standard. In melting point work of the highest precision from 450° to 800° C. there is some question as to whether the error resulting in a temperature gradient over the entire bulb of a resistance thermometer introduces as large an error as may arise with a thermocouple, which requires a much smaller region of temperature uniformity; for example, the errors due to inhomogeneity of the wires of the couple.

The general technique to be observed in melting point determinations with the resistance thermometer is the same as that required in thermocouple work of the highest precision. The large size of crucibles described in Table I. is necessary, since the bulb of the thermometer is from 5 to 8 cm. long. The most extensive paper on the application of resistance thermometers to melting point determinations is by Waidner and Burgess.* This paper contains a complete bibliography up to 1909. Later developments have been made only in the methods of measurement, such as bridges, etc., and are described by Waidner, Dickinson, Mueller and Harper and by Mueller.†

III.—USE OF OPTICAL PYROMETERS.

Metals and Alloys: Above 1,400° C. the difficulties involved in the use of thermocouples for melting point determinations are very great. Refractory tubes are attacked by the metals and are permeable to gases which contaminate the couple. The calibration of the couple changes, inhomogeneity develops, and troubles arise from electrical leakage. For these reasons the use of optical pyrometers is desirable, and, above 1,550° C., necessary. The disappearing filament type of optical pyrometer is most satisfactory, since it is capable of high precision, and requires a very small source upon which to sight. Special care must be given in the use of optical pyrometers to insure that black body conditions are closely approximated.

For metals and alloys melting below 1,750° C. the experimental device shown in Fig. 17 is suitable. The outer tube is made of sillimanite

---

* Waidner & Burgess, Sur. Stds. Sci. P. 124.
† Waidner, Dickinson, Mueller and Harper, " A Wheatstone Bridge for Resistance Thermometry," Bur. Stds. Sci. P. 241 ; Mueller, " Wheatstone Bridges and some Accessory Apparatus for Resistance Thermometry," Bur. Stds. Sci. P. 288.

porcelain, melting at 1,810° C., and constitutes the unit to be inserted into a furnace.   The crucible inside this tube is about 18 mm. in diameter and 20 mm. high, and is provided with a cover having two holes, 2 to 3 mm. in diameter, in the positions illustrated.   The pyrometer is focused on the outer hole, and the central hole is for observing the progress of a freezing or melting.   If the metal in the crucible is molten the central hole appears quite dark against a brighter background, because the level metal surface reflects the image of the upper and cold part of the furnace.   The surface under the side hole, however, is convex, on account of the surface tension of the metal, and the V-shaped depression formed between the metal and the side wall affords a satisfactory black body upon which to sight the pyrometer.   The outer tube should be uniformly heated for a distance at least twice its diameter, and the short
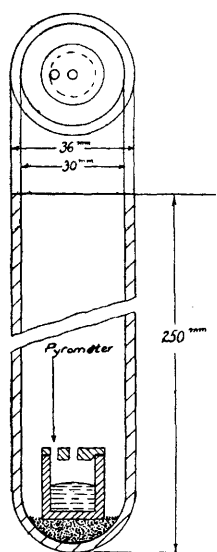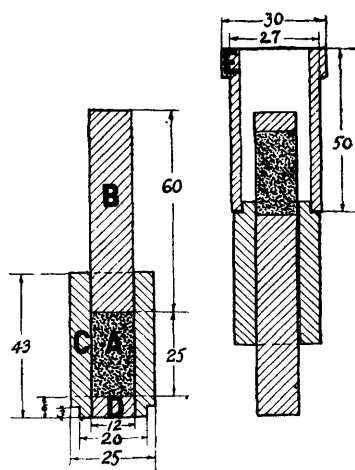

FIG. 17.

Dimensions in mm.

FIG. 18.

crucible should be filled about half full with metal.   Tall crucibles are not desirable, as they are less likely to be uniformly heated, and any non-uniformity disturbs the black body conditions.   Although it is realised that such a system is not ideal for producing black-body radiation, especially when the temperature is continually changing, as is necessary in melting point determinations, still it may be concluded on the basis of many careful observations that the error in general does not amount to more than 2° or 3° C.   For more precise work it is possible to fix to the cover of the crucible a re-entrant tube immersed directly in the metal, and into which the pyrometer is sighted.   This method is frequently employed for the standardisation of an optical pyrometer by direct melting point determinations.*

*Kanolt, Bur. Stds. Tech. P. No. 10.
Foote, Met. & Chem. Eng. 11, p. 97, 1913.

TURES: L. I. DANA, B.S., AND P. D. FOOTE, Ph.D. 207

Table of Melting Points : The following table gives the melting points of several pure metals which with their alloys may be investigated by the above method:—

TABLE IV.

Metal				Melting Point. °C.	Crucible Material.		Atmosphere.
Silicon	...	...	...	1420	MgO, Al$_2$O$_3$, or mixtures		Vacuum, N$_2$, H$_2$
Nickel	...	...	...	1452	,,	,,	Vacuum, N$_2$
Cobalt	...	...	...	1480	,,	,,	,,
Iron ...	...	...	...	1530	,,	,,	,,
Palladium	...	...	...	1550	,,	,,	Air
Chromium	...	...	...	1615	,,	,,	Vacuum, N$_2$
Platinum	...	...	...	1755	,,	,,	Air

Crucibles : Crucibles containing either graphite or silica must never be used for precision work with these metals and their alloys. Silica free crucibles are not sold by the porcelain manufacturers, but can be made in the laboratory without much difficulty from magnesia, alumina, or mixtures of the two. Pure magnesia aluminate does not begin to melt below 1,925° C., and hence is sufficiently refractory for the above metals. Pure fused alumina and pure fused magnesia made by the Norton Company are ground to 150 to 200 mesh and mixed in the approximate proportion 75% alumina and 25% magnesia (the exact proportion is immaterial). The powder is slightly moistened and compressed in a briquetting mould, similar to that illustrated by Fig. 18, into a cylinder having the outside diameter of the crucible. This cylinder is fired in a graphite crucible at a temperature of 1,700° C. for a few moments. The Arsem furnace described later, or any carbon resistor furnace having a clean atmosphere and capable of maintaining this temperature, is satisfactory. The cylinder sinters to a hardness sufficiently strong to be handled, and with care it is possible to drill out a hole large enough for the metal with an ordinary twist drill. The crucible is then refired at a temperature between 1,800° and 1,900° C. A cover is readily made in the same manner.

For ordinary testing with metals other than palladium and platinum the sillimanite crucible (" impervite " or " usalite ") may be employed. These are, of course, attacked, and must be discarded after each determination, but experiments indicate that the impurity introduced in the metal by a single heating affects the melting point less than 10° C. Such crucibles are useful for ordinary work with steels and nickel-chromium alloys.

Furnaces : None of the metals or alloys of high melting point, except the rare metals, can be melted in air without serious oxidation. The use of a vacuum furnace, the residual gases being CO and N$_2$, is satis factory except for palladium and platinum. Fig. 19 illustrates such a furnace designed by Arsem.* It is readily and accurately controllable, and a clear atmosphere is assured. The graphite spiral C is mounted

*Arsem. J. Am. Chem. Soc. 28, p. 921, 1906.
Kanolt. Bur. Stds. Tech. P. 10; Sci. P. No. 212.

in water-cooled copper electrodes. F is a radiation shield of graphite filled with magnesia. The pyrometer is sighted through the glass window D into the sillimanite tube B (see also Fig. 17), which is suspended
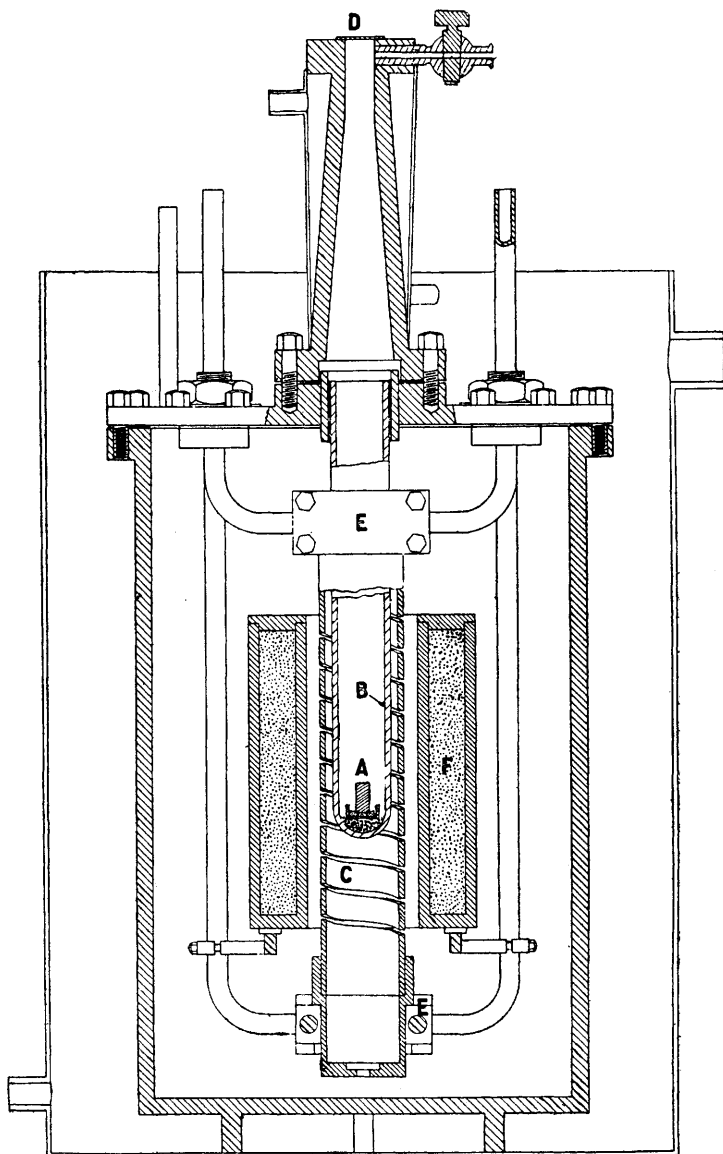
FIG. 19.

from the top of the furnace. In the place of A, the crucible shown in Fig. 17 is mounted on a bed of alundum. The porcelain tube is fairly impermeable to the hot gases and carbon vapour. With the first heating

in a vacuum furnace the liquid metal usually sputters on account of evolution of gases, and may throw off the cover of the crucible, but after the first melting satisfactory readings can be taken. Suitable rates of heating or cooling near the melting point are from 10° to 20° C. per minute. In this range, temperature measurements should be made very frequently, every ten seconds if possible. Fig. 20 illustrates typical freezing curves for pure iron and chrome-steel by this method.
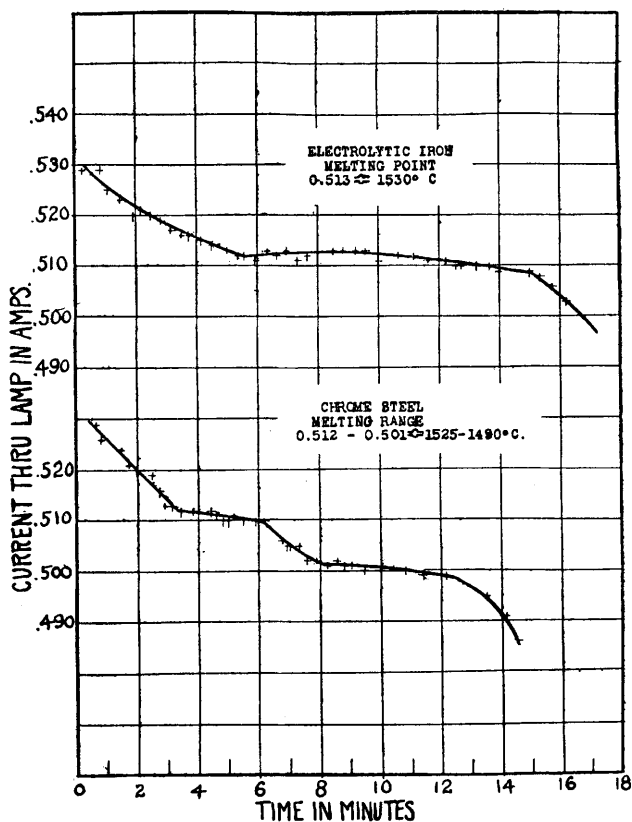

F IG. 20.

For temperatures below 1,550° C. the sillimanite tube of Fig. 17 may be heated in a platinum wound furnace if desired. The proper atmosphere for the metal can be obtained by fitting the sillimanite tube with a metal top containing a window and two side tubes through which N₂ is drawn. Another method is to insert a long porcelain tube through the furnace, in the centre of which is mounted the crucible. Gas is led in at the top of this tube and out at the bottom.

Crucible melts of palladium and platinum are seldom made. Both of these metals must be melted in an oxidising atmosphere, since in a reducing atmosphere the slightest trace of silica, which is present in nearly every type of furnace, is disastrous. Palladium may be heated

in a lime, alumina, magnesia, or magnesia aluminate crucible in a platinum-wound furnace. Platinum could be melted in a furnace wound with a platinum-rhodium alloy, but the method has never been attempted. In several cases a furnace consisting of an iridium tube, in which the tube serves as the resistor element, has been used. The method is open to serious objections, however, on account of the rapid volatilisation of iridium, even when the material is coated with a protective paint, such as a refractory earth mixture.*

Other Methods : For metals melting much above the range of platinum a modification of the wire method may be used. The material in the form of wire or ribbon is mounted as a filament of an electric lamp, and is gradually heated electrically until it melts. The apparent or bright-
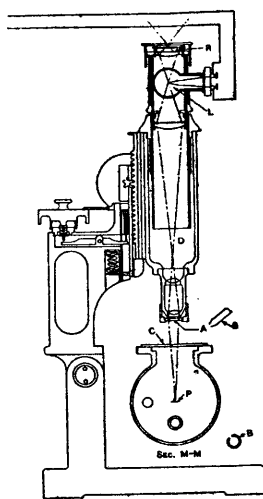

FIG. 21.

ness temperature is measured by an optical pyrometer at the instant of melting. In order to correct the observed temperature to true temperature the value of the emissivity of the material must be known. This involves a separate and difficult experiment. In some cases the material in sheet form is folded into a wedge and electrically heated, and the pyrometer is sighted into the opening of the wedge, the radiation from which is approximately black. Various other methods are employed, such as sighting on a bead of the molten metal in an electric arc, extrapolation of the temperature-current curve for a lamp filament, etc.†

*Waidner and Burgess. Bur. Stds. Sci. P. 55.
†Waidner and Burgess. Bur. Stds. Sci. P. 40, 55; J. d. Phys. ; 6, p. 830, 1907.
Forsythe, Astrophys. J. 12, p. 364, 1911.
Mendenhall & Ingersoll, Phys. R. 25, p. 1, 1907.
Pirani and Meyer, Verh. d. Deutsch. Phys. Ges. 14, p. 426, 1912.
Wartenberg, Verh. d. Deutsch. Phys. Ges. 12, p. 120, 1909.
Langmuir, Phys. R. 6, p. 152, 1915.
Worthing, Phys. R. 10, p. 377, 1917.

Micropyrometer : In order to determine the melting points of microscopic samples of materials Joly devised the meldometer. This consists of an electrically heated platinum strip, the linear expansion of which is a measure of its temperature. The relation between elongation and temperature is determined by placing samples of pure materials on the strip and observing the melting point through a microscope, while the elongation is measured by a vernier screw adjustment. A more satisfactory method is by use of the Burgess* micropyrometer, which operates on the same principle as the disappearing filament pyrometer, except that the lamp is mounted in a microscope instead of a telescope (see Fig. 21). This is sighted on a platinum strip, and on the strip in the field of view is placed a sample of the material to be melted, usually from 0.1 to 0.001 mg. in weight. The strip is enclosed in a water-cooled container having a clear glass window, and a reducing or neutral atmosphere is maintained. The temperature of the platinum strip is measured at the instant of melting, which is indicated with unmistakable evidence, since the material either gathers into a ball or spreads out on the strip. The pyrometer is calibrated by employing metals of known melting points. A natural question which arises is whether the sample actually takes up the temperature of the strip. If the sample were heated by radiation alone, since it receives radiation from a solid angle 2π and radiates through a solid angle 4π it can be shown on the basis of the Stefan-Boltzmann law that the absolute temperature of the sample would be roughly only 0.8 that of the strip. On the other hand, the microscopic sample acts as a shunt on the platinum strip, and more heat is developed at this point, tending to increase the temperature. Thermal conduction along the strip reduces this effect. The fact that samples of different sizes within a small range appear to give the same value for the melting point indicates that these effects are very small and that the sample actually assumes the temperature of the strip, the heat conduction and gas convection compensating for the deficiency in the direct radiation. The method must be used with caution, however, when applied to other materials than metals, especially in a vacuum. It has been found that errors of 50° or more resulted when gold was heated on a graphite strip in vacuo.

Refractory Materials, Refractory Oxides : Refractory oxides are the basic constituents of minerals and of ceramic refractory materials. Their melting points are very high, and it is necessary to adopt special precautions to avoid contamination and to eliminate the smoke produced by the vapourisation of the oxide. The Arsem furnace shown in Fig. 19 was used by Kanolt† for determining the melting points of magnesia, lime, alumina and chromium oxide. In each case heating curves by the temperature-time method were obtained with an optical pyrometer, and the results were confirmed by examination of the materials heated above and below the observed melting points. The rate of heating was about 100° C per minute near the melting point.

---

* Bur. Std. Sci. P. 198, 205, 242.
† Kanolt, loc. cit.

Table of Melting Points.—The following table is a summary of Kanolt's work :—

TABLE V.

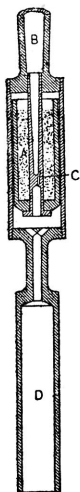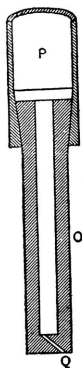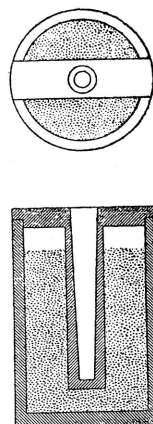| Oxide	M.P. °C.	Crucible material.	Atmosphere.
MgO	2800	Graphite	Stream of CO and N_2 at atmospheric pressure.
CaO	2570	Tungsten, CaO	Stream of H_2 at atmospheric pressure.
Al_2O_3	2050	Tungsten, Graphite	CO and N_2 vacuum; stream of CO and N_2 at atmospheric pressure.
Cr_2O_3	1990	Tungsten, Graphite	CO and N_2 vacuum.

FIG. 22.   FIG. 23.   FIG. 24.

Magnesia was melted in a special form of graphite crucible, Fig. 22, which was mounted in the Arsem furnace. The pyrometer was sighted through the tube B on the bottom of the tube A immersed in the magnesia. CO and N_2 at atmospheric pressure were passed through BCD, thus clearing the field of view from smoke. Lime was melted in a similar container, except that the parts in contact with the lime were made of tungsten. Fig. 23 shows another method employed for lime. The tube O, compressed from pure lime, was suspended in the furnace, and a stream of hydrogen was passed in at P and out at Q to avoid the presence of smoke. Alumina was melted in vacuo in the same form of crucible used for magnesia and also in a graphite crucible shown by Fig. 24. This latter method, with crucibles of both graphite and tungsten, was employed for chromium oxide.

*Fire Bricks and Ceramic Materials** : Refractory materials, such as fire bricks, fire clays and minerals, are composed of compounds of the refractory metallic oxides, solid solutions of the oxides, pure oxides, and mixtures of these classes, together with a variety of chemical compounds. The oxides, silica and alumina occur most commonly in refractory materials, and frequently in combination with these are the oxides of the alkali earth, the alkali, the iron group, and the rare earth metals.

Meaning of the Melting Point : In the case of refractory materials, which are either amorphous or heterogeneous mixtures of oxides and other substances, there is no definite melting point. The change from the solid state to one in which the material will flow is gradual over both a temperature and time interval. In addition, physical and chemical reactions which are not equilibrium reactions often take place during melting. These phenomena practically prohibit the use of melting curves, and for ordinary technical purposes the criterion of marked flow, although indefinite from the pure scientific standpoint, is adopted. Accordingly the practical definition of the melting point of a refractory material is that temperature at which, under specified conditions, a marked and distinct flow of the material begins. In terms of the deformation of a cone or cylinder, the melting point is midway between the temperature at which the deformation begins and the temperature at which the material fuses into a lump or ball, or is completely bent over. The softening or fusing point of a refractory should be defined in the same manner, making the three terms synonymous. If the refractory is a pure crystalline compound it possesses a true melting point, but often—as, for example, with quartz and albite—the change of state takes place so slowly at the melting point that the substance may be superheated. Thus with quartz the viscosity is so high that a marked flow is not perceptible until the material is superheated by 40° or 50° C.† For technical testing the criterion of marked flow is usually taken to define the so-called melting point, even for pure crystalline compounds, and thus on the basis of such a definition the melting point of quartz is about 1,750° C.

Conditions affecting observed Values of the Melting Point : The results obtained on the basis of the above definition of melting point are influenced by a number of experimental factors as follows:—

    (a) Chemical composition.
    (b) Size of the particles, and size, shape and orientation of the sample.
    (c) Time and rate of heating.
    (d) Pressure and chemical nature of atmosphere.

The relations between these factors are so complex that in most cases it is not possible to predict the magnitude or sign of the change in melting due to a variation in one or more of the above conditions. It must be noted that the melting point in actual use of the refractory material may differ considerably from that observed in the laboratory on account of the fact that the conditions of test in the laboratory are not reproduced. Thus contamination of the refractory by molten metals,

---

*For a more detailed discussion, see L. I. Dana, Bull. Am. Inst. Min. Eng. Sept., 1919.
†Quartz begins to flow at 1,750° C. (Kanolt, Bur. Stds. Tech. P. 10), while its true melting point is 1,710° C. (Ferguson and Merwin, Am. J. Sci. 48, p. 1, 1918.)

slags, flue dust, etc., may alter the melting point because of the chemical reaction; also the time and rate of heating may be different. Under load the softening or melting point of a refractory is lowered on account of plastic flow. For this and other reasons the value of the melting point determined in the laboratory is not the only factor as far as failure is concerned to be considered in the choice of a refractory for an industrial installation.

Method of Melting Point Determination—Sampling, Grinding and Moulding : Fire brick and other refractories of non-uniform texture and composition or with particles larger than thirty mesh should be carefully sampled. It is accordingly necessary to grind the material and mould the powder into the form of a cylinder or cone. If the refractory is of fine and uniform texture, however, a piece may be chipped off and shaped to the proper form. Fine refractory powders may be briquetted directly. Since the size of the particles may affect the melting point, the degree of fineness should be specified, at least approximately. For a large variety of substances, grinding to pass an eighty-mesh screen has proven satisfactory. The material is then slightly moistened and compressed into a cylinder about 2.5 cm. high and 1.2 cm. in diameter by means of the brass or polished steel mould shown in Fig. 18. In this figure C is a cylinder, B the piston, D a plug, and A the powder. In order to remove the compressed cylinder the mould is inverted, the cylinder E is placed on top, and the sample is slowly pushed out.

Time and Rate of Heating : The rate of heating, from room tempera ture to about 1,000° C. for substances melting above 1,500° C. may be very rapid. A satisfactory total time of heating is from thirty minutes to two hours, with a rate of from 5° to 10° C. per minute from about 50° below the melting point and during melting. Since the observed melting point depends to some extent upon the rate of heating, it is necessary to specify the temperature-time curve in order that results be reproducible. The following table illustrates the manner in which this may be done with sufficient exactness:—

Temperature interval.	Time.
Room temperature to 1,000° C.	20 minutes
1,000° to 1,650° 25	,,
1,650° to 1,700° M.P. 5	,,

Type of Furnace and Conditions Existing Therein : A furnace for melting refractories should be capable of easily maintaining a temperature of 1,800° C., and means must be provided for close temperature regulation. The atmosphere within the furnace must not react appreciably with the specimen, otherwise the material must be protected. Graphite or carbon tube and spiral resistance furnaces operated in air oxidise rapidly, but may be somewhat protected by passing a neutral or reducing gas through them. The gas may also serve the purpose of carrying away smoke, so that accurate optical temperature measurements may be made. Crushed carbon, graphite, kryptol, or carbon plate resistor furnaces do not permit of very precise regulation. Some forms of furnaces are so constructed that it is difficult to use an optical pyrometer. The vacuum furnace of the Arsem type, although requiring greater accessory apparatus, is more desirable on account of its freedom from smoke and because good control is possible at extreme temperatures, even at 2,500° C.

Furthermore, the atmosphere can be made much less reducing than that in an ordinary graphite furnace. Many refractories are seriously attacked in a carbon and carbon monoxide reducing atmosphere, and it is usually not possible to judge by simple inspection of the melted sample, whether or not the reduction is appreciable. In many cases the surface of the specimen is attacked, and a shell of higher melting point is formed, so that while the inner uncontaminated material may have been melted there is no outward evidence of this fact. In general the sample should be protected from the reducing atmosphere by a refractory tube of low porosity. In the Arsem furnace the sample A, Fig. 19, is protected by the sillimanite tube B. For temperatures beyond 1,800° C. no suitable protection tubes have been made. In certain special cases it may be desirable, if possible, to determine the melting point of a refractory under the atmospheric conditions to which it is subjected in actual use. Indirectly the pressure of the atmosphere may affect the melting point. For example, in a vacuum the more volatile and fusible substances, such as alkalies, may distil and thus cause a rise of melting point.

There appear to be some possibilities in the development of gas furnaces for high melting point determinations. With a suitable construction and air pressure of 10 lb. and more, temperatures of 1,650° C. may be maintained with illuminating gas and 1,800° C. with natural gas. By recuperating the waste heat or by preheating the gases, the above temperature limits may be increased. It should be pointed out that for reliable melting point work it is necessary to maintain a high temperature, not on a restricted small surface, but throughout a considerable volume.

Temperature Measurement : Pyrometric cones have been employed as a rough measurement of the melting temperature of refractories. The refractory is thus said to have a softening point corresponding to a certain cone number. Seger and similar cones serve a useful purpose under slow rates of heating in measuring heat effects during the firing of ceramic products, but in the laboratory, when the rates of heating are comparatively rapid and may vary considerably, the determination of the cone softening point is not of much significance. For it has been repeatedly shown by numerous investigators[*] that the softening point of Seger cones depends upon the nature of the atmosphere, and especially upon the time and rate of heating. Usually the more rapid the rate of heating the higher the softening temperature, variations of 50° C. being easily obtained. In order that the indications by a Seger cone possesses reliability, it is necessary to specify the atmosphere and the time-temperature curve in the manner illustrated above for refractories. Thus in the ordinary use of Seger cones a variable factor is introduced in the temperature scale defined by the cone numbers, which may have no relation to the properties and characteristics of the refractory being tested. Hence it is essential to use a strictly fixed and reproducible temperature scale. This is best accomplished by means of the disappearing filament type of optical pyrometer.

A very slight departure from black body conditions enables one to discuss the specimen and to watch the progress of melting. It is important to keep the eye fixed on the sample in order that the melting may be observed with certainty. Sintering and vitrification take place

---

*Sosman. Trans. Am. Cer. Soc. 15, p. 482, 1913.

on heating, sometimes producing shrinkage and bending; this must not be confused with the change in shape on melting. As in the case of metals, the pyrometer should be focused on a surface of the sample oblique to the line of sight, but it must be assured this surface is not reflecting light from a hotter section of the furnace, thus causing too high a reading. After the determination the sample is removed from the furnace, broken apart and inspected. The inside surface should appear homogeneous and amorphous or glassy. When the sample has been melted in a vacuum furnace a cellular structure is usually apparent, due to gases evolved during melting.

Softening Temperature of Coal Ash: The clinkering of coal ash is closely related to its softening temperature. Consequently the determination of this temperature is of considerable practical importance. The Bureau of Mines has made a very complete investigation of the factors and conditions affecting the fusibility of coal ash, and have recommended a standard procedure.* The results of their investigations will be briefly described.

Coal ash is composed principally of silica, alumina, iron oxides, and lime, together with small amounts of other oxides. The compounds which exert the greatest influence on the melting point are the iron oxides, because they exist in several states of oxidation depending on the chemical
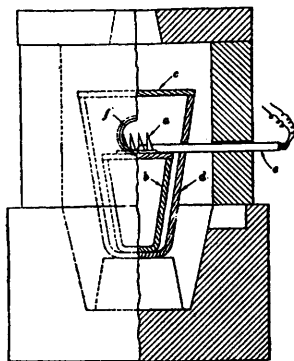

FIG. 25.

nature of the gases in which the ash is heated. When the ash is heated in air the iron is oxidised to its highest states of oxidation, Fe_2O_3 and Fe_3O_4. When heated in a very strongly reducing atmosphere, such as exists in a carbon resistance furnace, all the oxides are reduced to metallic iron. The ash in both of these atmospheres has a higher softening point than when it is heated in moderately reducing atmospheres, such as H_2 and H_2O or CO and CO_2. Under these conditions the oxides are reduced to the ferrous state FeO, forming low melting point ferro calcic silicates.

It has been found that the iron in the slag or clinker of an ordinary fuel bed exists in the ferrous state. Consequently it is preferable to heat the ash in a furnace which will reproduce as nearly as possible the conditions in the fuel bed. A carbon resistance furnace or one with air as the atmosphere are not suitable. A furnace wound with molybdenum

* Fieldner, Hall and Field, "U.S. Bureau of Mines Bulletin," 129.

with a gas-tight case, and equipped with a complicated arrangement for regulating the mixture of H_2 and H_2O has been used, but it is too complex for industrial use. The simplest and most satisfactory furnace has been found to be the gas furnace shown in Fig. 15 and Fig. 25, operated with the maximum excess of gas over air and containing an atmosphere approximately 50 per cent. CO and 50 per cent. CO_2. Since some samples of ash may melt as high as 1,500° C., it may be necessary to mix a small quantity of oxygen with the air to reach this temperature.

The following procedure is recommended. After thoroughly roasting the coal, the ash is ground to 200 mesh and roasted again in a current of oxygen. Using a 10 per cent. dextrin solution as a binder, small triangular pyramids, 20 mm. high and 6 mm. side at the base, are made from the powdered ash. These are placed vertically in a muffle or crucible, as shown in Fig. 25. A yellow flame burning at least 15 cm. above the cover is maintained, and the rate of heating before and during softening should be from 5° to 10° C. per minute. The softening temperature is the point at which the cone fuses down to a lump or ball, which, it will be noticed, is at a further stage of melting than is recommended by the Bureau of Standards for general ceramic materials. For the temperature measurements a thermocouple or optical pyrometer is employed.

Table of Melting Points of Refractory Materials : The melting points in the following table were determined at the Bureau of Standards principally by Kanolt, under conditions approximating those described in the section on refractory material. With the exception of pure kaolin and silica, different samples of the same general type of material may have melting points considerably different from the values tabulated.

TABLE VI.

MELTING POINTS OF COMMON REFRACTORY MATERIALS.

	Temperature. °C.
FIRE BRICKS.	
Fire Clay	1500—1750
Silica	1700—1750
Magnesia	2150
Bauxite	1600—1800
Chromite	2050
CLAYS AND SANDS.	
Kaolin, $Al_2 O_3 .2SiO_2 2H_2O$	1740
Fire Clays	1400—1740
Bauxite Clay	1800
Bauxite $Al_2O (OH)_4$	1820
Chromite, FeO, Cr_2O_3	2180
Silica	1750
Silica Sands	1700—1750
MISCELLANEOUS.	
Coal Ash	1100—1500
Alundum Cements	1750—2000