HIGH TEMPERATURES

396

apparatus sensible to $\frac{1}{40000}$ volt is necessary, and as the galvanometer should have at least 100 ohms resistance, as previously explained, when the deflection method is used, the corresponding current will be only a millionth of an ampere.

In those cases where it is permissible, as in many industrial measurements, to use certain alloys of the base metals which develop large E.M.F.'s, and whose resistance is so low that the galvanometer resistance may also be reduced, it is possible to realize pen recorders giving a strictly continuous record curve of a precision sufficient for many technical operations.

Temperature-rate Recorders. — As we have seen, it is sometimes of interest, more particularly in the laboratory, to measure directly the speed of the occurrence of certain phenomena, as the rate of cooling or chemical transformation. We require an apparatus that will give the rate of change of temperature of the sample in terms of its temperature.

Le Chatelier's Experiments. — Le Chatelier used this method in 1887 in his study of the properties of clays. He was also the first to employ a photographic apparatus for the recording of cooling- or heating-curve data, using an arrangement, to be described, in which the photographic plate remained stationary.

A luminous beam reflected by the galvanometer mirror falls periodically at regular intervals, of a second for instance, upon a fixed sensitive plate. The distance apart of two successive images gives the variation of temperature during unit time, that is, the rate of heating or of cooling; the distance from the same image to the image corresponding to the beginning of the heating will give the measurement of the temperature.

In all cases of photographic recording it is well to replace the ordinary galvanometer mirrors, which give images quite insufficient as to definition and brightness, by special mirrors made of a plano-convex lens, silvered on the plane surface. These mirrors are slightly heavier than parallel-face mirrors, but have two important advantages: the absence of extra images reflected by the front surface of the mirror, and a greater rigidity, which obviates accidental bendings of the mirror arising from the attachments to its support. One may easily get good mirrors of this type of 20 mm. diameter, and with more difficulty of 30 mm. diameter. These last give nine times more light than the mirrors ordinarily employed. It is easy to so choose the lens as to give a mirror of desired focal length. A plano-convex lens whose principal focus by transmission is 1 m. will give, after silvering the plane surface, an optical system equivalent to a spherical mirror whose radius of curvature would be 1 m.

Le Chatelier used discontinuous recording. In this manner of recording, the luminous source should possess periodic variations; one of the simplest to employ is the electric spark between two metallic points. The interruption of the current is produced by a pendulum at definite intervals of time.

In order to have a spark sufficiently bright, it is necessary to use an induction coil so worked as to give freely sparks of 50 mm., and to reënforce it by a Leyden jar which reduces the length of these sparks to 5 mm.; it suffices for this to use a jar of 1 to 2 liters. The choice of metals for the points is equally important; zinc, aluminium, and especially magnesium give sparks that are very photogenic. These metals possess the disadvantage of

oxidizing quite rapidly in the air, so that it is necessary from time to time to clean the points with a file. The metallic sticks may have 5 mm. diameter, and the distance apart of the points is 2 mm. One might without doubt, using mercury, which gives sparks as photogenic as does magnesium, construct an inclosed apparatus in which the metal would be preserved unchanged.

To produce the interruption, there is attached to the pendulum (Fig. 140) a vertical platinum fork which dips into two cups of mercury covered with alcohol.

Fig. 140. Clock Interrupter.

It is useful, in order to reduce to a minimum the resistance that the immersion of the fork opposes to the motion of the



399

HIGH TEMPERATURES

pendulum, to place this fork in the same horizontal plane as the axis of rotation of the pendulum. In this way one avoids the translatory movements in the mercury which cause the most trouble.

The only refinement with this intermittent lighting is to obtain, with a spark much too large and irregular to be photographed directly, the illumination of a very narrow slit. It is not sufficient to place the spark behind the slit and at a small distance away, because the slightest displacement of the spark would cause the luminous beam to fall outside of the mirror of the galvanometer. This difficulty is overcome by a well-known artifice. A lens is placed between the electrodes and the mirror (Fig. 141); the position of the electrodes is so adjusted that the image of the mirror is formed between them. With a distance apart of the electrodes



of 2 mm., a lens of 100 mm. focal length and a mirror of 25 mm. diameter, the image of the latter will touch the two points; the spark then necessarily crosses the image of the mirror, and the radiations passed by the lens will fall certainly upon the mirror. One is thus sure in placing before the lens a fine metallic slit that all the rays transmitted will reach the mirror and will be sent to the photographic plate, and that whatever may be the position of the slit in front of the lens.

To save time, it is advantageous to take several sets of observations on the same plate; this is easily done by arranging the plate so that it may be displaced vertically between two series, or in adjusting the slit so that it may be moved similarly before the lens.

The diagram (Fig. 142) is the reproduction of negatives relative to the action of heat on clays. The first line gives the graduation of the couple; it has been drawn from several different photographs which have been grouped to economize space. The following lines are reproductions of negatives made photographically without any intervention of the hand of the engraver. The second line, for example, represents the heating of an ordinary clay. A slight contraction of the lines between 150° and 350° indicates a first phenomenon with absorption of heat; it is the vaporization of the inclosed water. A second cooling much more marked between 550° and 650° shows the dehydration, properly so called, of the clay, the liberation of the two molecules of water in combination. Finally, the considerable spacing of the lines at 1000° shows a sudden setting free of heat corresponding to the isomeric change of state, after which the alumina be-



Fig. 142. Heating Curves of Clays.

comes insoluble in acids. The other rows refer to the heating of other varieties of clay, the third row to kaolin, the fifth to steargillite.

Dejean's Apparatus. — Another method of recording the rate of heating or cooling in terms of the temperature has been devised by Dejean. The new feature of this method, which gives a continuous record, is the use of an induction galvanometer or relay which may be inserted in the circuit of the more sensitive galvanometer G_1 of the Saladin system (Fig. 160). The principle of the apparatus is shown in Fig. 143. The induction relay is a modified d'Arsonval galvanometer having an electromagnet and a movable coil, the latter consisting of two distinct insulated windings, one of which is connected to a thermocouple. Heating or cooling one junction of this couple causes the coil to be

HIGH TEMPERATURES

deflected and its motion in the field of the electromagnet induces an E.M.F. in the second winding of the coil which is proportional to its angular speed and hence to the rate of change of E.M.F. of the couple, or approximately to the rate of cooling or heating, i.e., to $\frac{d\theta}{dt}$. The induced E.M.F. is measured by joining this winding to the sensitive galvanometer G_1 . The galvanometer

deflection passes through a minimum when the heating or cooling passes through a minimum, that is, for a region in which there is an absorption or evolution of heat. A second thermocouple in series with the other galvanometer G_2 of the Saladin system gives the temperature of the sample. We have, therefore, on the plate



Fig. 143. Dejean's Apparatus.

P (Fig. 134), when the record is taken photographically, the temperatures as abscissæ and the rate of cooling $\frac{d\theta}{dt}$ as ordinates. Dejean has used this method in the study of steels and has also investigated with it the copper-cuprous oxide system. The transition temperatures are very sharply marked. If desired, direct reading may be substituted for the photographic recording, with an increase in precision. Unless the temperature is changing rapidly, however, this method lacks sensitiveness. It is evidently a perfectly general method for recording the rate of change of E.M.F. $\left(\frac{dE}{dt}\right)$.

In neither Le Chatelier's nor Dejean's arrangement can differences in the rate of heating or cooling due to the substance itself be distinguished from those due to external causes, since no neutral piece is used (see page 382). **Temperature Time Recorders.**—There have been a great many types of instruments constructed for recording temperatures directly in terms of time for use with thermocouples. The early forms were for the most part photographic, giving continuous records, while many of the more recent ones are autographic, which usually give discontinuous results. We can mention only a few which illustrate sufficiently well the principles involved.

The Apparatus of Sir Roberts-Austen. — On account of its historical interest as well as its intrinsic usefulness, we shall first describe, with some of its modifications, the photographic apparatus of the late Sir Roberts-Austen, director of the royal mint at London.

A vertical slit lighted from a convenient source projects its image, by means of the galvanometer mirror, on a metallic plate pierced by a fine horizontal slit, and behind this slit moves a sensitive surface — plate or paper — which receives the luminous beam, defined by the intersection of the horizontal slit with the image of the vertical slit. If all were at rest, the impression produced by this luminous beam would be reduced to a point. If the plate alone is moved, a vertical straight line will be had; if the galvanometer mirror alone turns, a horizontal line. Finally, the simultaneous displacement of the plate and mirror gives a curve whose abscissæ represent temperatures, and whose ordinates, time. The illumination of the slit and the motion of the sensitive surface may be realized in many different ways.

Regarding the *lighting of the slit*, there are two quite distinct cases to consider, — that of laboratory researches by rapid heating or cooling, which last only a few minutes, and that of continuous recording of temperatures in industrial works, which may last hours and days, that is to say, periods 100 times to 1000 times longer. The rate of displacement of the sensitive surface, and consequently the time of exposure to the luminous action, may vary in the same ratio. The luminous source necessary will be therefore quite different, depending upon the case. For very slow displacements it is sufficient to use a small kerosene lamp with a flame of 5 to 10 mm. high. For more rapid displacements

400

HIGH TEMPERATURES

use may be made of an ordinary oil lamp, an Auer burner, or an incandescent lamp; finally, for very rapid displacements of the sensitive plate, 10 mm. to 100 mm. per minute, one may advantageously employ the oxyhydrogen flame or the electric arc. For oxyhydrogen light the most convenient is the lamp of Dr. Roux, with magnesium spheres; it consumes little gas and is inclosed in a metallic box which prevents all troublesome diffusions of the light. In more modern apparatus the Nernst lamp is often used.

The electric arc gives much more light than is needed, and the rapid wearing away of the carbon, by displacing the positions of the luminous point, renders difficult the permanence of suitable illumination of the slit. For very short experiments one may very conveniently use the mercury lamp in vacuo (Fig. 144) or



mercury lamp exist, however, which are free from this trouble. Fig. 144.

Mercury Lamp.

Whatever the luminous source employed, the slit may be always lighted by means of a lens

arranged as was indicated for discontinuous recording, that is, projecting upon the galvanometer mirror the image of the luminous source. When this is large enough, it suffices to place the slit before the luminous source, bringing it up close enough so as to be sure that some of the luminous rays, passing through, fall upon the mirror. But there is danger here of so considerably heating the slit that it may be altered; for this reason one is led to use more voluminous light sources than would otherwise be necessary. In the case of the use of a lens, the useful luminous intensity is as great as in placing

the slit immediately next to the luminous source, so long as the image of the latter is greater than the galvanometer mirror; now with the ordinary dimensions of the sources employed this condition is always fulfilled without any special precaution.

Instead of a slit lighted by a distinct luminous source, use may be made of a platinum wire, or better, as does Charpy, employ a carbon filament of an incandescent lamp heated by an electric current.

In order that the line traced by the recorder be very fine, it is necessary that the two slits, the luminous slit and the horizontal slit, be equally fine. Skillful mechanicians can cut such slits in metals. But it is easier to make them by taking a photographic plate of bromide gelatine that has been exposed to the light, developing until completely black, then wash and dry. By cutting the gelatine with the point of a penknife guided by a ruler, one may get transparent slits of a perfect fineness and sharpness.

For sensitive surfaces, use is made of plates or films of bromide gelatine. Professor Roberts-Austen employed exclusively plates which permit more easily the printing of a great number of positive proofs. Charpy, in his researches on the hardening of steel, made use of sensitive paper, which permits a much more simple installation.

For industrial recording, paper would allow of the employing large rolls lasting several days, as in the recording magnetic apparatus of Mascart. But in general one wants to have quickly the results of the record; this is always the case in laboratory investigations, and almost always in industrial studies. It is thus preferable to be content with quite short bands of paper rolled on a cylinder. There exists such a model quite well known and easy to use: the recording cylinders with an interior clock movement of the firm Richard, Paris. They may be ordered from the maker with any desired rate of rotation; unfortunately, this rate cannot be changed at the pleasure of the operator, a desideratum in laboratory investigations.

In the apparatus used by Charpy, or in its very elaborate form. as constructed by Toepfer of Potsdam, for Kurnakow, the ver-

HIGH TEMPERATURES

tically moving plate is replaced by a rotating cylinder wound with the sensitized paper on which the deflections of the galvanometer are registered. This form of recorder had also been used and discarded by Roberts-Austen. Fig. 145 represents the installation of the recording pyrometer used by Charpy in his researches on the quenching of steel. To the right is the galvanometer, to the left the Richard recording cylinder, and in the middle the electric furnace used for heating the samples of steel. It is interesting to note in passing that Charpy was the first to use electric heating in this kind of work. Kurnakow's apparatus, which must be placed in a dark room, is furnished with an



Fig. 145. Charpy's Apparatus.

auxiliary telescope and scale system using red light, so that the experiment may be controlled during the taking of a record. As constructed, five speeds may be given to the cylinder; and there is provided an E.M.F. compensating system for maintaining the maximum sensibility over a series of temperature ranges.

There is another device, used by C. L. A. Schmidt, by which the experiment may be watched while a photographic record of a cooling curve is being taken. It consists in shunting the sensitive photo-recording galvanometer G (Fig. 146), in series with a high resistance R, across a direct-reading millivoltmeter V. If the resistance of R + G is great compared with that of V, the readings of the millivoltmeter will not be altered appreciably by this operation. Schmidt moves the photographic plate, mounted as in the apparatus of Roberts-Austen, by means of a screw driven by a small motor. In this way any desired speed may be given to the plate.



If *plates* are used, they may be placed in a movable frame regulated by a clock movement; this is the first arrangement employed by Professor Roberts-Austen (Fig. 147). But this installation, somewhat costly and complicated, has the same disadvantage as the recording cylinders, in that but a single speed can be given to the sensitive surface. In order to drive the plate,



Fig. 147. Apparatus of Roberts-Austen.

Roberts-Austen later used a buoyed system in which the rate of rise of level of the water is controlled at will by the agency of a Mariotte's flask and a simple water cock. The plate is kept in an invariable vertical plane by means of two lateral cleats whose friction is negligible on account of the mobility of the float. The sketch (Fig. 148) gives the arrangement of a similar appa-

404

HIGH TEMPERATURES

ratus made by Pellin for the laboratory of the Collège de France. It carries a 13 by 18 cm. plate which is attached to the float by



means of two lateral springs not shown in the sketch. Neither are the two guides of the float, immersed in water, indicated; the play next the cleats is only two-tenths of a millimeter. The uncertainty that this play can cause in the position of the plate is quite negligible. The curve (Fig. 149) is the reproduction of an experiment made with such an arrangement by Roberts-Austen on the solidification of gold.

Fig. 148. Plate-holder.

During the whole period of freezing the temperature remained stationary, then lowering of temperature was produced at a regularly decreasing rate as the temperature of the metal approached that of the surroundings.



It is indispensable to trace, on each sensitive surface on which is to be recorded a curve, the line corresponding to the surrounding temperature, or at least a parallel reference line. This is very easy in the case of the guided plate or of the paper rolled on a cylinder. It suffices, after having brought the couple to the temperature of its surroundings, to displace in the opposite

direction the sensitive surface; the second curve traced during this inverse movement is precisely the line of the zero of the graduation of the temperatures. But this is a dependence that may be evaded by registering at the same time as the curve a reference line by means of a fixed mirror attached to the galvanometer in the path of the luminous beam which lights the movable mirror. Roberts-Austen likewise made use of the luminous beam reflected by the fixed mirror to inscribe the time in a precise manner. A movable screen driven by a second pendulum cuts off at equal intervals of time this second luminous beam. The reference line, instead of being continuous, is made up of a series of discontinuous marks whose successively corresponding parts are at intervals of one second, as is shown in Fig. 149.

The curves once obtained must be very carefully examined to recognize the points where the gradient presents slight anomalies, characteristic of the transformations of the body studied. Generally these irregularities are very insignificant, and it would be well, in order to recognize them with certainty, to obtain curves traced on a much greater scale. Practically this magnification is not possible without auxiliary devices which limit either the range or the sensibility; thus the sensitiveness of the galvanometer may be increased, and so the deflection, but then for the greater range of temperature the luminous image would fall off the sensitive plate.

In practice it has been found difficult to realize conveniently a sufficiently steady motion of the plate in the Roberts-Austen system of recording, and attempts have been made to devise methods in which the photographic plate remains fixed in position. This has been successfully accomplished by Saladin, whose apparatus (Fig. 160, page 419) has been modified by Wologdine to give the temperature-time curve by removing the prism Mand substituting for the second galvanometer G_2 a plane mirror turning about an horizontal axis. This mirror may be controlled by an hydraulic system as in Roberts-Austen's apparatus, or by clockwork as in the model constructed by Pellin of Paris. The deflection of the galvanometer G_1 gives to the beam of light an

406

HIGH TEMPERATURES

horizontal motion over the plate proportional to the temperature, while the vertical motion of the beam of light is given by the mirror turning at a uniform rate, and is therefore approximately proportional to the time as registered on a flat plate.

Autographic Recorders. — To obtain a satisfactory autographic or pen record with platinum thermocouples without sacrifice of sensibility of the galvanometer, it is necessary to eliminate the friction of the pen or stylus upon the paper. This has been accomplished by the use of mechanisms which cause the pen or stylus at the end of the galvanometer boom to make only momentary contact with the moving paper.*



Fig. 150. Siemens and Halske Recorder.

In the Siemens and Halske form of instrument (Figs. 150 and 151), the paper P is driven forward by the same clockwork that controls the pressing down, by means of the arm B, of the stylus N, which imprints dots periodically on the paper by means of a typewriter ribbon running across and beneath the record sheet. This system permits of taking a record continuously over very

* There are a considerable number of thermoelectric recorders. Among the manufacturers of these instruments are: Siemens and Halske, Berlin; Hartmann and Braun, Frankfort a. M.; Pellin, Chauvin and Arnoux, Carpentier, and Richard, Paris; Leeds and Northrup, the Thwing Instrument Company, and Queen of Philadelphia; the Scientific Instrument Company of Cambridge, England, and Rochester, N. Y.; the Bristol Company, Waterbury, Conn. long periods of time. In most of the other recorders the paper is wound upon a drum, and various devices are used to obtain the record; thus in the Hartmann and Braun type a silver stylus makes sulphide dots on a prepared paper, and in the Cambridge thread recorder rectangular coördinates are obtained by having the galvanometer boom strike an inked thread which runs parallel to the drum (Fig. 152).



Fig. 151. Principle of Recorder.

A Siemens and Halske drum recorder with pivot galvanometer, suitable for technical work, and which is inclosed in a dustproof metallic case, is shown in Fig. 153. It may be adjusted for seven-day records.

As previously stated, these autographic instruments all give intermittent records for the platinum thermocouples, and are limited to one or two speeds; and although they may be made very sensitive they are not adapted for the detection of transformations which take place very rapidly, since the recording

408

HIGH TEMPERATURES



Fig. 152. Thread Recorder.



Fig. 153. Drum Recorder.

interval cannot readily be shortened much below 10 seconds, and in most instruments this interval is greater than 15 seconds. In other words, they can be used advantageously only for slow cooling or heating.

A continuous pen record may be obtained with galvanometers suited for use with the base-metal couples developing high E.M.F.'s, such as the Bristol, Hoskins, Thwing, etc.

In order to eliminate the effect of irregularity of outside conditions which influence the rate of cooling, a method commonly



Fig. 154. Furnace and Charge Temperature Curves.

used when endeavoring to detect small transformations consists in placing a second thermocouple in the furnace, but sufficiently removed from the substance studied to be uninfluenced by its behavior. Alternate readings on the temperature of the test piece (θ) and of the furnace (θ') are then taken, preferably at definite time intervals. The data are most readily discussed by plotting the two temperature-time curves side by side as shown in Fig. 154, or by plotting the difference in temperature $\theta - \theta'$ against the temperature θ of the test piece.

This method may be made recording either by using two in-

HIGH TEMPERATURES

struments or by modifying one of the above-mentioned autographic recorders so as to trace the curves of two thermocouples on the same sheet. In practice, however, this method is usually resorted to only when great sensibility is desired, as in detecting minute internal-energy changes, when the potentiometer combined with the deflection galvanometer is the most sensitive and quick-working arrangement for taking the measurements. It is convenient to use thermocouples of the same composition so as



Fig. 155. Brearley Curve Tracer and Accessories.

to have readings of both the temperature of the sample and of the furnace given by the same potentiometer setting, and so depend upon the galvanometer deflections for measuring the residual parts of θ and θ' .

Regarding the precision of this method, it is to be noted that the quantity it is really desired to measure is $\theta - \theta'$ in terms of θ , and this is accomplished by measuring θ and θ' , hence the sensibility of $\theta - \theta'$ is no greater than that of θ or θ' . In other words, the method requires the maximum refinement of measurement to obtain the quantity sought, as well as the maximum of computation or plotting to reduce the observations.

Semi-automatic Recording. — The Brearley curve tracer, manufactured by the Cambridge Company, is a semi-automatic apparatus for registering the time-temperature curve. As shown with accessories in Fig. 155, a small tube furnace is connected to an electric supply main so as to heat the specimen within the furnace; a platinum-iridium couple, whose hot junction is within the specimen, is connected in series with a resistance and moving coil galvanometer of adjustable sensibility; a Nernst lamp furnishes



Fig. 156. Curves with Brearley Apparatus.

illumination and gives a sharp image at M on the scale G. The rotating drum L is surmounted by a sliding carriage N carrying two pointers, one of which, M, is fixed, and the second, immediately below, carries a pen and is depressed every second on the paper wound on the drum. The pointer M is made to follow the spot of light by the operator by turning a handle at the end of a long screw on which N runs. There is electromagnetic clock control of the drum and of the pen. The record is therefore a series of dots one second apart. The temperature scale may be made as open as desired, and a complete heating and cooling curve for a steel sample may be obtained in a few minutes. This instru-

412

HIGH TEMPERATURES

ment is also now made to give a continuous record. A sample curve is shown in Fig. 156.

Another method of working, in which the apparatus is completely autographic for relatively short temperature intervals, and at the same time very sensitive, is to use a recording galvanometer in connection with a potentiometer. This requires the operator to adjust the dials of the potentiometer to step from one temperature interval to the next, these intervals varying in length with the galvanometer sensibility, which should be capable of adjustment to give longer or shorter temperature intervals.

Differential Curves. — The method of page 411 may readily be modified so as to give $\theta - \theta'$, the difference in temperature between the test piece and furnace, by direct measurement instead of by computation, with the added advantage that the precision



Fig. 157. Method of Burgess.

of $\theta - \theta'$ may be made very great as compared with that of θ , the temperature of the sample. This may be accomplished, for example, by placing a commutator, which may be driven by a clock mechanism, in the thermocouple circuit at A, Fig. 157, so that alternate measurements on θ and $\theta - \theta'$ may be taken in terms of the time. Evidently the connections may be made so that either the galvanometer G_2 of the same direct-reading or potentiometer system that measures θ , or a separate instrument G_1 , as shown in the figure, may be used to measure $\theta - \theta'$. Both galvanometers may be photographic or autographic recorders.

Use of a Neutral Body. — Accidental variations in the indications of the auxiliary thermocouple giving θ' , the furnace temperature, may largely be eliminated by placing this couple within a blank or neutral substance. The material of the neutral body should be such that it undergoes no transformations involving an absorption or evolution of heat within the temperature range studied, such as a piece of platinum, porcelain, or even in some cases nickel or nickel steel. It is also desirable that the sample and neutral have as near as may be the same heat capacities and emissivities. The sample to be studied and the neutral piece are placed near together and arranged symmetrically with respect to the temperature distribution within the furnace.

To Roberts-Austen again was due the credit of first devising a sensitive differential method using the neutral body. He also modified his photographic recorder (Fig. 147) so as to give, by means of a second galvanometer, the $\theta - \theta' vs t$ curve on the same plate with the $\theta vs t$ curve, from which a curve giving $\theta - \theta'$ in



rig. 150. Ose of Neutral, Roberts-Austen.

terms of θ could be constructed. His arrangement of the directreading and differential thermocouple and galvanometer circuits is shown in Fig. 158 in which S is the sample or test piece, and N the neutral body possessing no transformations; the galvanometer G_2 measures the temperature θ of the sample, and G_1 measures the difference in temperature $\theta - \theta'$ between the sample and the neutral. Curves for steels and alloys were usually taken with the samples in vacuo.

It is evident that Roberts-Austen's final photographic apparatus, although very sensitive, was also complicated and very delicate of adjustment, and in practice it took great skill in its use, requiring for instance some three or four successive exposures adjusted to the proper adjacent temperature ranges, to take the cooling curve of a steel from 1100° to 200° C.

414