

CRITICAL RANGES A₂ AND A₃ OF PURE IRON

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INTRODUCTION

The question of the allotropy of iron, in spite of a vast amount of experimental work and perhaps an even greater amount of theorizing, is not yet settled. That there is a definite transformation in iron near 900° , the A_3 point, is generally recognized, as well as the fact that the temperature of this transformation is lowered by the addition of carbon and metallic elements. On heating the transformation Ac_3 is always found at a higher temperature than the transformation Ar_3 on cooling. Whether the A_3 transformation is sharp, like the melting point of a pure substance, or extends over a considerable range of temperatures, embracing perhaps as a lower limit the A_2 change, appears to be still an open question for pure iron. The nature and identity of the A_2 transformation, it would appear from recent publications, has not yet been satisfactorily settled.

In the present paper there is given a critical, historical summary of the experimental investigations of the location of A_2 and of A_3 in pure iron, together with brief mention of some of the theoretical aspects of the subject, and an account of a series of experiments carried out with several samples of very pure iron which were studied by two methods of thermal analysis in the range 500°C to 1000°C , and which it is believed furnish a contribution of considerable interest as to the location and nature of the A_3 and A_2 transformations.

Great attention has been given to the details of experimental manipulation and to the preparation of the samples, as it was soon found that some of the discrepancies noted in the work of many experimenters may be traced largely to lack of precautions which we have found essential.

For example, to anticipate somewhat, it is necessary to provide a suitable, practically gas-free furnace, the heating and cooling of which may be regulated to a nicety; to reduce to a minimum the deforming effects on the cooling and heating curves due to the poor conduction of the sample, it must be of a form and mass to pass on its heat rapidly and completely to the thermocouple; and finally, the sample itself should be free from gases, which, if present, further mask the definiteness of the heating and cooling curves. We have also varied within wide limits the sev-

eral factors which may influence the determination of the exact location and shape of the transformation ranges, especially the mass and preparation of sample, rate of heating and cooling, design of furnace, and finally, as nearly as it is experimentally possible, we have worked with a substance approaching pure iron, free from occluded gases and other impurities and contained within a vacuum.

A preliminary notice of some of the experiments carried out in 1911 and 1912 has already been published,¹ but since this work the experimental method has been greatly improved and several newly prepared samples investigated.

The methods of this investigation are described in considerable detail, as they are the same now being used in a new study of the iron-carbon system and because they are believed to be of some interest in themselves.

THEORIES OF THE ALLOTROPY OF IRON

Several explanations have been offered for the existence and nature of the transformations in iron, and the discussion of this subject has usually been linked with the transformations occurring in the iron-carbon system. For the consideration of *pure* iron, however, it seems simpler and sufficient to forget for the moment the iron-carbon system which has no more relation to pure iron than, say, the iron-manganese or iron-sulphur series of alloys. Furthermore, if there were agreement as to the facts concerning these transformations, the establishment of a satisfactory explanation in terms of well-known physicochemical principles should not be difficult. But we are in the presence of a double uncertainty, both as to facts and as to theory. Until the facts are well established and recognized any theory can be at best only a working hypothesis.

Briefly stated, the current hypotheses regarding the A₃ and A₂ transformations in iron are:

1. The critical points A₃ and A₂ divide iron sharply into three allotropic forms, γ -iron above A₃, β -iron between A₃ and A₂, and α -iron below A₂.
2. The critical point A₃ is the seat of an allotropic change, but the A₂ point is not, the transformation at A₂ being associated

¹ J. Iron and Steel Institute, 87, p. 335, 1913; J. Washington Academy, 3, p. 329, 1913.

mainly with the loss of magnetism which is accompanied by a small thermal change. Hence, there is no β -iron according to this theory, and the A2 transformation may be abrupt or spread over a considerable temperature interval as experiment may require

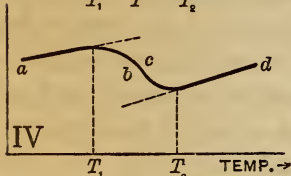
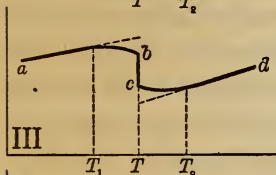
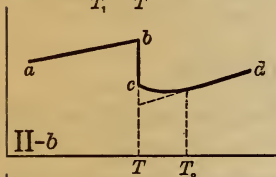
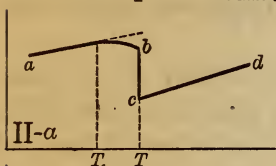
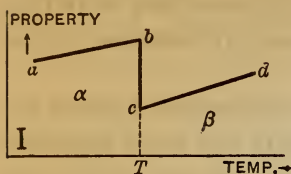


Fig. 1.—Types of allotropy
(Benedicks, Smits)

3. The critical range A2 is not independent of A3 but forms a part of the A3 transformation. Here, again, we have no β -iron, but to account for an evolution of heat on cooling at A2 requires assumptions regarding the mutual solubility of γ -iron in α -iron, and even the simultaneous existence in meta-stable equilibrium of two kinds of molecules of the same substance.

This last type of physicochemical equilibrium has been studied both theoretically and experimentally by Smits for several chemical systems, and for any particular case may be verified by noting the change in location of the transformation temperatures with rate of cooling.

Benedicks has put forth a theory of allotropy in which the allotropic change may be of several types,² as illustrated in Fig 1. Applied to iron, he would assign Type IIa, which relegates A2 to the end point of A3 or the temperature at which γ and α irons cease to interact. If A2 can be shown to be constant in position independently of rate of cooling, then Smits' analysis will not apply, and if A2 persists in magnitude and location for heating and

cooling through the A2 range and holding the sample a long time below A3 but above A2, Benedicks's hypothesis becomes of little meaning.

There are various other minor modifications of the above three hypotheses, all of which have been useful and perhaps none of which is without value in furnishing some part of a satisfactory explanation of the transformations in iron.

² These types may also be deduced from the theory of Smits.

PREVIOUS DETERMINATIONS OF A_2 AND A_3 IN IRON

We shall pass in review briefly the experimental evidence as to the existence and nature of transformations in iron at A_2 and A_3 , as shown from observations on the physical properties of iron, including dilatation, electrical and magnetic changes, specific heat, heat evolution and absorption, crystalline structure, and deformation under stress. As we are dealing with a single element, purely chemical changes would not be expected to shed any light on the question of such transformations, and there appear to be no strictly chemical data bearing on the subject, except some inconclusive work on the dissolving power for carbon.

In quoting the numerical values of the temperatures assigned to transformations as noted by the several observers (see Tables 1 and 2), it should be borne in mind that there are considerable discrepancies in the temperature scales used, and sometimes the method of experimental operation leads to incorrect temperatures of the phenomena measured. No general attempt is made here to correct the temperatures as given by the several observers, as for the most part such correction would be extremely uncertain. This uncertainty is further enhanced in some cases by the impurity of the samples of iron operated upon.

In this historical summary we are more concerned with the qualitative aspect of the transformations—their very existence, in fact—than their exact location, which latter we believe is most exactly defined by our own experiments.

Critical Ranges as Determined by Expansion.—Both from the work of Charpy and Grenet and of Broniewski, observations on the expansion of iron give no indications of the existence of A_2 . The former places the contraction observed as lying in the interval 860° to 890° for iron, with 0.03 carbon, while the latter finds it above 950° for electrolytic iron.

The disagreement is here great enough to again raise the question, as was done by Le Chatelier in 1899, of the rate and other conditions of heating, and also whether the sensibility of the methods used was great enough to detect A_2 . Even its non-existence, in so far as expansion is concerned, would prove only that iron immediately above and below A_2 has the same coefficient

of expansion, or simply that the A₂ transformation is unaccompanied by appreciable change in volume—a not unreasonable possibility. The more recent experiments of Rosenhain and Humfrey would appear to indicate a slight volume change accompanying A₂.

Critical Ranges by Thermoelectric Observations.—This method of operation is open to the serious objection, for the exact location and description of critical ranges, that the iron which forms one element of a thermocouple must be partly in a hot region and partly in a cold. The reactions due to whatever transformations take place will be progressive along the iron and thereby may mask any transformation on heating, for example, after the one taking place at the lowest temperature.

Using a Fe-Cu thermocouple, Broniewski finds for electrolytic iron a hazily defined point of inflexion at 730° and another at 950° on heating (or at 850° for 0.07 per cent carbon), but with a Fe-Pt couple he is able to detect only the point at 1020° which Müller claims is due to hydrogen. Both Harrison and Belloc fail to get any thermoelectric discontinuity with Fe against either Cu (Harrison) or Pt (Belloc) but appear to find a maximum for the curve of thermoelectric power at about 800°.

Thus, the thermoelectric data on the critical ranges of iron appear to be meager and of little value, and the thermoelectric method can not register transformations sharply except with an indefinitely short furnace, or one having no appreciable length between the inside and outside temperatures along the iron sample.

Critical Ranges in Terms of Crystalline Structure.—There appears to be practical unanimity of opinion concerning the evidence offered by the various investigations (Osmond and with Cartaud, Carpenter and Stead, Rosenhain and Humfrey, and others) concerning the existence of changes of crystalline structure, namely, that the A₂ region is not accompanied by any appreciable crystalline change while the A₃ transformation in pure iron is so accompanied. All these experiments appear to show there is no crystallographic difference between β and α iron, although there does not appear as yet to be perfect accord as to the nature of the crystalline change taking place at A₃.

Critical Ranges as Detected by Mechanical Methods.—The study of the mechanical properties of metals at high temperatures offers very great experimental difficulties, and as far as approximately pure iron is concerned the only experiments which shed any light on the detection of A₂ and A₃ by mechanical means are those of Rosenhain and Humfrey, who have carried out two series of measurements on tensile strengths, the first of a more qualitative nature in which an iron 99.76 pure, containing 0.03 carbon, was used, and the second, much more elaborate, with iron containing 0.1 per cent carbon. Both series show a distinct discontinuity for the A₂ range and for the A₃ range. (See Fig. 2.)

Critical Ranges as Given by Electrical Resistance.—The electrical resistance of approximately pure iron at high temperatures has been studied among others by Le Chatelier, Hopkinson, Morris, Boudouard, Harrison, A. R. Meyer, and Broniewski.

The observations show, when plotted as resistance (or ratio of resistance hot to resistance cold, R_t/R_{20}) against temperature, a continuous curve which begins to inflect at temperatures ranging from 700° (A. R. Meyer) to 800° or higher (Le Chatelier, Hopkinson). At about 900° to 950° the curve becomes nearly horizontal, as found by all observers, and according to Broniewski has another inflection at 1020°. This observer, however, took observations with the iron in an atmosphere of hydrogen, but Müller has shown that with electrolytic iron a critical point is obtained thermally in this region only until the hydrogen is removed by successive heatings.

The observations of Meyer appear to have been taken with considerable care on very pure samples of iron, and when plotted as dR/dt against t give a cusp at 700° and are strikingly similar to the magnetic susceptibility curves obtained by Curie and others, as shown in Fig. 2. The observations of Morris, who used iron 99.92 pure, give a sharp maximum for dR/dt at 765°, and Somerville gets one at 750° with an undefined "iron," while Boudouard finds two breaks in the $R:t$ curve, one at 775°, the other at 885°.

As in the case of nickel with a transition point in the region about 370°, the electrical resistance curve appears to anticipate, as it were, the A₂ transformation for iron, which as

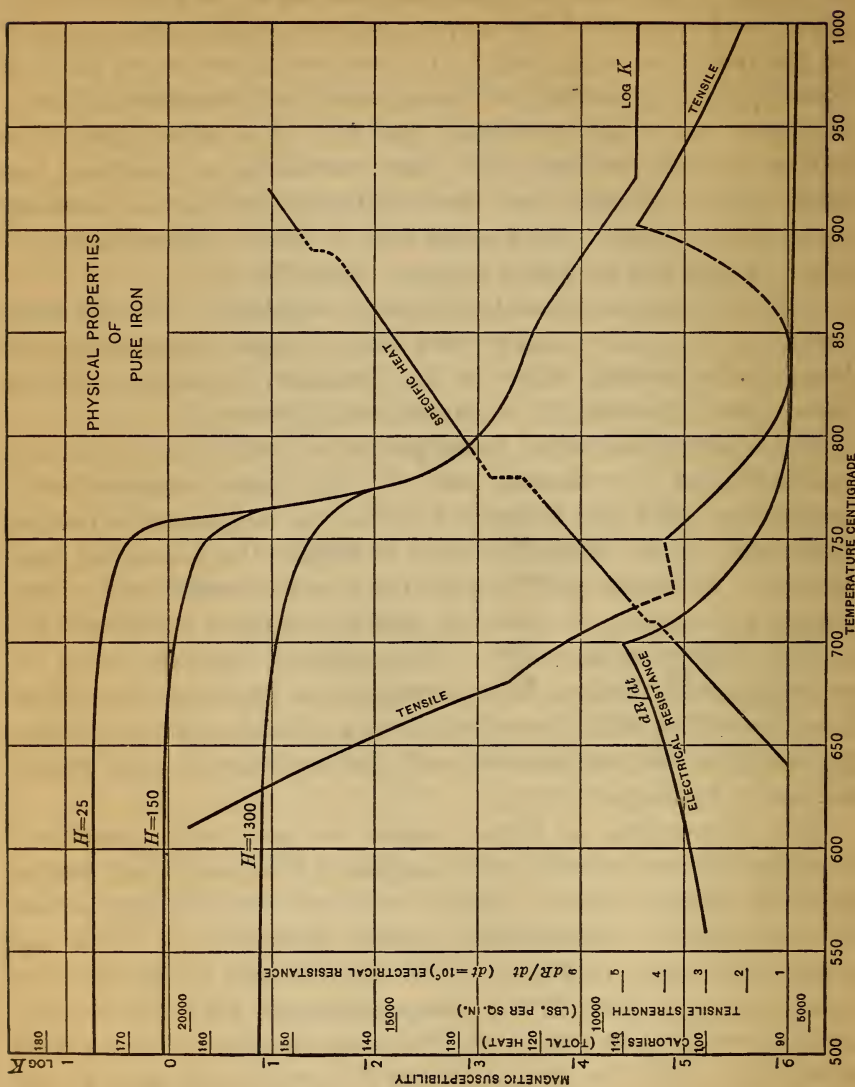


Fig. 2.—Physical properties of pure iron

measured by this phenomenon may be considered as starting some 60° or 70° below the maximum; or, in Benedick's nomenclature, is a transformation of Type IIa. The observations of Broniewski also show a second inflection (for A_3 ?) at about 950° , although, if present, this inflection should have been detected by Morris, Meyer, and others.

Critical Ranges as Determined Magnetically.—Hopkinson, using a wrought iron containing 0.01 per cent carbon and 0.362 per cent of other impurities, mostly slag, finds a cusp in the permeability curve at 775° , the permeability for a magnetizing force of 0.3 falling from 11 000 at 775° to 1 at 785° . With a mild steel containing 0.126 per cent carbon and 0.244 Mn, the peak is at 730° for the same small magnetizing force.

The exhaustive experiments of P. Curie show that the intensity of magnetization (I) is markedly dependent upon the value of the magnetizing force (H) for iron containing only 0.04 per cent carbon, and decreases (for all values of H) at first gradually with rise in temperature and above 700° with increasing rapidity, reaching almost to zero at 750° , where there is an abrupt turn in the $I:T$ curve. Above 750° the $I:T$ curve possesses no considerable variations until 1280° C. The magnetic susceptibility $k = I/H$ (plotted as $\log k:T$ in Fig. 2) decreases with great abruptness at about 750° , although the decrease in k begins gradually from below 625° (high values of H decreasing k at lower temperatures than low values of H). There is a further abrupt drop in k , beginning at about 860° , terminating sharply at 920° . Terry, and very recently Honda, find that ferromagnetism disappears on heating and reappears on cooling at 785° . At the laboratories of Schneider & Co. the loss and gain of magnetism are found to be associated with A_2 at about 770° .

The magnetic behavior of iron in the region about 750° appears in all respects similar to the behavior of other ferromagnetic substances, such as nickel, cobalt, and magnetite, in the region of their single magnetic transformation points, which for these substances, it is of importance to note, are also transformation regions as measured by other physical properties, such as electrical resistance, thermoelectricity, and thermal or calorimetric effects.

This last is well shown by the experiments of Weiss and his associates, who are able to compute from purely magnetic data obtained at higher temperatures the transformation points by means of the equation $k(T - \theta) = \text{const.}$, and compare them with the values obtained calorimetrically. In this way Weiss and Beck find:

Transformation points= θ -273	Calculated magnetically	Observed calorimetrically
Iron.....	753°	758°
Nickel.....	376	376
Magnetite.....	588	580

Later magnetic observations by Weiss and Foëx, who used less than 0.5 g, place the Curie point, θ , ($=A_2$) at 774° for electrolytic iron, divide the β region into two parts, β_1 and β_2 , and locate the transition from β_2 to γ iron with great sharpness at 920° .

Magnetically speaking, therefore, it appears reasonable to claim that the critical range A_2 for iron is strictly similar to the transformation taking place generally in ferromagnetic substances as they pass over into the feebly magnetic state. In addition, the iron undergoes a further distinct magnetic modification accompanying the A_3 transformation.

Critical Ranges as Determined Calorimetrically.—There have been several determinations of the specific heat of iron at high temperatures but for most of them in the range 700° to 950° the observations are not closely enough spaced to locate the critical ranges with definiteness.

Weiss and Beck were able to identify the Curie point computed from magnetic data with an abrupt change in the specific heat of iron at about 755° to 760° (or A_2) but did not go high enough in temperatures to reach A_3 .

Meuthen, using the vacuum furnace and calorimeter of Oberhoffer, has been able to locate both A_2 and A_3 with considerable exactness for iron containing 0.06 per cent carbon, in terms of the specific heat. (See Fig. 2.) He places A_2 at 770° to 790° and A_3 at 880° to 900° . Also A_2 remains constant in temperature to the point O in Fig. 3.

The calorimetric data, therefore, give positive evidence of the existence of A₂ for iron containing about 0.06 carbon.

From Meuthen's calorimetric observations, the amount of heat evolved at A₂ is about the same as at A₃, while by cooling curve methods all observers find the heat effect at A₃ at least three times that at A₂.

Critical ranges from heating and cooling curves.—An enormous amount of work has been done by thermal methods on the location of the critical ranges of steels and other ferrous alloys, much of which is very contradictory. This is discussed at length in several papers and especially in a recent one by Prof. H. M. Howe.³ While some light may perhaps be thrown on the position and properties of A₃ for pure iron from an examination of the behavior of impure irons, for the A₂ transformation in pure iron, we would expect to learn little or nothing from a study of impure iron, on account of the very small quantity of heat involved in the transformation, which one would expect to be considerably masked or attenuated by the impurities present.

It appears to be a remarkable fact, however, that, generally speaking, whenever A₂ is detected at all, it is always found at the same temperature, whatever the composition of the iron alloy. For example, the discussion by Prof. Howe would place the break at O in the line GOS, Fig. 3, at 769° C., which is exactly the temperature we find experimentally for A₂ maximum in pure iron. In other words, the A₂ line for the Fe-C system is horizontal, as shown by practically all existing data, and the A₂ point viewed in this way would appear to have the characteristics of a Fe-C eutectoid with the possible important if not crucial exception, of which we do not appear as yet to have sufficient experimental proof, that the quantity of heat

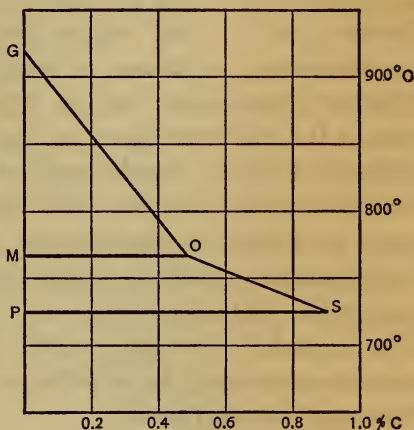


Fig. 3.—Part of Fe-C diagram

³ H. M. Howe; "Discussion of the existing data as to the position of Ac₃," Trans. Am. Inst. Mining Engrs., 46, p. 1099; 1913.

involved in the A₂ transformation does not vary appreciably with the carbon content from zero to 0.48 per cent. This constancy of heat of transformation, together with its constancy in temperature, if both be definitely proved by using a pure Fe-C system, lend force to the idea that A₂ is a transformation independent of the carbon present, and from the work of Moore and others A₂ appears to be independent in position also of metallic components.

As to A₃, the comprehensive discussion by Prof. Howe leads to an equilibrium temperature Ae₃ of 917° for pure iron. This temperature A₃=917° also satisfies the observations of practically all recently published work with very pure iron.

Returning to the A₂ range in pure iron and its location by heating and cooling curves, we are confronted by considerable contradictory evidence as to its existence, location, and type, whether possessing one or two cusps. Prof. Benedicks⁴ discusses the evidence given by the thermal experiments of Osmond, Roberts-Austen, Arnold, and others and gives as well a concise critical summary of the whole subject of the nature of A₂ in pure iron, as shown by experiment, and concludes that A₂ is not an independent transition point but forms a part—a tailing off—of A₃, which latter is taken as a transformation of Type IIa (see Fig. 1) and, “according to this, the nature of the β -iron is to be α -iron containing in solution a limited amount, increasing with temperature, of γ -iron.”

Since Benedicks's publication we have the experiments of Carpenter, which he would have taken as verifying Benedicks's (or Smits's) theory; of Guillet and Portevin, who appear to find A₂ and A₃ as distinct transformations; and of Broniewski, whose results are ambiguous.

Let us consider the experiments of Carpenter more closely. His observations of 1904, taken in association with Mr. Keeling on iron containing 0.01 per cent carbon, showed Ar₂ sharply defined at 762° and Ar₃ at 900°. Carpenter's observations of 1913, using iron with 0.007 per cent carbon or of a carbon content hardly detectable in difference from his iron of 1904, also show

⁴ C. Benedicks: “On allotropy in general and that of iron in particular,” *Jl. Iron and Steel Inst.*, 86, p. 242; 1912.

Ar₂ as present but not sharply defined and ranging from 768° to 741°, while Ac₂ is not in general clearly defined by his curves except as a swell. The main differences in these two series appear to be that solid, rolled cylinders of iron five-eighths by five-eighths inch were used in the earlier, while in the later sheets of electrolytic iron 0.01 inch in thickness were rolled into a cylinder weighing 42 g. The curves differ in the main, as one would expect, the poorer conductivity and the presence of gases in the wound-up sheets of otherwise untreated electrolytic iron, producing a flattening out, distortion, and displacement of the critical regions, especially of the feebler A₂. Similar remarks apply to the recent experiments of Honda, who used iron cylinders 3.25 cm long, and concludes that A₂ is not sharply defined.

Several experimenters, notably Arnold, insist that A₂ has a double cusp for pure iron, while it would appear from the work of several others, notably Carpenter and also Rosenhain, that A₂ is erratic, sometimes showing a double and sometimes a single cusp.

Considering all the hitherto available data, there can be hardly any doubt that thermally there is a critical range for pure iron in the neighborhood of 770° (A₂); but whether this be separate from the higher critical range near 900° (A₃) and whether it (A₂) be single or double cusped, the existing thermal observations do not prove conclusively, but a fair inference would be that A₂ is single and independent of A₃.

TABLE 1

Thermal Maxima of Critical Ranges of Pure Iron by Various Observers

Observer	Date	Carbon content, per cent	Iron content by dif- ference	Ac2	Ar2	Ac3	Ar3	Remarks
Osmond	1887	750	890	Ar3 corrected from 855. Two maxima for Ar2.
Roberts-Austen	1891	0.007	(?)	895	
Arnold	1894	.003	99.967	740	740	860	854	Ar2 is double.
Charpy	1895	.007	740	730	865	840	
		.009	744	731	903	860	
Charpy and Grent	1903	tr.	775	730	935	900	
		.05	755	730	885	860	
Osmond	1899	Electrolytic Fe	800	780	905	880	
Carpenter and Keel- ing.	1904	.01	99.803	762	900	
Harkhort	1907	99.89	691 to 763	764 to 759	910 to 917	888 to 875	
A. Müller	1909	.017	99.803	770	763	917	894	23 observations in vacuo, all agreeing very closely.
Rosenhain and Hum- frey.	1909	.029	99.66	770	763	941	904	
E. Colver-Glauert	1910	Fe "Kahl- baum."	A2 is double.
H. C. H. Carpenter	1913	.008	99.967	(?)	768 to 741	902 to 938	898 to 886	Ac2 not detected; 2 samples of same analysis; 10 ob- servations.
Guillet and Portevin	1913	Not detected.	99.96	791 788	778 778	937 932	902 902	As deposited } Electro- Annealed } lytic.
Honda	1913	Fe "Kahl- baum."	795	787	933	915	A2 not sharp.

Summary of previous determinations of A₃ and A₂ in pure iron.—Without for the moment considering any theory concerning the meaning of the transformations in pure iron, let us consider what is the present experimental basis for the existence of A₂ and A₃, either as separate or associated transformations.

A summary of most of the experiments that have been made is given in Tables 1 and 2; the former includes only heating and cooling curve methods and the latter all others. These tables, taken in connection with the preceding paragraphs, show that

there is overwhelming evidence for a discontinuity in properties of pure iron for the intervals of temperatures roughly defined as 700° to 780° and 850° to 950°, or corresponding to the critical ranges A2 and A3. (See also Fig. 2.)

TABLE 2

Critical Ranges in Pure Iron by Other than Cooling Curve Methods

Observer	Date	Carbon content per cent	Iron content by difference	A2	A3	Method and remarks
P. Curie.....	1895	0.04	99.9+	750	920	Magnetic
Morris.....	1897	{ 0.006	99.925	765	Electrical resistance
		{ 0.010	770 to 780	Magnetic
Hopkinson.....	1889	{ 0.006	99.515	(?)	880	Electrical resistance
		{ 0.010	99.128	775	Magnetic, cusp μ vs. T curve
Le Chatelier.....	{1890	780	Electrical resistance
	{1899	0.057	99.763	(?)	840	Expansion
Osmond.....	1900	Electrolytic	(?)	Detected	Crystallographic
Harrison.....	1902	(?)	(?)	{ Uncertain	Thermoelectric Cu-Fe couples, H atmos.
				760?	Electrical resistance
Belloc.....	1903	(?)	"Pure iron"	(?)	(?)	Thermoelectric
Charpy and Grenet..	1903	0.03	860 to 890	Expansion
Boudouard.....	1903	? Commercial	775	885	Electrical resistance
Weiss and Beck....	1908	(?)	760	Calorimetric; A3 not measured
Rosenhain and Humfrey	{1909	0.029	99.767	Detected	Detected	Tensile and crystallographic, quali- tative only
	{1913	0.106	99.374	750	910	Tensile strength
Terry.....	1910	0.012	99.30	785	910	Magnetic
Somerville.....	1910	0.012	"Iron"	750	(?)	Electrical resistance
A. R. Meyer.....	{1911	{ 0.00	99.976	700	(?)	Fe "Kahlbaum" } Electrical resist-
		{ (?)	99.94	700	(?)	Ingot Iron } ance, cusp of
		{ 0.00	99.85	705	(?)	Electrolytic } dR/dt curve
Weiss and Foëx....	1911	Electrolytic	774	Magnetic; A3 not measured
Meuthen.....	1912	0.06	99.960	780	890	Calorimetric
Broniewski.....	{1913	{ 0.07	99.87	730	850	Thermoelectric
		{ Electrolytic	950 (a)	(a) by Fe-Cu,
				730 (a)	1020 (b)	(b) by Fe-Pt couple
				750 to	950 and
				850	1020
				700?	890 to 950	Expansion
Stead and Carpenter.	1913	0.007	99.967	Not detected	Detected	Crystallographic
Schneider et Cie....	1913	0.060	99.378	770	Magnetic
Honda.....	1913	"Kahlbaum"	785	Magnetic

The existence of A_3 is not open to question, it having been readily located by practically all methods of physical analysis, with the possible exception of electric resistance and thermoelectricity for which any discontinuity is not well defined. The magnetic change is also small, but abrupt and unmistakable. The thermal observations, which give the sharpest definition of A_3 , show that the maximum of Ar_3 is always lower in temperature than that of Ac_3 .

Controversy has raged for a quarter century not only about the nature and extent but as to the very existence of A_2 , which has, however, been generally identified with the loss of ferromagnetism in iron. The point of inflection of the electrical resistance curve appears to be associated with the A_2 region, as well as an abrupt change in specific heat of the same magnitude as at A_3 . The thermoelectric effect appears not less uncertain than at A_3 ; there is a small but an abrupt change in tensile strength at A_2 ; and there is a small thermal effect on heating and cooling which appears to remain at a constant temperature for the addition of carbon or metallic components in considerable quantities. Apparently the only phenomenon studied, which has hitherto always given negative results for A_2 , is crystalline structure.

Most, although not all, of the phenomena appear to indicate that A_2 differs from A_3 , in that for the latter the transformation is abrupt, taking place at a higher temperature with ascending temperature than with descending, while for the former, the transformation is more gradual (of Type II *a*, Fig. 1), but has the same location of maximum on heating and cooling. That A_2 and A_3 are parts of a single transformation, A_2 being subordinated to A_3 , is a conclusion to be drawn with some difficulty from the data, and as pointed out by Guertler it is difficult to construct any plausible physicochemical theory which would admit of a distinct heat evolution at A_2 and still have A_2 a part of the A_3 transformation, for "the end point is never marked by a sudden evolution of a new and constant thermal effect at a given temperature."

THE PRESENT INVESTIGATION

The object of the present investigation is to determine, with several samples of pure iron of different sizes, prepared by various methods, the exact location and nature of the A_2 and A_3 ranges,

using the most refined methods of thermal analysis and keeping the samples free from the masking influences of occluded gases.

Experimental Method.—Two methods of taking heating and cooling curves have been used simultaneously on the same sample; one, the inverse-rate method of Osmond in which the times required for the specimen to rise or fall successive, equal temperature intervals are noted in terms of the temperature or $(dt/d\theta$ vs $\theta)$; the other, the derived differential method of Rosenhain, in which the observations are taken by the differential method of Roberts-Austen, using a “neutral” of platinum,⁵ and in which for equal decrements or increments of temperature the difference in temperature between specimen and neutral is taken in terms of the temperature of the specimen $(\theta - \theta'$ vs $\theta)$ for $\Delta\theta = \text{const.}$ The results so obtained by the differential method are transformed into the derived differential curve by the operation of dividing the differences $\theta - \theta'$ for each temperature interval $\Delta\theta$ by this interval and plotting in terms of θ , or giving:

$$\frac{d(\theta - \theta')}{d\theta} \text{ vs } \theta$$

These two methods of thermal analysis supplement each other most excellently as each is subject to different disturbing effects; and although obtained by totally different operations, the resulting heating or cooling curves are strictly similar, except for certain minor details which we shall mention later. To operate both methods simultaneously requires no more apparatus or observers than the differential method alone, although in this latter case the chronograph may, less conveniently, be replaced by any sufficiently exact timepiece. It is preferable to have two observers, although this is not essential.

The inverse-rate method is subject to error, due to drafts, sudden changes in current feeding the furnace, or any cause which may impress upon the specimen thermal changes not proper to it. Inversion of $dt/d\theta$ at recalescence, or an actual increase of temperature on cooling, is not readily expressible by other than a horizontal line in the plot; this weakness of analysis is of minor import, however, as the data on which the inverse-rate curve is

⁵ For a detailed description of the methods of taking cooling curves, see G. K. Burgess, Reprint 99, Bull. Bur. Standards, 1909.

based give, nevertheless, very sharply the beginning, maximum, end, and also, when present, the elevation in temperature accompanying a transformation. This last effect, of course, only accompanies a violent evolution of heat and is of no interest here.

The derived differential method is less subject to error due to extraneous influences; recalescence can not be any more readily expressed by this method of plotting than the other. The presence and properties of a neutral free from transition ranges, as is platinum, have no appreciable effect on the location of the critical points of a substance such as iron.

Arrangement of the Apparatus.—The general appearance and arrangement of the apparatus is shown in Plate I, and a schematic diagram, Fig. 4, gives the layout of connections.

Measurement of Temperature.—For this purpose thermocouples were used connected to a five-dial, low-resistance potentiometer designed to be free from thermal electromotive forces, of the Diesselhorst type as constructed by Otto Wolff.

The moving coil galvanometer (from Leeds & Northrup) used with the potentiometer had a constant sensibility for all parts of the range of the potentiometer as used, and gave when critically damped a deflection of 25 mm on scale and telescope at 2 meters for each 20 microvolts of emf of the thermocouple. As used, it had a resistance of 57 ohms and a period of two seconds. This sensibility, which was ample, could have been increased if necessary. The zero shift was not troublesome and the instrument was glass inclosed, reducing temperature inequalities. The method of operation, whether for calibration, inverse rate, or differential curves, was to note times, preferably on the chronograph, and this invariably, when taking inverse-rate curves, every time the zero of the scale passed the cross hair of the telescope; the dial of the potentiometer was then turned, say, two steps, corresponding to about 2° , throwing the zero of the scale back about 25 mm, and the operation repeated indefinitely. The sensibility is about 0.01° with the Pt, Pt-Rh thermocouples.

Measurement of Time.—For recording the time measurements necessary for the inverse-rate method and convenient with the calibration of the couples and with the differential methods use was made of a cylindrical, motor-driven Geneva chronograph together with a telegraph key which, when depressed, gave a dash

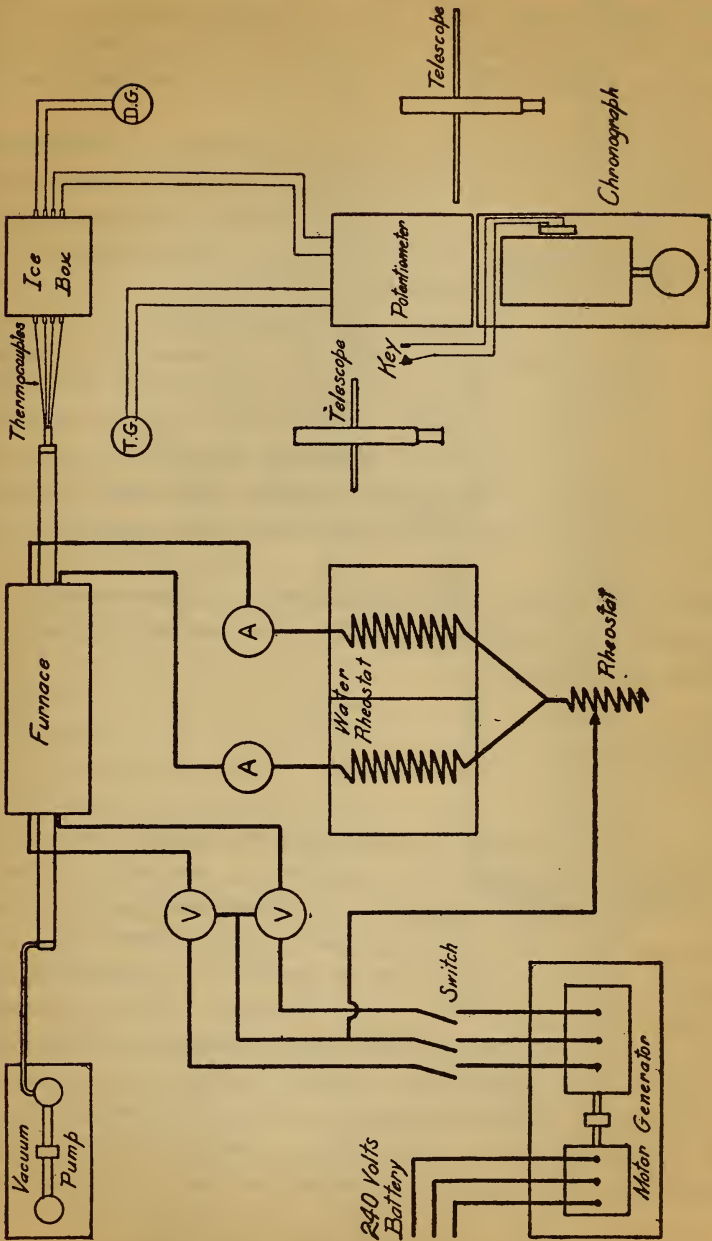


Fig. 4.—Diagram of apparatus

on the chronograph sheet easily distinguishable from the seconds marked on the same sheet with the same pen when actuated through a relay by a standard clock situated in a distant constant-temperature room. The time observations were easily obtained to 0.1 second.

Thermocouples.—In some of the preliminary work various thermocouples of 0.6 mm diameter were used, but the later more reliable measurements were all taken with three Heraeus 0.4 mm × 150 cm thermocouples of platinum, 90 platinum–10 rhodium, marked M_1 , M_2 , and M_3 , and all cut off the same batch of wire. These couples were frequently interchanged during the investigation. A differential thermocouple, M_4 , for measuring the difference in temperature between the iron sample and the platinum neutral, was made by fusing a length of 45 mm of 90 Pt–10 Ir wire between two lengths of platinum wire of the same grade as in the temperature-measuring couples. The cold junctions of all thermocouples were always kept at 0° in a suitable ice box. (See Fig. 4.)

Temperature Scale and Calibration of Thermocouples.—The temperature scale used is that defined by the freezing points of the following pure metals:

	°C
Zinc.....	419.3
Antimony.....	630.0
Silver.....	960.0
Copper.....	1083.0

The calibration of the thermocouples was carried out as follows: The metals were melted in crucibles 14 cm deep of Acheson graphite of about 300 cc capacity in an Heraeus electric resistance furnace wound with platinum foil. The thermocouples while immersed in the metal were protected by out-glazed Berlin porcelain tubes of about 5 mm diameter. Both freezing and melting points were taken several times for a first calibration, and the couples were occasionally checked at the silver point during the progress of the investigation and recalibrated at the close, when they showed no appreciable change. All (M_1 , M_2 , M_3) satisfied the same equation between 400° and 1100° C, namely,

$$\text{emf} = -313.8 + 8.259t + 0.001666t^2$$

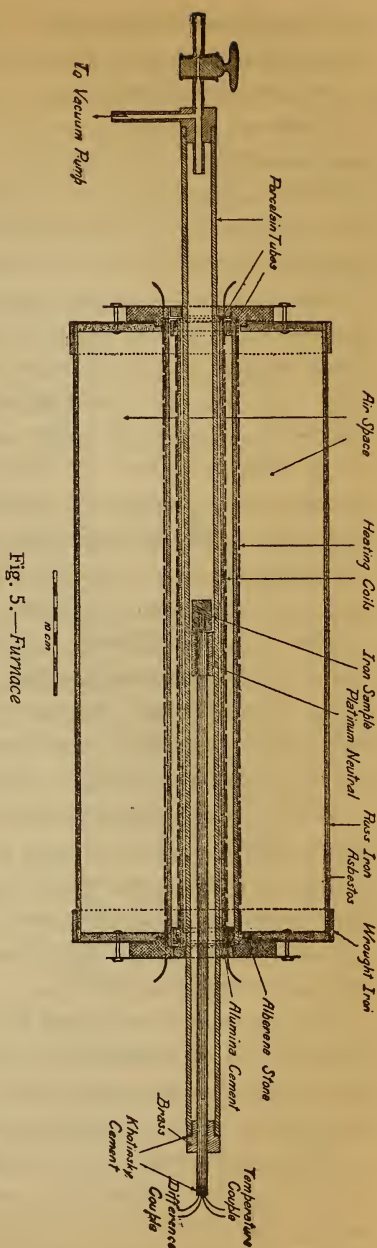
$t_0 = 0$

where emf is expressed in microvolts and t is temperature centigrade. All thermocouple wires were electrically annealed at about 1400°C before using.

It is interesting to note the excellent behavior of these thermocouples in direct contact with iron. The fact that there was practically no oxidation of the iron together with the fact that the metals were always in a vacuum of the order of 0.01 mm Hg probably accounts for this constancy.

Mounting of Thermocouples.—One junction of the differential couple together with the hot junction of the temperature measuring couple were inserted in the iron specimen under observation and the other differential junction, which was about 4.5 cm away, was inclosed within the neutral, a platinum cylinder weighing 98 g. The bare wires were in direct contact with the iron, and in fact when very small samples were used, as the 0.7-g sample of iron from Prof. Carpenter, the iron was hammered onto the couples. The sketch, Fig. 5, gives an idea of the arrangement when small cylinders (10 to 30 g) were used.

Differential Measurements.—The differential couple was connected directly to a Siemens & Halske moving coil galvanometer of 200 ohms resistance. Deflections were read by means of a telescope and scale 2.5 m distant. As connected, the galvanometer gave a deflection of 60 mm for 100 microvolts, corresponding to a sensitiveness of nearly 0.01°



with the Pt-Ir couple used. This was ample, and there would have been no advantage in increasing this sensitiveness, as could easily have been done fourfold by changing the galvanometer connections.

Furnace and Accessories.—The furnace, shown in Fig. 5, was constructed in the laboratory and consists essentially of four concentric tubes, three of Berlin porcelain and an outer one of iron backed with a one-eighth inch layer of asbestos. The innermost tube, which carries the specimens under study, is glazed both inside and out, so as to hold a vacuum, and extends beyond the furnace to receive seals of hard wax and metal for pump and thermocouple. There was no trouble in holding a vacuum of 0.01 mm Hg up to a temperature of 1050°. The two unglazed porcelain tubes each carry a separate heating coil of platinum foil 2 cm wide by 0.001 cm thick. In some of the preliminary work a furnace was used in which a single heating coil was wound directly on the glazed tube carrying the specimen. This earlier arrangement is less satisfactory than the one above described since the tube deteriorates sooner, and the uniformity of temperature is less well maintained. As will be noted, the furnace is provided with no other insulation than these concentric tubes, thus permitting, when desired, the use of faster rates of cooling and reaching more conveniently lower temperatures than when the furnace is packed with insulating material.

With the construction described there was no trouble whatever from drafts. The furnace was tested for freedom from critical ranges by taking several blank series of heating and cooling curve observations, using the usual platinum neutral and replacing the iron specimen with a cylinder of palladium. Some of these blanks are shown in Plate VIII.

The vacuum pump used is a two-cylinder motor-driven Geryk pump kept in condition to maintain a vacuum of 0.01 mm Hg in the furnace as measured with a mercury gauge and provided with drying tubes of phosphorus pentoxide.

The energy supply for heating the furnace was furnished by a 5-kw Siemens-Schuckert motor-generator set delivering alternating current to the furnace and operated on a 240-volt storage battery circuit. Two of the three phases generated by the alternator were used at a voltage which could be set anywhere between

50 and 170 volts. This somewhat elaborate arrangement was found to be highly desirable, when, as here, one is seeking minute thermal effects and every extraneous cause of variation in the rate of heating or cooling of the sample must be eliminated. There are two further advantages gained by using alternating current instead of direct for heating the furnace; it permits use of a liquid rheostat without polarization or electrolysis, and it eliminates any magnetic field about the iron sample. This last, if present, might conceivably influence the magnetic transformation in iron.

The rheostat, Fig. 6, deserves special mention, as it was specially designed to give automatically a constant rate of heating and cooling, variable at will within wide limits. In addition to the salt-water rheostat, wire rheostats were placed in the heating circuit.

It consisted of a cypress box of two compartments, each measuring 30 cm by 35 cm by 35 cm, in each of which were two copper plates (35 cm by 26 cm), placed 30 cm apart at the bottom and 1 cm apart at the top. A metal box through which cold water was circulated for the purpose of keeping the salt water cool was placed on each side of the partition. The outside copper plate in each compartment besides performing its functions as an electrode also formed one side of a wedge which opened at the top and could be filled with water before starting a run. This was done to cause the water which was fed at a constant rate from a Mariotte bottle to rise between the copper plates at a faster rate as the temperature of the furnace increased, thus overcoming the greater radiation losses to which the furnace is subjected at the higher temperatures and thereby giving a very constant rate over the whole range.

When taking cooling curves the water in the wedges was kept at the same level as the water in the compartment by connecting the two with a siphon; thus all the water was siphoned off at the same rate. A series of brass outlets were constructed and calibrated for this rheostat which gave a series of definite times of heating or cooling of the furnace, ranging from a few minutes to several hours.

THE MATERIALS INVESTIGATED

Sources of Iron.—It was considered worth while to examine the thermal behavior of several samples of pure iron prepared by different methods and subjected to various preliminary treatments.

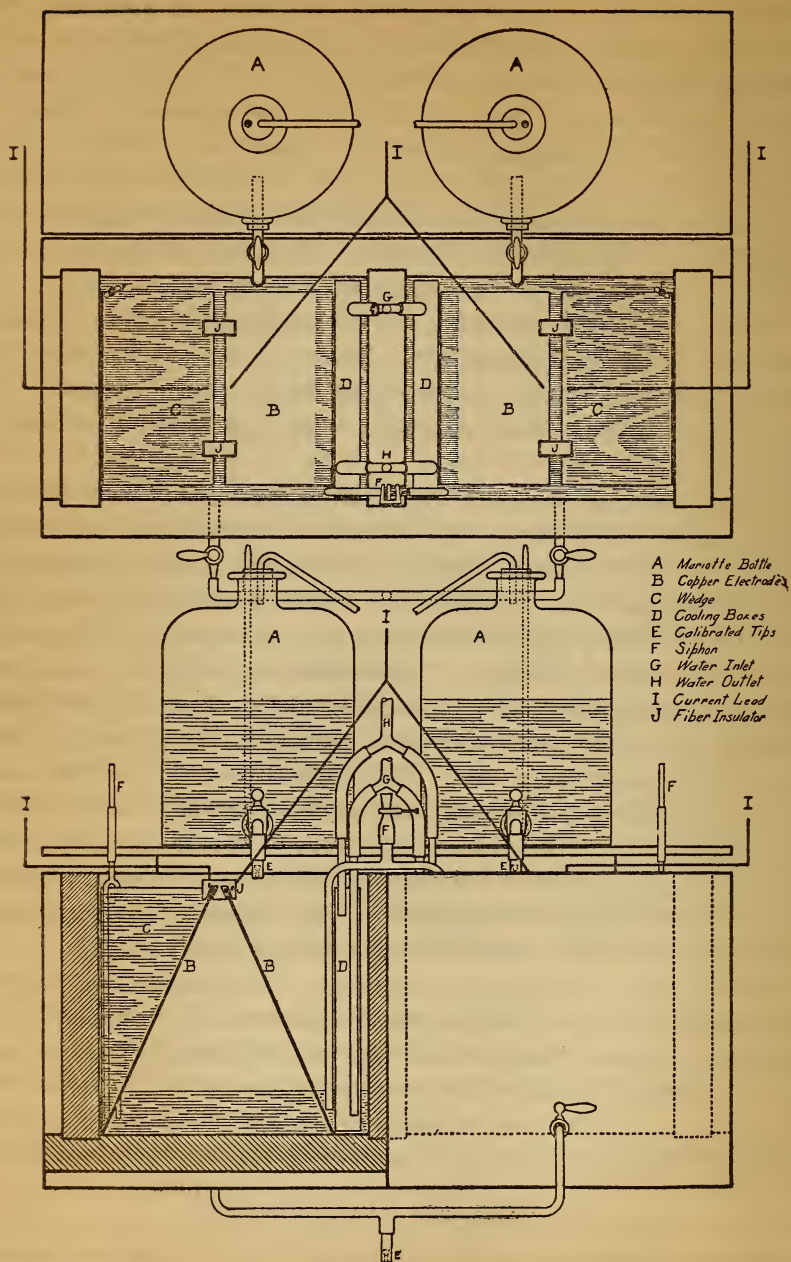


Fig. 6.—Rheostat

We are indebted to Prof. C. F. Burgess, of Wisconsin, who furnished three samples of his electrolytic iron in the form of cathode plates together with an analysis; to Messrs. H. Goldschmidt and Cuntz, who furnished electrode plates and an analysis of iron obtained from the German firm of Langheim-Pfanhauser; to Prof. H. C. H. Carpenter, of Manchester, England, who kindly sent us some of the electrolytic iron he had used in his experiments on the critical ranges in pure iron, and which had been analyzed by Prof. J. E. Stead. Several samples of electrolytic iron were also prepared for this investigation at the Bureau of Standards by Messrs. Cain and Cleaves using a method which is to be described elsewhere. There is also included a sample of "ingot iron" for which we are indebted to the American Rolling Mill Co., of Middletown, Ohio.

Preparation and Description of Samples.—The samples were prepared for taking heating and cooling curves by cleaning with alcohol and ether. In the case of the untreated electrolytic irons of C. F. Burgess and Langheim-Pfanhauser the samples 1, 16, 17, and 26a, in the form of plates one-eighth to one-fourth inch thick, were bored out to receive the thermocouples. Some preliminary but less satisfactory measurements were made with small pieces packed about the thermocouples and within a thin-walled platinum cylinder of 3.5 cm length and 1.5 cm diameter. With this last arrangement the transition points were not always very sharply defined, due apparently to a progression of the reaction from one piece to another.

The first and often several of the succeeding curves taken with untreated electrolytic plates which are known to be heavily charged with gas, especially hydrogen, was erratic, an effect due for the most part to the presence of these gases within the sample, producing parasitic evolutions and absorptions of heat. (See Pl. XI.) This gas effect has been noticed by other observers.

To obviate this troublesome effect it was decided to melt some of the samples of iron before taking the heating and cooling curves, which melting was carried out successfully both in a vacuum electric furnace and in gas-fed furnaces. This melting of iron, provided contamination from crucible or furnace atmosphere is avoided, has the great advantage of further purifying the iron by

the removal of all or nearly all of the contained gases. Electrolytic iron, for example, bubbles very violently on first melting in vacuo, showing that a considerable quantity of gas remains occluded to the temperature of fusion and is only removed by melting the iron. Melting in vacuo, as is shown for samples 25 and 26, as compared with 1 and 26a, Table 3, appears also to lower the already very small carbon content of the iron to almost nothing, again increasing the purity with respect to the most undesirable element, carbon. Finally, electrolytic iron, which has been melted either in vacuo or in gas furnaces, possesses a sharply defined heating curve the first time such iron is reheated, so that a very troublesome source of uncertainty is removed by this melting. That the presence of gases in the iron has a considerable effect on the location and range of the critical ranges is also shown in later paragraphs.

For all these reasons it appeared to us desirable, when making a thermal study of iron and its alloys which occlude or contain gases, to remove these gases by a previous melting of the metal, preferably in vacuo.

There was considerable range in mass (0.7 to 35 g) from one sample to another used in taking heating and cooling curves, as is shown in Tables 4 and 6. It is our experience that it is advantageous to work with as small samples as the precision of the experimental method will permit when it is desired to locate the exact temperatures of the critical ranges of the material. The apparent advantage to be gained with larger samples, which absorb or set free greater quantities of heat, appears to be more than offset by the conductivity of the larger sample not being sufficient to transmit promptly enough the heat generated to the thermometric device. If there is nonuniformity of temperature throughout the sample, this effect is enhanced, and a phenomenon which really takes place at a single temperature will then appear to be spread over a range of temperatures.

We believe this spreading and attenuation of the reaction is a principal reason why Prof. Carpenter was not able to detect Ac_2 with certainty when using 42 g of metal in the form of a thin

sheet coiled into a cylinder, while with only 0.7 g of his iron we were able to locate Ac₂ with great sharpness. (See Pl. VI.)

For melting in vacuo the Arsem furnace was used, the iron being contained in a crucible of pure magnesia placed within a tube of Marquardt porcelain. For melting in the gas furnace covered clay crucibles brasqued with pure fused magnesia were used.

Chemical analyses.—The chemical analyses of the different preparations of iron used are shown in Table 3, including mention of who furnished the analyses. Those at the Bureau of Standards were made by Messrs. Cain, Cleaves, Tucker, and Witmer. In all cases the analyses were made of the metal in the condition stated in the column headed "Description," and the pieces for analysis were cut from the cylinder or plate used for taking the heating and cooling curves. It will be noted that the purest iron is 99.983 Fe, obtained by remelting electrolytic iron in vacuo in magnesia crucibles. The two samples remelted in vacuo are also the lowest in carbon content, 0.003 and 0.001 per cent, respectively. The average carbon content of all samples is 0.009 and the range 0.001 to 0.015. It is of interest to note that with the exception of the Mn and Cu contents, the "ingot iron" is nearly as pure as the average of the electrolytic irons.

Where there are check analyses by different chemists, and in the case of the carbon determinations by different methods, when one considers the difficulty of exact determination of such small quantities of impurity, the agreement is extremely satisfactory, and in most cases may well be within the degree of homogeneity of the samples. None of the samples was analyzed for oxides, but their amount, if present, must be very small.

TABLE 3

Description and Chemical Analyses of Pure Iron

Source	Description	Analysis furnished by—	No.	C	S	P	Si	Mn	Cu	Fe by difference
H. C. H. Carpenter.	Electrolytic 0.01-inch sheet.	Stead	F5	0.008	Tr.	0.002	0.014	0.009	99.967
American Rolling Mill Co.	“Ingot iron” remelted in gas furnace.	Bureau of Standards.	F1	.012	0.020	.001	.003	.029	0.03	99.905
J. R. Cain.....	Electrolytic remelted in gas furnace.do.....	F2	{ .008 .009	{ .045 .045	Tr.	.004	Tr.	<.001	99.941
Langheim - Pfauhauser.do.....do.....	F3	.007	.011	<.001	.004	Tr.	99.977
C. F. Burgess.....do.....do.....	F4	.009	{ .010 .009	<.001	.006	Tr.	.006	99.968
J. R. Cain.....do.....do.....	F6	{ .019 .013 .015	<.001	Tr.	.007	Tr.	<.001	99.975
Do.....do.....do.....	F7	.014	<.001	Tr.	.003	Tr.	<.001	99.971
C. F. Burgess.....	Electrolytic remelted in vacuo.do.....	25	.003	.006	.004	.004	.000	99.983
Langheim - Pfauhauser.do.....do.....	26	.001	.004	.006	.007	.000	99.982
Do.....	Electrolytic plates.do..... H. Goldschmidt. Bureau of Standards. C. F. Burgess ...	26a	{ .008 .00	{ .004 .00	<.001 .007	.006 .00	Tr. .00	.011 .008	99.970 99.98
C. F. Burgess.....do.....	{ Bureau of Standards. C. F. Burgess ... }	1	{ .009 .012	{ .003 .00	<.001 .004	.006 .013	Tr. .00	.006	99.975 99.971

⁶ By solution. ⁷ First burning, 0.008 C; second burning, 0.006 C.

EXPERIMENTAL DATA

We have divided the data into two chronological portions:

1. A preliminary series of observations carried out with a furnace and rheostat of somewhat less satisfactory form than that of Figs. 5 and 6, with less precautions for holding a good vacuum and steady current, and in part with the iron samples in a less concentrated form; nor was the thermocouple calibration as carefully checked in all cases. These preliminary observations, although we do not place the reliance on all of them, for the exact

location of temperatures that we do on the definite series, are, nevertheless, quite instructive in showing some of the things that should be avoided in the exact thermal analysis of a substance occluding gases, and also furnish data for discussing the effects of varying some of the factors that influence the location of the critical ranges.

2. The definite series of observations were then carried out with all the precautions and improvements in method and manipulation our preliminary measurements had shown to be necessary; it is on this definite series, together with the last two of the preliminary series, that we mainly base our conclusions regarding the allotropy of iron as shown by thermal analysis.

In all cases, attention should be given mainly to the location of the maxima of the critical ranges, as the beginnings and endings, especially the former, on heating are, in general, not to be located with exactness.

Preliminary observations have already been reported on briefly, but are here included in full for the sake of completeness. (See Table 4.) The numerical values here given are in some cases slightly different from those previously published, due to some of the indications of one of the thermocouples needing correction. Three Pt-Rh. thermocouples, C₁, W₁₁, and W₁₄, were used in these preliminary observations.

All but one of the samples of iron are electrolytic. Three from Prof. C. F. Burgess, Nos. 1, 16, and 17; sample No. 25 remelted in vacuo is from the same lot as No. 17; and No. 26 is from the Langheim-Pfanhauser A-G. iron, also remelted in vacuo. The electrolytic plates were relatively thick, from one-eighth to nearly one-fourth inch.

The mass of the samples ranged from 15 to 31g, and for the first three series the iron sample consisted of more than one piece of metal. The first three, 1, 16, and 17, were from the electrolyte plates as deposited, 25 and 26 were remelted in vacuo, and 22 is ingot iron remelted in a gas furnace, of similar quality as sample F₁ of Table 3.

1912	Feb. 16.	W14	22	29	.118	.127	784	875	902	-27	768	772	-04	908	890	+18	782	742	+ 40-	925	875	+50	
	19.	W14	22	29	.150	.124	737	893	895	-02	768	772	-04	913	887	26	784	926	873	53		
	19.	W14	22	29	.319	.256	746	- 38	893	893	00	768	772	-04	913	881	32	793	937	866	71		
	21.	W14	22	29	.160	.202	756	- 38	893	896	-03	768	772	-04	913	887	26	784	926	862	64		
	23.	W14	22	29	.175	.153	784	893	902	-09	768	772	-04	913	887	26	788	928	866	62		
	26.	W14	22	29	.137	.148	756	- 28	893	893	00	769	772	-03	913	885	28	784	751	+ 33	928	866	62	
1913	Mar. 5.	W14	22	29	.066	.062	746	- 38	893	902	-09	768	772	-04	913	892	21	782	756	+ 26	924	878	46	
	12.	W14	22	29	.167	.156	746	- 38	875	895	-20	772	771	+01	917	887	30	932	866	66	
1912	Mean.				748	785	- 36	888	897	-09	769	772	-03	913	887	+26	785	750	+ 33	928	869	+59
	July 19.	W14	25	31	.121	.181	773	909	905	+ 4	769	769	0	918	900	+18	781	733	+ 48	931	887	+44	
	22.	W14	25	31	.070	.063	728	- 50	913	905	8	768	768	0	914	03	11	774	751	23	928	893	35	
	22.	W14	25	31	.247	.289	809	913	904	9	768	768	0	918	00	18	779	747	32	929	884	45	
	29.	W14	25	31	.132	.155	821	911	905	6	768	768	0	913	00	13	779	742	37	931	886	45	
	Aug. 5.	W14	25	31	.066	.079	772	911	906	5	768	769	- 1	913	02	11	775	761	14	924	894	30	
1912	6.	W14	25	31	.094	.051	773	911	907	4	768	769	- 1	04	775	761	14	893	
	Oct. 22.	C1	25	31	.078	.126	777	909	906	3	769	770	- 1	915	04	11	775	929	894	35	
	Mean.				728	787	- 50	911	905	+ 6	768	769	0	915	902	14	777	749	28	929	890	+48
	Aug. 14.	W14	26	21	.217	.248	773	907	909	- 2	768	768	0	911	904	+ 7	779	929	893	+36	
	15.	W14	26	21	.209	.192	826	913	909	+ 4	765	768	- 3	918	904	14	779	733	+ 46	930	891	39	
	16.	W14	26	21	.096	.142	835	912	910	+ 2	768	767	+ 1	915	905	10	773	737	36	926	895	31	
1912	16.	W14	26	21	.082	.095	913	909	+ 4	766	915	906	9	925	897	28	
	21.	W14	26	21	.099	.153	826	912	910	+ 2	767	768	- 1	915	907	8	774	742	32	925	895	30	
	28.	W14	26	21	.063	.054	907	913	912	+ 1	768	768	0	915	908	7	775	747	28	925	899	26	
	29.	W14	26	21	.248	.275	819	913	913	0	764	768	- 4	918	904	14	928	891	37	
	Mean.				831	912	910	+2	767	768	- 1	915	905	10	776	740	+36	927	894	+32	

Several facts stand out prominently from these preliminary observations. In the first place, in contrast to the samples remelted in vacuo, before taking heating and cooling curves, which samples show the Ac_2 and Ar_2 maxima sharply defined at a single temperature, 768° , the untreated electrolytic samples show a wide and variable interval between the Ac_2 and Ar_2 maxima, an interval in some individual cases greater than 50° . With untreated electrolytic iron, Ac_2 is always higher and Ar_2 always lower than the single A_2 point at 768° , as found with the remelted irons. Again, the position of the maxima of Ac_3 is higher and of Ar_3 lower, with very considerable variations for the untreated samples; or, in other words, the interval Ac_3 – Ar_3 (maxima) is considerably less, 10 to 14° , for the samples reheated in vacuo than for the untreated samples, for which this interval ranges from 20 to 40° .

These results show the important rôle played by the occluded gases and an examination of the data of the tables shows that several reheatings to 1050° in vacuo are not sufficient to put thick electrolytic iron plates into a satisfactory condition for making a thermal analysis of its critical ranges. When there are several pieces making up a sample (as Nos. 16 and 17) the retarding effect of poor conduction also enters somewhat.

Remelting appears from these observations to be an essential preliminary treatment to which the iron should be subjected, unless several rates are used, as we shall show below. We desire to emphasize this point, for we believe that one of the main reasons why many of the previously published results with electrolytic iron show inconsistencies and variations in the location of A_2 and A_3 , is due to the fact that the gases have never been sufficiently removed or the samples were not in a compact enough form, or both these effects superposed and sometimes associated with a too wide temperature interval between observations.

A property that appears to be common to all these samples is that, on the average, for A_3 the beginning of Ac_3 is at the same temperature as the beginning of Ar_3 , within the limit of accuracy with which these somewhat indefinitely defined temperatures can be located. This characteristic sharply distinguishes A_3 from

A₂; for the latter, as we have seen, the maxima of Ar₂ and Ac₂ coincide when the samples are compact and gas free.

As to the effect of rate of heating or cooling upon the location of the critical ranges, it will be noted, Table 4, that for the rates here used, 0.06° to 0.35° per second (or 17 to 3 seconds per degree), there is no effect on the location of A₂ (max) for the samples 25 and 26 premelted in vacuo, or for sample 22, ingot iron remelted in gas furnace, while for the untreated samples a fast rate accompanies a greater difference in Ac₂–Ar₂. For the A₃ range the effect of rate is less pronounced for the untreated samples but appears to be appreciable for the premelted samples. Table 5 shows that reducing the rate to zero gives 769° for A₂ (=Ac₂=Ar₂) for all samples; and for A₃ we find for zero rate Ac₃–Ar₃=12° with Ac₃=912° and Ar₃=900° on the average.

TABLE 5

Maxima of Critical Ranges for Zero Rate—Preliminary Series

Sample	Ac ₃	Ar ₃	Ac ₃ –Ar ₃	Ac ₂	Ar ₂	Ac ₂ –Ar ₂
1.....	914	900	14	768	767	+1
16.....	913	900	13	769	769	0
17.....	911	896	15	770	769	+1
22.....	909	895	14	769	772	–3
25.....	912	903	9	769	769	0
26.....	913	909	4	768	768	0
Mean.....	912	900	12	769	769	0

It therefore appears that in spite of the wide variations noted in Table 4, the nature of the sample, whether or not gas free or whether in one or several pieces, does not influence the location of the maxima of the critical ranges when reduced to zero rate of heating and cooling.

The definite series of observations is shown in Table 6, in which are recorded all the observations taken with the improved apparatus of Figs. 4, 5, and 6 on the samples here included. There are three samples of electrolytic iron, prepared by Messrs. Cain, Cleaves, and Schramm (F₂, F₂', F₇); an electrolytic sample (F₃), prepared by Langheim-Pfanhauser; another (F₄), from Prof. C. F.

Burgess; and one of ingot iron (F1), from the American Rolling Mill Co., all of which were remelted in a gas furnace before taking observations. In addition, F8 and F9 are small samples from Nos. 25 and 26, respectively, of the preliminary series; and F5 is a piece from an electrolytic sample which had been studied thermally by Prof. Carpenter.

Considering first the existence and location of the maxima of the A₂ range, the observations on all these nine samples show most emphatically the existence of a common maximum for Ac₂ and Ar₂ at 768°, with agreement of 1° among the samples. This result is identical with that found in the preliminary series for the samples Nos. 25 and 26, reheated in vacuo, and for the others of this series when reduced to zero rate. This constancy of (maximum of) $Ac_2 = Ar_2 = 768^\circ \text{C} \pm 0.5$ is seen, therefore, to persist for variations in mass from 0.7 to 35 g. in rate of heating or cooling from 0.05° to 0.35° per second, for iron remelted in vacuo or gas furnace, whether of electrolytic or "ingot" preparation, as determined in two differently constructed furnaces, with five separately calibrated thermocouples and using two methods of thermal analysis.

TABLE 6
Definite Series of Observations

Date	Couple	Sample No.	Mass in g	Rate= Degs/Secs		Run No.	Beginning						Maximum						End					
				Up	Down		Ar2	Ar3	Ar3-Ar3	Ar2	Ar3	Ar3-Ar3	Ar2	Ar3	Ar3-Ar3	Ar2	Ar3	Ar3-Ar3	Ar2	Ar3	Ar3-Ar3			
1913 May 19 20 27 27 28 29	M1	F2	33	0.143	0.155	1		776		868	891	-23	767	765	+2	911	876	+35	774	736	38	923	849	+74
	M1	F2	33	.101	.131	2	748	776	-28	858	891	-33	769	767	2	912	879	33	774	739	35	922	858	64
	M1	F2	33	.121	.093	3		808		874	892	-18	768	767	1	912	882	30	775	729	46	922		
	M1	F2	33	.138	.128	4		808		876	889	-13	768	768	0	912	880	32	775	736	39	923	858	65
	M1	F2	33	.053	.063	5		808		893	893	00	768	768	0	912	883	29	772	748	24	919	863	56
	M1	F2	33	.075	.083	6		779		894			768	768	0	912	881	31	773	744	29	922	858	64
June 5 5 5 7 14	M1	F2	33	.102	.092	7		819					768	768	0				775	741	34			
	M1	F2	33	.115	.078	8		775					768	767	1				774					
	M1	F2	33	.131	.222	9							768			911	880	31	773			920	855	65
	M1	F2	33	.088	.100	10	755				891			767		910	879	31				919	858	61
	M1	F2	33	.068	.107	10		790		892	889	-03	767	768	0	910	880	30	772	767	05	921	849	72
	M1	F2	1.5	.128	.090	1		804		888			768	768	0	910	880	30	772	767	05	921	849	72
Mean						752	794		877	891	-15	763	767	+1	911	880	+31	774	742	+51	921	856	+65	
June 11 11 12 Mean	M1	F3	32	.130	.125	1		776		891	891	00	768	763	0	914	880	+34	776			920	858	62
	M1	F3	32	.151	.143	2		776		890	890	00	768	768	0	914	882	32	776			922	863	59
	M1	F3	32	.053	.064	3		775		858	894	-36	768	768	0	911	886	25	771			920	880	40
	Mean							776		880	892	-12	768	768	0	913	883	+30	774			921	867	+54

TABLE 6—Continued
Definite Series of Observations—Continued

Date	Couple.	Sample No.	Mass in g	Rate= Degs/Sec		Run No.	Beginning						Maximum						End						
				Up	Down		Ac2	Ar2	Ac2-Ar2	Ac3	Ar3	Ac3-Ar3	Ac2	Ar2	Ac2-Ar2	Ac3	Ar3	Ac3-Ar3	Ac2	Ar2	Ac2-Ar2	Ac3	Ar3		
1913 July 8..... 10..... 14.....	M1	F4	37	.164	.144	1	762	775	-13	894	894	0	768	768	0	916	886	+30	776	743	+33	925	868	+57	
	M1	F4	37	.051	.062	2	751	771	-20	885	897	-12	768	769	-1	912	890	22	771	753	18	921	879	42	
	M1	F4	37	.136	.081	3	759	773	-14	897	895	+2	768	768	0	914	890	24	776	750	16	920	877	43	
	Mean.....						757	773	-16	892	895	-3	768	768	0	914	889	+25	774	749	+22	922	875	+47	
July 17..... 17.....	M2	F5	0.7	.131	.107	8	769	769	911	904	+07	768	766	+2	912	888	+24	772	753	+19	921	893	+28	
	M2	F5	0.7	.057	.054	2	769	769	912	903	09	767	766	1	910	889	21	771	756	15	920	895	25	
	Mean.....						769	769	912	904	+08	768	766	+1	911	888	+23	772	754	+17	920	894	+26	
	July 31..... 31.....	M2	F7	13	.147	.125	1	776	774	876	892	-16	768	766	+2	912	888	+24	774	748	+26	916	876	40
Mean.....	M2	F7	13	.103	.105	2	774	775	872	895	-23	768	766	2	910	889	21	773	748	919	872	47	
	Mean.....						775	775	874	894	-20	768	766	+2	911	888	+23	774	748	918	874	+44	
	July 23..... 24.....	M1	F1	35	.177	.112	1	785	785	880	894	-14	768	766	+2	916	884	+32	774	748	+26	925	858	+67
	Mean.....	M1	F1	35	.057	.043	2	785	785	867	896	-29	768	768	0	911	889	22	772	748	24	920	867	53
Aug. 11..... 13.....	M2	⁹ F8	1.0	.064	.095	1	785	785	874	895	-21	768	767	+1	914	886	+28	773	738	+25	922	862	+60	
	M2	¹⁰ F9	2.1	.099	.101	1	786	786	907	901	+06	768	766	+2	913	898	+15	773	748	921	890	+31	
	Mean.....						786	786	912	905	+07	768	766	+2	916	903	+13	774	748	925	897	28	

¹⁰ Piece of No. 26 which has been run.

⁹ Piece of No. 25 which has been run.

⁸ By Bureau of Standards.

The small electrolytic sample, F5, from Prof. Carpenter, which had been heated by him six times to 1000°C , also behaves exactly like the others.

Turning now to the maxima of A_3 we see that for all the samples, Ac_3 is located at $912^{\circ} \pm 2$, while the agreement for Ar_3 is apparently not so good, the range being from 880° to 903° for the different samples, and the mean value of Ar_3 is 889° . It is to be noted that the samples F8 and F9, preheated in vacuo, are in agreement with Nos. 25 and 26 of the preliminary series, again showing the smallest interval, namely, $Ac_3 - Ar_3 = 14^{\circ}$.

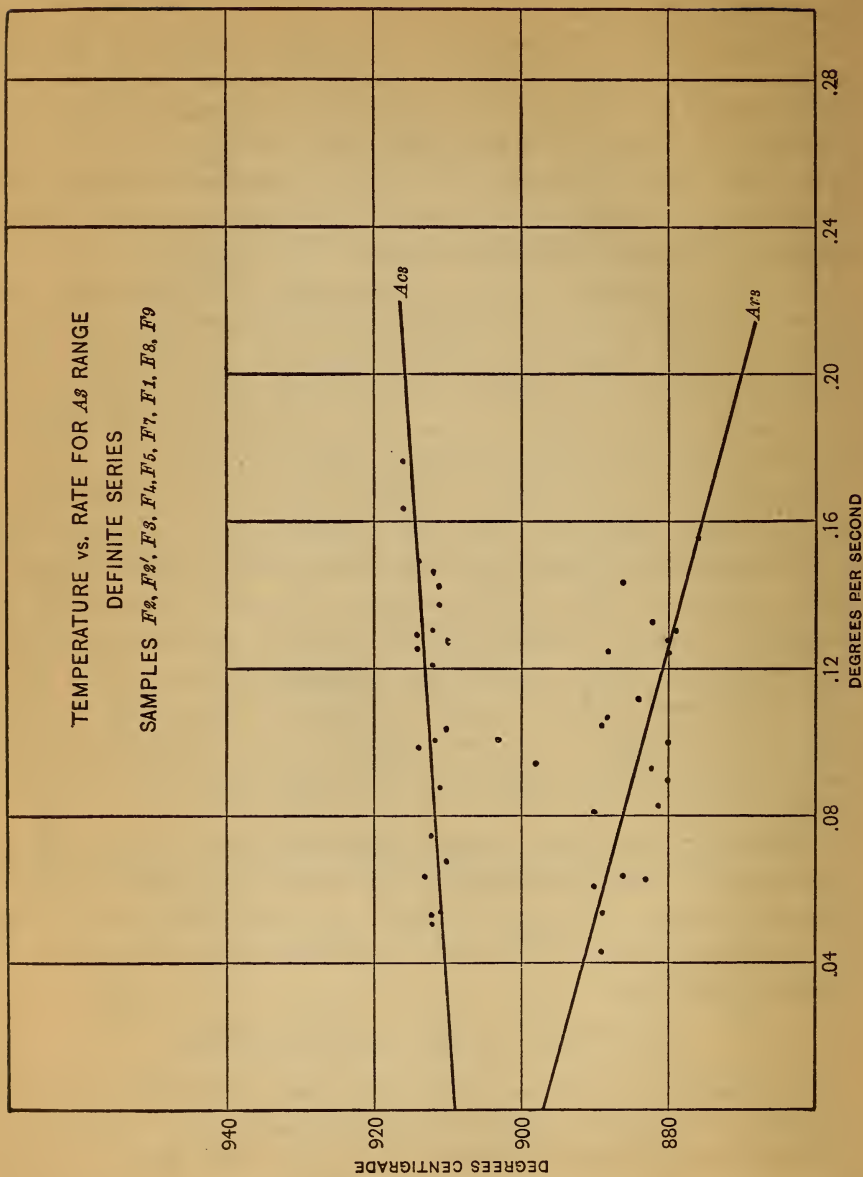
As in the preliminary series, the beginning of Ar_3 is located, in general, at about the same temperature as the beginning of Ac_3 , although these beginning temperatures are not defined with sufficient sharpness to warrant certainly the statement that the A_3 transformation begins at the same temperature on heating and on cooling, although this appears highly probable.

No effect of rate of heating or cooling can be seen in the location of the critical range A_2 . For the critical range A_3 , when the observations on Ac_3 and Ar_3 are plotted in terms of rate of heating or cooling (see Fig. 7), the anomalies in location of Ar_3 largely disappear, although extrapolating Ac_3 and Ar_3 to zero rate again fails to give a single equilibrium temperature Ae_3 . For zero rate, $Ac_3 = 909^{\circ}$ and $Ar_3 = 897^{\circ}$, or there is apparently a real difference of some 12° in the location of the maxima of this transformation, which result is in exact agreement with the preliminary series.

Considering both series, it seems safe to say that we may place $Ac_3 = 909^{\circ} \pm 1$ and $Ar_3 = 898 \pm 2$ and $Ac_2 = Ar_2 = 768^{\circ} \pm 0.5$ for pure iron passing through A_3 and A_2 at zero rate and through A_2 at any rate provided the iron is gas free and in the form of a single compact piece.

DESCRIPTION OF THE PLOTTED CURVES

An examination of the actual heating and cooling curves is also essential. For most of the samples both inverse rate (marked I) and derived differential (marked D) heating and cooling curves are recorded. Observations were usually taken at 2° intervals, although others were sometimes used, namely, 1° and 4° steps,

Fig. 7.—Temperature vs. rate for *A3* maxima

which are evident from inspection. For all curves the ordinates represent temperatures centigrade; for the inverse rate curves the abscissas represent time in seconds to change the temperature of the sample by the unit interval (1° , 2° , or 4°); and for the derived differential curves the abscissas represent deflections on the differential galvanometer scale expressed in millimeters.

Effect of plotting at different intervals is shown in Plate III for the observations of a single heating and cooling curve of sample F1. It would appear that there is no advantage in reducing the interval at which temperatures are taken to as small as 1° in the desire not to miss any very slight transformation; on the contrary, the sensibility is thereby reduced proportionally, since what is measured is only the effect between two successive taps of the key. On the other hand, with wide intervals, such as 4° , missing a single observation may be sufficient to throw the whole series into doubt. The interval chosen, 2° , appears to avoid, satisfactorily, the two pitfalls of lack of sensibility and danger of missing the cusp of a transformation.

Curves of the definite series are shown in Plates IV to VIII. The most detailed study was made of sample F2, consisting of 33 g of premelted electrolytic iron, prepared by Mr. Cain. In contrast to the observations by ourselves and others on untreated electrolytic iron which show irregular curves for the first three or four heatings, with this premelted iron the first curve is about as regular and sharply defined as the succeeding ones. The similar character of the two types of curve is well shown here, the only considerable difference being that for very slow and for rapidly changing rates the inverse-rate curve shows marked departures from the vertical. It is apparent from an inspection of the curves that although the maxima and to a less degree the ends of the critical ranges are sharply defined, the exact location of the beginnings, especially on heating, is attended with considerable uncertainty for both types of curve.

The curves of Plate IVa show the results of an effort to attenuate or eliminate, if possible, by various operations, the A₂ point. As the curves indicate, it is impossible to influence the position or nature of Ac₂ or Ar₂ by any thermal operations performed upon the iron above or below this temperature. Thus, during the

sixth heating the sample was held 71 minutes at 825° , then heated to above A_3 and then cooled; in the seventh it was heated to just below the beginning of A_3 and then cooled; in the eighth and ninth it was heated and cooled twice over a short range including the A_2 point; in the tenth it was held 60 minutes just below A_3 and then carried up and down three times over the A_3 range before cooling. In all these operations, Ac_2 and Ar_2 remain unchanged in any way, and the evidence is abundantly conclusive that the critical range A_2 is in no sense related to the A_3 transformation, as has been suggested it might be, particularly by Benedicks.

A small piece (1.5 g = F_2') of the above sample was also examined with the same results (Pl. IV).

The observations, with several other samples of electrolytic iron, F_3 , F_4 , and F_7 premelted in the gas furnace, are shown in Plates V, VII, and VIII, corroborating the previous observations. It will be seen that in each case the first heating gives as definite results as the succeeding ones. A sample of 35 g of remelted ingot iron F_1 (Pl. VII) gives the same type of curve as the remelted electrolytic irons.

A sample of particular interest is F_5 , it being 0.7 of a gram of Prof. Carpenter's electrolytic iron, which is seen (Pl. VI) to behave exactly like the others, showing Ac_2 and Ar_2 both clearly located on the curves at 768° .

The advantage of using small samples for sharply defining the magnitude of the critical ranges is well shown for the curves of F_5 (0.7 g), F_8 (1.0 g), and F_9 (2.1 g), Plates VI and VII, the last two being pieces remelted in vacuo. These very small samples were also inclosed within the platinum neutral in the furnace, a proceeding which appears to be advantageous, since the sample F_2' of 1.5 g not so inclosed (Pl. IV) shows the A_3 range much less sharply.

The curves of the preliminary series are not all presented here, but a sufficient number are included to indicate the constancy of behavior attained with the variously prepared samples with the imperfect apparatus and at times an unsteady heating current. All the observations taken of one of the electrolytic samples premelted in vacuo (No. 26) are given and this series of curves (Pls.

X, Xa, and Xb) gives a fair example of them all. Some of the untreated electrolytic samples give somewhat erratic results, as shown for sample No. 1, Plate XI. The curves for the ingot iron, sample No. 22, Plates IX and IXa, are also representative of the results obtained with the earlier apparatus. Plate XI is interesting mainly in that it contains about all the errors to which thermal analysis is subject. This was our first series for pure iron.

Existence of Other Critical Ranges.—Several observers have announced the existence of transformation points in addition to A₂ and A₃; notably, Sir Roberts-Austen, who considered he had found several points below A₂; Carpenter, one at 600°, which Rosenhain later attributed to the heating tube; Arnold a “fourth recalcrescence point” between A₃ and A₂ (or a doubling of A₂); Robin, two critical regions below A₂ near 400° and 100°, respectively; and P. Curie, Broniewski and others, one or more points above 1000°.

A few of our observations extend to as low as 300° and as high as 1050° without indicating the presence of any critical regions above A₃ or below A₂.

Some of the curves, particularly on cooling, give slight evidence of a minute transformation at about 805° (see in particular several of the cooling curves for sample F₂), although with the other samples this point can hardly be said to be present. If a point between A₃ and A₂ is really present, this would corroborate the magnetic observations both of Curie and of Weiss and Foex, whose susceptibility curves show an inflection between A₂ and A₃. (See Fig. 2.)

There is more positive evidence of a slight absorption of heat in the heating curves corresponding in temperature to the maximum of A₃. Although not always present in the heating curves, this doubling of A₃ is well shown, mainly for the inverse-rate curves, in the following of the definite series: Sample F₇, both curves; the curves of very slow rate of sample F₂, especially the fifth; F₄, all curves; F₃, F₁, and F₈, slightly evident; while this doubling is apparently absent in F₉ and F₅ (Carpenter's sample), both of very small mass.

Some of the curves of the preliminary series also show one or another of these secondary points (see Pls. IXa and Xb), usually more marked in the inverse-rate curves; but due to the relative irregularity of the preliminary series, as compared with the definite series with the perfected apparatus, we do not place any considerable reliance on the former series for this purpose.

In view of the apparent impossibility of finding experimentally a common equilibrium temperature Ae_3 for the heating and cooling curves, the presence of an inferior, even if slight, transformation on heating at the temperature of Ar_3 would be an aid in explaining this anomaly, although the allotropy of iron would thereby be further complicated, a step we are by no means anxious to champion, unless the facts are considered sufficiently convincing.

ILLUSTRATIVE SERIES OF OBSERVATIONS

In Table 7 are given the actual observations taken for our heating and cooling curves of sample F_3 , showing the method of recording and reducing such observations. These observations are plotted in Plate XII both as differential and derived differential curves. The abscissas of the differential curves are millimeter deflections on the galvanometer scale, as given by the differential thermocouple. It is evident from inspection why the derived differential method is to be preferred over the differential as a method of expressing graphically the results of thermal analysis.

The inverse rate curves deduced from Table 7 are given in Plate VIII.

In Table 7, the column headed " M_1 " gives emfs of thermocouple M_1 measuring the temperature of the sample F_3 ; the one headed "Time," the intervals in seconds as obtained from the chronograph sheet for M_1 to change 20 micro volts; " M_4 ," the corresponding deflection in millimeters of the galvanometer measuring the difference in temperature between sample and neutral; and " dt " the successive differences of M_4 .

TABLE 7

Sample No. F3. Run first up. Observers, J. J. C. and H. S. Couples $\left(\frac{dt}{T} \frac{M4}{M1}\right)$. Maximum temperature, 1005°. Date, June 11, 1913. Pot. Wolff. E. M. F. S. & S. Machine on battery. Time: Beginning, 10.49; ending, 11.42; total time, 53 minutes. Remarks: Weight of sample, 31.7 g; length of sample, 25 mm; diameter of sample, 15 mm. Hole, 17 mm deep; 5 mm diameter.]

M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt
500		684		546		640		592		587		638		466	
	18.6		00		15.5		+01		14.3		+04		13.6		+07
02		684		48		639		94		583		40		459	
	19.0		+01		15.5		+02		14.1		+01		13.5		+05
04		683		50		637		96		582		42		454	
	18.3		+01		15.4		00		14.3		+03		13.7		+08
06		682		52		637		98		579		44		446	
	18.3		+02		15.4		00		14.2		+06		13.8		+08
08		680		54		637		600		573		46		438	
	18.1		+02		15.1		+04		13.9		+05		13.5		+08
10		678		56		636		02		568		48		430	
	18.1		+03		15.2		+03		14.0		+05		13.6		+07
12		675		58		633		04		563		50		423	
	18.1		+03		15.3		+01		14.1		+05		13.7		+09
14		672		60		632		06		558		52		414	
	17.8		+02		14.9		+02		13.9		+04		13.7		+09
16		670		62		630		08		554		54		405	
	17.8		+03		14.9		+01		13.9		+05		13.6		+09
18		667		64		629		10		549		56		396	
	17.6		+04		15.0		+02		14.0		+05		13.6		+08
20		663		66		627		12		544		58		388	
	17.9		+06		14.8		+02		13.8		+07		13.7		+10
22		657		68		625		614		537		60		378	
	17.8		+08		14.7		+01		14.0		+04		13.5		+08
24		649		70		624		16		533		62		370	
	17.4		+05		14.7		+01		13.9		+06		13.8		+10
26		644		72		623		18		527		64		360	
	17.0		+01		14.8		+03		13.8		+04		13.6		+09
28		643		74		620		20		523		66		351	
	16.4		00		14.5		+04		13.7		+07		13.6		+10
30		643		576		616		22		516		68		341	
	16.6		+01		14.7		+04		13.9		+04		13.7		+11
32		642		78		612		24		512		70		330	
	16.3		+01		14.5		+04		13.7		+06		13.5		+11
34		641		80		608		26		506		72		319	
	16.2		+01		14.6		+03		13.9		+07		14.0		+11
36		640		82		605		28		499		74		308	
	16.2		00		14.5		+03		13.5		+06		13.8		+12
538		640		84		602		30		493		76		296	
	15.8		00		14.3		+02		13.7		+07		13.9		+11
40		640		86		600		32		486		78		285	
	15.9		00		14.4		+04		13.5		+06		13.8		+12
42		640		88		596		34		480		80		273	
	15.9		+01		14.3		+05		13.8		+07		14.0		+12
44		639		90		591		36		473		82		261	
	15.7		-01		14.3		+04		13.7		+07		14.0		+16

TABLE 7—Continued

M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt
684		245		734		300		784		544		834		532	
	14.0		+14		11.6		-14		12.2		-07		14.1		+06
86		231		36		314		86		551		36		526	
	13.8		+14		11.6		-12		12.5		-05		14.3		+06
88		217		38		326		88		556		38		520	
	14.1		+14		11.6		-14		12.4		-05		14.6		+08
90		203		40		340		90		561		40		512	
	14.1		+16		11.7		-12		12.6		-05		15.0		+10
92		187		42		352		92		566		42		502	
	14.3		+16		11.5		-13		12.4		-05		15.1		+11
94		171		44		365		94		571		44		491	
	14.6		+19		11.6		-12		12.6		-04		14.8		+11
96		152		46		377		96		575		46		480	
	14.6		+19		11.8		-11		12.7		-04		15.0		+14
98		133		48		388		98		579		48		466	
	14.7		+25		11.7		-10		12.8		-04		15.3		+16
700		108		50		398		800		583		50		450	
	15.0		+26		11.8		-11		12.9		-01		15.5		+19
02		82		52		409		02		584		52		431	
	13.7		+04		11.7		-11		13.0		-01		15.8		+22
04		78		54		420		04		585		54		409	
	12.2		-10		11.9		-10		13.1		+01		16.4		+29
06		88		56		430		06		584		56		380	
	11.9		-13		12.0		-10		13.2		+01		17.0		+34
08		101		58		440		08		583		58		346	
	11.9		-14		11.8		-10		13.3		+01		17.5		+40
10		115		60		450		10		582		60		306	
	11.6		-18		11.9		-10		13.6		+02		18.8		+49
12		133		62		460		12		580		62		257	
	11.5		-14		11.9		-09		13.7		+04		19.8		+59
14		147		64		469		14		576		64		198	
	11.5		-17		12.1		-08		13.4		+03		18.2		+34
16		164		66		477		16		573		66		164	
	11.5		-16		12.1		-08		13.7		+04		13.4		-30
18		180		68		485		18		569		68		194	
	11.4		-15		12.0		-09		13.9		+06		10.2		-56
20		195		70		494		20		563		70		250	
	11.6		-16		12.2		-09		13.7		+03		9.4		-58
22		211		72		503		22		560		72		308	
	12.0		-15		12.1		-07		13.8		+06		9.4		-55
24		226		74		510		24		554		74		363	
	10.9		-16		12.3		-07		14.1		+04		9.8		-49
26		242		76		517		26		550		76		412	
	11.4		-15		12.1		-07		13.8		+04		10.0		-42
28		257		78		524		28		546		78		454	
	11.5		-14		12.2		-08		14.0		+04		10.5		-39
30		271		80		532		30		542		80		493	
	11.6		-15		12.2		-06		13.8		+05		11.0		-31
32		286		82		538		32		537		82		524	
	11.5		-14		12.5		-06		14.1		+05		11.2		-20

TABLE 7—Continued

M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt
784		554		902		697		920		734		938		732	
	11.5		-24		13.2		-07		14.7		-01		15.6		+01
86		578		04		704		22		735		40		731	
	11.6		-24		13.7		-06		14.6		-01		15.2		+01
88		602		06		710		24		736		42		730	
	12.2		-20		13.6		-06		14.6		+01		15.2		+01
90		622		08		716		26		735		44		729	
	12.3		-16		13.7		-04		15.0		-01		15.6		+03
92		638		10		720		28		736		46		726	
	12.5		-16		14.0		-04		14.6		00		12.5		+02
94		654		12		724		30		736		48		724	
	12.7		-12		13.8		-03		13.1		+01		15.4		+01
96		666		14		727		32		735		50		723	
	13.0		-12		14.4		-03		15.0		+01				
98		678		16		730		34		734					
	13.1		-10		14.2		-02		14.9		+01				
900		688		18		732		36		733					
	13.3		-09		14.2		-02		15.1		+01				

[Sample No. F 3. Run first down. Observers, J. J. C. and H. S. Couples. $\frac{dt M 4}{T M 1}$ Maximum temperature 964. Date June 11, 1913. Pot., Wolff. E. M. F. S. & S. Machine on battery. Time: Beginning 1.32; ending, 2.27; total time, 55 minutes.]

M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt
950		175		930		97		908		53		886		30	
	26.5		-11		18.4		-06		16.2		-03		15.3		-02
48		164		28		91		06		50		84		28	
	24.5		-10		18.3		-05		16.1		-02		15.1		-03
46		154		26		86		04		48		82		25	
	24.3		-10		18.0		-04		16.3		-01		15.1		-01
44		144		24		82		02		47		80		24	
	22.2		-06		17.7		-04		15.8		-03		15.1		-01
42		138		22		78		900		44		78		23	
	21.8		-09		17.5		-04		15.9		-01		15.0		00
40		129		20		74		898		43		76		23	
		-07		17.2		-05		15.8		-03		14.8		-02
38			18		69		96		40		74		21	
					17.0		-04		15.7		-02		14.8		-01
	2)40.8 20.4		-07	16		65		94		38		72		20	
					16.9		-02		15.5		-02		15.2		-01
36		115		914		63		92		36		70		19	
	19.9		-07		16.7		-03		15.6		-03		14.7		-01
34		108		12		60		90		33		68		18	
	19.3		-07		16.7		-04		15.3		-01		14.7		-01
32		101		10		56		88		32		66		17	
	18.7		-04		16.3		-03		15.3		-02		14.7		-02

TABLE 7—Continued

M1	Time	M4	dt	Mi	Time	M4	dt	Mi	Time	M4	dt	Mi	Time	M4	dt
964		15		914		768		764		461		714		523	
	14.9		-01		13.5		-07		13.3		-04		14.4		+09
62		14		12		761		62		457		12		532	
	14.6		-01		13.8		-12		13.3		-03		14.2		+08
60		13		10		749		60		454		10		540	
	14.6		-01		13.2		-15		13.3		-02		14.6		+12
58		12		08		734		58		452		08		552	
	14.5		-01		13.0		-17		13.3		-02		14.7		+14
56		11		06		717		56		450		06		566	
	14.5		-01		12.7		-18		13.4		-01		14.9		+16
54		10		04		699		54		449		04		582	
	14.7		-01		12.6		-19		13.4		00		14.8		+24
52		09		02		680		52		449		02		606	
	14.4		-01		12.7		-21		13.7		00		18.0		+41
50		08		800		659		50		449		700		647	
	14.6		00		12.4		-19		13.4		00		16.8		+35
48		08		798		640		48		449		698		682	
	14.3		-01		12.3		-18		13.4		+01		16.4		+25
46		07		96		622		46		450		96		707	
	14.5		00		12.4		-19		13.6		+01		15.6		+22
44		07		94		603		744		451		94		729	
	14.4		00		12.5		-16		13.9		+01		15.5		+17
42		7		92		587		42		452		92		746	
	14.3		00		12.6		-16		13.5		+03		15.0		+14
40		7		90		571		40		455		90		760	
	14.3		00		12.6		-14		13.5		+02		14.7		+11
38		7		88		557		38		457		688		771	
	14.5		+04		12.6		-14		13.8		+04		14.7		+10
36		11		86		543		36		461		86		781	
	14.9		+09		12.6		-11		13.7		+03		14.4		+07
34		20		84		532		34		464		84		788	
	15.7		+20		12.9		-11		14.0		+03		14.2		+06
32		40		82		521		32		467		82		794	
	17.2		+40		12.9		-11		13.6		+04		14.2		+03
30		80		80		510		30		471		80		797	
	20.9		+95		12.8		-10		13.9		+04		13.9		+04
28		175		78		500		28		475		78		801	
	32.4		+235		12.9		-07		13.8		+05		12.8		+03
26		410		76		493		26		480		76		804	
	34.8		+200		13.1		-08		14.0		+07		13.8		+02
24		610		74		485		24		487		74		806	
	24.4		+90		13.1		-07		13.9		+06		13.7		+01
22		700		72		478		22		493		72		807	
	19.5		+40		13.2		-05		14.0		+07		13.6		00
20		740		70		473		20		500		70		807	
	17.5			13.0		-05		14.1		+07		13.7		-01
18			68		468		18		507		68		806	
	16.5			13.0		-05		14.2		+08		13.4		-01
16			66		463		16		515		66		805	
	14.0			13.5		-02		14.1		+08		13.4		-02

TABLE 7—Continued

M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt	M1	Time	M4	dt
664		803		622		732		580		654		538		600	
	13.5		—01		13.0		—02		13.0		—04		13.2		—04
62		802		20		730		78		650		36		596	
	13.2		—02		13.0		—05		13.0		—03		13.3		—03
60		800		18		725		576		647		34		593	
	13.3		—02		13.0		—03		12.9		—02		13.3		—03
58		798		16		722		74		645		32		590	
	13.3		—03		12.9		—04		13.3		—02		13.2		00
56		795		14		718		72		643		30		590	
	13.1		—02		13.1		—05		13.3		—02		13.3		—01
54		793		12		713		70		641		28		589	
	13.3		—03		12.8		—04		12.8		—02		13.5		—02
52		790		10		709		68		639		26		587	
	13.2		—04		12.9		—04		12.8		—03		13.2		—03
50		786		08		705		66		636		24		584	
	13.3		—03		13.0		—03		13.3		—03		13.3		—04
48		783		06		702		64		633		22		580	
	13.1		—03		13.0		—04		13.2		—03		13.5		—02
46		780		04		698		62		630		520		578	
	13.1		—04		13.0		—04		13.2		—04		13.3		—01
44		776		02		694		60		626		18		577	
	13.0		—03		13.0		—03		13.0		—03		13.3		—01
42		773		00		691		58		623		16		576	
	13.1		—05		12.9		—03		13.3		—03		13.4		—02
40		768		598		688		56		620		14		574	
	13.3		—03		13.0		—04		13.1		—03		13.5		+01
38		765		96		684		54		617		12		575	
	12.9		—04		13.2		—03		13.2		—02		13.7		—01
36		761		94		681		52		615		10		574	
	13.1		—04		12.8		—04		13.1		—02		13.4		—03
34		757		92		677		50		613		08		571	
	12.8		—05		13.1		—04		13.2		—02		13.5		—02
632		752		90		673		48		611		06		569	
	13.2		—04		12.9		—04		13.2		—04		13.8		—00
30		748		88		669		46		607		04		569	
	12.9		—03		13.2		—04		13.4		—01		13.4		—03
28		745		86		665		44		606		02		566	
	13.0		—04		13.1		—03		13.0		—03		13.8		—01
26		741		84		662		42		603		00		565	
	13.0		—05		13.1		—04		13.1		—02				
24		736		82		658		40		601					
	12.9		—04		13.0		—04		13.4		—01				

MICROSCOPICAL EXAMINATION

By H. S. RAWDON

Figs. 1 and 8 of Plates II and IIa, which are micrographs of a sample of electrolytic iron prepared by Mr. J. R. Cain, Bureau of Standards, illustrate the appearance of the metal upon deposition. The iron is quite different in its properties from iron under ordinary conditions. It is quite brittle and hard, and the samples for microscopic examination are prepared with much less difficulty than after the iron has been melted. This difference is undoubtedly due to the hydrogen which saturates the metal as a result of its method of preparation.

All of the other specimens examined show some spherical gas bubbles due to the liberation of the dissolved gases during the processes of melting and which did not escape from the iron on account of its viscosity. These bubbles have a peculiar appearance under vertical illumination, resembling inclusions of MnS. This is due to the absence of all oxide film from the walls of the bubble. Fig. 5 shows this appearance of the bubbles somewhat. These bubbles occur in all the specimens regardless of their method of melting, and also very small ones occur in samples which were heated for the cooling curve determination without previous melting. Fig. 3 is interesting in showing the interior veinings in the iron crystals which appear upon deep etching after the sample has been heated considerably.

All of the photomicrographs, unless otherwise stated, are at a magnification of 100 diameters. Picric acid was used as an etching agent.

SUMMARY AND CONCLUSIONS

In the first part of this paper, after a brief statement of the current theories of the allotropy of iron, we have given what we hope will be considered an impartial account of the numerous experimental efforts of others to locate and define the critical ranges A₂ and A₃ of pure iron in terms of the various physical phenomena which have been found to change with temperature.

These observations are embodied in Tables 1 and 2, from which we see that all the physical properties of iron which have been

studied, with the single notable exception of crystallographic structure, have shown, in the hands of one or more skillful experimenters, a distinct discontinuity for the A₂ range as well as for the A₃ range. For several of the phenomena, such as electrical resistance, thermoelectricity, specific heat, and magnetism, it would appear that the discontinuity is at least as great for A₂ as for A₃, while the thermal effect has, of course, been long recognized as being much the more pronounced at A₃.

The investigation proper consisted in taking in vacuo some 130 heating and cooling curves by two methods simultaneously, the inverse rate and differential, for 15 samples of pure iron prepared by various methods and analyzed by several chemists. Unusual precautions were taken to secure uniformity of heating of the samples, and it was also possible to take observations for samples of widely different mass, and over a wide range of rates each maintained strictly constant. Two furnaces were used and temperatures were taken with six separately calibrated thermocouples. The observations show that in order to get consistent and reliable results in the thermal analysis of a substance such as iron, the properties of which are so readily susceptible to many minor influences, it is necessary to get rid of all the disturbing influences.

We find essential the following precautions:

1. The iron should be pure—our purest samples were 99.983 and contained 0.003 per cent carbon or less—and it should be kept pure by heating it only in vacuo; a pressure of 0.01 mm Hg suffices.

2. Either the occluded gases should be removed by premelting the iron, preferably in vacuo, or it will in general be found necessary to take a series of heating and cooling curves at widely different rates, in order to determine correctly the location of the critical ranges A₃ and A₂.

3. The iron should be in a single piece, entirely surrounding and in contact with the thermocouple junction; otherwise the thermocouple will integrate the irregular progress of the heat through the sample and the curves will lose their sharpness. Small samples (1 g. or so) give sharper results than large samples.

4. The interval of recording temperatures should be wide enough that sufficient sensibility is attained and narrow enough

that the contour of the curves is not distorted; we have found a 2° interval satisfactory.

5. The sensibility of the apparatus indicating temperatures and differences of temperature should be of the order of 0.01° and time should be measured to better than 0.2 second.

Among the results of this investigation may be mentioned the demonstration that the inverse rate and differential methods, the latter plotted as the derived differential curve, give identical results of the same sensibility for the critical ranges, and the two sets of curves are strictly similar, save for minor particulars.

The plotted curves give what seems to us conclusive evidence of the independent existence of A_3 and A_2 , all of the 130 curves, without exception, showing both these critical ranges sharply defined and unquestionably distinct. It was found impossible to eliminate or attenuate A_2 by thermal treatment. The A_2 transformation has not a double cusp, nor do there appear to be other transformations above A_3 and below A_2 between 300° and 1050° . With electrolytic iron, unless the sample has been premelted into a compact mass, erratic results will be obtained for both A_3 and A_2 , the location of the critical points apparently depending in the main upon the rate of heating or cooling. The critical points may even be displaced by over 50° . (See Tables 4 and 6.) It is possible, however, to reduce the observations on untreated electrolytic iron to exactly the same temperature basis as the gas free, compact material by taking curves at several rates and reducing to zero rate. This would appear to indicate that the gases occluded, mainly hydrogen, play no essential chemical rôle in modifying the iron equilibrium.

Even with gas-free iron the A_3 point is not entirely independent of the rate of heating or cooling, so that it is necessary to reduce the observations to zero rate in order to obtain correct results for Ac_3 and Ar_3 . The range in the location of Ar_3 , for example, with premelted samples was found to be 876° at 0.155 degree seconds to 898° at zero rate. (See Fig. 7.)

All preparations of pure iron, even those containing gases, when reduced to the common basis of zero rate of heating or

cooling, have the same maximum for the A₂ critical range,¹¹ namely, A₂ = Ac₂ = Ar₂ = 768° ± 0.5. All but one of the 15 samples gave this result to within 2°; the other to 3°.

Similarly for zero rate, the value of the maxima of A₃ are found to be Ac₃ = 909° ± 1 and Ar₃ = 898° ± 2.

It was not possible to infer a single equilibrium temperature Ae₃ from these experiments, the Ac₃ transformation on heating always being at a higher temperature than Ar₃, the transformation on cooling.

It was found, however, that the beginning of Ac₃ coincides in temperature with the beginning of Ar₃ as closely as could be judged. It is as if the crystallographic changes at A₃ required, so to speak, a temperature inertia to complete itself both on heating and on cooling, although the effect of rate on the equilibrium (see Fig. 7) appears to be slightly the greater on cooling.

It is possible that the A₃ transformation is somewhat more complex than this, as there are indications from some of the heating curves of a doubling of Ac₃, although not of Ar₃. This effect may be fortuitous.

The relative amounts of heat accompanying the two transformations, A₃ and A₂, is approximately 3 to 1, respectively.

An examination of some of the heating curves will perhaps give the erroneous impression that Ac₂ is an evolution rather than an absorption of heat. The swing back at the maximum is very abrupt, following what appears to be a gradual building up of this maximum from an indeterminate low temperature. This behavior would be in accordance with the gradual change in certain physical properties, such as magnetism and electrical resistance, as A₂ is approached. On the other hand, the opera-

¹¹ Prof. Benedicks having raised the question of the effect on A₂, due to an alternating current heating supply, the authors have taken heating and cooling curves of a sample in vacuo within an ordinary gas-heated muffle furnace, with the following results for A₂ maxima:

Date	Sample	Rate = Degree seconds		Ac ₂	Ar ₂
		Up	Down		
1913.				.	.
Dec. 1.....	F7	0.08	0.33	766	768
Dec. 1.....	F7	.14	.24	768	770
Dec. 1.....	F7	.15	.05	768	768
Dec. 1.....	F7	.23	.23	768	770

tions carried out on sample F2 (Pl. V) failed to diminish sensibly the intensity of Ac_2 , which would imply that this thermal transformation is limited to a narrow temperature interval; also some of the curves of Ac_3 show that this long back swing appears to be in part at least a property of the heating conditions. The shading off on cooling through Ar_2 , if this effect is a real one, might be marked by a similar swing back from this peak, and therefore be indistinguishable. (Compare also Plate XII.)

We hesitate to express an opinion on the nature of the allotropy

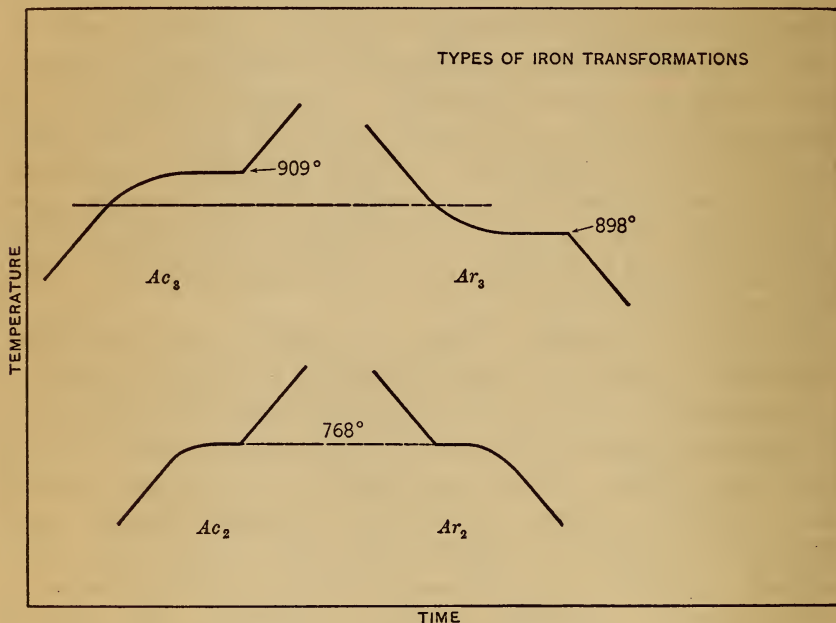


Fig. 8.—Types of transformation in iron.

of iron. These thermal observations appear to show that the transformations A_3 and A_2 are of the types illustrated in Fig. 8. The fact that A_2 appears to be accompanied by no crystallographic change, such as accompanies A_3 , requiring a violent rearranging of relatively large crystal masses and involving a considerable quantity of heat, may account for the sharpness with which Ac_2 equals Ar_2 , and the A_2 transformation may be merely molecular, not involving the crystallographic structure as such. Whether we have any β iron or not to inhabit the region between A_2 and A_3

will depend on our definition of allotropy, but we hope that we have proved beyond a reasonable doubt that under standard conditions there is a definite transformation at 768° and a less well defined although more intense one at 898° to 909° in terms of their maxima on cooling and heating.¹²

In conclusion, we take great pleasure in acknowledging the samples of iron and analyses from Prof. C. F. Burgess, Prof. H. C. H. Carpenter, Dr. H. Goldschmidt, Mr. J. R. Cain, and the American Rolling Mill Co., and the cooperation of the chemical

¹² The authors would suggest the following concerning the theory of allotropy of iron:

1. Some of the experimental facts that any theory must satisfactorily account for are: A definite thermal effect, independent of rate of heating or cooling, located at $768^{\circ} \pm 0.5 = Ac_2 = Ar_2$, i. e., with no measurable lag; a much greater thermal effect, but dependent upon rate, accompanying a marked crystallographic change, and, as extrapolated for zero rate, located at $Ac_3 = 909^{\circ}$ and $Ar_3 = 898^{\circ}$. Both the Ac_2 and Ac_3 maxima appear to be anticipated by gradual changes in physical properties below these temperatures defining the maxima. Finally, A_2 and A_3 are distinct transformations.

2. Among the experimental uncertainties are, whether with A_2 there is associated any crystallographic change, however slight—it being recalled that the thermal change is also very slight—and whether there is any slight volume change accompanying A_2 . Concerning A_3 , we are not sure whether, as zero mass and zero rate are approached, Ac_3 exactly equals Ar_3 or not. For neither A_2 nor A_3 has the beginning of Ac_2 or Ac_3 been exactly located.

3. We may define an allotropic transformation in many ways. Confining ourselves to a pure substance in the solid state, let us make the simple definition: *An allotropic transformation is one accompanied by crystallographic change.*

4. There appears to be no doubt that A_3 is an allotropic transformation under this definition, whether or not for zero rate and mass $Ac_3 = Ar_3$, so long as there is observed a crystallographic change. It is not necessary in the case of iron to add to the definition the complications of Smits's theory, actually observed with the masses hitherto used experimentally, namely, that $Ac_3 > Ar_3$, and the faster the rate the greater the interval $Ac_3 - Ar_3$.

5. Sufficient experimental evidence is yet wanting to decide in favor of A_2 being an allotropic transformation according to the above definition.

6. So much for facts and theory. We still have the realms of analogy and hypothesis to work upon to guide us as to the probable nature of A_2 in terms of allotropy. One of the greatest experimental difficulties encountered is due to the nontransparency of iron crystals rendering an adequate optical examination of iron passing through A_2 well-nigh hopeless.

Turning to the transparent substance quartz, however, we have a material which appears to present a close analogy in certain of its transformations to those in iron. At 575° , quartz has a very minute transformation although a definitely defined one by thermal analysis, corresponding evidently to our A_2 in iron. At about 900° there is a violent crystallographic change in quartz accompanied by a correspondingly large thermal effect and also by a very considerable volume change; in iron, exactly our A_3 . Now it is interesting to note that for the reversible point at 575° in the transparent quartz, there is a very slight crystallographic change accompanied by a minute volume effect which anticipates the sharp maximum at 575° by many degrees in the same way that the numerous physical properties of iron appear to anticipate the sharp maximum of iron at $Ac_2 = 768^{\circ}$.

7. Reasoning from the quartz analogy, therefore, the following hypotheses may be made regarding the nature of the A_2 transformation in iron, namely, that A_2 is an allotropic point accompanied by a very minute but as yet undetected crystallographic change and differing from A_3 mainly in magnitude; that when sufficiently exact expansion measurements are made on pure iron, a minute but abrupt volume change will probably be found at A_2 preceded by a very feeble anticipatory region in the expansion curve below A_2 .

If experiment eventually proves the first of the above hypotheses incorrect, we have the oft-expressed alternative that the A_2 transformation is mainly if not entirely associated with the passage from the ferromagnetic to the paramagnetic state; and under the above definition, A_2 would not be an allotropic transformation, and β iron would be really dead.

WASHINGTON, December 1, 1913.

division of this Bureau, in making check analyses. The care and skill with which Mr. H. Scott has assisted us in taking and reducing the observations has greatly expedited the investigation, and we are indebted to Mr. H. S. Rawdon for the photomicrographic examinations.

WASHINGTON, September 22, 1913.

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This list of references to the literature of the critical points of pure iron makes no pretense of being complete. Many of the papers dealing mainly with the theoretical and controversial aspects of the subject are omitted, but it is believed that a sufficient number of titles concerning the experimental aspects of the subject are included to enable anyone to readily get in touch with the subject. The papers are grouped in terms of the principal phenomena studied by the authors.

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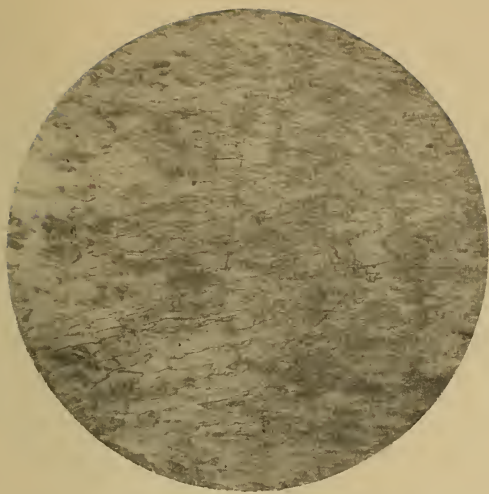


FIG. 1.—Cain's electrolytic iron as deposited. Section perpendicular to the electrode



FIG. 2.—C. F. Burgess's electrolytic iron heated to 1050° C several times but not remelted

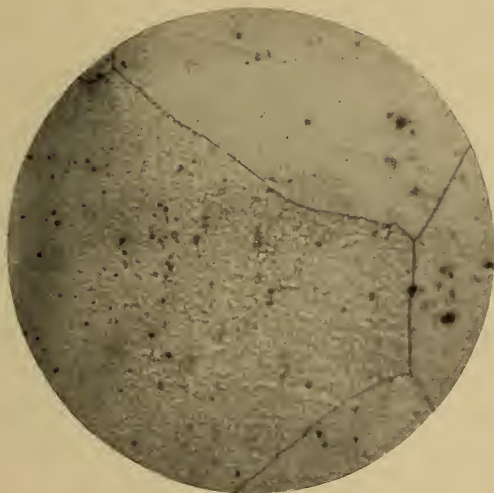


FIG. 3.—Same as Fig. 2, but at 500 x. Small bubbles are seen at this magnification

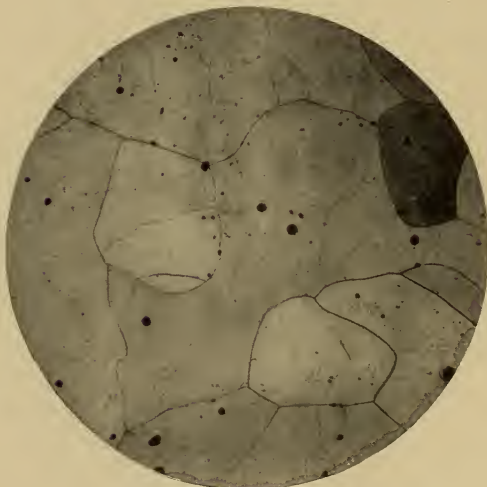


FIG. 4.—Cylinder Fr, remelted from American ingot iron in gas furnace

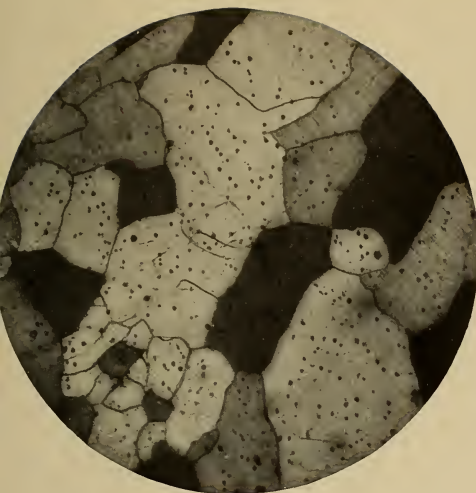


FIG. 5.—Cylinder F6. Cain's electrolytic iron, remelted in gas furnace

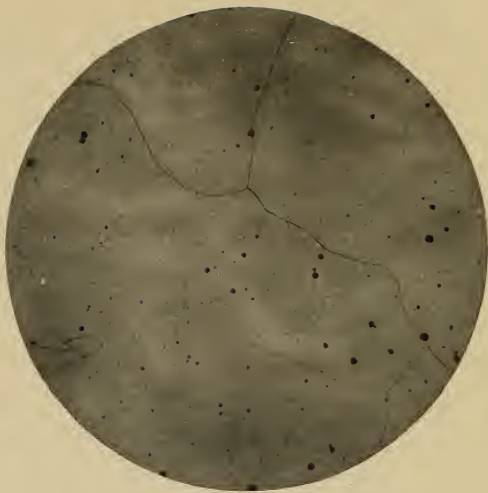


FIG. 6.—Cylinder 26 (Langheim-Pfanhauser) remelted in Arsem furnace in vacuo

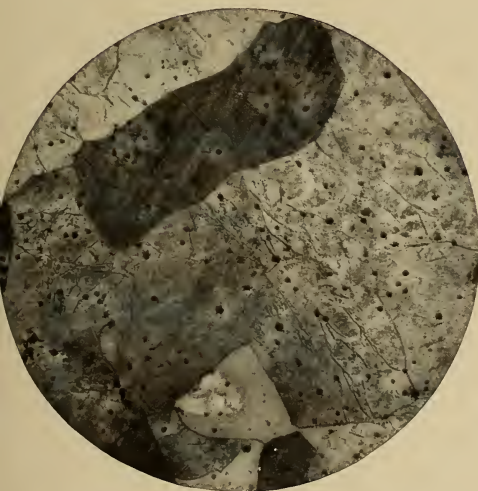


FIG. 7.—Cylinder F₃ (Langheim-Pfanhauser) remelted in gas furnace

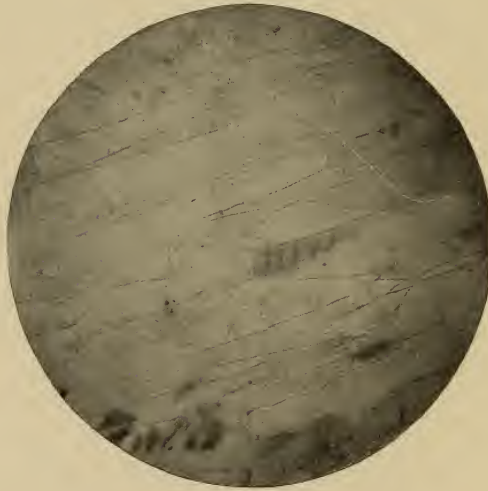


FIG. 8.—Same as Fig. 1, but 250 diameters

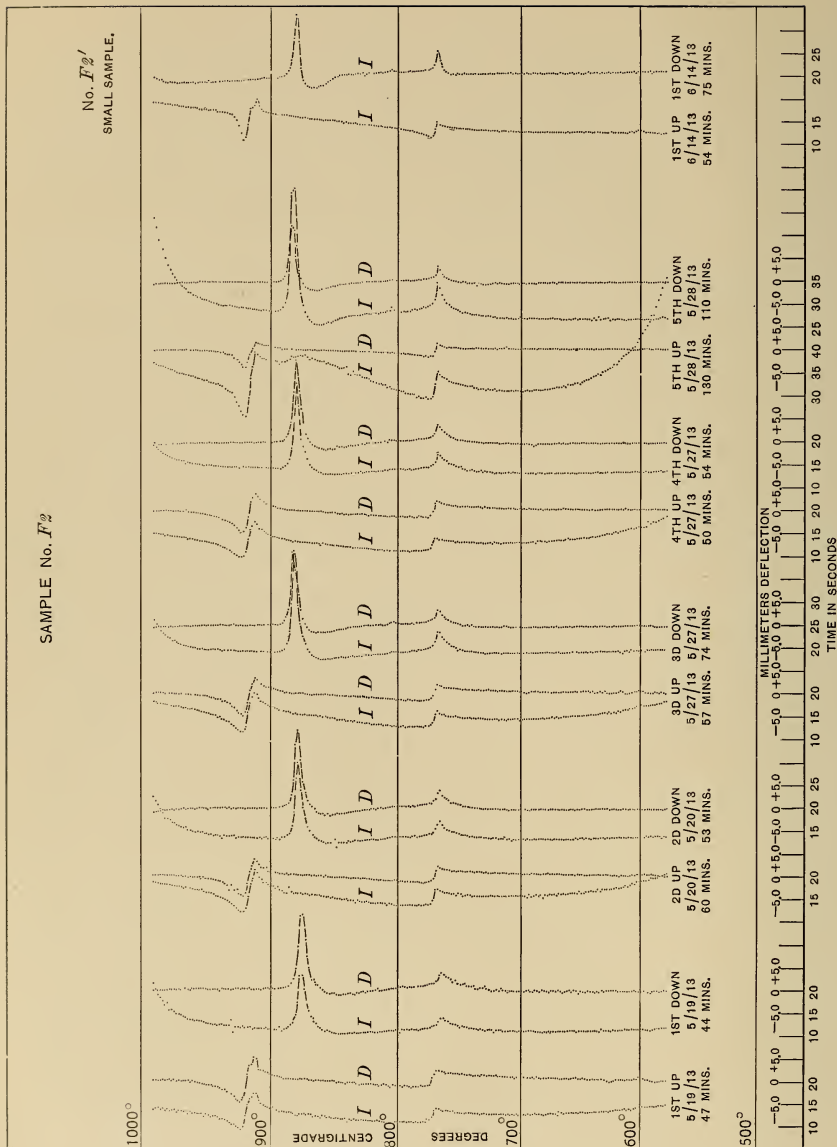


Plate IV.—Curves for samples F_2 and F_2

SAMPLE No. F_2

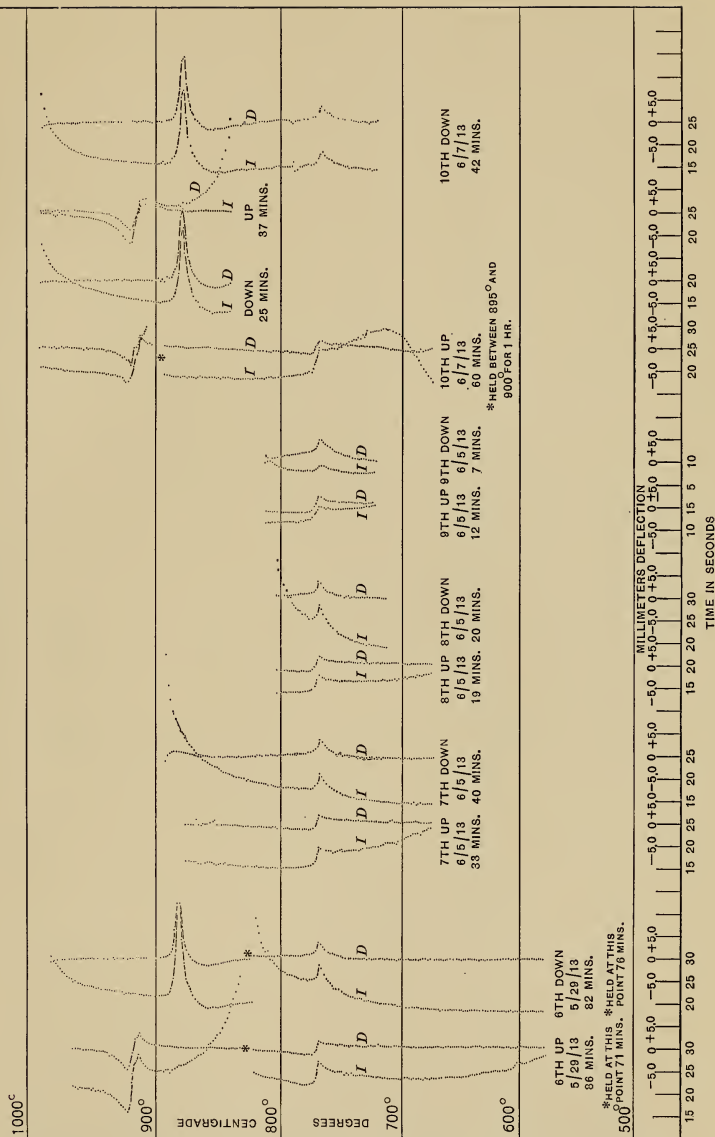


Plate IVa.—Showing persistence of A2

SAMPLE No. $I^{7/4}$

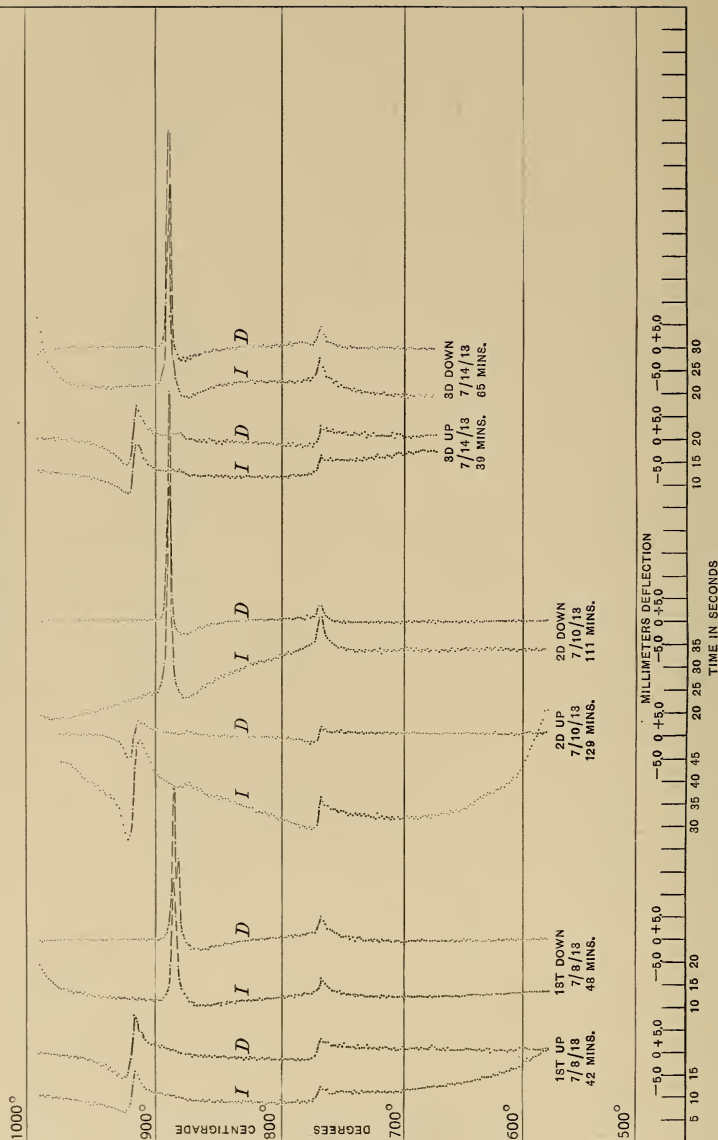


Plate V.—Curves for sample F_4

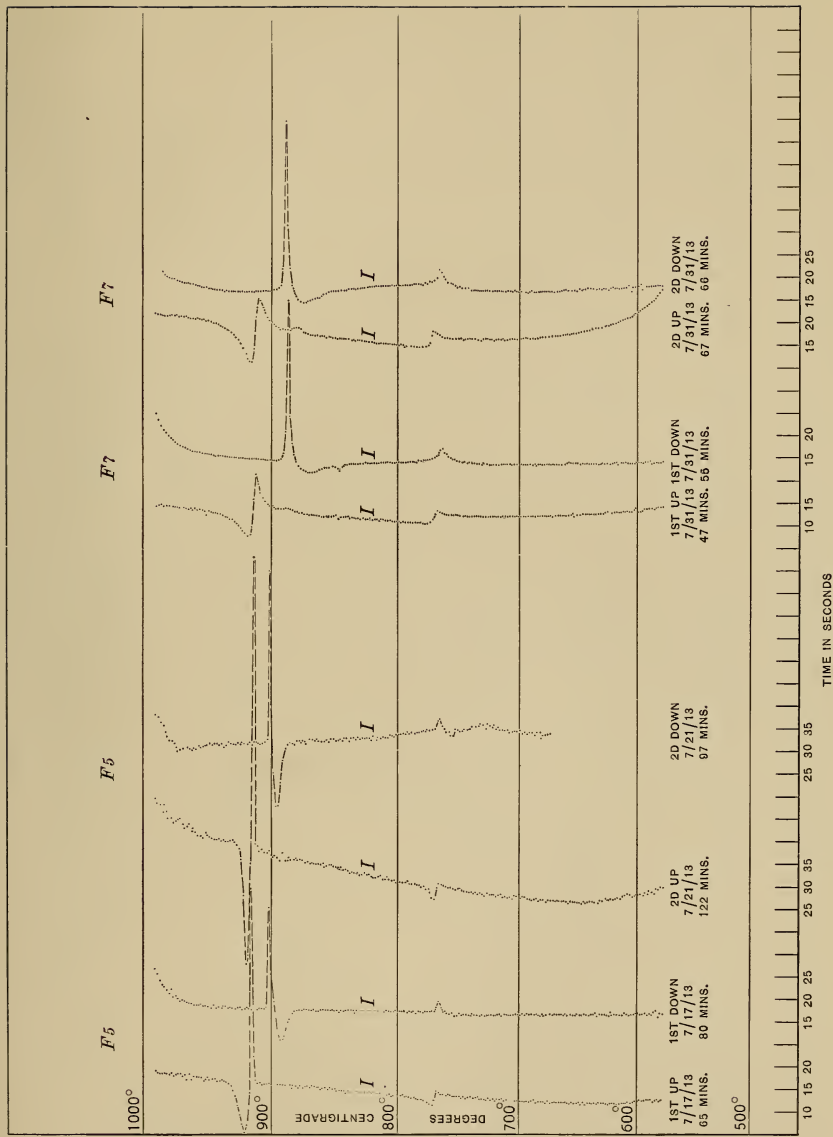


Plate VI.—Curves for samples F5 (Carpenter's sample) and F7

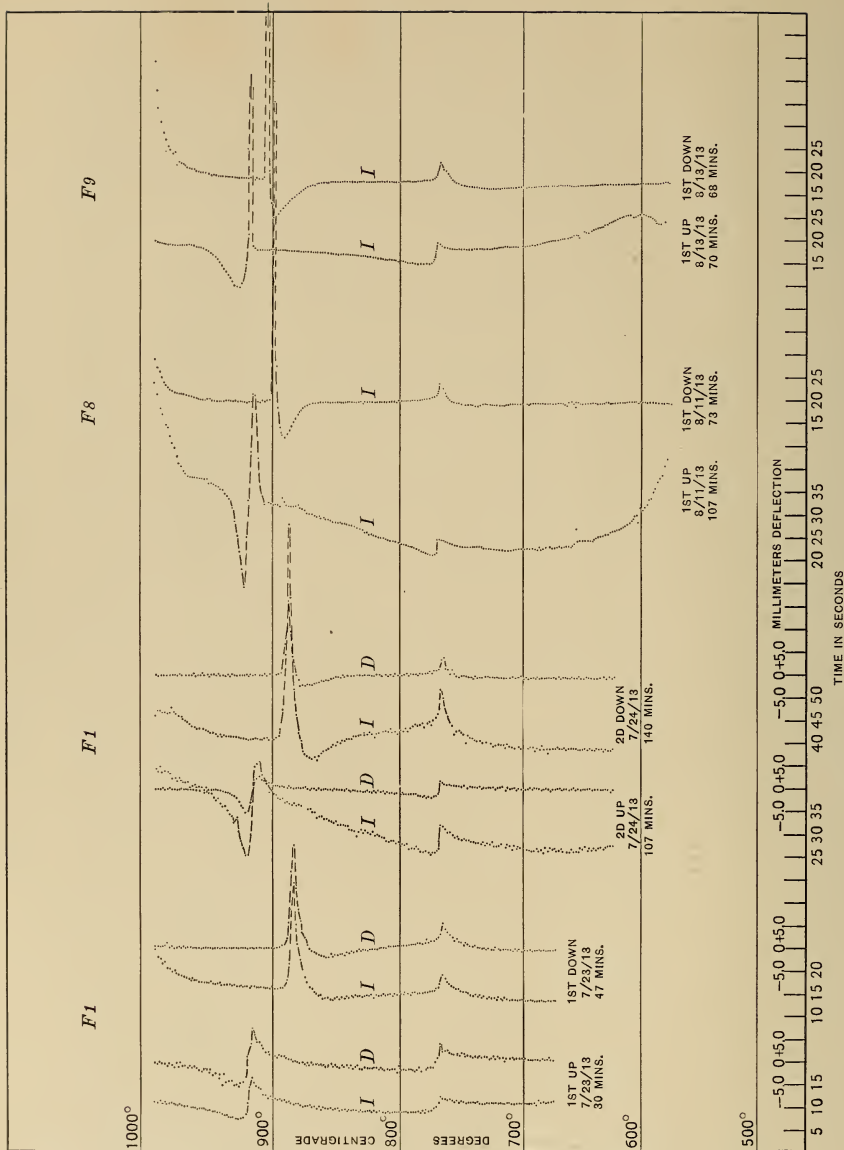


Plate VII.—Curves for samples *F1*, *F8*, and *F9*

SAMPLE No. *F3*

PLATINUM vs. PALLADIUM

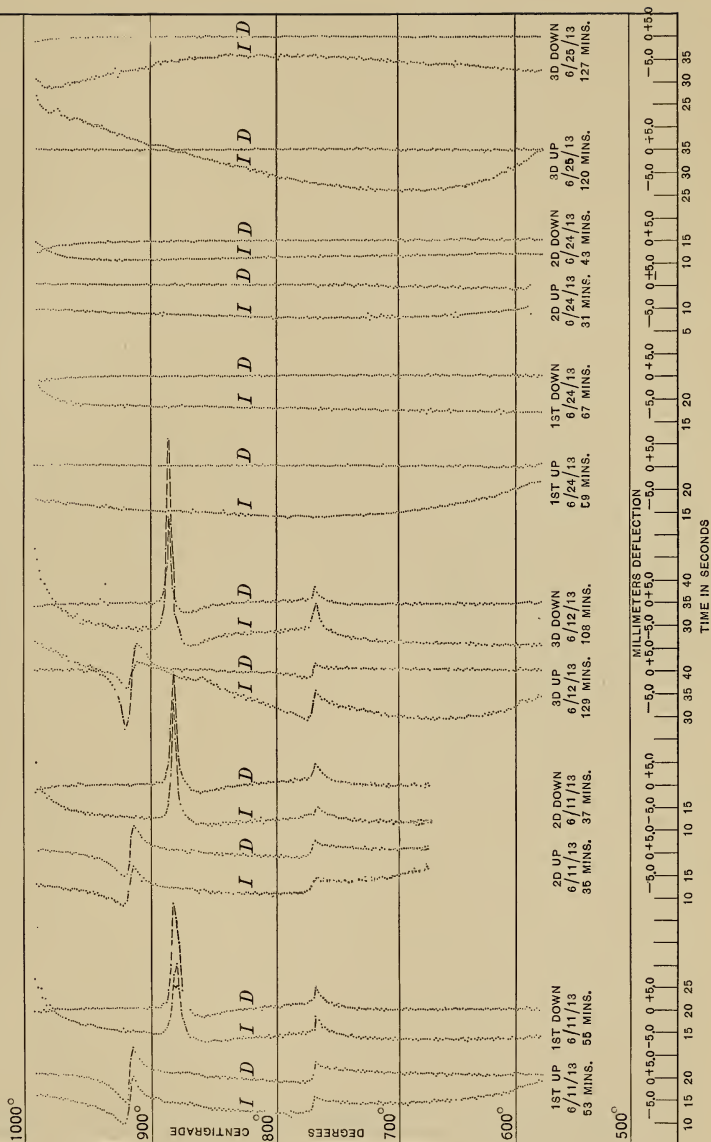


Plate VIII.—Curves for sample *F3* and *Pt-Pd* blank

SAMPLE No.22

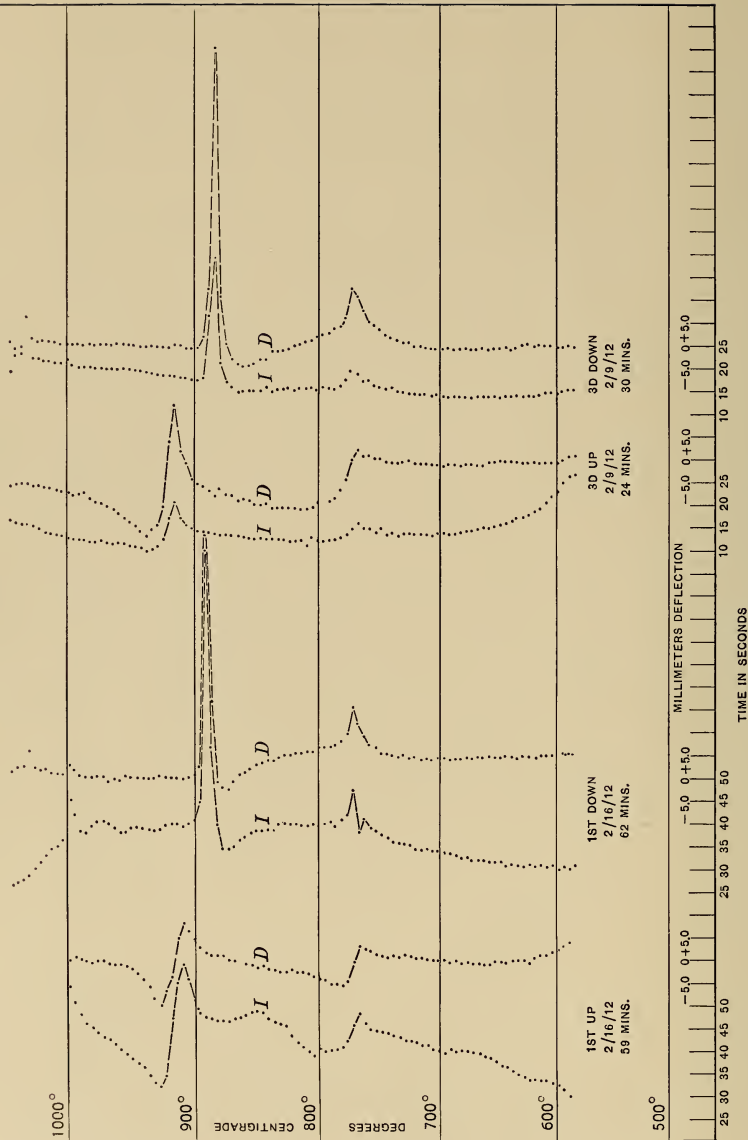


Plate IX.—Curves for sample 22

SAMPLE No.22

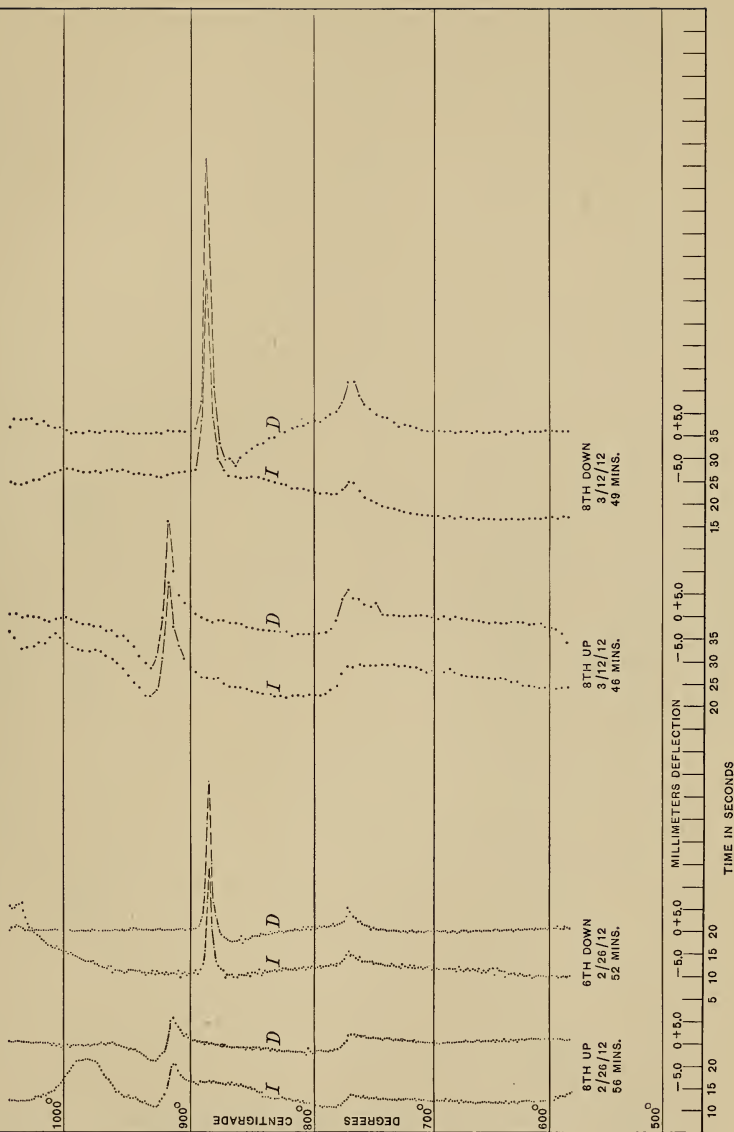


Plate IXa.—Curves for sample 22

[illegible]

Plate X.—Curves for sample 26

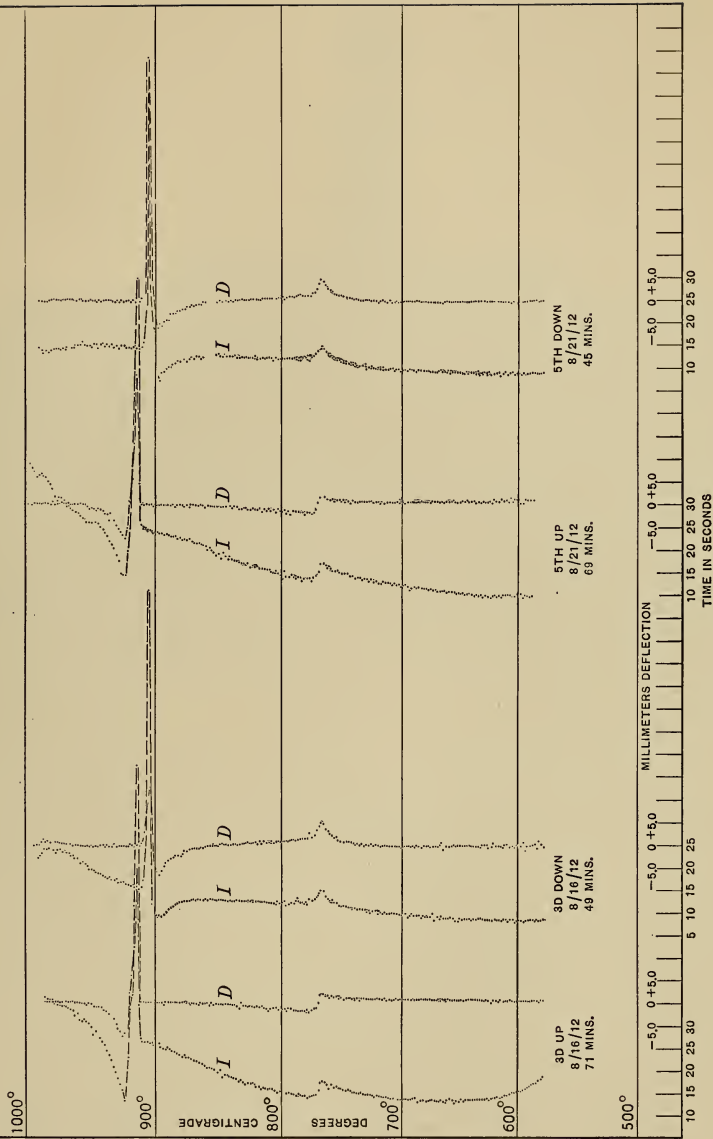


Plate Xa.—Curves for sample 26

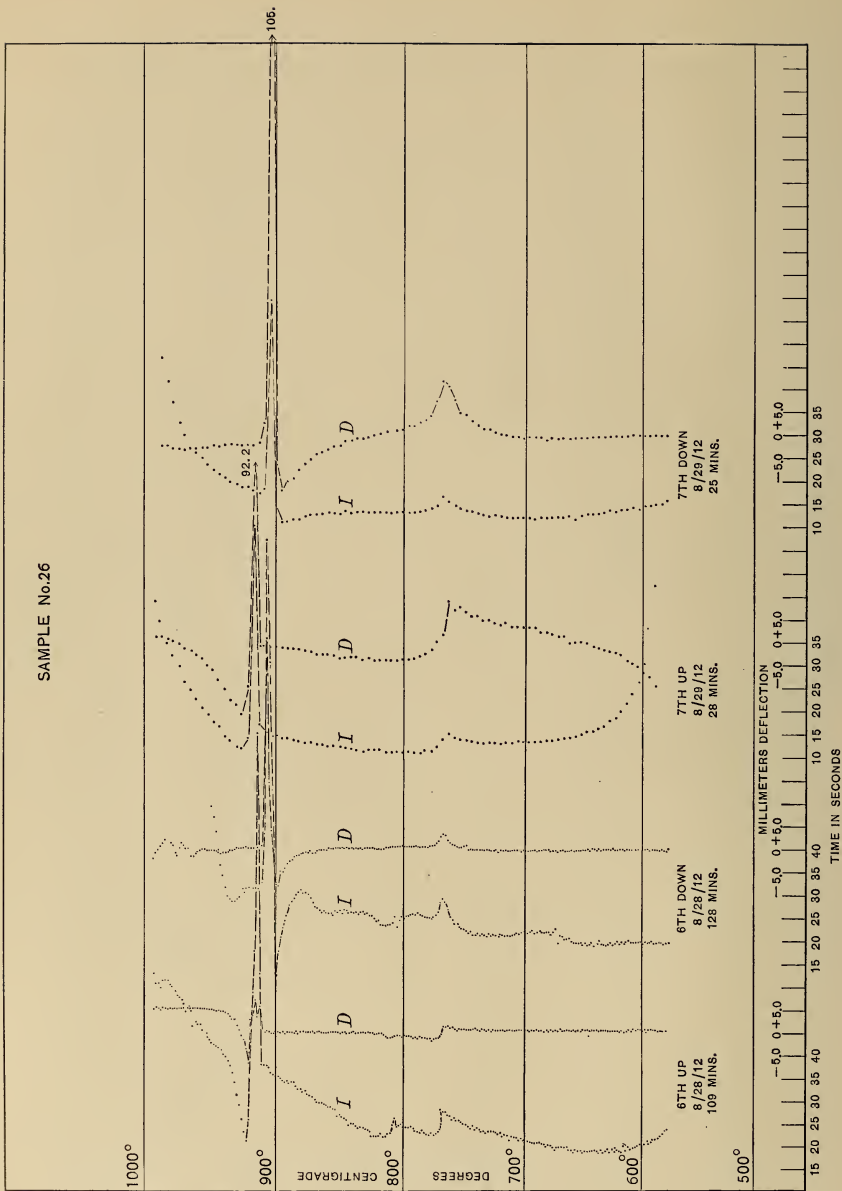
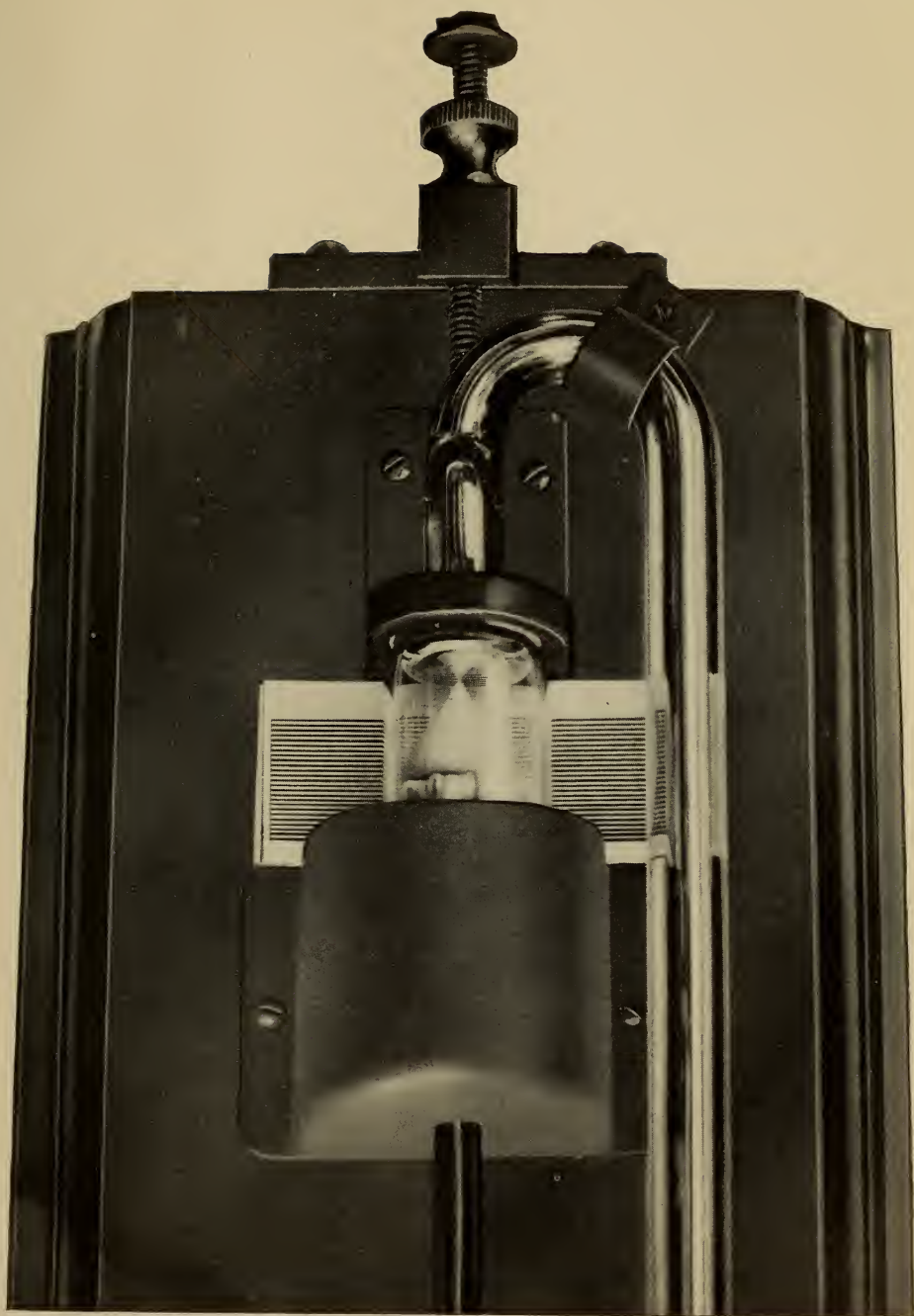


Plate Xb.—Curves for sample 26

Fig. 1



SAMPLE No. *F*₃

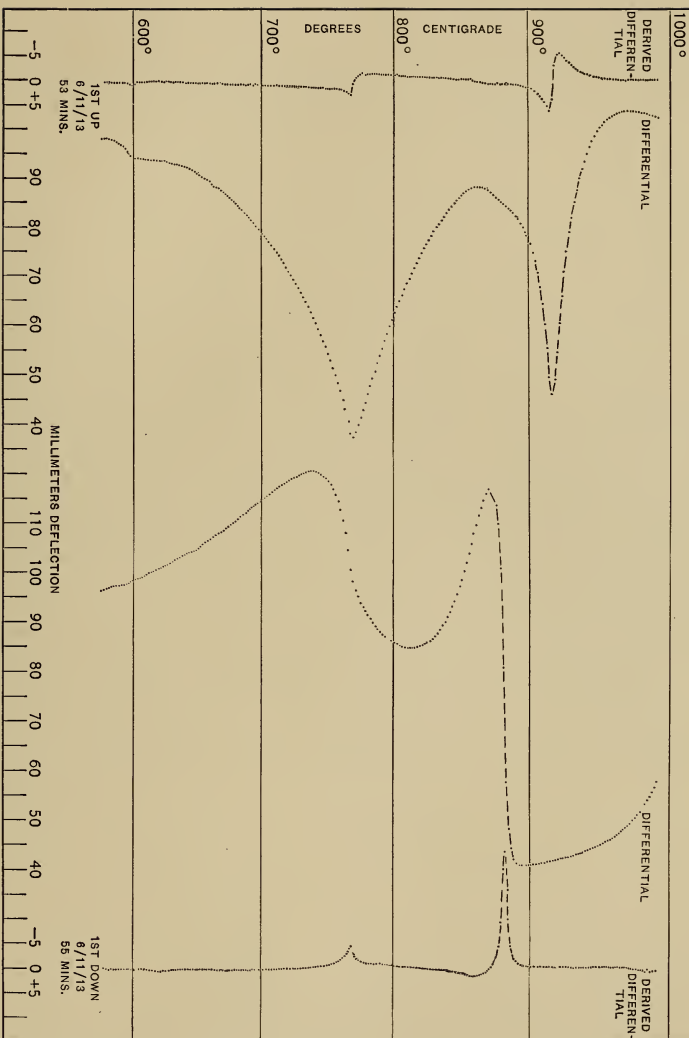


Plate XII.—Comparison of differential and derived differential curves

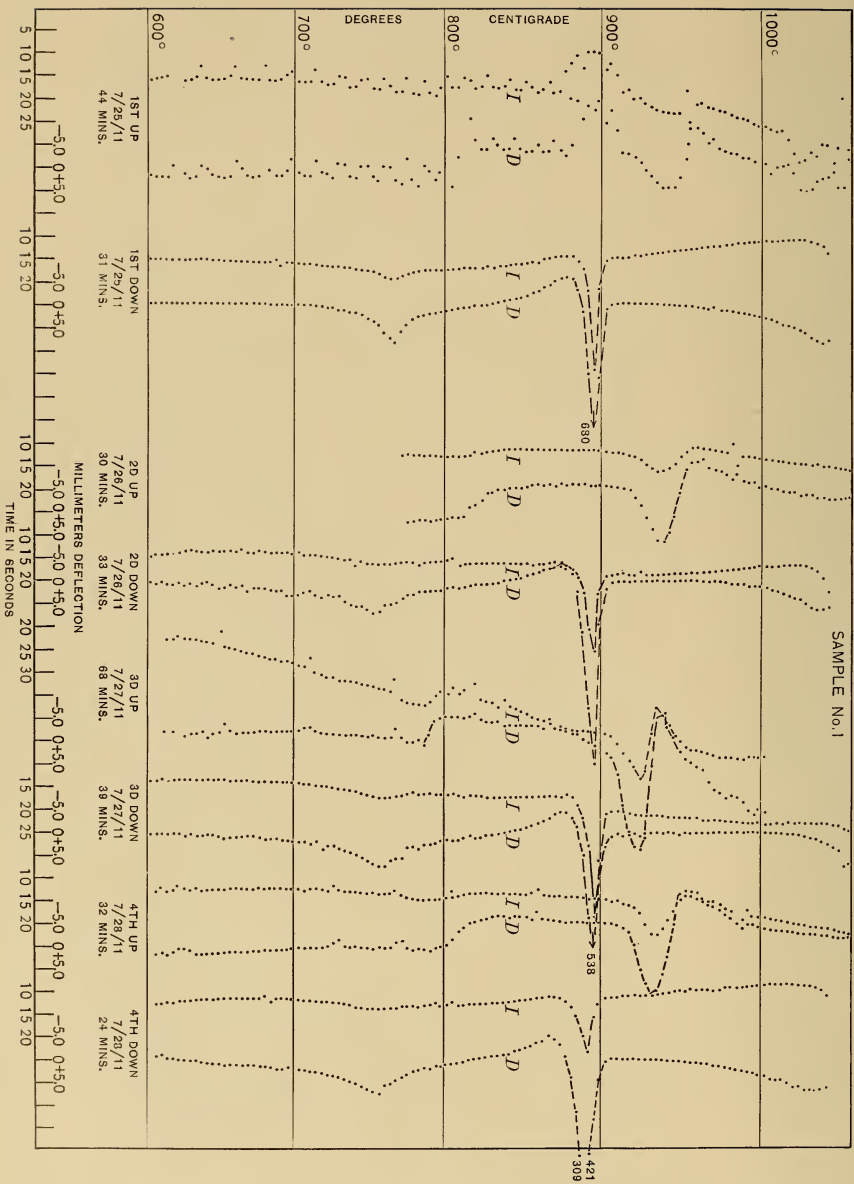


Plate XI.—Curves for sample 1 (first series taken)



