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FREEZING TEMPERATURES OF HIGH-PURITY IRON AND OF SOME STEELS

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ABSTRACT

The freezing temperature of high-purity iron (99.99+ percent) in an atmosphere of helium was measured with an optical pyrometer and found to be 1,539° ±1° C. The same samples of iron were found to freeze 1° C lower in an atmosphere of hydrogen. In addition, the initial freezing temperatures in an atmosphere of helium of some irons of lesser purity and of some steels were measured to determine the effects of various impurities and alloying elements. The results of measurements on 23 samples of irons and steels, together with the chemical analyses, are reported. The freezing-point depressions of the various elements are listed in a table which may be used to calculate the initial freezing temperatures (liquidus points) of iron containing many combinations of 17 elements, which include all those generally found in commercial irons and steels.

The samples containing less than 0.1 percent of impurities were melted in beryllium oxide crucibles and the other samples, in all but two cases, were melted in crucibles of aluminum oxide. Temperatures were determined by means of an optical pyrometer sighted into refractory blackbodies immersed in the freezing metal.

CONTENTS

I. INTRODUCTION

The wide variety of purposes for which iron and steel are used makes their properties of the greatest importance. Furthermore numerous alloys with special properties are required to satisfy the needs of modern industry. It is for this reason that the effect of various impurities and alloying elements upon the properties of iron is of such great interest. The effect of such constituents upon any property of pure iron can be established only after the value of that particular property has been determined for pure iron. One property, which is of particular interest to those investigating or producing iron or steel, is the melting, or freezing, point.

Although many values for the melting point of iron have been reported, there is still some uncertainty regarding the melting point of pure iron, because iron of high purity has not been available for the measurements and because no determination under entirely satisfactory experimental conditions has been reported. Even after a relatively pure iron has been produced and its purity established, precautions must be taken to maintain its purity during the measurement of the melting point, because it is so readily contaminated by many crucible materials and gases during melting [1].[1]

II. PREVIOUS WORK

A summary of the various determinations of the melting or freezing point of iron since 1904 is given in table 1. Many of the earlier determinations are included primarily for their historical interest. In comparing the reported values in table 1 with one another, it should be borne in mind that in nearly all of these investigations one or more of the following conditions prevailed: (1) The investigators were primarily interested in establishing phase equilibrium or constitutional diagrams and were not primarily interested in an accurate determination of the melting point of iron. (2) The impurities reported were so great and so diverse that the various results can scarcely be considered as determinations of the melting point of the same material. (3) No consideration was given to gases, which have a significant effect upon the melting point. (4) The iron was subjected to contamination, particularly by gases, during the determination. (5) The temperature-measuring instruments used in the various investigations were not calibrated on the same basis.

If a complete chemical analysis, including gases, had been given in each case, the value which each observer would have obtained on his particular temperature scale with metal of any specified purity could be computed from the effects of various impurities upon the melting point, but the analyses in most cases are inadequate to give any significance to such a calculation. It was decided to accept the values reported as applying to the melting point of the particular iron used in the particular atmosphere employed, and to reduce the reported values of temperature to a common basis as far as possible. However, even this adjustment has certain limitations.

In most of the determinations listed in table 1, the reported value is based upon a calibration of the temperature-measuring instrument at either the melting point of nickel or the melting point of palladium with various values for each. The adjustment of the reported values to the same temperature scale requires the selection of one particular value for the melting point of nickel and another for the melting point of palladium. The two values selected for these two melting points must be on the same temperature scale. The procedure is questionable because there is no reason to believe that all the nickel or all the palladium used in these calibrations melted at the same temperature and because there is no way of determining what the respective values were.

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[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1.—*Determinations of the melting or freezing temperatures of iron*

Observers	Reference	Year	Reported impurities	Crucible material	Atmosphere	Value reported	Type of instrument used	Basic calibration point	Reported values adjusted for Ni-1,455° C Pd-1,554 Pt-1,773
			% by wt			*°C*		*°C*	*°C*
Carpenter and Keeling	[2]	1904	0.11	Magnesia	CO	1,505	Thermocouple	Extrapolated above 1,000° C	
Guertler and Tammann	[3]	1905	.2 to .6			1,555 ±5	do	Ni-1,484	1,521
Isaac and Tammann	[4]	1907	.29	Porcelain	N_2	1,527 ±5	do	Ni-1,451	1,532
G. K. Burgess	[5]	1907	.05		H_2	1,505	Optical	Pt-1,753	1,517
H. Karkort	[6]	1907	.73	Magnesia	CO	1,504	Thermocouple	Pd-1,535	1,532
R. Sahmen	[7]	1908	.27	Porcelain	N_2	1,532	do	Ni-1,451	1,537
B. Saklatwalla	[8]	1908		Magnesia	N_2	1,510	do	Cu-no value	
A. Müller	[9]	1909	.20	Magnesite	Vacuo	1,485 to 1,525	do		
N. Konstantinow	[10]	1910	.50	do	Under $BaCl_2$	1,514	do	Ni-1,451	1,519
Ruer and Shüz	[11]	1910	.20	do		1,502	do	Ni-1,451	1,507
Loebe and Becker	[12]	1912	.16	Porcelain	CO	1,525	do	Ni-1,451	1,530
Ruer and Kaneko	[13]	1913	.20	do	N_2	1,524	do	Ni-1,451	1,529
Ruer and Fick	[14]	1913	.20	do	N_2	1,524	do	Ni-1,451	1,529
Ruer and Klesper	[15]	1914	.04	do	N_2	1,528	do	Ni-1,451	1,533
Burgess and Waltenberg	[16]	1914	.015 to .03		Vacuo and H_2	1,530	Optical	Pd-1,549 Ni-1,452	1,534
Rümelin and Fick	[17]	1915	.04	Porcelain		1,526	Thermocouple	Ni-1,451	1,531
Ruer and Goerens	[18]	1917	.04	do	N_2	1,528	do	Ni-1,451	1,533
Hanson and Freeman	[19[	1923	.13	Alumina	N_2	1,530	do	Ni-1,452	1,534
Tritton and Hanson	[20]	1924	>.08	Porcelain	N_2 and A	1,535	do	Pd-1,555	1,534
W. P. Sykes	[21]	1926	.025	Alundum	H_2	1,532	Optical and thermocouple.	Ni-no value	
Andrew and Binnie	[22]	1929	(1)	do	Cracked ammonia	1,537	Thermocouple	Extrapolated above 1,200° C	
Jenkins and Gaylor	[23]	1930	.02 to .10	Alumina	H_2	1,527	Optical	Pd-1,555	1,526
Chipman and Marshall	[24]	1940	.031	Beryllia support	Moist H_2	1,535	Thermocouple	Pd-1,555	1,534
Present work		1940	<0.01	Beryllia	He	1,539	Optical	Au-1,063	1,539

[1] Decarburized Armco.

Most of the values for the melting point of iron were determined with thermocouples. The difference between the iron and palladium points is so small, about 20° C, that this difference will be very nearly the same on practically any temperature scale. The difference between the iron and nickel points, however, is large enough to make the extrapolation from one point to the other depend significantly upon the emf-temperature relation used. The values obtained with thermocouples calibrated with nickel, therefore, are subject to an additional uncertainty not present in those values determined with thermocouples checked with freezing or melting palladium.

The values generally accepted for the melting points of pure nickel and pure palladium on the International Temperature Scale are 1,455° and 1,554° C, respectively. Although the assumption that the various investigators had available nickel or palladium as pure as the metals used in establishing these points is very doubtful, the values reported for the melting point of iron have been adjusted on that assumption, as shown in the last column of table 1. This adjustment brings the values into much better agreement, reducing the spread from 53° to 22° C and the average deviation from 10° to 5° C, and probably adjusts most of the reported values in the right direction—but the uncertainties involved in the adjustment should be kept in mind.

Three determinations in which relatively pure iron was used and in which the temperature scale employed is definitely stated deserve special consideration. These are the determinations of Burgess and Waltenberg [16], Jenkins and Gaylor [23], and Chipman and Marshall [24].

Burgess and Waltenberg reported a result of 1,530° C as the mean of two values by different methods, 1,533° C by the micropyrometer method in which the iron was heated on a platinum strip in hydrogen and 1,528° C by melting the iron in an Arsem furnace both in vacuo and in hydrogen. We attribute the lower value obtained in the Arsem furnace to carbon contamination from the furnace atmosphere and to poor blackbody conditions. Considering only the micropyrometer value, the adjusted value of Burgess and Waltenberg becomes 1,537° C.

Jenkins and Gaylor used several methods, including a crucible method with partially immersed blackbodies. They obtained a value of 1,527° C and reported that the presence of iron vapor interfered with their observations. In our opinion, the low value they obtained is not surprising in view of the arrangement of their blackbodies.

Chipman and Marshall suspended strips of carbonyl iron in hydrogen and melted them in a uniformly heated enclosure with the measuring junction of a thermocouple near the specimen of iron. The melting temperature was taken as the temperature at which drops of metal fell from the specimen. The value 1,535° C reported apparently applies for iron in equilibrium with hydrogen, inasmuch as the iron was heated very slowly as the melting point was approached. Part of the difference of 4° C between this value and the value obtained in the present work is undoubtedly due to hydrogen, and it is also probable that the iron was slightly contaminated by silicon due to the reduction of the silica in the porcelain tube which was close to the sample. On the whole, however, their result and the micropyrometer result of Burgess and Waltenberg are the two values to which the most weight should be given.

III. PRESENT WORK

1. MATERIALS

The materials used in this work consisted of 2 samples designated as "high-purity" iron, 1 sample of slightly lower purity than the above, 1 sample of Armco ingot iron, and 19 steels.

The high-purity iron was prepared by Thompson and Cleaves [1] by reducing purified iron oxide to sponge iron, melting the sponge, and remelting first in hydrogen and then in vacuo. The samples used were taken from the ingots designated in their paper as numbers 3 and 15 and have been numbered to correspond with the ingots from which they were taken. These ingots were examined spectroscopically and by chemical methods for the presence of 55 elements. The impurities detected were chiefly sulfur, oxygen, and silicon, with lesser amounts of carbon, phosphorus, copper, hydrogen, and nitrogen. The total of impurities detected was less than 0.01 percent. The complete analyses of the ingots are given in the paper by Thompson and Cleaves. All of the impurities detected are listed in table 4.

The sample of iron identified as Y in table 4 came to us indirectly from the Westinghouse Research Laboratory in 1934. The analysis of this sample as reported by that laboratory is given in table 4.

The samples of Armco ingot iron and the 19 steels were machined from bars which had been used for the preparation of the Standard Samples corresponding to the designations given in table 4. The analyses, with the exception of the oxygen content of Sample 55, are those given in the February 18, 1935 Supplement to National Bureau of Standards Circular C398.

No analyses were made of the samples after the freezing-point determinations.

The temperature coefficient of electrical resistance of relatively pure materials will serve as a criterion of purity after a correlation between the two has been established. To provide data for such correlation for iron, we have given, in table 2, corresponding values for some of the samples used in this work. However, unless the wires are given essentially the same heat treatment before the measurements, differences in physical condition may mask the differences due to composition.

The values in table 2 are the coefficients for the intervals 0° to 100° C, $(R_{100}-R_0)/100R_0$, measured on wires 0.02 inch in diameter which had been heated in vacuo for 2 hours at 800° C.

TABLE 2.—*Corresponding values of temperature coefficient of resistance and amount of impurities in iron*

Sample	$\frac{R_{100}-R_0}{100R_0}$	Impurities	
		Weight percent	Atomic percent
3 and 15	0.00652	<0.010	<0.028
Y	.00644	<.028	<.081
Ingot iron	.00590	.18	.32

2. GENERAL PROCEDURE

The procedure followed was, in a general way, similar to that employed by the authors in determining the freezing temperatures of several of the platinum metals [25, 26]. The sample of iron or steel, about 75 grams in weight, was machined from an ingot or rod to the size and shape required to fit the crucible and an axial hole was drilled to accommodate a sight tube. The sample, together with the refractory blackbody sight tube, was placed in a refractory oxide crucible, as shown in figure 1 or 2. This entire assembly was then placed inside a Pyrex glass enclosure in which a desired atmosphere could be maintained. The metal was heated by means of a high-frequency induction furnace and the temperature measured by means of a precision optical pyrometer sighted into the blackbody.

In any experiment of this nature, every effort should be made to select a crucible material and atmosphere which will not alter the chemical composition of the metal during heating at temperatures above its melting point and to arrange the apparatus so that the atmosphere admitted to the enclosure will surround the metal and not be significantly contaminated by adsorbed gases released by the refractory during heating.

3. CRUCIBLES

At the time the freezing-temperature measurements were made on steels, accounts of investigations with iron and steel indicated that these materials could be melted in aluminum oxide crucibles without any appreciable contamination from the crucible. Consequently, aluminum oxide crucibles were used for all the steels except two. In these two cases beryllium oxide was used, not because it was considered superior to aluminum oxide, but merely to gain some information regarding its suitability for use with pure iron. Subsequently, Thompson and Cleaves reported that beryllium oxide was preferable to aluminum or magnesium oxide for melting pure iron. Beryllium oxide crucibles were therefore used exclusively in the later work on pure iron.

The beryllium oxide crucibles and accessory parts were prepared by the general method described by Swanger and Caldwell [27]. Pure unfused beryllium oxide was heated to 1,800° C in a graphite container by means of a high-frequency induction furnace. The calcined oxide was then heated to about 1,100° C in oxygen to remove any carbon either combined or in discrete particles, and was then broken up and ground in a steel ball mill to pass a 200-mesh screen. The finely divided material was treated with HCl to remove iron and then washed with distilled water. The crucibles were formed by tamping the material moistened with a solution of beryllium chloride (4 g of $BeCl_2$ in 100 ml of water) into a graphite mold lined with a layer of paper. The interior of the crucible was formed by drilling with a properly shaped tool while the material was still moist. The mold containing the crucible was heated in air to about 1,100° C for 2 hours. This enabled the crucible to be slipped out of the mold. It was then placed on a tungsten sheet inside a graphite container and fired to 1,800° C by means of an induction furnace.

The crucible cover and the cone above it were made separately in the same way except that before finally firing to 1,800° C, they were cemented together with a paste made from beryllium oxide and the beryllium chloride solution. The blackbody sight tubes were formed by rolling a small amount of the paste on a brass rod, as described by Swanger and Caldwell. The sight tubes were also fired to 1,800° C.

The aluminum oxide crucibles and accessory parts were made in the same way, with the following exceptions: (1) The material was commercially available crystalline alumina which was prepared for tamping by grinding in a porcelain ball mill; and (2) aluminum chloride was used as a binder.

4. ATMOSPHERE

By a process of elimination, helium was selected as the atmosphere in which to melt both the irons and steels. Atmospheres containing oxygen or carbon were immediately rejected because both of these elements are readily taken up by iron. According to Smithells [28], nitrogen at a pressure of 1 atmosphere is soluble in liquid iron at 1,540° C to the extent of about 0.03 percent by weight, and hydrogen at the same pressure is soluble in liquid iron at the melting point to the extent of about 0.0023 percent and in solid iron at the melting point to the extent of about 0.0011 percent by weight. These percentages may appear small, but according to Van't Hoff's law of the freezing-point lowering, 0.0023 percent of hydrogen (by weight) will lower the freezing point of iron about 3° C. Our experience with the volatility of metals and refractories at high temperatures led us to expect very little success in obtaining an accurate measurement of the freezing temperature of iron in vacuo.

Helium was selected as the atmosphere in which to measure the freezing temperature, because all the available evidence indicates that the solubility of helium in either iron or steel is considerably less than that of nitrogen or hydrogen.

For comparison purposes the freezing temperature of high-purity iron was also measured in an atmosphere of hydrogen and in vacuo. The value obtained for the freezing temperature in hydrogen was lower than that in helium, indicating that helium was less soluble than hydrogen. The value obtained in vacuo is lower than that in either helium or hydrogen. This is attributed to the absorption of light by iron vapor present in the line of sight.

The helium used was sufficiently freed of oxygen to prevent any noticeable oxidation of the samples. Commercial helium was passed through copper chips at about 700° C to remove oxygen and then through magnesium perchlorate and phosphorus pentoxide to remove water vapor. The hydrogen used was passed through the same system.

5. ARRANGEMENT OF APPARATUS

The samples of pure iron were mounted as shown in figure 1, and the samples of steel, for greater convenience in changing samples, were mounted as shown in figure 2. In the first case we were primarily interested in obtaining accurate values for the freezing temperatures of a few samples of pure iron, whereas in the latter case we were interested in obtaining values for the initial freezing temperatures of a large number of steels and were willing to make some sacrifice of accuracy for the sake of convenience.

For the pure iron, figure 1, the sample was insulated on all sides to promote temperature uniformity in the metal. Large temperature differences at the time of freezing must be avoided if an accurate measurement of the freezing temperature is to be obtained. The insulating material immediately surrounding the crucible will prevent the excessive loss of metal if, by chance, any cracks should develop in the crucible during repeated heating and cooling. The comparatively coarse insulating material permits the ready passage of gas.

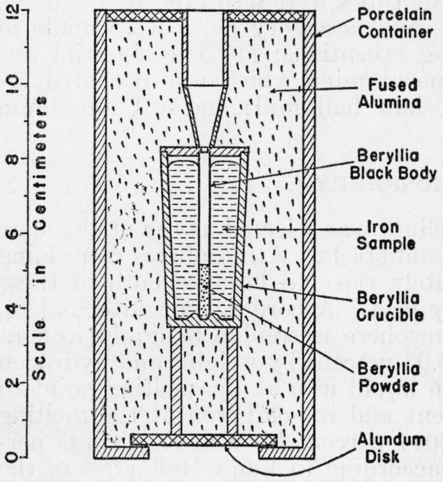

FIGURE 1.—*Cross section showing method of mounting iron samples for the measurement of the freezing temperature.*

In the mounting for the steels, figure 2, any one sample could be easily replaced by another. Unfused aluminum oxide was used for the insulation because it is a better thermal insulator than the fused material. The unfused oxide might also have been used for the pure iron except for the fact that the particles are much smaller and pack more closely, making it difficult to pass a gas through it to the melting-point sample. In all of these measurements no difficulty of any nature was encountered with either type of crucible.

The Pyrex enclosure in which the samples were heated in the desired atmospheres is shown in figure 3. The mica diaphragms, with central openings to permit sighting into the blackbody, reduce the convection currents. The Pyrex tube was closed with a Pyrex plate sealed to the tube with Cementyte. The cemented joint was cooled by a number of small air jets. Thin sheets of mica between the porcelain container and the Pyrex tube restricted the flow of gas around the porcelain container. The alundum disk in the bottom of the porcelain container permitted the gas, admitted to the top of the tube, to flow through the porcelain container. Before heating a sample, the gas (helium or hydrogen) was passed slowly through the enclosure for approximately

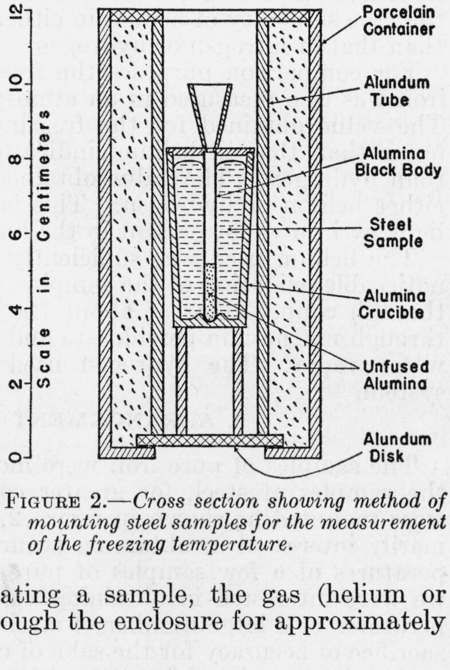

FIGURE 2.—*Cross section showing method of mounting steel samples for the measurement of the freezing temperature.*

16 hours. The sample was then heated slowly so that the gases released from the refractory during heating would be carried off.

The Pyrex tube fitted closely inside of the water-cooled coil of the induction furnace.

6. TEMPERATURE MEASUREMENTS

The optical pyrometer used was the one designed by Fairchild and Hoover [29] and has been briefly described elsewhere [25]. It was fitted with a 45° total-reflecting prism for sighting into the blackbody.

The temperature measurements are expressed on the International Temperature Scale of 1927, in which

$$\log_e\frac{J_2}{J_1}=\frac{C_2}{\lambda}\left(\frac{1}{1336}-\frac{1}{t+273}\right),$$

where J_2/J_1 is the ratio of brightness at the wavelength, λ, of blackbodies at temperature t° C and at the gold point (1,336° K), and C_2 is a constant equal to 1.432 cm-degrees. In these measurements the effective wavelength, λ, of the red screen in the optical pyrometer was 0.6532 μ. For the measurements on high-purity iron, the brightness ratio, J_2/J_1, was measured by utilizing a sector disk of such an opening that it reduced the brightness of the blackbody at the freezing temperature of iron to very nearly that of a blackbody at the gold point. The transmission of the sector disk used was determined on a circle dividing engine as 0.01406 with an uncertainty of 0.00002. An uncertainty of 0.00002 in the transmission corresponds to about 0.25° C in the determination of the freezing temperature of iron.

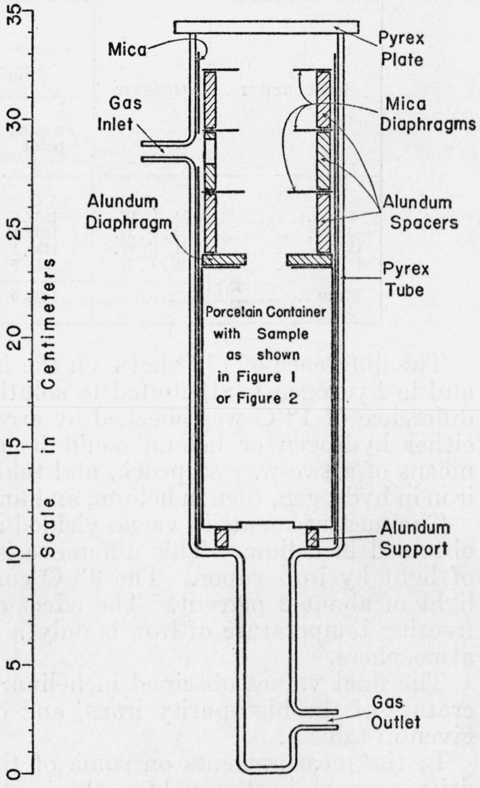

FIGURE 3.—*Assembly used for heating samples in a controlled atmosphere.*

For the observation on the blackbody at the gold point, an assembly of the same dimensions as that shown in figure 1 was used. The only difference was that for the gold, thorium oxide refractories were used.

For the measurements on the steels, an absorption glass was used instead of a sector disk.

IV. RESULTS

The results obtained on the two samples of high-purity iron in helium and in hydrogen are given in table 3. Each freeze represents the mean of from 12 to 24 photometric settings. During the course of these measurements, approximately the same number of observations was taken on the blackbody at the gold point.

TABLE 3.—*Summary of observations on the freezing temperature of high-purity iron*

Ingot number	Observer	Atmosphere			
		Helium		Hydrogen	
		Freezing point	Number of freezes	Freezing point	Number of freezes
		° C		° C	
3	H. T. W.	1538.8	4	1537.5	4
3	W. F. R.	1539.1	5	1538.3	7
15	H. T. W.	1539.1	3	1537.7	3
15	W. F. R.	1538.6	3	1538.0	6
Mean		1538.9		1537.9	

The difference of 1° C between the freezing point of iron in helium and in hydrogen is attributed to solution of hydrogen in iron. This difference of 1° C was checked by arranging an experiment in which either hydrogen or helium could be admitted to the enclosure by means of a two-way stopcock, and taking a series of freezes with the iron in hydrogen, then in helium, and finally shifting back to hydrogen.

The measurements in vacuo yielded a result about 3° C below that obtained in helium. This difference is attributed to the absorption of light by iron vapor. The 3° C corresponds to an absorption of light of about 2 percent. The effect of pressure, as such, upon the freezing temperature of iron is only a small fraction of a degree per atmosphere.

The final values obtained in helium for the initial freezing temperature of the high-purity irons, and other irons, and the steels are given in table 4.

In the measurements on some of the steels, there was a decided drift upward in the values obtained for successive freezes. The maximum drift observed was 4° C per freeze for Sample 12d. This was attributed to changes in the chemical composition. In such cases, the value reported is that obtained by plotting the values for the various freezes as a function of time of heating and extrapolating the curve back to zero time.

It is recognized that, in general, a steel does not freeze completely at any one temperature but instead has a freezing range. In a few cases we were able to detect the lower limit of the freezing range, but these were exceptional. However, no difficulty was encountered in establishing the temperature of initial freezing.

TABLE 4.—*Chemical analyses and initial freezing temperatures of irons and steels*

Sample	Percentage, by weight, of—																		Initial freezing temperature	
	C	Mn	P	S	Si	Cu	Ni	Cr	V	Mo	As	Sn	Al	W	Co	O_2	H_2	N_2	Measured	Computed [c]
																			°C	°C
Pure irons:																				
15	([a])	nil	([b])	0.0013	nil	<0.002	nil	nil	nil	nil	nil	nil	<0.001	nil	nil	0.0019	0.0002	0.0006	1,538.9	------
3	0.001	nil	([b])	.0026	0.003	<.002	nil	nil	nil	nil	nil	nil	nil	nil	nil	.0005	.0001	.0004	1,538.9	------
Y	<.005	<0.002	<0.002	<.005	<.004	------	------	------	------	------	------	------	------	------	------	<.01	------	------	1,537.4	>1,537.5
Ingot iron:																				
55	.013	.019	.003	.017	.001	.041	0.020	0.002	------	0.002	0.012	0.008	0.002	------	0.006	.03	------	.005	1,534.5	1,534
Steels:																				
15b	.101	.559	.032	.038	.292	.145	.083	.064	0.005	.003	.008	------	------	------	------	------	------	------	1,527	1,524
8d	.078	.482	.099	.083	.018	.013	.004	.007	.003	.003	.007	------	------	------	------	------	------	------	1,525	1,526
11d	.202	.430	.006	.041	.027	.010	.008	.008	.002	.001	.008	------	------	------	------	------	------	------	1,520	1,522
111	.202	.662	.023	.020	.292	.122	1.75	.272	.003	.215	.016	------	------	------	------	------	------	------	1,513	1,510
72	.294	.651	.016	.020	.137	.064	0.288	.911	.012	.149	.012	------	------	0.045	------	------	------	------	1,509	1,511
106	.343	.484	.020	.020	.250	.142	.129	1.29	.008	.164	.009	------	1.06	------	------	------	------	.009	1,507	1,506
12d	.418	.344	.013	.036	.016	.015	.007	0.015	.002	.002	.008	------	------	------	------	------	------	------	1,506	1,508
32b	.413	.624	.016	.018	.217	.117	1.21	.638	.006	.005	.017	------	------	------	------	------	------	------	1,496	1,499
73	.314	.276	.023	.031	.360	.033	0.072	13.93	.034	.005	.011	------	------	------	------	------	------	------	1,494	1,491
30c	.489	.707	.019	.014	.237	.099	.080	0.977	.235	.010	.016	------	------	------	------	------	------	------	1,494	1,497
33b	.366	.700	.037	.032	.233	.114	3.48	.029	.005	.003	.016	------	------	------	------	------	------	------	1,493	1,492
21c	.574	.630	.062	.030	.107	.050	0.152	.166	.007	.005	.008	------	------	------	------	------	------	------	1,484	1,492
22b	.674	.935	.084	.042	.123	.009	.003	.003	.005	.002	.004	.0004	------	------	------	------	------	------	1,483	1,484
100	.617	.39	.023	.022	.192	.123	.151	.180	.011	.005	------	------	------	------	------	------	------	------	1,481	1,486
14b	.817	.493	.008	.031	.009	.017	.074	.018	------	.008	.012	.018	------	------	------	------	------	------	1,477	1,478
101	.061	.554	.011	.013	.763	.056	8.44	17.56	.044	.006	------	.005	------	------	------	------	------	.028	1,464	1,462
50a	.660	.287	.020	.007	.48	.047	0.045	3.52	.970	.009	.042	.026	------	18.25	------	------	------	------	1,460	1,461
35a	1.03	.345	.037	.036	.387	.267	.254	0.264	.011	.004	.009	------	0.005	------	------	------	------	------	1,456	1,457
51	1.29	.271	.011	.014	.250	.044	.02	.02	------	------	------	------	------	------	------	------	------	------	1,434	1,442

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[a] This lot of iron was not analyzed for carbon. The carbon content of other lots of iron prepared by the same methods was 0.001 percent or less.

[b] These lots of iron were not analyzed for phosphorus. The phosphorus content of other lots of iron prepared by the same methods was less than 0.0005 percent.

[c] The values in this column were computed by summing up the effects of the individual elements.

V. EFFECT OF IMPURITIES AND ALLOYING ELEMENTS

The effect of certain individual elements upon the initial freezing temperature of iron can be obtained from phase-equilibrium diagrams, but these give no information as to the effect produced when two or more foreign elements are present in the iron. The effect of certain elements, individually or in combination, upon the freezing temperature of iron can be calculated, on certain assumptions regarding dilute solutions, from Van't Hoff's law of the freezing-point lowering; but, in many of the cases, the assumptions regarding dilute solutions do not hold even for very small percentages of the foreign elements. Consequently the effect of several elements upon the freezing temperature, when all are present at the same time, can only be found from experiments.

The measurements of the initial freezing temperatures of the steels, and the chemical analyses, provide data for establishing the effects of various impurities and alloying elements on the freezing temperature of iron when several of the elements are present at the same time. Our results indicate that, in general, when a number of other elements are present in iron, the effect of any one is the same as it would be if the other elements were not present and that the total effect of all the elements is the sum of the effects of the elements taken separately.

The lowering of the freezing temperature of iron by the individual impurities and alloying elements usually present in steels is given in table 5. These values for the individual elements, other than silicon, tungsten, and the gases, were obtained from phase-equilibrium diagrams, chiefly from the International Critical Tables. It was found that the sum of the individual freezing-point depressions could be made more nearly equal to the observed depressions by reducing the value obtained from the phase-equilibrium diagram for silicon from 14° to 8° C per percent and by making the freezing-point depression for tungsten equal to 1° C per percent. The value for tungsten is based upon the observation on only one sample, 50a, and consequently does not apply generally. The values for the gases were computed by using Van't Hoff's law for the freezing-point depression. The values for the freezing-point depressions in table 5 have been found to apply within reasonable limits for amounts of the elements within the ranges given in the last column of table 5.

The initial freezing temperatures of the various irons and steels computed from the chemical analyses and the lowering effects of the individual elements are given in the last column of table 4. The agreement of the temperatures calculated by use of table 5 with the observed temperatures is very good, the average difference being less than 3° C. In general, the computed values are slightly higher than the observed values. However, the amount of the gases present in the steels was determined only in a few instances, and in these instances the agreement between the observed and computed freezing temperatures is exceptionally good. If the gases present in the other steels had been determined and taken into consideration, the computed values would have been lowered and consequently, in most cases, brought into better agreement with the observed values.

This method of computing the initial freezing temperature from the analysis cannot be expected to hold for percentages of impurities or alloying elements outside of the range in which it has been verified by experiment. Table 6 shows how well it holds for cast irons. The analyses and experimentally determined initial freezing temperatures were taken from a paper by Ash and Saeger [30]. The initial freezing temperatures, computed by adding the effects of the separate elements, are given in the last column. With the exception of the values for samples XIII and XIV, the average difference between the observed and computed values is 5° C.

TABLE 5.—*Depression of the initial freezing (liquidus) temperature of iron per percent by weight for each of the impurities or alloying elements usually found in steels, and the amounts of the various elements in the materials investigated*

Element	Depression of freezing point per percent by weight	Range of elements in materials investigated (percentage by weight)
Hydrogen	1,300° C (computed)	0 to ?
Nitrogen	90° C (computed)	0 to 0.03
Oxygen	80° C (computed)	0 to 0.03
Carbon	Varies as follows: 65° C at 0% 70° C at 1% 75° C at 2% 80° C at 2.5% 85° C at 3% 91° C at 3.5% 100° C at 4%	0 to 3.8
Phosphorus	30° C	0 to 0.7
Sulfur	25° C	0 to 0.08
Arsenic	14° C	0 to 0.5
Tin	10° C	0 to 0.03
Silicon	8° C	0 to 3
Manganese	5° C	0 to 1.5
Copper	5° C	0 to 0.3
Nickel	4° C	0 to 9
Molybdenum	2° C	0 to 0.3
Vanadium	2° C	0 to 1
Chromium	1.5° C	0 to 18
Aluminum	0	0 to 1
Tungsten	1° C	18% W with 0.66% C

TABLE 6.—*Chemical analyses and initial freezing temperatures of cast irons*

Sample number	Percentage, by weight, of—					Initial freezing temperature	
	C	Mn	P	S	Si	Measured	Computed
						° *C*	° *C*
XI	1.96	0.25	0.14	0.06	0.85	1,380	1,378
X	2.00	.24	.15	.06	.84	1,380	1,375
XII	1.97	.27	.14	.06	1.50	1,365	1,372
VI	2.29	.35	.27	.04	1.24	1,350	1,341
III	3.08	.44	.35	.04	1.68	1,250	1,249
IV	3.10	.48	.35	.04	1.69	1,250	1,245
XIV	2.89	.44	.66	.03	2.88	1,195	1,251
XIII	3.27	.52	.59	.03	2.87	1,155	1,207
IX	3.60	.58	.67	.03	2.86	1,150	1,157
VIII	3.63	.59	.68	.03	2.87	1,150	1,154
VII	3.76	.54	.46	.05	2.10	1,150	1,147

We hesitate to suggest that a value computed from the data in table 5 is more accurate than an experimentally determined value, but it is difficult to see why sample XIV with 2.89 percent of carbon should melt 55° C lower than sample IV with 3.10 percent of carbon. The other constituents are about the same with the exception of silicon, which according to the observations on other samples has an effect of only 8° C per percent. In the case of samples XIII and IX, the compositions are practically identical except for the carbon content, and it is difficult to believe that 0.33 percent of carbon would lower the freezing temperature by only 5° C. The discrepancy between the observed and computed values for samples XIII and XIV may be due to the presence of some impurity that was not sought for in the analysis, since in both cases the measured value is lower than the calculated one.

VI. DISCUSSION OF RESULTS

The mean of the observations on the freezing point of the high-purity iron in helium, 1,539° C, is believed to be accurate to ±1° C. The recognized sources of error and the magnitude of the uncertainty introduced in the final result by each, are estimated to be as follows: (1) Transmission of sector disk, 0.25° C; (2) effective wavelength of red screen, 0.3° C; (3) photometric matching, 0.25° C; and (4) departure from blackbody conditions, 0.2° C.

If the impurities in the samples of high-purity iron were all present in the maximum amounts reported and if helium is not soluble in iron, the freezing point of absolutely pure iron would not be more than 0.5° C higher than that of the high-purity irons used in this investigation.

The mean of the observations on the freezing point of the high-purity iron in hydrogen, 1,538° C, is somewhat less accurate than the value in helium, because it is subject to all the uncertainties listed above in addition to the uncertainty in the amount of absorbed hydrogen at the beginning of freezing. According to Smithells [28], the amount of hydrogen, at a pressure of 1 atmosphere, absorbed by iron increases from about 0.0001 percent, by weight, at 400° C to about 0.0011 percent in the solid at the melting point and to about 0.0023 percent in the liquid at the melting point. These are equilibrium values which require some time to establish. In our experiments the iron was heated only about 20° C above the melting point and was maintained molten for only a few minutes before freezing. It is very doubtful that the iron absorbed the equilibrium amount of hydrogen in these few minutes. Our experience with silver in air [31] would indicate that only a small percentage of the difference between 0.0011 and 0.0023 percent would be absorbed under these conditions.

The value of 1,536° C obtained for the freezing point of the high-purity iron in vacuo does not mean that the iron was freezing at 1,536° C. It was evident from the deposits of iron on the inner surfaces of the cone directly above the opening in the blackbody that iron vapor had been present in the light path. Jenkins and Gaylor reported seeing clouds of iron vapor in their experiments and went to considerable trouble to devise methods to eliminate them. The difference between 1,539° and 1,536° C can be accounted for by an absorption of light of 2 percent. No "clouds" of vapor were detected in our experiments.

The freezing temperature of the iron identified as Y was measured in the same way as the high-purity irons, and the result obtained should be just as accurate. The value obtained for the initial freezing temperature of the Armco ingot iron is the result of 10 freezes and should be accurate to ±2° C. Each of the values for the initial freezing temperature of the steels is the result of from three to five freezes and should be accurate to ±3° C.

The method of computing the initial freezing temperatures of the steels from the chemical analyses and the lowering of the freezing point by the separate elements is entirely empirical and should be used with discretion. However, this method seems to hold reasonably well for considerable ranges of composition.

VII. SUMMARY

1. The freezing temperature of high-purity iron in helium at atmospheric pressure is 1,539°±1° C.
2. The freezing temperature of high-purity iron is 1° to 3° C lower in hydrogen than in helium.
3. The freezing temperature of Armco ingot iron in helium is 1,534°±2° C.
4. The depression of the initial freezing temperature of an iron or steel by most of the elements commonly found in steels is independent of the presence of other elements.
5. The initial freezing temperature of a steel can be calculated from the chemical composition.

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