[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Reactivity of Amalgams

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The oxidation of zinc amalgams proceeds very simply[1] when the experimental conditions are properly chosen. Provided agitation is sufficiently violent, the rate of oxidation is virtually independent of the zinc concentration and is limited mainly by the rate at which fresh amalgam surface is exposed; when the latter rate is constant, the rate of oxidation is roughly proportional to the concentration of oxidizing agent and almost independent of temperature. These results led to the important conclusion that the two elementary processes involved in the reaction—electron capture by the oxidizing agent, and expulsion of the resultant positive charges as zinc ions—occurred separately and (practically) simultaneously. This conclusion has now been strengthened by an investigation of other amalgams, which was undertaken because of its bearing on the cleaning of mercury: obviously, if it is true that all base metals dissolved in mercury can be oxidized at rates nearly independent of their concentrations, the removal of these impurities ought to become progressively easier as their concentration decreases.

Air as the Oxidizing Agent.—When zinc amalgams are shaken with 1 *N* sulfuric acid in contact with air, oxygen—not hydrogen ion—is the principal oxidizing agent.[1] The separatory funnel method of ref. 1 (pp. 452-453) was used to measure the rates at which five other representative base metals reasonably soluble in mercury were oxidized by air in contact with acid solutions. The results for these amalgams are abstracted in Table I, which summarizes also the results from ref. 1, Table I, for zinc amalgams; by and large, a detailed picture of the new experiments can be constructed from the latter table. All amalgam concentrations are percentages by weight; rates

TABLE I

OXIDATION OF AMALGAMS BY AIR IN CONTACT WITH ACID

No.	Initial concentration, %	$10^4 \times$ average rate
a. Thallium amalgams shaken with *N* H_2SO_4; electrolyte solution for e. m. f. measurements: 0.1 *M* $TlNO_3$–0.02 *M* HNO_3–0.001 *M* HgAc[a]		
1	1.0	10
2	0.1	14
3	.1	21
4	.01	9
5	.01	13
	Over-all average rate	13
b. Lead amalgams shaken with 1 *N* $HClO_4$; electrolyte solution for e. m. f. measurements: 1 *M* $Pb(NO_3)_2$–0.02 *M* HNO_3–0.001 *M* HgAc		
6	0.1	2.9
7	.01	3.1
8	.001	3.8
	Over-all average rate	3.3
c. Zinc amalgams shaken with 1 *N* H_2SO_4; electrolyte solution for e. m. f. measurements: 1 *M* $ZnSO_4$–0.05 *M* H_2SO_4		
9	0.1	3.3
10	.01	3.1
11	.005	3.7
12	.001	3.2
13	.001	2.5
	Over-all average rate	3.2
d. Cadmium amalgams shaken with 1 *N* H_2SO_4; electrolyte solution for e. m. f. measurements: 1 *M* $Cd(NO_3)_2$–0.01 *M* H_2SO_4–0.001 *M* HgAc		
14	0.1	3.2
15	.01	2.0
16	.001	3.0
	Over-all average rate	2.7
e. Tin amalgams shaken with 1 *N* H_2SO_4; electrolyte solution for e. m. f. measurements: 0.1 *M* $SnCl_2$–0.15 *M* HCl[b]		
17	0.1	1.7
18	.1	1.5
19	.01	2.4
20	.01	1.4
21	.001	2.3
	Over-all average rate	1.9
f. Copper amalgams[c] shaken with 1 *N* H_2SO_4; electrolyte solution for e. m. f. measurements: 1 *M* $CuSO_4$–0.01 *M* H_2SO_4–0.001 *M* HgAc		
22	0.00148	0.29
23	.00112	.25
	Over-all average rate	0.27

[a] Mercurous acetate was added to stabilize cell reading for exhausted amalgam; this salt could not be used in the tin experiments owing to its reaction with stannous chloride. [b] 0.15 *M* hydrochloric acid necessary to repress hydrolysis. [c] Copper amalgams prepared by electrolysis; others by dissolving metals in hot mercury in the absence of oxygen. Electrolysis is resorted to because the solubility of copper in mercury near room temperature is only 0.002%, according to unpublished results from this Laboratory agreeing with earlier measurements.

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(1) Liebhafsky, THIS JOURNAL, 59, 452 (1937).

are the decreases each second in the percentage of base metal for 25 cc. of amalgam.

Table I leads to these conclusions. (1) For each solute metal listed, the rate of oxidation is virtually independent of the amalgam concentration. (2) These rates vary over only a 50-fold range. (3) At least a rough parallelism exists between the character of the metal and the rate of oxidation; copper, the most noble of these metals, is oxidized least rapidly. These conclusions show that ridding mercury of dissolved base metals is a relatively simple matter, for the removal of such metals becomes progressively easier as their concentration decreases.

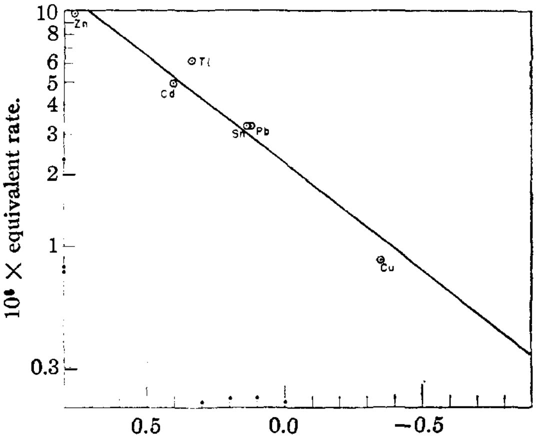

Fig. 1.—Equivalent rate of oxidation for base-metal amalgams as a function of the standard electrode potential for the metal.

If the elementary process of electron capture by the oxidizing agent is involved in the oxidation of base-metal amalgams, there might be a correlation between the rates of oxidation and the electrode potentials of the various metals. The standard electrode potentials naturally do not apply for the conditions existing at the acid–amalgam interface, but they can serve as a measuring stick for the potentials that make the electron capture possible. The rates of Table I have been divided by the equivalent weights of the respective metals, since the faraday is the rational unit for measuring the amount of electricity transferred in unit time. The resulting quotients, or *equivalent rates*, have been plotted on semilogarithmic paper in Fig. 1 against the standard electrode potentials[2] of the metals. Within the experimental error, the logarithm of the equivalent rate is proportional to the electrode potential, a decrease of one volt causing a decrease of about one power of ten in this rate.

The functional relationship in Fig. 1 is of the kind to be expected when the rate of a process is proportional to the free energy decrease that accompanies it. Such correlations between kinetics and thermodynamics usually occur only for very simple processes; the logarithm of the rate of evaporation into high vacuum, for example, is often proportional to the free energy decrease for the vaporization. In other words, that such a simple relationship should be even approximately valid for the oxidation of base-metal amalgams is supporting evidence for the idea that electron capture as an elementary process is involved in these reactions. Furthermore, Fig. 1 can be used to explain why the rates of oxidation are virtually independent of the amalgam concentrations: according to the Nernst law, changes in these concentrations produce relatively slight changes in the electrode potentials, thus leaving the rates practically unaffected.

A general, thermodynamic picture like the foregoing cannot, of course, be a close-up of the oxidation process. The following detailed mechanism is consistent with the experimental results. The violent shaking continually re-forms the amalgam-solution interface so that a typical element of interface has in effect a very limited lifetime ($<<1$ sec.). Since dilute amalgams obey the Nernst equation, the concentration of solute metal atoms in the interface may be considered equal to that in the body of the amalgam. For each element of interface, this concentration, even for the most dilute amalgams studied, provides more solute metal than is equivalent to the oxygen captured and retained (*i. e.*, adsorbed) by the interface during its lifetime. The oxygen molecules thus adsorbed migrate rapidly over the amalgam surface. During this migration, they necessarily penetrate the regions near the solute atoms, where the shape of the potential barriers favors the flow of electrons from the base-metal solute atom to the oxygen. As this electron capture occurs, a corresponding number of solute-metal cations are ejected into the solution. This picture yields an absolute rate of oxidation that is virtually independent of the amalgam concentration (since an excess of solute atoms is always present on the surface), that is proportional to the concentration of oxygen, and that varies from

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(2) All standard electrode potentials are taken from Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

one solute to another since the height and width of the potential barrier hindering the electron capture by oxygen will be determined by the character of the base metal. It implies, furthermore, that the shape of the potential barrier will be changed if oxygen is replaced by other oxidizing agents.

These ideas receive further (though only qualitative) support from our experiments with sodium, aluminum[3] and magnesium amalgams. In accord with a linear extrapolation of Fig. 1, these amalgams of strongly metallic elements all proved too reactive for rate measurements by our method. Considerable time and effort were expended in unsuccessful attempts to obtain quantitative results for these amalgams (acidity, solvent and apparatus were varied): the principal difficulties encountered were the rapidity of the reactions; the reactions of the amalgams with hydrogen ion and with water to liberate hydrogen, which swept oxygen out of the solutions; and the insolubility of reaction products (especially those of magnesium amalgam) under certain conditions.

The standard electrode potentials[4] used in plotting Fig. 1 are for half-cells only; but no half-cell is involved in the oxidation process. A more rational measuring-stick would be the electrode potential for the entire reaction, which can be obtained by subtracting from the abscissas of Fig. 1 the standard electrode potential of the proper oxygen half-cell.

Hydrogen Ion as Oxidizing Agent.—Rate measurements were made on the six amalgams of Table I in the virtual absence of gaseous or dissolved oxygen, this element being removed by prolonged bubbling of hydrogen through the acid solution in the separatory funnel. The following results for 0.01% lead amalgam shaken with *N* perchloric acid and measured against 0.1% lead amalgam are representative. Values for a similar experiment in which air was not removed are given for comparison. More refined measurements are required to decide whether hydrogen ion or air introduced during sampling is the oxidizing agent principally responsible for the slight reaction indicated by the 32 mv. reading. But there is no doubt that hydrogen ion oxidizes the amalgams of Table I much more slowly than does oxygen. Similar experiments have shown that sodium, aluminum, and magnesium amalgams, on the other hand, are oxidized readily by hydrogen ion.

Time, sec.	0	15	30	45	75	
E. m. f., mv.	30.2	30.2	30.3	...	32.0	(air removed)
E. m. f., mv.	30.0	39.8	64.8	782.2	782.8	(air present)

With Fig. 1 as a guide, this difference of reactivity toward hydrogen ion can be qualitatively explained. Since the standard potential for the hydrogen–hydrogen ion couple is zero, the maximum potential available for electron capture for the Table I amalgams is measured by 0.76 volt, the standard electrode potential of zinc. The "overvoltage" of hydrogen on mercury is about 0.9 volt. For these amalgams, therefore, the driving force available for oxidation by hydrogen ion is not sufficient to overcome the overvoltage. For sodium, aluminum, and magnesium, this driving force does exceed the overvoltage.

The older explanations postulate some change at the electrode surface (for example, film formation, or the accumulation of hydrogen in some electromotively active form) to be responsible for overvoltage. In our experiments, a constantly renewed metallic surface is presented to the solution; and the discovery of something analogous to overvoltage in our work therefore tends to discredit these older explanations—it would appear that "overvoltage" acts to retard electron capture from amalgams, thus acting *before* hydrogen atoms or similar species could form. This view of our work is in harmony with the quantum mechanics treatment of overvoltage given by Gurney,[5] in which salient experimental observations of Bowden[6] and others are quantitatively explained on the theory that the penetration of a potential barrier by electrons is the fundamental process underlying the overvoltage phenomenon. Perhaps the most important of these experimental observations shows the increment in the logarithm of the current density to be proportional, under properly chosen conditions, to the increment in the applied voltage. The close analogy between this observation and Fig. 1 is obvious.

Oxidation of Noble Metals.—Several experiments, in which 25 cc. of pure mercury or of 0.01% silver amalgam was shaken for six minutes with 50 cc. of *N* sulfuric acid in contact with

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(3) Work with aluminum amalgams is difficult because of the low solubility of the metal (0.002% near room temperature according to unpublished results from this Laboratory).

(4) When there are two or more standard electrode potentials to choose from (as in the case of copper), the potential corresponding to the main reaction commonly observed was taken.

(5) Gurney, *Proc. Roy. Soc.* (London), **134**, 137 (1931).

(6) Bowden, (a) *ibid.*, **125**, 446 (1929); (b) **126**, 107 (1929).

air, gave rather erratic results. Several tenths of a mg. of silver and about ten times that much mercury were oxidized in the amalgam experiments, and about 0.5–5 mg. of mercury when that element was used.[7] The equivalent rate from Fig. 1 for −0.8 volt, the standard potential for these metals, corresponds to the formation of 40 mg. of silver and 80 mg. of mercurous ion in six minutes of shaking. We may conclude that both metals are oxidized at a rate below that predicted by Fig. 1, although a higher rate for silver would probably have been obtained with a saturated amalgam.[8]

The standard electrode potential for the oxidation of these noble metals is near 0.4 volt. When this potential is zero, no net reaction can occur. It is not surprising, therefore, to find that the net rate of oxidation decreases below that required by Fig. 1 as this potential approaches zero. In the language of quantum mechanics, an increasing probability that electrons will penetrate the potential barrier in the reverse direction is responsible for this decrease in rate.

Other Oxidizing Agents.—Exploratory experiments were undertaken to discover whether the relationship of Fig. 1 held for one amalgam and several oxidizing agents. The likelihood of its holding accurately is not great, for the oxidizing agents differ more among themselves than do the metals given in Fig. 1.

In all experiments 25 cc. of 0.01% zinc amalgam was shaken for five seconds with the oxidizing agent or agents present in 40 cc. of N perchloric acid. Air, when not intended to act as an oxidizing agent, was expelled by bubbling hydrogen through the solution in the separatory funnel. It has been shown in several cases (ref. 1, Table II) that the rate of oxidation is roughly proportional to the concentration of oxidizing agent; this relationship was accordingly assumed in calculating the new experimental results. The concentration of zinc does not, of course, enter into the rate law.

The specific rates of the less reactive oxidizing agents were determined directly. For air, this rate is the quotient of the over-all average, 3.2 (10^{-4}), for zinc from Table I, divided by the constant concentration of dissolved oxygen, $9(10^{-4})N$; or 0.34. The decrease in hydrogen peroxide concentration in an experiment of the kind described above was obtained from a measurement of the final zinc amalgam concentration; k was then calculated to be 0.20 from the integral form of the first-order rate law. For cupric ion, it was necessary to determine the final concentration directly on the solution because the formation of a saturated copper amalgam vitiated zinc e. m. f. measurements; the same logarithmic formula gave 0.31 for the specific rate.

The *relative* specific rates for oxidizing agents more reactive than cupric ion were obtained as follows.[9] The perchloric acid contained an amount of cupric ion equivalent to the zinc (taken as 0.0010 equivalent) in the amalgam, and an equivalent amount of the competing oxidizing agent. In every case, the five-second shaking oxidized completely the zinc in the amalgam. If x equivalents of cupric ion are consumed in the process, and $y = 0.001 - x$ equivalents of competing oxidizing agent disappear, the relative specific rate is

$$\frac{k}{k_{\mathrm{Cu}^{++}}} = \frac{\log 0.001/(0.001 - y)}{\log 0.001/(0.001 - x)}$$

x was obtained from e. m. f. measurements of the copper amalgam formed against a two-phase copper amalgam, unpublished results from this Laboratory being used for the solubility of copper in

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(7) With 0.01 N acid, the rates of oxidation of silver and mercury appeared to be higher and more concordant. The situation is probably complex and will be dismissed with the observation that the formation of fine bubbles during shaking, which usually occurs only when the mercury contains no dissolved base metals, is probably one of the complicating factors involved. The formation of mercury bubbles during shaking with acid is an interesting phenomenon *per se*, which no doubt results from an adsorption of electrical charges at the mercury-solution interface. Tin amalgams show it under certain conditions, but other base-metal amalgams do not; it can be quite a good indicator for the exhaustion of such amalgams. It occurs more readily, and the bubbles persist longer, with N than with 0.01 N sulfuric acid. The presence of zinc sulfate and of some other salts also promotes it. The adsorption of zinc ion may be responsible for the pronounced decrease in the rate of oxidation of zinc amalgams observed when N sulfuric acid was saturated with zinc sulfate; this adsorption may retard the expulsion from the amalgam of the zinc ion formed during the oxidation.

(8) Experiments with 10^{-3} and 10^{-4}% silver amalgams have shown that the rate at which the silver is oxidized by air decreased sharply with the concentration, in marked contrast with base-metal amalgams. Silver differs from the base metals in that it must compete with mercury for the oxygen molecules reaching the amalgam surface; as the amalgam concentration decreases, silver is at greater disadvantage in this competition so that the decrease in its rate of oxidation is not surprising. Our results are not precise enough to warrant the formulation of a quantitative picture.

(9) The method outlined above, which assumes the competing reactions to be independent, gave low values for the relative specific rates of oxidizing agents less reactive than cupric ion. When oxygen and hydrogen peroxide were allowed to compete for zinc amalgam, on the other hand, the relative rates measured agreed with the quotient of the specific rates directly determined; which suggests, reasonably enough, that the formation of copper in excess of that required to saturate the mercury was responsible for the low relative rates when cupric ion was the most reactive oxidizing agent present. These "specific rates," unlike those for unimolecular reactions, are not dimensionless; they are the decrease per second in the concentration (expressed in weight per cent.) of 25 cc. of amalgam when the oxidizing agent is 1 N.

mercury. It is clear that relative specific rates obtained in this way cannot be very accurate; but, owing to the great speed of the reactions, they are probably more reliable than the quotients of independently determined specific rates would have been.

The relative specific rates, together with those calculated for the less reactive oxidizing agents, are plotted semilogarithmically in Fig. 2. In the simplest case, the points in Fig. 2 would lie along a line with a slope equal and opposite to that of the line in Fig. 1—opposite in sign because the more powerful oxidizing agents have the greater negative electrode potentials. This simple case is obviously not realized. But one can say that a relationship of the kind in Fig. 1 holds for positively charged oxidizing agents, or metal ions; the evidence for this statement is reinforced somewhat by the circumstance already mentioned that hydrogen ion is quite inert to zinc amalgams, as it ought to be according to Fig. 2. The oxidizing agents not positively charged evidently are much less reactive by comparison with the metal ions than their standard potentials alone would indicate, perhaps owing to the greater complexity of the process by which they capture electrons; the oxygen point would be nearer the line were it plotted against the oxygen–peroxide potential as abscissa. Further work obviously is required.

Summary

The reactivities of five base-metal amalgams, or of practically all those adapted to convenient investigation, have been studied under experimental conditions that had yielded simple results for zinc amalgam. For each amalgam, as for that of zinc, the rate of oxidation with a given oxidizing agent at a given concentration is limited mainly by the rate at which fresh surface is exposed—it is virtually independent of the amalgam concentration.

Qualitative observations on three amalgams (those of sodium, magnesium, and aluminum) too reactive for quantitative investigation are in accord with the foregoing quantitative results.

An important practical consequence of these conclusions is that the removal of dissolved base metals from mercury by oxidation becomes progressively easier as their concentration decreases, placing the complete removal of traces of such impurities among the easiest purification processes known.

The new experimental evidence demonstrates the generality of the mechanism—electron capture by the oxidizing agent accompanied by the (practically) simultaneous expulsion from the amalgam of the positive ions resulting—assumed for the oxidation of zinc amalgams.

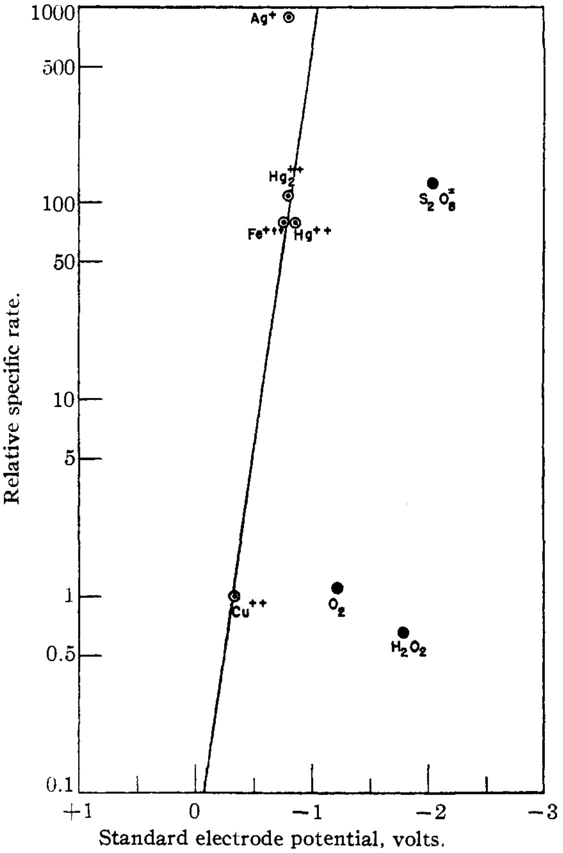

Fig. 2.—Specific rates relative to that for cupric ion for the oxidation of zinc amalgam by several oxidizing agents.

With oxygen as oxidizing agent, the increment in the logarithm of the rate of oxidation is proportional to the increment in the standard electrode potential of the dissolved base metal for six amalgams. This relationship points to a proportionality between the rate of oxidation and the free energy decrease for the reaction. It resembles the relationship that has been found in overvoltage studies to exist between current and applied voltage.

The inertness of the six amalgams toward hydrogen ion likewise indicates a similarity between overvoltage phenomena and the processes involved in the oxidation of amalgams. It seems reasonable to assume that the penetration of a potential barrier by electrons, which Gurney has applied quantitatively to explain overvoltage, is also occurring in the oxidation of amalgams.

The results with zinc amalgam and eight oxidizing agents reveal no general relationship of rate to electrode potential; but there is some basis for the belief that such a relationship exists provided the nature of the oxidizing agent (metal ions as contrasted with other substances) is taken into consideration.

SCHENECTADY, N. Y. RECEIVED SEPTEMBER 10, 1941

[CONTRIBUTION FROM THE METALLURGICAL FUNDAMENTALS SECTION, METALLURGICAL DIVISION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

A Modified Calorimeter for High Temperatures. The Heat Content of Silica, Wollastonite and Thorium Dioxide Above 25°[1,2]

BY J. C. SOUTHARD[3]

Introduction

The thermodynamic properties of metallurgically important substances have been investigated for a number of years at the Pacific Experiment Station of the Federal Bureau of Mines. Data are now available which permit the calculation of reaction free energies, at room temperature, of a large number of such substances. However, the high-temperature heat content data necessary to calculation of equilibria and heat balances at the elevated temperatures at which most metallurgical processes occur are lacking in a large number of instances. This is particularly true of oxides and sulfides.

Description of Apparatus

The present apparatus for heat contents at high temperatures (to 1500°) is a modification of the standard one in which a capsule containing the sample is heated in a furnace to a determined temperature and at a given moment dropped into a calorimeter of known heat capacity. The modifications described below were introduced primarily to remove the necessity for dismantling a considerable portion of the apparatus to return the sample to the furnace in preparation for another determination. This permits more rapid operation than has previously been consistent with good work.

Capsule (A) (Fig. 1) containing the sample is a 2.0 × 2.0-cm. cylinder made of 0.2-mm. 90% platinum–10% rhodium alloy.

The furnace (B) has a heating element made of B. and S. no. 20 80% platinum–20% rhodium alloy wire wound on a 1 × 14 inch alundum tube. The furnace is surrounded by a water jacket, except for a 1-inch hole at the top and at the bottom for passage of the capsule. When the capsule is in position the top hole is closed with a refractory plug 3 inches long, and the bottom hole with a water-cooled gate (D) which rotates on a shaft (E) eccentric with the center line of the furnace. The heat exchange of the furnace with the calorimeter is thus made virtually zero even when the furnace is at 1500°.

The temperature distribution in the furnace at 1100° is such that a 1.25-inch length is isothermal to 1°. This length is sufficient to hold the capsule and thermocouple junction. This isothermal space is made possible without elaborate precautions by the favorable length to bore ratio of 14 to 1.

The temperature of the capsule was measured by a platinum–platinum–10% rhodium thermocouple (not shown in Fig. 1) which was within 0.25 inch of the top of the capsule and within the above-mentioned isothermal space. The thermocouple was first calibrated by comparison with another bearing a Bureau of Standards certificate and during the course of the determinations on each substance by melting a 0.25-inch length of gold wire and a similar one of palladium wire between the elements of the couple as described in Bureau of Standards Research Paper 768. All calibrations were made with the thermocouple in its usual place in the furnace. Repeated calibration was necessary when working at 1500°.

The capsule is suspended in the furnace by a B. and S. no. 32 90% platinum–10% rhodium alloy wire. The wire is led out through a small hole in the top of the furnace and attached to a steel plunger fastened by a spring trigger at the top of a vertical brass tube. The brass tube is slotted throughout most of its length to permit free fall of the plunger. The lower 6 inches (15 cm.) is not slotted, so that the fall of the plunger

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[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior.

[2] Not copyrighted.

[3] Chemist, Metallurgical Division, Bureau of Mines.