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High-Temperature Research

By means of "liquid containers," liquid metals can be studied at much higher temperatures than heretofore.

Aristid V. Grosse

The field of high-temperature research is a great frontier of science. But it is by no means a new frontier. Since prehistoric times the attainment of higher and still higher temperatures has characterized successively more advanced civilizations. Thus, the stone age gave way to the bronze age, and the bronze age, to the iron age. In the last 20 years men have learned how to produce temperatures equivalent to those of the sun and stars, if only for an instant, and we have the atomic age and the space age. But space technology requires the production of exceedingly high temperatures for long periods, not just instants, for powering rockets and producing the components of spacecraft. This we must accomplish if we are to continue our scientific advance and lead the way into space.

High-temperature research is a field of very broad scope, involving as it does the sciences of chemistry, physics, metallurgy, and ceramics. An important problem is that of producing high temperatures by chemical reactions, which necessarily must have thermally stable reaction products. This can be achieved in several ways—through combustion of metals in oxygen; through combustion of gaseous mixtures; or through plasma jets. In every case, there is a corollary problem—that of confining or containing chemical substances at temperatures which conventional containers cannot withstand. In this article I discuss the high-temperature research conducted by the Research Institute of Temple University, since it illustrates several important aspects of the subject. The Research Institute has devoted its main efforts to this field for the last 16 years. I will attempt to give a more or less historical outline of our studies and to show how our investigations led to new possibilities—to the attainment of high flame temperatures, the development of a "liquid crucible," and the establishment of some relationships for liquid metals.

The first problem we considered was, How high a temperature can be reached for extended periods through chemical reactions? Combustion of wood, charcoal, and coal has been for ages the standard method of producing heat. In contrast, the combustion of metals in oxygen had hardly been studied at all, and our first efforts were devoted to this subject.

The chemical production of high temperatures requires not only the evolution of great heat in particular chemical reactions but also thermal stability of the reaction products. As the temperature increases, the dissociation of the reaction products into atoms, radicals, or intermediate unstable molecules increases until a balance between the evolution of heat and the energy of dissociation is reached at a particular temperature, usually defined as the flame temperature.

At the temperature of the sun's disk —that is, about 5000° to 5500°K— only about a dozen compounds can exist, as one may easily deduce from spectroscopic analysis (*1*). This group of compounds can be divided into metallic and nonmetallic compounds. The metallic compounds include four oxides (AlO, MgO, ZrO, TiO), two fluorides (MgF and SrF), and two hydrides (MgH and CaH). The five nonmetallic compounds are N_2, CO, C_2, CN, and OH. The heats of combustion of various metals in oxygen are given in Table 1 and compared with the heats of combustion of hydrogen, carbon, methane, and carbon monoxide. As Table 1 shows, hydrogen and hydrocarbons generate, on an equal weight basis, more heat than the metals generate; this is due to their high heats of combustion and their low atomic

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The author is president of the Research Institute of Temple University, Philadelphia, Pa. This article is adapted from a lecture presented at the institutes of inorganic chemistry of ten West German universities and at "Technische Hochschülen" in ten cities of West Germany between 19 November and 6 December 1962.

Table 1. Heats and products of combustion in oxygen.

Fuel	Atomic or molecular weight	Kcal/g of fuel	Kcal/g-atom or g-mole of fuel	Product of combustion
		Metals		
Mg	24.32	5.920	143.940	MgO
Al	26.97	7.410	199.525	Al_2O_3
Zr	91.22	2.840	258.800	ZrO_2
Fe	55.85	1.670	95.350	Fe_2O_3
		Nonmetals		
H_2	2.016	34.20	68.400	H_2O
C(graphite)	12.000	2.20	26.428	CO
C(graphite)	12.000	7.88	94.385	CO_2
CH_4	16.032	13.20	210.800	H_2O and CO_2
CO	28.000	2.42	67.797	CO_2

weights. However, on a molar basis, all the metals listed (with the exception, of course, of iron) generate more heat than either hydrogen or carbon, in accordance with their positions in the periodic system as electropositive elements. It is because the metals are much more costly than either coal or oil, since they have to be produced from their oxides by reduction, that we do not use them as fuel in our daily lives.

Methods were developed at our institute to burn many metals at atmospheric pressure. The metals were burned in the solid state (as rods, pipes, balls, sheets, and powders), in the liquid state, and in the vapor state. The expected adiabatic temperatures in the range of 3000° to 5000°K were reached (*2*). The highest temperature, close to 5000°K, was attained (*3*) through burning zirconium powder in a torch-type apparatus. Beryllium, at pressure of 1 atmosphere, in oxygen produces a temperature of 4300°K, and aluminum and magnesium, temperatures of 3800° and 3350°K, respectively.

Various types of apparatus have been developed for the combustion of metals (see *2–4*). A typical autoclave for the combustion of metals, either under pressure (up to 75 lb/in.^{2}) or in a vacuum (down to 4 mm-Hg) is shown in Fig. 1. Metals are fed in the form of a rod through the stuffing box at right or, as balls or small rods, by gravity through the side arm at left. The combustion phenomena may be observed through the sight glass (diameter, 4 in.) at the top of the autoclave. One combustion phenomenon of general interest is the so-called "skating sun" observed during the burning and boiling of aluminum metal (*5*); this was first observed on 29 December 1948. It was called a "sun" because of its brilliance and disk-like shape; the vapor of boiling aluminum burns in oxygen in a regular flame front, a fraction of a millimeter above the surface of the boiling metal. Suns up to 6 inches in diameter were observed; these burned down to minute drops if the metal was pure. The suns "skate" on the surface of the liquid alumina because of their lower density; because of their surface tension, thickness, and vapor pressure they have great mobility.

Whereas aluminum, as every housewife knows, does not burn in air, it does burn readily in the apparatus shown in Fig. 1, even at 4 mm-Hg oxygen pressure, a concentration of oxygen 35 times less than that in air.

The experiments on metal combustion gave the Institute valuable experience in containing and handling large quantities—1 or more liters—of liquid alumina, liquid magnesia, and other materials at high temperatures.

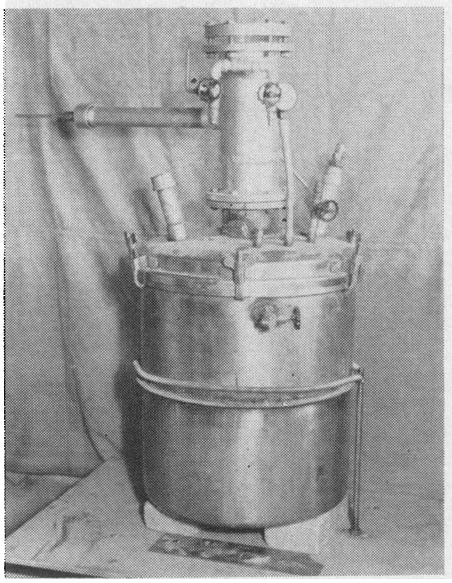

Fig. 1. Autoclave for the combustion of metals either under pressure (up to 75 lb/in.^{2}) or in a vacuum (down to 4 mm-Hg). Metals are fed either in the form of rod through the stuffing box or through the side arm by gravity feed. Observation is through the sight glass (diameter, 4 in.) at the top of the autoclave.

Combustion of Gases

While study of the combustion of metals was being continued, we turned our attention to conventional flames, with the objective of reaching higher temperatures. As I mentioned earlier, the production of very high temperatures depends in part on the thermal stability of the reaction product. Fluorine is the most electronegative element known, and thus many fluorine compounds are more stable than the corresponding oxides, because of the greater strength of the fluorine bond. A good example is hydrogen fluoride. When it is formed from hydrogen and fluorine a flame temperature of 4000°K is reached (*6, 7*). At a total pressure of 5 atmospheres the temperature is raised to 4200°K (*6*). In contrast, the maximum temperature of the hydrogen-oxygen flame is only 2930°K at atmospheric pressure.

Two of the most stable nondissociating, nonmetallic compounds are CO and N_2. Thus, if we can burn an organic compound (particularly an endothermic one) to form these products we will have attained high flame temperatures. Useful endothermic compounds are cyanogen and the carbon subnitrides (or dicyanoacetylenes) $N{=}C{-}(C{=}C)_n{-}C{=}N$, for which the general formula is $C_{(2n+2)}N_2$.

When a mixture of cyanogen and oxygen was burned according to the equation $(CN)_2 + O_2 \longrightarrow 2CO + N_2$, one of the highest flame temperatures so far attained, 4800°K (at atmospheric pressure), was produced (*8*). By burning the same mixture under a total pressure of 100 pounds per square inch, a temperature of 5050°K was attained (*9*).

It was found that the unstable colorless liquid, carbon subnitride, C_4N_2—the first member of the dicyanoacetylene series—can be burned with oxygen (*10*) in either a diffusion flame or a flame of premixed type, according to the equation $C_4N_2 + 2O_2 \longrightarrow 4CO + N_2$. The calculated flame temperature is 5260°K at atmospheric pressure.

Since the flame temperature calculated for the cyanogen-oxygen flame has been checked experimentally (*8*), the enthalpy data for CO and N_2 may be used with confidence. The accuracy of the calculated flame temperatures is ±2°. In all these combustion studies ordinary oxygen, O_2, was used. It was recognized that significantly higher temperatures could be obtained if ozone, O_3, were substituted for O_2. The heat of formation of ozone from oxygen is +33.98 kilocalories per mole of ozone; thus, the amount of heat liberated is increased, and, provided the stoichiometry of the combustion is adjusted to produce the same reaction products as with oxygen, the flame temperature is also increased.

However, pure ozone in either gaseous, liquid, or solid form may detonate with great violence to molecular oxygen, although with proper handling it can be made to burn in a regular, but faint and nonluminous, blue flame (*11*) to oxygen, according to the equation $2O_3 \longrightarrow 3O_2$. Because of the experience we had gained in handling and burning 100-percent ozone we were able to premix and burn various mixtures of hydrogen (*12*) and cyanogen (*13*) with ozone. The mixture $3(CN)_2 + 2O_3$ burns uniformly, noiselessly, as brightly as an electric arc, and with a pink-violet color: $3(CN)_2 + 2O_3 \longrightarrow 6CO + 3N_2$. At pressures of 1 and 10 atmospheres, its calculated temperatures are 5208° and 5506°K (±2°), respectively. The temperatures of the corresponding oxygen flame, $3(CN)_2 + 3O_2 \longrightarrow 6CO + 3N_2$, are 4856° and 5025°K, respectively.

The cyanogen-ozone and the carbon subnitride-oxygen flames, with temperatures of 5208° and 5260°K, respectively, produce the highest chemical-flame temperatures achieved to date at pressure of 1 atmosphere. Calculations indicate (*10*) that substitution of ozone for oxygen in the carbon subnitride-oxygen flame, provided explosions and detonations could be avoided, particularly under pressure, would produce a temperature higher than 6000°K (see Table 2). These flame temperatures represent the ultimate goals with chemical reactions.

Table 2. Temperature attainable through substitution of ozone for oxygen in the carbon subnitride-oxygen flame.

Reaction	Flame temperature (deg K)		
	1.0 atm	10.0 atm	600 lb/in.^{2} (atmospheric)
$(C_4N_2)g + 2O_2 \longrightarrow 4CO + N_2$ $\Delta H_{298°} = 254.6$ kcal	5,261	5,573	5,748
$(C_4N_2)g + 4/3\ O_3 \longrightarrow 4CO + N_2$ $\Delta H_{298°} = 299.9$ kcal	5,516	5,936	6,100

Plasma Jets

We recognized long before our flame studies were completed that to achieve higher temperatures and to be able to heat gases of low molecular weight for extended periods, in order to get high specific impulses, other means of generating energy were necessary. As a parallel project, it was necessary to develop new methods of confining or containing chemical substances at high temperatures.

In 1958 the Institute started research on plasma jets (*14, 15*). The use of electrical energy, particularly in the form of the well-known electric arc, offers great possibilities for chemical research.

Plasma is often referred to as the "fourth state of matter," since in a plasma the number of positive ions and electrons exceeds the number of neutral atoms or molecules.

The development of plasma jets resulted from the work of various investigators, primarily in Germany. In 1910 Beck described the high-current carbon arc. Next came Gerdien's researches in 1923 on the steam arc. Having improved the Gerdien arc, Maecker and Peters, in 1951, were able to attain a plasma temperature of 50,000°K, using currents of 1500 amperes. In 1954 Peters inserted a nozzle into the anode of a steam arc burning under pressure and produced a high-temperature plasma jet which emerged from the nozzle at supersonic velocity; thus, the prototype of the modern plasma jet flame was created (*16*).

Use of the noble gases helium and argon makes it possible to produce a chemically inert "flame" of temperature up to 25,000°K. The ionization of argon to $A^+ + e^-$ begins to occur at 10,000°K; due to the rapid increase in ionization between 15,000° and 20,000°K, the heat content rises sharply. The first ionization potential of argon is 15.68 volts, equivalent to 362 kilocalories per gram atom; that of helium is 24.46 volts or 565 kilocalories per gram atom. Helium begins to ionize appreciably only in the 20,000° to 25,000°K range, and therefore its heat content is lower than that of argon. Up to 10,000°K both gases exist as neutral atoms.

Liquid Metals as High-Temperature Substances

Let me emphasize the difference between the problem of containing hot gases and that of containing hot liquids or solids. The densities of liquids or solids at high temperatures are about 100,000 times greater than the densities of gases at pressure of 1 atmosphere, and consequently the concentrations of energy are that many times greater. For this reason, to confine hot gases is comparatively easy.

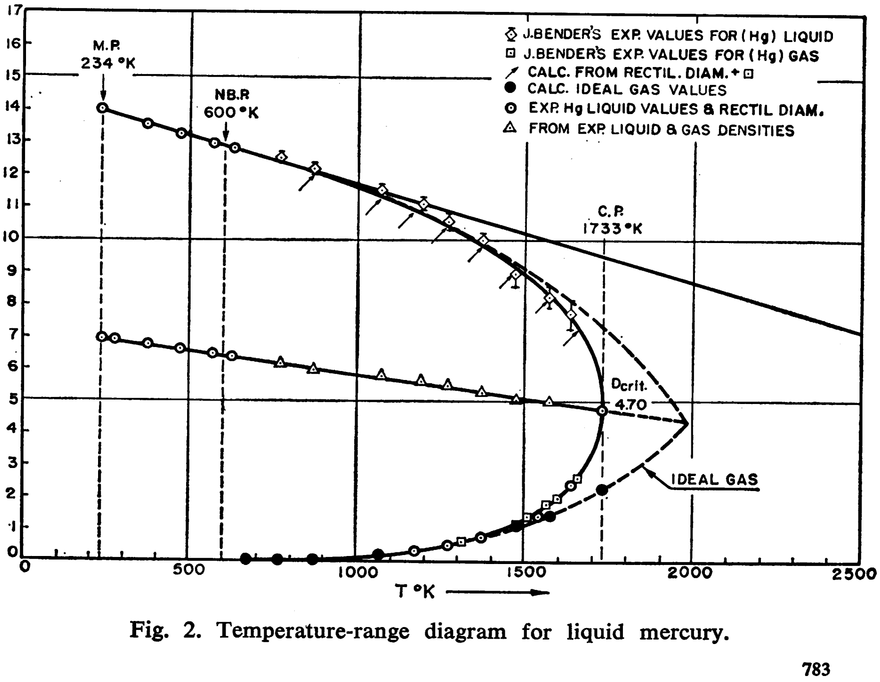

Fig. 2. Temperature-range diagram for liquid mercury.

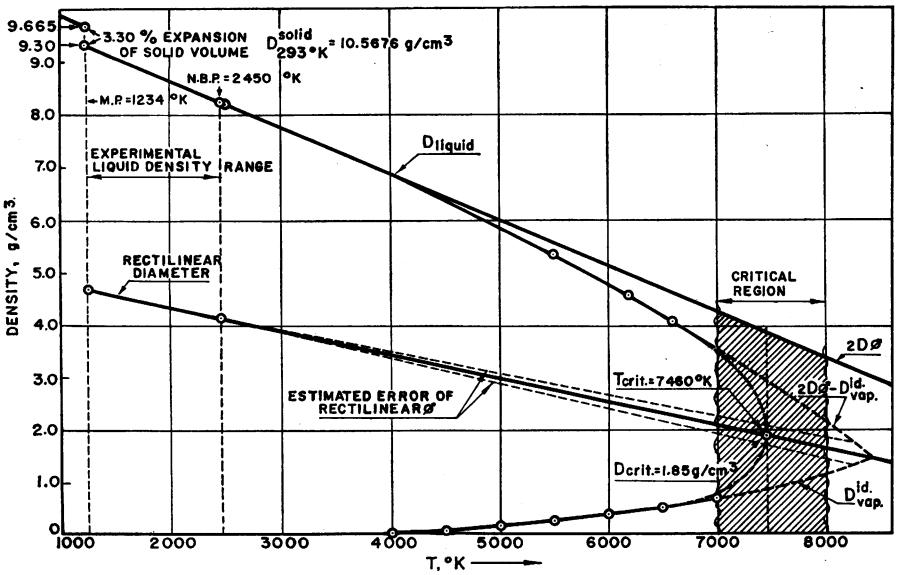

Fig. 3. Temperature-range diagram for liquid silver.

Another problem relates to the nature of chemical substances that can be heated to extremely high temperatures. As I have said, the highest temperature attainable through ordinary chemical reaction is in the range 5000° to 6000°K. This is the limit of existence of chemical compounds. At these temperatures all chemical bonds break and all molecules are dissociated into transient radicals or atoms. Thus, flame temperatures higher than these cannot be produced through chemical reaction.

The temperature above which no known solid can exist has been reached. The metal with the highest melting point is tungsten, which melts at 3643°K, and the oxide with the highest melting point is thorium dioxide, which melts at 3300°K. Tantalum carbide, which melts at 4200°K, has the highest melting point of any known substance. For purposes of containment, in practice at our laboratories, these maxima are attained and used only rarely, because of (i) chemical reaction between the high-melting substance and any other substance being investigated; (ii) the occurrence of eutectic mixtures, which lower the melting point; and (iii) thermal shock. And it is not likely that substances will be found with melting points many hundreds of degrees higher. Thus, we are compelled to find, if possible, thermally stable liquids if we want to contain higher temperatures in some useful way.

Fortunately for the future development of high-temperature research and technology there are substances which will exist as liquids up to very high temperatures—much higher than any at which we had thought liquids could exist. These substances are the refractory metals, which will eventually be useful in our rocket and space technology. Some of them remain as rather dense liquids even up to temperatures of 20,000°K. Since they are *elementary* monatomic liquids they cannot undergo any chemical change (except for ionization), even at extremely high temperatures.

A question which arises in this connection is: What is the liquid-temperature range of a metal—that is, the range from the melting point to the critical point? It had been assumed until very recently that the critical temperature T_c was 1.5 to 1.75 times the normal boiling point T_b, or that (*17*)

$$T_c = 1.4732 \times T_b^{1.0818}$$

where T is expressed in degrees Kelvin. As may be seen later, this is not the case; the critical temperatures of metals are 2.75 to 4 times the normal boiling points. Mercury is the only metal for which the critical constants have been determined. They are as follows: T_c = 1733°K (±50°); P_c = 1587 atm (± 50); D_c = 4.70 g/cm³.

Let us look at the data for mercury in greater detail. Figure 2 shows the temperature-range diagram for liquid mercury. Here the densities of liquid and of saturated vapor (in grams per cubic centimeter) are plotted against absolute temperature; they are based primarily on Julie Bender's determinations made during World War I. All values for the half sum of the densities of liquid and of saturated vapor—that is ½ $(D_{\text{liq}} + D_{\text{sat vap}})$—fall, within the limits of experimental error, on a straight line, the so-called rectilinear diameter. Thus, mercury follows the law of Cailletet and Mathias, as do all other thermally stable liquids. The value for critical density D_c lies on the rectilinear diameter at the critical point (that is, 1733°K).

Table 3. Critical temperatures, heats of vaporization, and entropies at normal boiling points for various metals.

Metal	Boiling point at 1 atm (deg K)	ΔH_{vap} (cal/g-atom)	ΔS_{vap} (cal/g-atom deg K)	T_{red} from Hg curve, Fig. 3	T_c (deg K)
Cs	958	15,750	16.95	0.445	2,150
Rb	974	16,540	16.99	0.445	2,190
K	1,039	18,530	17.88	0.425	2,440
Na	1,163	21,280	18.40	0.415	2,800
Bi	1,832	36,200	19.75	0.397	4,620
Pb	2,024	42,880	21.15	0.375	5,400
Ga	2,510	61,200	24.40	0.330	7,620
Sn	2,960	69,400	23.42	0.340	8,720
U	4,200	101,000	24.05	0.333	12,500
Mo	5,100	142,000	27.85	0.295	17,000
Re	5,900	169,000	28.63	0.287	20,500
Ta	5,700	180,000	31.60	0.260	22,000
W	5,800	191,000	32.90	0.250	23,000

Table 4. Critical constants of the alkali metals.

Metal	T_c (deg K)	V_c (cm³/g-atom)	D_c (g/cm³)	P_c (atm)	Compressibility factor Z_c [= $(P_c \times V_c)/(R \times T_c)$]
Na	2,800	130	0.18	~500	0.28
K	2,450	230	0.17	230	0.29
Rb	2,200	265	0.32	210	0.31
Cs	2,150	320	0.42	160	0.29

The experimental vapor density is practically equal to the ideal-gas density of mercury up to about 85 percent of the critical temperature. By extrapolating from the curve for the ideal-gas density to the rectilinear diameter, one obtains a temperature which always lies above the critical point. Furthermore, it is known that the density of the saturated vapor is only a fraction of the density of the liquid below the critical temperature. Thus, the measurements of Julie Bender, which were made up to 1650°K, were not far from the critical point (see Fig. 2). The T_c and P_c were actually measured for the first time by Birch (*18*) in Bridgeman's laboratory at Harvard University.

It was assumed that the law of Cailletet and Mathias holds for other metals also, and on this basis I developed a semi-empirical method of estimating the critical temperatures of all metals for which density data for the liquid state are available over a substantial temperature range.

Use of the method is illustrated in Fig. 3, with silver as the example (*19*). Here, T_c is estimated to be 7500°K, and D_c, to be 1.85 g/cm^3. Diagrams of the temperature range for the liquid phase of many other metals, such as lead, tin, bismuth, magnesium, sodium, potassium, and gallium, were constructed in the same way, and it was found that the critical density of metals is usually about one-fourth the density at the normal boiling point.

The big differences in density between liquid metals and gases, at a given temperature and pressure, may be illustrated by comparing the density of liquid tungsten at 6000°K and the density of argon at the same temperature and at pressure of 1 atmosphere. The density of tungsten is estimated to be 16.40 g/cm^3 and that of argon, 8.10 × 10^{-5} g/cm^3; the ratio of the densities is 200,000 to 1!

A second and independent semi-empirical method for estimating critical temperatures is based on van der Waals's theorem of corresponding states. The theorem requires (*20*) that, for example, the entropy of vaporization of various liquids should be equal at corresponding temperatures, and vice versa.

The heat of vaporization of mercury, ΔH_{vap}, is known over an appreciable temperature range and the entropy of vaporization, ΔS_{vap} (or ΔH_{vap} T), can be readily extrapolated to the critical temperature on a reduced temperature plot. Figure 4 is a plot of the entropy curve and the reduced-temperature curve for mercury and of corresponding curves for a number of well-known normal liquids, such as carbon dioxide, carbon tetrachloride, ammonia, benzene, and water. Mercury has a markedly distinct behavior. Let us assume for the present that other metals behave in the same manner. By assuming the principle of corresponding states to be valid for other metals and by using the experimentally determined values for entropy of vaporization of other metals—for example, at their normal boiling points—we can, from Fig. 4, derive their reduced temperatures and thus their approximate critical temperatures. Table 3 contains a summary of critical temperatures of a number of metals, arranged, in ascending order, from 1733°K for mercury to 23,000°K for tungsten.

Data on liquid sodium (*21*) have recently become available which give ΔH_{vap} and ΔS_{vap} over the whole range from 800°R (445°K) to 3000°R (1667°K). In the case of liquid sodium, a close fit to the mercury curve can be obtained only if the critical temperature for sodium is assumed to be 2800°K. Usually the critical temperatures estimated by the two methods are in good agreement (*22*). They cover a wide temperature range, and many metals—for example, uranium, zirconium, molybdenum, rhenium, tantalum, and tungsten—have critical temperatures above 10,000°K. The predicted critical constants of the alkali metals, based on a combination of the two methods, are given in Table 4.

The important point is not so much the particular critical temperature of a metal as the fact that many metals can be heated to over 10,000°K and still remain liquid (at saturated-vapor pressure).

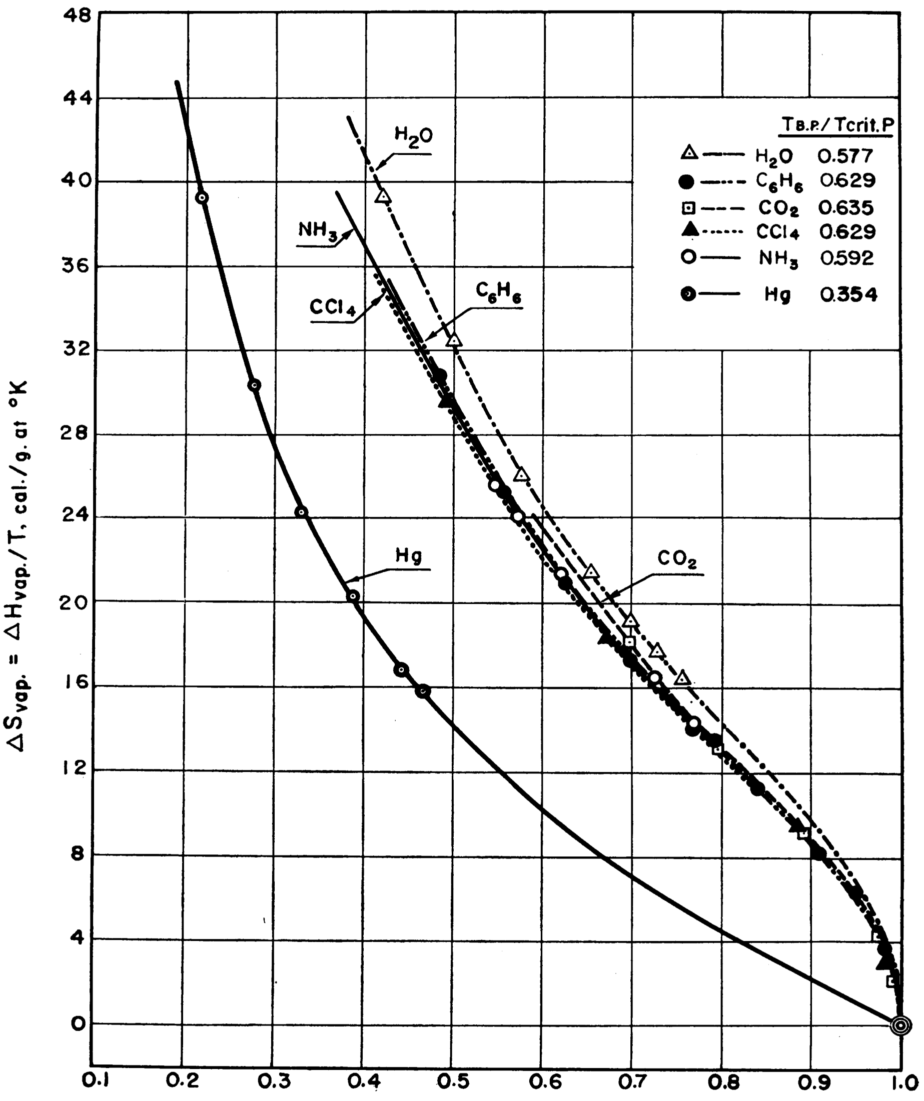

Fig. 4. Entropy plotted against reduced-temperature curve for mercury and other liquids.

Containment above the Melting Point of the Container

It occurred to me that it might be possible to contain substances at high temperatures in *liquid* containers—that is, in a "liquid pipe" or "liquid crucible." The practical problem was solved, in principle, in 1950 (*4, 23*) through use of a centrifugal chemical reactor, shown schematically (to scale) in Fig. 5. In this reactor, liquid aluminum metal was boiled at about 2700°K in a container of *liquid* aluminum oxide (melting point, 2320°K).

In this particular case the reactor, consisting essentially of a large steel cylinder lined with aluminum oxide bricks, was rotated horizontally at a few hundred rotations per minute. Aluminum metal, in the form of a rod, was fed, together with oxygen gas, through the stuffing box at right, where it burned in the free cylinder, with a dazzling flame and the evolution of great heat, to aluminum oxide at a temperature of about 3800°K.

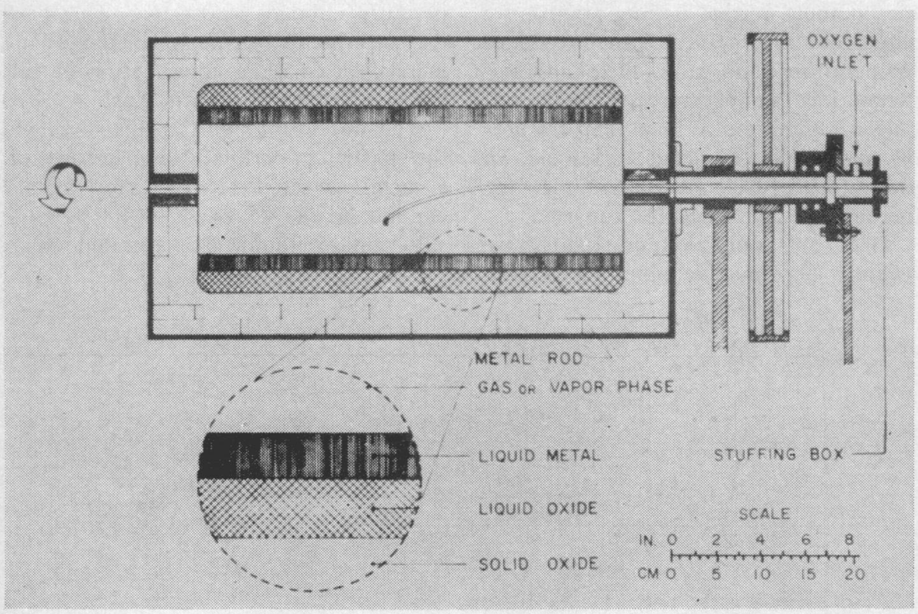

Fig. 5. Schematic diagram of the centrifugal chemical reactor.

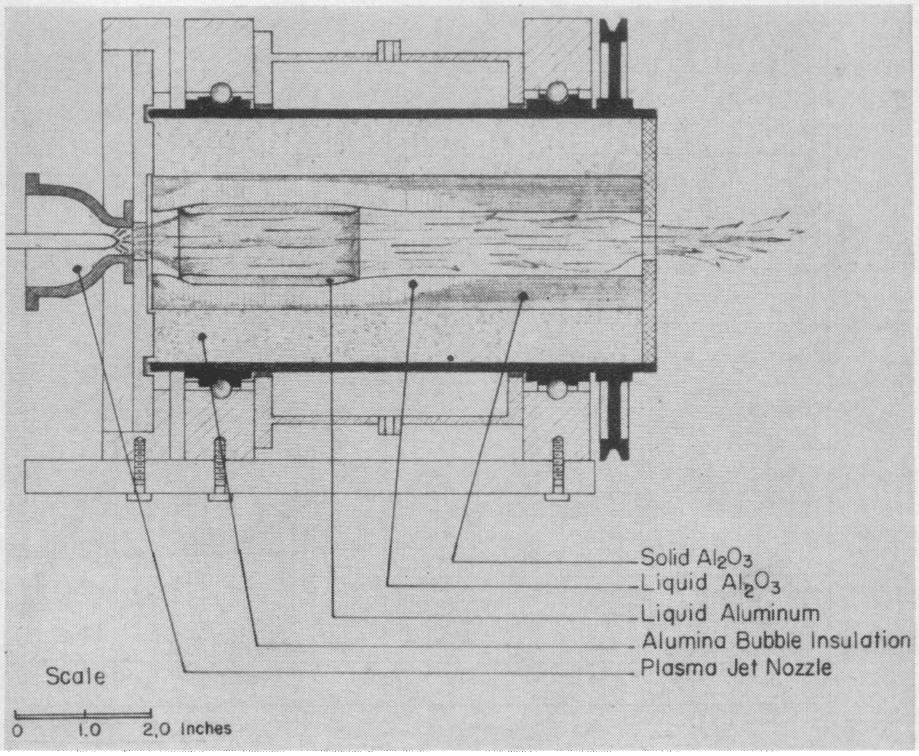

Fig. 6. Schematic diagram of the plasma jet centrifugal furnace.

In the centrifugal reactor, liquid boiling aluminum in the form of a pipe, burning in oxygen, floats on the surface of the heavier liquid aluminum oxide [also in the form of a pipe (see Fig. 5)], which in turn is supported on solid aluminum oxide. The melting surface gradually recedes toward the walls of the steel pipe. The number of rotations per minute should be sufficient to produce "rimming" (*24*) of the liquid aluminum and liquid aluminum oxide.

The whole free volume (except in the vicinity of the side plates) is at a temperature of about 3800°K; most of the combustion product (aluminum oxide) boils out through the open port at left. The operation can be carried out for periods up to 1 hour without special cooling. The reaction can be carried out with an excess either of aluminum or of oxygen. The thickness of the liquid-aluminum pipe can be varied at will from about 1 millimeter to about 2.0 centimeters or more.

The density of liquid aluminum oxide was recently found to be 3.053 g/cm^3 at the melting point (2288°K) and 2.569 g/cm^3 at 2720° (*25*); the density of liquid aluminum is estimated, according to the method reported for magnesium (*26*), to be 2.050 g/cm^3 at the normal boiling point (2720°K). Thus, liquid aluminum always floats, as a perfectly separate, clearly defined phase, on liquid aluminum oxide.

A true "liquid crucible" was produced by rotating liquid aluminum oxide *vertically*, thus producing a paraboloid of revolution, and by introducing aluminum rod and oxygen into this paraboloid through a tube of solid aluminum oxide placed, from the top, along the axis of rotation. The boiling aluminum (also in the shape of a paraboloid) was burned in the crucible thus formed. A limiting disadvantage of such chemical centrifugal furnaces is the fact that their operation requires exothermic chemical reactions. Thus, no chemical reaction can be studied except the one actually taking place.

It recently occurred to me (*27*) to utilize a high-temperature plasma jet (*15, 28*) operating in the range 5000° to 17,500°K as a centrifugal furnace, with a noble gas such as helium or argon as a source of heat. Such a furnace has now been operated successfully. It is shown schematically in cross section in Fig. 6.

The centrifugal furnace consists of a steel cylinder approximately 12 centimeters in diameter, surrounded by a water jacket. The unit is rotated in a ball-bearing mount by a 1-horsepower variable-drive unit. The range of rotation for this unit is from 500 to 1500 rotations per minute. The interior of the steel pipe can be filled with any desired insulating material, such as aluminum oxide bubbles or Thermax carbon. The reaction section of the furnace consists of a number of coaxial tubes of any oxide or other refractory material, depending upon the substance to be contained.

The power consumed in operating a furnace of this type varies from 8 to 15 kilowatts at 25 to 30 volts, and from 350 to 500 amperes. The flow of helium is from 15 to 30 liters per minute, at normal temperature and pressure. The average temperature of the plasma is 10,000° to 17,500°K.

In the example shown in Fig. 6, aluminum was boiled in liquid aluminum oxide. An aluminum oxide tube was first melted by being heated for about 5 minutes in the plasma jet. The liquid aluminum oxide could be readily observed through the exit port. A solid rod of aluminum of known weight was then introduced through the exit port, at a slight angle; it melted in a few seconds and floated on the liquid aluminum oxide container and came to a boil in about 3 minutes. It distilled through the exit port and burned in the air with the usual brilliant flame.

Subsequent examination revealed that the innermost aluminum oxide tube had melted over a length of about 10 centimeters and that the remaining aluminum metal formed a sharp cylindrical band, about 3 centimeters wide and 3 millimeters thick, on the aluminum oxide. The two phases were perfectly defined and separate, as shown in Fig. 7. We have melted a thorium dioxide tube in the plasma jet, also.

The range of use of liquid oxide containers should be, on the average, for Al_2O_3, 2288° (melting point) to about 3800°K; for ZrO_2, 3000° (melting point) to about 4600°K; and for ThO_2 3300° (melting point) to about 4700°K.

The ratio of the vapor pressure of the container material to the total pressure can be adjusted, if desired, by operating the plasma jet and furnace at a higher total pressure. Thus, a way is now open to extend inorganic chemical research, particularly on chemical reactions in liquid phase (for example, between the container and any added substance lighter than the container), to a much higher temperature range.

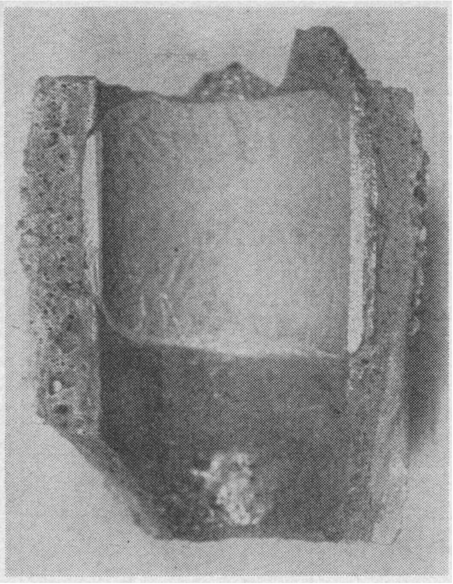

Fig. 7. After solidification, aluminum is clearly defined inside the aluminum oxide tube. The light gray area is aluminum.

The method just described is not well suited for making physical measurements (such as measurements of density and electrical resistivity) because of imperfect geometry. These measurements may be made by means of centrifugal furnaces heated by ohmic resistance, as illustrated in Fig. 8. That liquid metals may be used in this way as conductors was not realized in the past, due to the fact that the magnetic field created by the large electric current that is needed constricts and finally "pinches off" the liquid metal, thus breaking the circuit.

The phenomenon of the "pinch" was first discussed in Philadelphia by Carl Hering at the 3 May 1907 meeting of the American Electrochemical Society (*29*) and was further described by him in subsequent publications (*30*). The phenomenon was investigated quantitatively by Edwin F. Northrup (*31*), who established the relationship between the pressure P of the pinch (in dynes per square centimeter), the current strength I (in absolute centimeter-gram-second units), and the cross-sectional area of the liquid metal, A (in square centimeters). The relationship is $P = I^2/A$. If the current is measured in amperes, $P = \text{amp}^2/100\,A$.

Two methods have been found to counteract the pinch: (i) arranging the geometry of the current path to take advantage of the hydrostatic pressure of the liquid metal, and (ii) using a centrifugal force greater than the pinch pressure, as illustrated in Fig. 8. The liquid metal can be heated in a solid tube or in a "liquid pipe" of significantly greater electrical resistance than the metal.

It has been found possible to overcome the pinch effect and to use ohmic-resistance heating to boil bismuth, lead, tin, and other metals at or slightly above atmospheric pressure. We can now reflux bismuth or lead at about 2000°K for long periods. It is also possible, therefore, to construct thermostats by means of boiling liquid metals.

Physical Properties of Liquid Metals

Liquid metals are monatomic substances, and thus the relationships between their physical properties and temperature are simpler to comprehend than the corresponding relationships that exist for molecular liquids. For example, electrical conductivities may be extrapolated to higher temperatures, and from them thermal conductivities

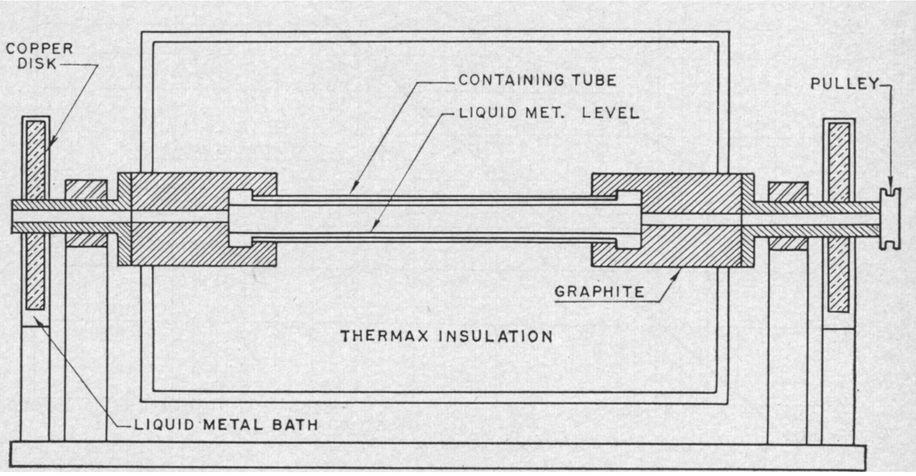

Fig. 8. Schematic diagram of the centrifugal electrical furnace.

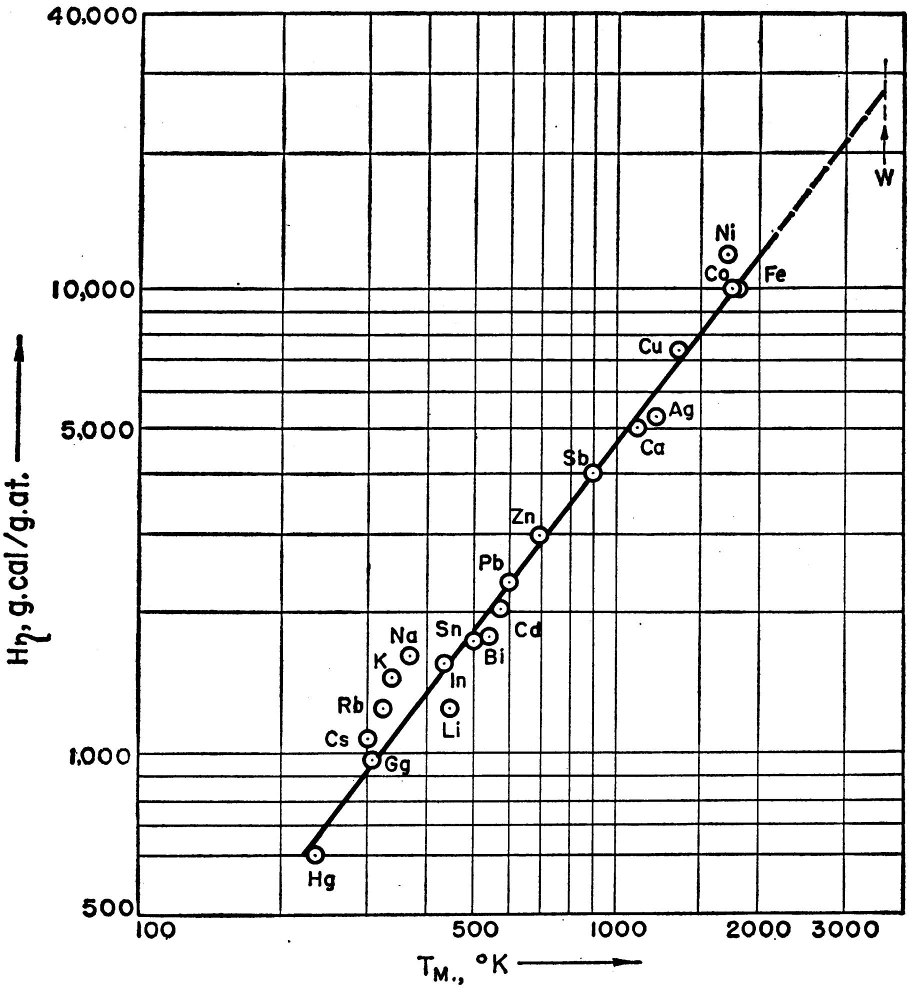

Fig. 9. The activation energy of viscosity, H_η (in g-cal/g-atom), plotted against melting point (in degrees Kelvin) for various metals.

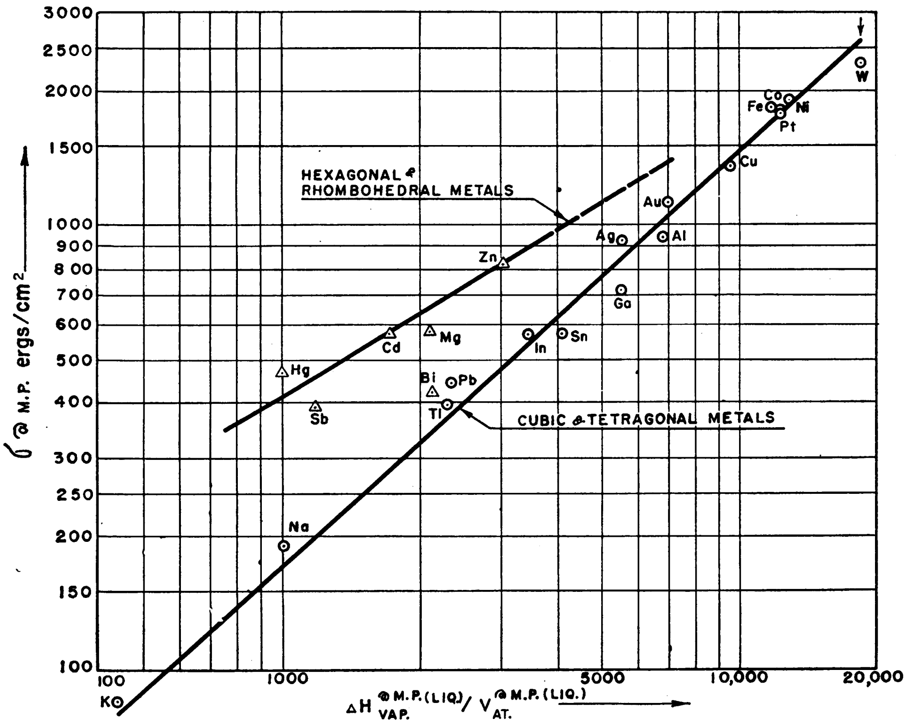

Fig. 10. Surface tension at melting point plotted against heat of vaporization per cubic centimeter at melting point for various metals.

can be readily estimated in accordance with the Widemann-Franz law. I will discuss here, however, only the viscosity and surface tension of liquid metals.

Andrade's simple formula (*32*) relates the viscosity η (in poises) and T (in degrees Kelvin) according to the expression

$$\eta_T = a \times \exp(H_\eta/RT)$$

It has been found recently (*33*) that the logarithm of the activation energy of viscosity $H\eta$ is a linear function of the logarithm of the melting point of the metal, as shown in Fig. 9.

Expressed in algebraic form, the relationship is

$$\log H_\eta = 1.348 \log T_{mp} - 0.366$$

(where the logarithm is to the base 10), or

$$H_\eta = 0.431 \times T_{mp}^{1.348}$$

This relationship, coupled with Andrade's expression (*34*) for the viscosity of a liquid metal at the melting point,

$$\eta_{mp} = 5.7\ (A \times T_{mp})^{1/2}/(10^4\ V_{at}^{2/3})$$

where A is atomic weight and V_{at} is atomic volume, permits us to estimate the viscosity of any metal at any temperature.

A simple relationship, shown graphically in Fig. 10, exists between the surface tension (in dynes per centimeter or ergs per square centimeter) of a liquid metal (at saturated-vapor pressure) at its melting point, σ_{mp}, and its heat of vaporization per cubic centimeter, $\Delta H_{vap}{}^{liq}/V_{at}$, at its melting point. Clearly, the surface tensions of metals belonging to the cubic or tetragonal systems lie along one straight line, while those of metals of the hexagonal or rhombohedral systems fall on a second and higher line. This fact tends to support the current belief that some elements of the crystal structure or space configuration of the solid state persist in the liquid state.

A practically equivalent relationship, also represented by two lines for the two types of metals, exists between the total surface energy Σ [which equals the product of σ and O_{at}, where O_{at} is the total surface in square centimeters per gram atom ($1.091 \times V_{at}^{2/3} \times N^{1/3}$ for close-packed spheres)] and the heat of vaporization.

This relationship was first deduced theoretically by Skapski (*35*); Taylor (*36*) used it to predict unknown surface tensions. Another relationship, proposed by Strauss (*37*), is very similar to that shown in Fig. 10.

The value of all such relationships depends on the reliability of the experimental data on which they are based. A critical review of all pertinent data from the literature will be published elsewhere.

The straight line of Fig. 10 for cubic or tetragonal metals is given by the equation

$$\sigma_{\text{mp}} = 0.274 \left(\frac{\Delta H_{\text{vap}}}{V_{\text{at}}}\right)^{0.931}$$

or

$$\log \sigma_{\text{mp}} = 0.9309 \log \left(\frac{\Delta H_{\text{vap}}}{V_{\text{at}}}\right) - 0.5623$$

(the logarithms here and in the equations that follow are to the base 10). The relationship for hexagonal and rhombohedral metals is

$$\sigma_{\text{mp}} = 5.740 \left(\frac{\Delta H_{\text{vap}}}{V_{\text{at}}}\right)^{0.620}$$

or

$$\log \sigma_{\text{mp}} = 0.6204 \times \log \left(\frac{\Delta H_{\text{vap}}}{V_{\text{at}}}\right) + 0.7587$$

(σ_{mp} is in dynes per centimeter, ΔH_{vap} is in calories per gram atom, and V_{at} is in cubic centimeters per gram atom, all for the liquid at the melting point.)

At the critical temperature T_c, the surface tension of any substance is zero. It has been shown (*38*) that, at least in first approximation, σ should be a linear function of temperature. If we know T_c (see Table 3) we can readily calculate the temperature coefficient over the whole liquid range:

$$d\sigma/dT = -\sigma_0/T_c = -\sigma_{\text{mp}}/(T_c - T_{\text{mp}})$$

or

$$d\sigma/dT = -\sigma_T/(T_c - T)$$

where σ_0 is the extrapolated surface tension at 0°K and σ_T is the surface tension at any temperature T (see *38* for a table giving $d\sigma/dT$ for 20 metals and for discussion of this relationship).

Nuclear Rocket Reactor

The obvious way to produce rocket thrust with a high specific impulse is to use atomic energy and operate a nuclear reactor containing the critical mass of fissionable material in the form of a "liquid pipe," as illustrated in Figs. 5 and 6; then to bubble or blow hydrogen gas radially through the liquid metal to heat the gas to as high a temperature as possible and then allow the atomic hydrogen to expand through the rocket nozzle. The thickness, diameter, and length of the "liquid pipe" can be varied to suit the design requirements.

The first step toward realization of this goal should be the study of the chemistry (at as high a temperature as is now experimentally possible) of appropriate metals with various refractory oxides, carbides, nitrides, sulfides, and other substances useful for such a nuclear program (*39*).

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