Dinner Speaker

Chemistry at High Temperatures and Pressures

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About two years ago, at the time I was changing my place of employment from the General Electric Research Laboratory at Schenectady, New York, to the Brigham Young University at Provo, Utah, I planned to continue the high-pressure work in which I had been engaged. Events following the successful synthesis of diamonds, however, raised considerable doubt as to whether or not this work could be continued. Company attorneys and others gave caution as to the limits that would be imposed on my work for reasons of proprietary interest; and the placing, shortly thereafter, of a governmental secrecy order on the high-pressure apparatus that was being used severely restricted what I might do. Because of these complications, I began to cast about for another research area. Research at high temperatures seemed appealing, particularly high temperatures in condensed phases. A search of the literature with respect to methods of producing high temperatures showed that, outside the use of atomic bombs, four general means for obtaining high temperatures had been used:

(1) Exploding wires by high voltage discharge (Anderson, 19,700°C.);
(2) Use of shock waves (approximately 50,000°C.);
(3) High pressure electric arcs (C. G. Suits, 6,440°C.);
(4) Solar furnaces (approximately 5,000°C. maximum).

More recently much higher temperatures have been obtained than those just mentioned.[†] However, these temperatures are not produced in condensed phases.

Methods (1) and (2) above are very transient, inasmuch as the temperature exists only for periods of micro to milli-seconds. The maximum temperatures obtainable in methods (1) and (3) are limited by ejection of hot material from the arc or from the wire and by adiabatic expansion. The temperature obtainable in method (4) cannot exceed the temperature of the sun's surface. An unexplored area would be the region above 5,000°C. in condensed phases where the temperatures could be maintained for second to minute periods. Time periods of this duration for temperatures of this magnitude would be sufficient for many chemical reactions to take place. It seemed reasonable that it should be possible to generate temperatures of the order of 10,000°C. that could be maintained for a few minutes by resistance heating of some electrically conducting element confined with a bomb such as is shown in Figure 1. The bomb serves to confine the electrical heating element so that cooling by expulsion of material cannot occur. Also, the heating element is held together (so that it cannot explode as do Anderson's wires) so that large currents can be passed through it for a reasonable period of time. The thermal insulation immediately surrounding the heating rod, and indeed the rod itself, will be molten and will grade-off radially into solid material with the radial temperature gradient that is established. The heat loss out the ends of the bomb along the axis will be such as to provide a thermal gradient from the mid-point of the bomb toward the ends so that material will grade from molten to solid here and in this wise the container problem has been eliminated. The material within the bomb is confined by tightening the nuts on the tension bolts. The pressure exerted upon the material within the bomb by this technique is small; indeed, it is insufficient to close up any voids initially present, so it is important to have good fitting components in order that the phases with the bomb might remain as condensed systems when the material becomes molten at the high temperature.

A proposal was submitted in January of 1956 to the U.S. Army Office of Ordnance Research requesting financial aid to construct and test some experimental bombs similar to that of Figure 1 to determine the maximum temperatures that might be obtained in such a device. The scope of work was also to include the estimation of temperatures and pressures by various means and to conduct some chemical reactions at the highest temperatures obtained. The proposal was accepted. Let me express, at this point, my appreciation to the U.S. Army Office of Ordnance Research for their financial aid. Organizations, of course, are made up of individuals and I especially wish to thank Dr. Peter R. Kosting, Director of the

Metallurgical and Engineering Sciences division, and Dr. Humbert Morris of the Los Angeles Ordnance district for their interest and support.

In the first bombs constructed, the heating element was a carbon rod and the thermal insulation was a readily machinable, stony material known as pyrophyllite. Pyrophyllite is a naturally occurring, extremely fine-grained, hydrous aluminum silicate, which, when confined, melts to a glass-like substance at a temperature around 1,500°C. A platinum, platinum-rhodium thermocouple element was imbedded in the carbon rod for the measurement of temperature. Power input, measured as watts, to the carbon heating element as a function of temperature indicated by the thermocouple was recorded. A plot of these two variables yields a straight line function, which was extrapolated to indicate higher temperatures. An additional point on this plot was obtained by finding the power input necessary to melt a small tungsten wire passing through, or adjacent, to the graphite rod. A sample of such a power input-versus-temperature plot is shown in Figure 2.

With a carbon rod heater and pyrophyllite insulator, it is possible to obtain extrapolated temperatures of the order of 6,000°C. for periods of 15 seconds. For periods of minutes it is possible to obtain temperatures of the order of 4,000°C. The maximum temperature obtainable in such a system is limited because of intrusion of molten pyrophyllite material across the carbon heating element. This intrusion, which seems to be a combination mechanical and chemical effect, results in interruption of the electric current. Substitution of thermal insulation materials for the pyrophyllite surrounding the carbon rod was attempted in order to eliminate or minimize this current cut-off effect. Alumina, porcelain, silica, and glass were tried. Alumina and porcelain were no better than the pyrophyllite, silica was inferior, but pyrex glass increased the temperature that could be obtained before cut-off occurred. A pyrex glass sheath of approximately 1/32-inch wall thickness immediately surrounding the carbon rod allowed extrapolated temperatures of 15,000°C. to be obtained for 15-second periods. Some attempts were made to substitute compressed refractory powders for the pyrophyllite thermal insulation for use with various heating elements. This was without success. In the first place, it was difficult to obtain a dense compact mass free of minute voids. Of course, on heating such material, the voids would be filled with molten liquid and condensed phase would not be maintained. Secondly, it soon became apparent that when operating at 10,000°C., it matters little whether the refractory being used melts at 1,500°C. or 2,500°C. In view of this, most of our experiments have been conducted with pyrophyllite as the refractory element. Of course, the principal advantage of pyrophyllite is that it can be readily machined to any shape.
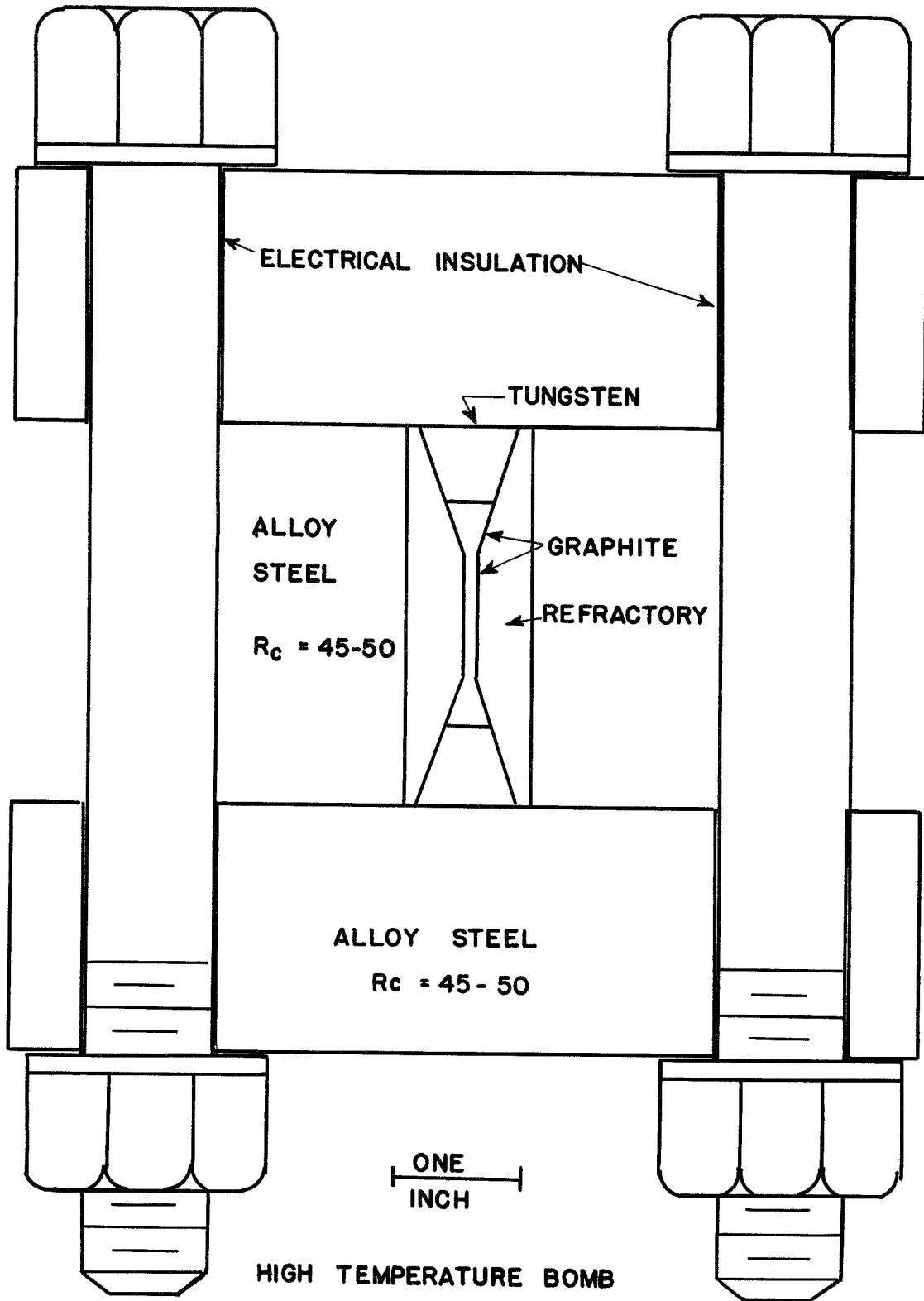
Because there seemed to be some chemical reaction between carbon and the materials used as thermal insulation as the high temperatures being produced, we though it advisable to experiment with some high melting metallic materials such as tungsten and molybdenum in these materials over that of carbon, it was found that much larger wattages were required to obtain a given temperature with these substances. All other conditions of geometrical arrangement, etc., remained the same. (A new temperature calibration must be obtained for each change of materials or geometrical dimensions and arrangement.) With molybdenum and tungsten, the cut-off phenomena was observed again. As before, the highest temperatures were obtained when the heating element was sheathed with pyrex glass. With this arrangement, temperatures of 10,000°C. were maintained for 15 seconds before cut-off. With tungsten and molybdenum, there appeared to be no evidence of chemical reaction between the metal and the refractory. Cut-offs seemed to be caused by the molten metal withdrawing into a ball and the molten refractory material flowing into the space from which the metal withdrew. The forming of this ball of metal might be due to two effects: (1) an actual electrical "pinch" effect due to the high current flowing through the metal; and (2) an attempt by the metal to reduce its surface area because of the large difference in surface energy between the metal and the refractory.

At this point, it seemed that this cut-off phenomena might be eliminated if the heating element were composed of some material that when molten would possess cohesive forces more like that of the ceramic insulator and also if the electrical resistance of this element were a factor of 100 or so higher than that of tungsten. The higher resistance would require much lower currents to obtain the same wattage within the element and hence the electrical "pinch" effect would be reduced. The materials experimented with in this connection were, in general, semi-conductors such as silicon carbide, copper oxide and sulfide, elemental silicon, etc. From these experiments heating elements were developed which usually do not cut-off at power inputs available to us. These heating elements are composed of an approximately 50-50-by-volume mixture of silicon carbide and graphite powders or of 50-50 graphite and powdered pyrophyllite.

Extrapolations of power input—temperature curves such as that of Figure 2 are hazardous above 10,000°C. Consequently, equipment is being assembled to attempt to utilize thermal noise power in the measurement of temperatures that might be produced in bombs with C—Si C heating elements. If power inputs corresponding to 10,000°C. are maintained in C—Si C heaters for periods greater than one minute, considerable mixing of molten material ensures, the C—Si C mixture is dispersed throughout a relatively large volume of molten material, with resultant enlargement of the cross section of the electrical conduction path. This certainly leads to lower temperatures within the bomb.

Application of very high pressures to the contents of the bomb would tend to stiffen the molten materials by squeezing out the holes. The holes, of course, are necessary for liquid flow. High pressure would thus tend to maintain the original geometry of components within the bomb, thus allowing higher temperatures to be obtained and maintained. To carry out high-temperature experiments within the bomb, it is necessary to surround the heating element with a sheath of the materials to be reacted. In some instances, it may be possible to construct the heating element of the reacting materials. Limitations on the reactions will be imposed in many cases because of the reaction with the heating element or the refractory liner. Regardless of these limitations, there are numerous high-temperature experiments that can be performed with this equipment.

The basic thermodynamic relationships for predicting the course of a chemical reaction involve pressure—volume, internal energy, and entropy terms. Pressure and temperature are the most important intensive properties over which we have control and through which we may influence the course of a chemical reaction. Extremely high temperatures and pressures are important in that they offer the possibility of causing radical changes to take place in the electronic configurations of atoms. Since the chemical properties of atoms depend upon the external electronic configuration of the elements, application of high pressure and high temperature may produce entirely new chemical substances.

ELECTRICAL INSULATION

TUNGSTEN

ALLOY STEEL

$R_c = 45\text{-}50$

GRAPHITE

REFRACTORY

ALLOY STEEL

Rc = 45 - 50

ONE
INCH

HIGH TEMPERATURE BOMB

# TYPICAL  TEMPERATURE  CALIBRATION