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I. An apparatus for use with condensed phases at 10,000°[1]
II. Some thermodynamic and rate considerations at very high temperatures

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An apparatus is described wherein condensed phases may be heated to temperatures of 10,000° or higher for second to minute periods. Temperature is obtained by resistance heating of an electrically conducting element confined by a steel bomb. At the highest temperatures of operation, both the heating element and adjacent refractory material are molten. Some consideration is given to the various quantities that determine the equilibria between reactants and products under constant volume and also under constant pressure conditions. Kinetic problems at very high pressure and at very high temperature are discussed. Finally, there is some speculation as to the possibility of forcing external electrons into inner unfilled orbitals when condensed phases are maintained at constant volume and then subjected to extremely high temperatures.

I

An unexplored area for scientific research exists in the region above 5,000° wherein temperature could be maintained for second to minute periods in condensed phases. We have found it possible to obtain temperatures of at least 10,000° by resistance heating of an electrically conducting element confined within a bomb such as is shown in Fig. 1. During operation the thermal insulation immediately surrounding the central heating rod will grade-off radially from liquid to solid material with the radial temperature gradient that is established. The heating element will, of course, be liquid at the higher operating temperatures. The heat loss out the ends of the bomb along the axis will be such as to provide a thermal gradient from the central regions of the bomb toward the ends so that material will also grade from molten to solid here and in this wise eliminate the container problem. 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 within the bomb might remain as condensed systems when the material becomes molten at the high temperature.

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°. A 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 adjacent to the graphite rod. A sample of such a power input versus temperature plot is shown in Fig. 2.

With a carbon rod heater and pyrophyllite insulator, it is possible to obtain extrapolated temperatures of the order of 6,000° for periods of 15 seconds. For periods of the order of minutes it is possible to obtain temperatures of the order of 4,000°. The maximum temperature obtainable with carbon heaters is limited by intrusion of

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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 and consequently limits the temperature obtainable. Substitution of thermal insulation materials for the pyrophyllite immediately 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 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 a 1/8-inch diameter carbon rod allowed extrapolated temperatures of 15,000° 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, vaporization would take place into the voids and a condensed phase would not be maintained. Secondly, it soon became apparent that when operating at 10,000°, it matters little whether the refractory being used melts at 1,500 or 2,500°. 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 at the high temperatures being produced, we though it advisable to experiment with some high melting metallic materials such as tungsten and molybdenum in place of carbon. Because of the much higher thermal conductivity of 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 phenomenon 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° were maintained for 15 seconds before cut-off. There seemed 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 by 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-off" 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.

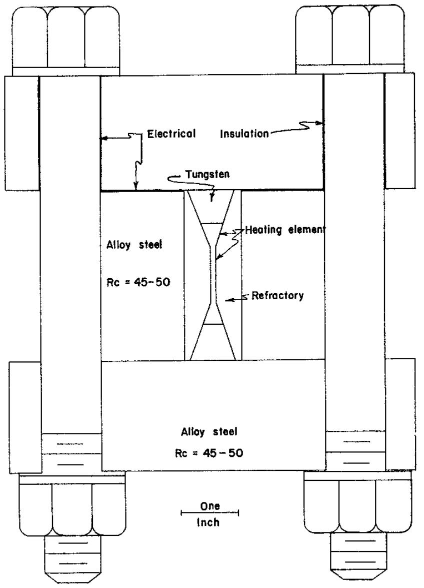

Fig. 1.—High temperature bomb.

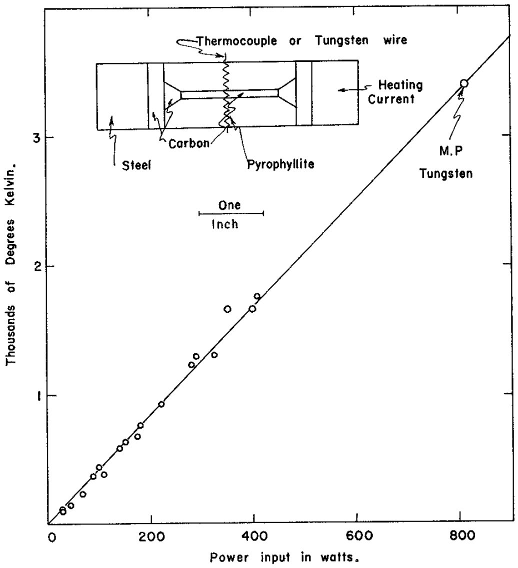

Fig. 2.—Typical temperature calibration.

At this point, it seemed that this cut-off phenomenon 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-off” 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. Through these experiments a heating element was found in which it has not been possible to produce cut-off at power inputs available to us (20 kw.). This heating element is composed of an approximately 50-50-by-volume mixture of silicon carbide and graphite powders.

Extrapolations of power input-temperature curves such as that of Fig. 2 are hazardous above 10,000°. Consequently, equipment is being assembled to try to utilize thermal noise power in the measurement of temperatures that might be produced in bombs with C-SiC heating elements. If power inputs corresponding to 10,000° are maintained in C-SiC heaters for periods greater than one minute, considerable stirring of liquid material ensues, the C-SiC mixture is dispersed throughout a large volume of molten material with resultant enlargement of the cross section of the electrical conduction path. This leads to lower temperatures within the bomb. Initially, 3,000 watts corresponds to a conservative 10,000° when the conducting cross section is 1/8-inch diameter. However, when the conducting cross section is ½-inch diameter, 3,000 watts corresponds to only 3,000°. Application of very high pressures to the contents of the bomb would tend to stiffen the molten materials by squeezing out the molecular holes. The holes, of course, are necessary for liquid flow. High pressure would tend to maintain the original geometry of components with the bomb, thus allowing higher temperatures to be obtained and maintained for longer periods of time. 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 is 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 experiments that can be performed with this high-temperature device.

II

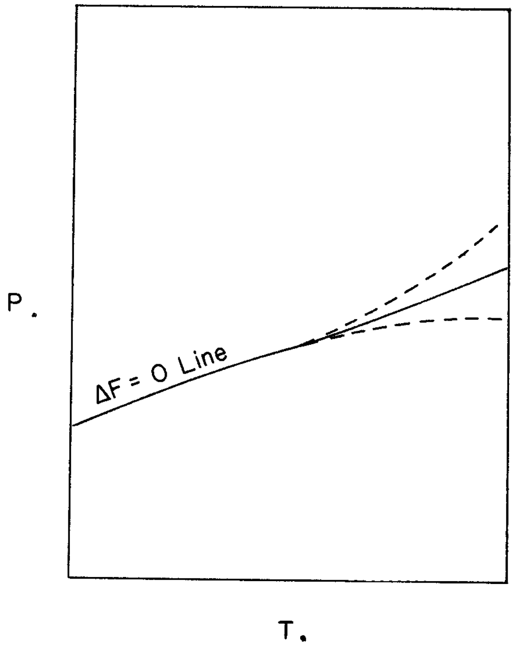

Fig. 3.—Plot showing $\Delta F = 0$ line on a P–T diagram.

A substance is completely characterized thermodynamically if the volume is known as a function of the two intensive properties, pressure and temperature, and if the specific heat at constant pressure, say one atmosphere, is known as a function of temperature. If this information (in addition to ΔE and S at some pressure and temperature) were available for all possible substances, the thermodynamicist would have an easy time in predicting the course of chemical reactions. However, the amount of such information available even at moderate pressures and high temperatures is meager. The basic thermodynamic relationships for predicting the course of a chemical reaction are give below for the reaction A = B where A represents the reactants and B represents the products of the reaction. The difference in free energy between

$$F_B = P_BV_B + E_B - T_BS_B \qquad \text{(a)}$$
$$F_A = P_AV_A + E_A - T_AS_A \qquad \text{(b)} \qquad (1)$$
$$\Delta F = F_B - F_A \qquad \text{(c)}$$

the products and the reactants gives a measure of the extent to which the reaction will proceed in the direction A → B under the thermodynamic conditions involved. The points where the difference in free energy equals zero give convenient places of reference, since at such points the equilibrium is displaced toward the reactants. The most common conditions under which a reaction takes place are those of constant pressure and constant temperature. The free energy equation 1c under these circumstances becomes equation 2 below.

$$\begin{aligned} \Delta F &= P(V_B - V_A) + (E_B - E_A) - T(S_B - S_A) && \text{(a)} \\ &= P\Delta V + \Delta E - T\Delta S && \text{(b)} \qquad (2) \\ &= P\Delta V + \Delta D && \text{(c)} \end{aligned}$$

Again, whether or not a chemical reaction will take place depends upon the sign of the change in free energy, ΔF. The balance between the various thermodynamic quantities which determine this sign may at times be quite delicate. The possibilities existing with respect to this balance are shown below.

Case I For ΔV positive, ΔD positive:
ΔF is positive everywhere
II For ΔV positive, ΔD negative:
ΔF is negative for $|\Delta D| > |P\Delta V|$
III For ΔF negative, ΔD positive:
ΔF is negative for $|P\Delta V| > |\Delta D|$
IV For ΔV negative, ΔD positive:
ΔF is negative everywhere

From the standpoint of utilizing high pressure to bring about a chemical reaction in a condensed system that would not go otherwise, Case III is of primary interest. In such a situation, the positive thermal term ΔD would be larger than the negative mechanical term $P\Delta V$ at low pressures and would establish equilibrium in favor of reactants. At sufficiently high pressure, however, the $P\Delta V$ term would become significant and favor the formation of the products. This true in general (for reasonable volume decreases) because of the small effect of pressure on thermal terms. The internal energy E changes with pressure as shown below. The first term in equation 3 gives the thermal expansion and the second term the compressibility.

$$\left(\frac{dE}{dP}\right) = -T\left(\frac{dV}{dT}\right)_P - P\left(\frac{dV}{dP}\right)_T \qquad (3)$$

Since these terms are of the same magnitude and of opposite sign, the change of internal energy with pressure is small.

The effect of pressure on entropy (see equation 4) is generally small.

$$\left(\frac{dS}{dP}\right)_T = -\left(\frac{dV}{dT}\right)_P \qquad (4)$$

The effect on potassium should be larger than for any other material. In this case a pressure of 12,000 atm. reduces the entropy by 30%. Pressures of millions of atm. are indicated to cause the entropy to approach zero. These pressure effects on E and S will generally be of the same magnitude for products and reactants and hence will have little effect on the outcome of the reaction providing ΔV is large.

When the change in free energy equals zero ($\Delta F = 0$), equation 2b transforms to equation 5

$$P = \frac{T\Delta S}{\Delta V} - \frac{\Delta E}{\Delta V} \qquad (5)$$

For Case III reactions above, a plot of pressure versus temperature would appear as shown in Fig. 3. The slope of the line equals the ratio of the change in entropy to the change in volume and the pressure axis intercept equals the ratio of the change in internal energy to the change in volume. The reaction A → B becomes thermodynamically more favorable in P ® T regions above this line, whereas the reverse reaction, B → A, becomes increasingly favorable below the line. Actually, the changes in entropy, volume and internal energy are not constants, but depend on P and T so that $\Delta F = 0$ line may deviate in either direction from the straight line, as shown by the dashed curves in the figure.

The reaction A = B may be useful or of interest only if the amount of B produced within a given time exceeds a certain minimum. By utilizing the absolute reaction rate theory as developed by Henry Eyring a minimum rate curve may be drawn on a pressure-temperature diagram. Three typical samples of the form taken by this curve for a positive $\Delta V^{\ddagger}$ are shown in Fig. 4. In a $P - T$ region below a curve of Fig. 4, the elementary rate process proceeds faster than the pre-chosen value selected. Above the curve the rate is slower. For negative $\Delta V^{\ddagger}$ the curve on the $P - T$ diagram will have a negative slope and the rate will proceed faster than the pre-chosen value in regions above the curve.[2]

In order to utilize the foregoing equilibrium considerations it is necessary to have enough actual or estimated thermodynamic information to produce the $\Delta F = 0$ line on the $P - T$ diagram. The rate information will be even more difficult to obtain. In some cases it is possible to obtain rate data on the reverse transformation, B → A. Then, making the assumption that the reaction proceeds in either direction along the same reaction path, it is possible to construct the *minimum rate line*. Figure 5 shows the $\Delta F = 0$ line and *minimum rate line* on the same diagram. In the region of overlap the products will be formed. Prediction of the course of a reaction at

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[2] These considerations are given in detail by the author in the paper, “Chemistry at High Temperature and Pressure.” “High-Temperature—A Tool for the Future,” published and distributed by Stanford Research Institute, Menlo Park, California, 1956, pp. 161-166.

high pressure and high temperature is not only handicapped by lack of thermodynamic data for reactants and products, but is handicapped by not knowing what the products might be because the products of high pressure—high temperature experimentation might be substances heretofore unknown. An expression of this idea was recently given by Wentorf in regard to his synthesis of cubic boron nitride.[3] He reputedly said, "Attempting to make this material was like fishing for an unknown fish in an unknown lake." Of course, the making of cubic boron nitride was aided by analog-type reasoning, the analog being the diamond. However, the amount of analog-type reasoning that can be used in the synthesis of new materials is limited. The he only course open seems to be one of "going out on a limb" with some unconventional ideas. One possibility is that at extremely high pressures, atoms will be forced into such close proximity that normal electronic configurations are grossly affected. Under such conditions the addition of high temperature and catalysts to the system to overcome activation barriers could lead to the formation of hitherto unknown compounds wherein the chemical bonding would be entirely new. Perhaps these compounds might have some properties that would be superior to those of materials in use today. In general these "new compounds" could be returned to ordinary condition of pressure and temperature without disruption by reducing the temperature to normal before reducing the pressure. In some instances, rapid temperature quenching may be required.

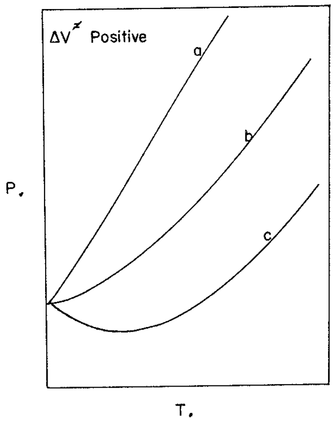

Fig. 4.—Minimum rate curves on *P–T* diagram for positive volume of activation.

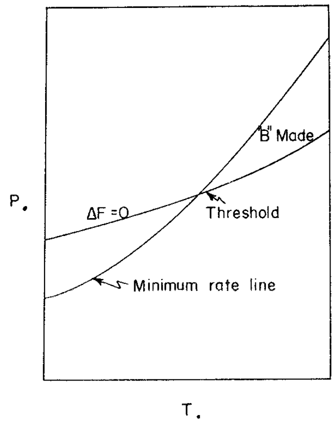

Fig. 5.—Minimum rate line and $\Delta F = 0$ line showing region of overlap where products are made.

The high-temperature bomb described above is loaded at a fixed volume and then high temperature is applied to the system. The bomb will, of course, try to maintain the volume existing at its initial loading. Because the materials of construction are compressible, however, there will be some increase in volume. Nevertheless, constant temperature, constant volume thermodynamics will be most applicable to this situation. Equation 1 shows that, at constant temperature and volume, equation 6 will apply.

$$\Delta F = V\Delta P + \Delta E - T\Delta S \qquad 6)$$

The balance established between the quantities ΔE, ΔP and ΔS will determine whether or not ΔF is negative. It will be important, therefore, to know the effect of temperature on the above quantities. The manner in which the pressure within the bomb changes with temperature is give by equation 7 below.

$$\left(\frac{dP}{dT}\right)_V = -\left(\frac{dV}{dT}\right)_P \Big/ \left(\frac{dV}{dP}\right)_T \qquad (7)$$

The data necessary to make an estimate of the magnitude of $(\delta P/\delta T)v$ at the temperatures of interest here are non-existent. However, something can be gained from examining data available at low temperature. Bridgman has measured *P-V-T* relationships for several liquids at temperatures from 0 to 95° and pressures to 12,000 atm.[4] A perusal of his data shows that the pressure generated by confining certain organic liquids to the volume they occupy at 0° and atmospheric pressure followed by heating to 95° will generate a pressure of about 1,200 atm. (This is an average for 30 organic liquids.) On a temperature *versus* pressure plot, curves for these liquids bend toward the temperature axis, indicating that the pressure generated by the temperature tends to fall off at higher

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[3] R.H. Wentorf, Jr., *J. Chem. Phys.*, **26**, 956 (1957).

[4] Consult P.W. Bridgman, "The Physics of High Pressure," G. Bell and Sons, London, 1949.

temperatures. Mercury is in a different class than the organic liquids. If it is confined to the volume which it occupies at -30° and 1 atm. and then heated at constant volume to 200°, the pressure generated will be 7,000 atm. Curves for these materials cannot be extrapolated with any degree of reliability to temperatures greater than two or three hundred degrees.

Some measure of the pressures attained in the high-temperature bomb have been obtained by increasing the temperature until they explode. A bomb constructed similar to that shown in Fig. 1 except that the inside diameter in 1.5 inches will withstand an internal pressure in the neighborhood of 16,000 atm. Temperatures of 10,000° in the core of this bomb will cause it to burst. For the present, then, the approximate pressure developed within the bomb at 10,000° has been set at 16,000 atm. If, in the reaction A = B, the ratio of thermal expansion to compressibility is less for the products than for the reactants, high temperature will make the $V\Delta P$ component of ΔF more favorable with respect to product formation.

The internal energy of a substance is given by equation 8.

$$E = E_0 + \int_0^T C_v dT + \Sigma E_{latent} \qquad (8)$$

Other things being equal, the important quantity affecting the change of internal energy with temperature is C_v. If this quantity is smaller for the products than for the reactants (again, other things being equal) at the high temperature, ΔE will be negative and the reaction will be favored.

The entropy of a substance is affected by temperature, as shown below in equation 9.

$$\left(\frac{dS}{dT}\right)_v = \frac{C_v}{T} \qquad (a)$$

$$S = S_0 + \int_0^T \frac{C_v}{T} dT + \Sigma \frac{E_{latent}}{T} \qquad (b) \qquad (9)$$

Here, as in the case of internal energy, the quantity of importance as temperature is increased is the specific heat at constant volume. The relative change of the quantity TS with temperature will be larger than the change of internal energy E.

Thermodynamic data are not available to make quantitative use of the above relationships at very high temperatures. However, the influence of the various quantities in determining the sign of ΔF can be qualitatively weighed in some instances and the efficacy of the use of the high-temperature bomb in causing a reaction to proceed in the desired direction can be determined. Again, as in the constant *P-T* situation, the nature of the products that can be formed at high-temperature constant volume may not be known. *A priori*, it seems reasonable to state that "things resistant to heat must be born of heat." Perhaps solid materials could be produced that would remain solid at temperatures considerably above the melting points of the highest melting solids known today (on increasing the temperature of such a material at atmospheric pressure a melting point would not be reached, rather a transition temperature would be reached where the material would transfer into its natural form).

At very high temperature and constant volume a process may take place that is reminiscent of that taking place at very high pressures, *i.e.*, electrons seeking empty orbitals closer to the nucleus. When a substance is heated at low pressure a temperature is eventually reached (approx. 7,000°) where ionization begins to take place. If the condensed material being heated is confined to constant volume, ionization of electrons, *i.e.*, electron escape, cannot take place in the usual sense. As an alternative to ionization, sufficiently high temperature could conceivably drive the electrons to occupy unfilled orbitals, thereby changing the ordinary chemistry of the atoms concerned. New chemical compounds might be formed under such conditions and could be "captured" for study at normal room temperature and pressure by rapid thermal quenching.

Up to the present time, the pressure inside the bomb prior to application of heat has been substantially one atm. There are certainly circumstances where it would be desirable to place an initial pressure on the contents of the bomb before increasing the temperature.

A limitation on the maximum pressure obtainable in conventional high-pressure apparatus is imposed by piston failure. Failure occurs because the piston must protrude a short distance from the cylindrical hole into which it is being driven. This leaves an unsupported portion of the piston wherein lies the region of greatest stress. Failure begins here. The maximum pressure obtainable with cemented tungsten carbide pistons is about 50,000 atm. It would be possible to make the piston of such length that at a pressure of 50,000 atm. the top of the piston would be driven flush with the top of the cylindrical hole, thereby eliminating any unsupported surface. The driving ram abutting the top of the piston and the top of the cylinder could now be driven with greater force against these components. The inside arrangement of the cylinder could be made similar to that of the high-temperature bomb. The temperature inside could then be raised to the neighborhood of 10,000° whereupon a pressure of 15,000 atm. or so would be generated from the inside. The total pressure inside would then be near 65,000 atm. The pistons, however, would not fail because there would be no unsupported surface.

Many reactions will proceed rapidly at very high temperature. The rate will depend especially on terms of the type exp $(-\Delta F^{\ddagger}/RT)$ which means that rates may be appreciable at 10,000° even for $\Delta F^{\ddagger}$'s of 100 kcal. This fact ensures the usefulness of a high-temperature device such as that described herein even though the high temperatures can be maintained only for relatively short periods of time.