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**AN INVESTIGATION OF TEMPERATURE MEASURING
TECHNIQUES FOR USE IN HIGH POWER DENSITY
NUCLEAR REACTORS**

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ABSTRACT

Temperature measuring techniques for application to temperatures up to 3000°C have been investigated. Emphasis has been placed on those methods suitable for use in the environment of a high power density nuclear reactor of particular design. A survey of available techniques is made and evaluated in the light of the general problem. The properties and behavior of materials at high temperatures and in a high flux of particle radiation are discussed. As a result of the preceding considerations and a comprehensive literature search thermoelectric thermometry emerges as the most favorable method. A discussion of thermoelectric thermometry is given and recommendations as to materials and construction of a proposed expedient thermocouple are given. An experimental program leading to a more satisfactory thermocouple assembly is discussed.

CHAPTER I

INTRODUCTION

1.1. General Remarks

In the nuclear rocket propulsion project reactor now under consideration, it is necessary to have a detailed knowledge of temperatures throughout the reactor at all times. Many of the points whose temperatures are to be measured are not easily accessible, and at some of them the temperature is expected to be very high. Some information can be obtained by measuring the temperature of the emerging gas, but this is not adequate. Probes are therefore necessary, which will give a direct reading of the temperature at interior points. In this study we attempt to survey the field of temperature measurement and to recommend an experimental approach which will lead to a satisfactory temperature measuring instrument.

Among the special difficulties attending the measurement of temperatures in the reactor are:

- 1) The wide range of temperatures, which may be expected to preclude the use of any single type of instrument throughout the reactor.
- 2) The very high temperatures involved. Conventional methods of measuring very high temperatures are optical. These cannot apply unchanged to measurements inside the reactor. Hence unconventional high temperature methods must be developed.
- 3) The radiation density inside the reactor is very appreciable, and the effect of radiation on all processes and materials must be taken into account.
- 4) Neutron balance. Materials with high thermal neutron absorption cross section must be used very sparingly or not at all.
- 5) Inaccessibility. Signals must be transmitted outside the reactor, and then must be relayed some distance. Electrical signals are definitely indicated.
- 6) High pressure. Three separate pressure shells exist in the reactor. Inside the innermost one the pressure is of the order of 300 psi. Any temperature measurement signal must be transmitted through the pressure shells.

7) Vapors. Because of the high temperature, structural materials such as carbon have measurable vapor pressure. They are therefore liable to condense on the cooler portions of a temperature probe or as a suspension in the gas phase, thus impairing electrical insulation or optical transmission.

8) Dimensional instability. Sintering, recrystallization and evaporation processes at high temperatures cause dimensional changes in all substances. No method can be used which relies on the maintenance of exact physical dimensions.

9) Loss of strength. All structural elements lose mechanical strength at high temperatures.

10) Chemical attack. Certain chemical reaction rates may be greatly increased at high temperatures.

1.2. Outline of General Approach

A preliminary examination appeared to indicate that conventional methods could be used, and indeed were being used for the measurement of temperatures up to 1500°C . The chromel-alumel thermocouple has good accuracy, reproducibility and stability in the range -200°C to $+1150^{\circ}\text{C}$. In the lower part of this range (-200°C to $+750^{\circ}\text{C}$) the iron-constantan couple offers slightly higher thermoelectric power. In the range 600° - 1700°C the Le Chatelier thermocouple platinum against platinum with 10% rhodium can be used; indeed in the lower portion of this range (630° - 1063°C) it is the international standard. Insulation throughout this range of temperatures is adequately furnished by high-purity, large-grain alumina. Care should be taken not to use oxides like zirconia above the temperature at which their insulating properties fail. Protection from physical and chemical corrosion can be furnished by stainless steel tubes up to about 1400°C , and the Norton Company procedure of swaging the couple, with insulation, into an air tight tube appears very acceptable.

The main problem arises in the measurement of temperatures above 1500°C . We have therefore devoted practically all our time to the consideration of the measurement of high temperatures under the handicaps enumerated above.

At temperatures below 1500°C , the advantages of thermocouples are so outstanding that other methods would probably hardly even be considered. It soon became evident that at high temperatures, too, thermocouples required more consideration than any other method. However, we have surveyed a number of other methods for the measurement of temperature, and examined their suitability for this particular application.

This is done in Chapter II.

Chapter III deals with the properties of materials in general at very high temperature. The main emphasis is on materials with melting points above 2400°C .

Chapter IV deals with the effects of radiation on possible materials of construction and with the magnitude of spurious electrical signals induced by the environment.

Chapter V deals with the literature on suitable methods of high-temperature measurement.

Chapter VI treats the theory and practice of thermoelectric thermometry.

In Chapter VII we discuss our recommendations for a high temperature probe and outline a proposed course of further investigation.

CHAPTER II

SURVEY OF TEMPERATURE MEASURING TECHNIQUES

In this chapter we treat a number of temperatures measuring techniques and examine their suitability for high temperature use. We base our survey on the list of accepted temperature measuring devices given in our proposal, with suitable additions.

It will be seen that many of the methods which appear feasible depend on the introduction of a solid material into the measuring cavity, and the retention of some physical property such as length or shape for an extended period.

2.1. Thermal Expansion of Liquids and Solids

2.1.1. Liquid Thermometry

A thermometer consists of a liquid contained in a solid of different thermal expansion coefficient. The relative volumes are observed, and the temperature is obtained as a function of the volume difference. How can this be done at high temperatures? There is not much difficulty in selecting a suitable liquid; there are a number of suitable metals. For the range below 2100°K, tin, gallium or aluminum come to mind; for the range above 2100°K, platinum seems eminently suitable. It is harder to conceive of a solid container. If the liquid is metallic, the container should either be non-metallic or of a metal which is completely insoluble in the liquid. The latter condition is in practice an impossible one, as all solid metals are more or less corroded by liquid metals at temperatures over 2000°C. So we want a non-metallic container of a refractory material. The rate of corrosion of refractories by melts is discussed by Kingery ("High Temperature - a Tool for the Future" p.126). Possibly a coated material (e.g. MoSi_2 over Mo) or an oxide (e.g. BeO) could serve as a container.

The design of a high temperature thermometer must provide for a constant internal volume of the solid container. If any deformation occurs, no mechanism exists which will prevent a volume change during this deformation. Therefore little deformation can be permitted. Oxides like BeO and MgO are already at or above their sintering temperatures. Metals like tungsten and molybdenum are at their annealing temperature. High-melting carbides or nitrides, coated with a non-metallic coating or glaze, appear to offer the best hope. No specific combination can be suggested at present. However, there seems

* Stanford Research Institute, 1956.

to be good reason to believe that carbide structures resist deformation to higher temperatures than other materials.

Finally, the volume differential must be observed, preferably in the form of an electrical signal than can be obtained outside the reactor. A possible mechanism would be as follows: A circuit is set up which includes the thermometer liquid. (See Fig. 2.1) All resistances are kept very low except that of the thin wire, so that the total resistance of the circuit is proportional to the length of wire which is exposed. Thus ΔR is proportional to $\Delta(V_{\text{solid}} - V_{\text{liq}})$.

The difficulties in actually building such a device would, however, be quite formidable. Perhaps the greatest would be: dissolution of the wire in the thermometer liquid; changes in resistance of wire due to annealing, which may lead to irregularities in shape as well as changes in resistivity due to changed microstructure; temperature dependence of all resistances; and chemical attack on wire by surrounding atmosphere. In fact, we are not able to suggest a suitable wire material, or an alternative way to get the signal out.

2.1.2. Bimetals

A bimetal thermometer takes advantage of the differential expansion of two solids. If the solids are two joined strips, curvature will result which can be readily measured. Readings will be reproducible only if the elastic limit of the materials is not exceeded, so that there is little or no mechanical hysteresis. This is a condition which is difficult to fulfill at high temperatures, at which elasticity of metals is very low. Sagging and multiple bending are to be expected.

2.2. Gas Thermometry

The expansion of a gas is measured. It is possible to measure a) the volume change of a permanent gas at constant pressure; b) the pressure change of a permanent gas at constant volume, and c) change of vapor pressure in presence of the condensed phase. Method c) is especially sensitive, but the temperature range for any given thermometric substance is correspondingly limited.

In the high temperature range and at the pressures we are considering, the ideal gas law will be fairly accurate for permanent gases, so that the readings in methods a) and b) will be proportional to the absolute temperature. In method c) the vapor pressure P is related to the absolute

Fig. 2.1. Schematic Representation of High-Temperature Liquid Thermometer.

temperature T by the equation

$$\log P = A - \frac{B}{T} \quad (2.1)$$

where A and B are specific constants for each material.

In principle, gas thermometry can be used at all temperatures. However, at high temperatures there are great practical difficulties. First, the gas has to be contained in a strong, rigid, gas tight container, and we have encountered no material which would fulfill these conditions at temperatures of the order of 2500°K . It is possible, however, that a satisfactory coated tungsten or metal carbide tube might be developed in an experimental program. Second, a gas thermometer measures temperature over the entire volume of the gas. In methods a) and b), the average temperature of the gas is measured; method c) measures (under equilibrium conditions) the temperature of the liquid-gas interface. If the proposed device is to measure the temperature of a small region, the gas volume must be kept very small. In our case, this means that the entire gas volume must be deep inside the reactor. We thus again encounter the problem of how to get the signal out. In case a) a movable manostat, such as a piston, is needed. A gas-tight piston could be connected rigidly to a recording device in the cool region. Let us say that we want the piston to move at least 1 mm per 100°K in the 2500°K range. The total volume of gas is of the order of 1 ml., so that a 100°K rise in the temperature means a volume increase of 0.04 ml. The area of the piston head is then at most 0.4 cm^2 . This appears feasible. The question of a gas-tight container and a gas-tight fit between piston and container is, however, more difficult. It can be safely predicted that if a tight fit is indeed achieved at low temperatures, the piston and barrel will sinter together when high temperatures are reached. We therefore discard method a). Methods b) and c) depend on the development of a high-temperature pressure transducer. At the present time (1957) no pressure transducer can operate continuously much above 600°F .

2.3. Fixed Point Methods

By their nature, these methods measure only one temperature -- the one at which the phase change occurs. This makes them unsuitable for a continuous temperature-measuring device. We should not, however, ignore the possibility of using a fixed point as an indicator of undue or catastrophic temperature rise. Such a device could be made very simple and would serve as an alarm. It would consist of a wire of arbitrary high melting point, which completes an electrical circuit.

The leads can be rods of a very high-melting material such as zirconium carbide or tantalum carbide. The wire could be a tungsten-molybdenum alloy. Tungsten and molybdenum form a continuous series of solid solutions, with melting points varying continuously from 2620°C to 3380°C, and the desired failure point can be chosen anywhere in this range. A voltage is applied through the circuit, and interruption of the circuit can actuate a safety device.

Practical problems for such a device resemble those encountered in a thermocouple assembly (See Chapter VI): the leads must be prevented from shorting and the wire must be protected from chemical change. It is possible that the former aim can be attained by inserting the leads through two adjacent instrument holes and passing the wire between the holes horizontally. The second condition is more difficult. Carburization of tungsten and molybdenum leads to the formation of lower-melting eutectics. If we start out with a carbide, the melting point may still be changed by the absorption of carbon. For instance, TaC (m.p. 3800°C) forms an eutectic with carbon (10% C by weight) with a melting point of 3300°C. If, on the other hand, we start with an eutectic composition, deviation from the initial composition will result in a raising of the liquidus point. However, some liquid phase will always form at the melting point of the eutectic, and it is probable that circuit failure will result. A method must also be found to prevent a spurious signal from being produced by shorting through the body of the reactor.

Nevertheless, problems here appear easier than in the case of thermocouples and it is desirable to consider the fixed-point method for an interim or supplementary program.

2.4. Thermoelectric Effects

These will be treated in a separate section.

2.5. Thermochemical Effects

These depend on measuring an equilibrium or reaction rate, the temperature dependence of which is known. The number of reactions which have been investigated at very high temperatures is small; mostly they are gas reactions. We could choose, for example, the reaction $N_2 + O_2 = 2NO$. The following table gives some data on this reaction's temperature dependence:

T(°K)	% of gases combined at equilibrium	Time for half decomposition of NO ($P_{\text{total}} = 1 \text{ atm.}$)
1000	0.0	81.6 years
1500	0.1	1.3 days
1900		2.1 min
2000	0.6	
2100		5.1 sec
2500	1.8	
2900	3.2	3×10^{-5} sec
3200	4.2	
4200	10.0	

Utilization of this reaction depends on whether the following conditions can be fulfilled:

a) Gas-tight container and gas lead tubes. The difficulties of this have already been discussed.

b) No side reactions. In this case, oxygen will be expected to react with most construction materials. Possibly a gas-tight container and leads can be made from fused oxides.

c) Equilibrium attained at high temperatures. This means that the stay of gas in the container must be comparatively long.

d) No reaction while gas is in leads. The stay in that portion of the leads in which the rate is still fast must be very short compared to the stay in the container. The volume of the container must, then, be much larger than that of the leads. If we limit the container to a reasonable size, the leads must be very narrow indeed. But this again implies an unwarranted reliance on dimensional stability.

2.6. Radiation Effects

The measurement of the radiation from a hot body is the standard method of measuring high temperature. In most optical pyrometers the image of the hot body as seen through a telescope is projected onto the plane of the filament of an incandescent lamp. An observer matches the brightness of the image with the brightness of the filament by observing the "disappearance" of the filament. The lamp heating current is then a measure of the temperature of the body. Usually filters are employed to restrict the range of light wave lengths viewed, and a rotating sector mechanism may be used to reduce the brightness of the hot body image. The lamp filament is calibrated against a black body.

From Wien's law we have

$$J_{\lambda T} = C_1 \lambda^{-5} e^{-C_2/\lambda T} \quad (2.2)$$

where $J_{\lambda T}$ is the brightness at wave length λ of a blackbody at absolute temperature T . If the rotating sector transmits a fraction X of the light from a source at temperature T_2 , and this is matched in brightness against the light from a filament at T_1 at wave length λ , then:

$$X J_{\lambda T_2} = J_{\lambda T_1} \quad (2.3)$$

and

$$X = \frac{J_{\lambda T_1}}{J_{\lambda T_2}} = \frac{e^{C_2/\lambda T_2}}{e^{C_2/\lambda T_1}} \quad (2.4)$$

so that

$$\frac{\lambda \ln X}{C_2} = \frac{1}{T_2} - \frac{1}{T_1} \quad (2.5)$$

λ , X , C_2 , and T_1 being known, T_2 can be determined.

Neutral gray screens can be used instead of rotating sectors.

One of the big problems in the use of this method is that most materials are not blackbodies, so that an emissivity correction has to be taken into account. Values of the emissivity are not always well known.

If the emissivity is independent of wave length (a "graybody"), it is advantageous to compare the intensity of radiation at two wave lengths from the same body by means of a photocell. Filters or a monochromator may be used. The ratio of intensities at the two wave lengths is a function of the temperature ("color temperature").

Thus the optical method furnishes an excellent way of measuring high temperatures. We are informed that an attempt has already been made to use this method and that some difficulties have been encountered. These concern the provision of an optical path from the inside to the outside of the reactor, collimation of the light beam so that only the desired region will be "seen", and absorption, contamination and scattering of light by hot carbon vapor and solid particles

of condensed graphite in the optical path. In view of the fact that investigation of this aspect of temperature measurement is already under way, we have not concerned ourselves with it. However, it is our opinion that if no acceptable thermocouple can be developed, this may be the best method. Light can be brought out of the instrument hole and through the pressure shell through a tube fitted with mirrors. We believe that it will be more profitable to compare the intensity of emission at two wave lengths, rather than to attempt to measure the total emission of light. The two wave lengths should be chosen so as to reduce absorption by carbon vapor and CN to a minimum. The carbon arc spectrum suggests that 4900 Å and 6800 Å would be acceptable wave lengths. (See also Section 2.20.)

2.7. Sound Velocity in Gases

For a given ideal gas, the velocity of sound is directly proportional to the square root of the temperature. This fact has been used to measure the temperature of gases and might conceivably be used in the reactor. We would, then, measure the temperature of a gas assumed to be in equilibrium with a solid portion of the reactor. A common mechanism uses two spark gaps. The sonic wave from a spark across the first gap introduces a discontinuity in a discharge across the second.

This is one of the few methods which may be rendered impractical by the presence of ionizing radiation. Charge leakage across the spark gap and its leads would probably render it inoperative. The usual high temperature insulation and dimensional problems are also expected.

The amount of charge leakage naturally depends on the voltage applied and the intensity of the radiation. At high enough voltage (1000 V) and intensities it is possible to get a total discharge when a gamma ray passes through the spark gap - an effect similar to that observed in a spark discharge counter.

2.8. Spectroscopic Methods (Doppler broadening etc.)

The main problem here, as in Section 2.6, is providing an optical path; therefore, the discussion will not be repeated.

2.9. Phosphor Luminescence

This method utilizes the decrease of luminescent efficiency of a phosphor with increasing temperature. This is a very sensitive method since the efficiency may decrease by several per cent per degree Centigrade. For instance, a

ZnS-CdS phosphor decreases in efficiency by a factor of 100 when heated from 5°C to 40°C. This method has no known high temperature applications because of material difficulties.

2.10. Radiation and Absorption Properties of Gases

This heading refers to the temperature dependence of the intensity of spectral lines and bands in gases. In transitions from one electronic state to another, the relative intensities of the lines which correspond to different vibrational states of origin depend on the relative populations of these states, which are temperature dependent. This method is not applicable in our case, since we desire to measure the temperature of a solid.

2.11. Noise Generation in Electrical Elements

This is a specific high temperature method, and therefore of particular interest. Unfortunately, its development is not yet adequate to permit of practical use.

Noise in an electrical circuit can be reduced only to a finite lower limit. At this limit the residual noise (Johnson noise) is due to the random unevennesses in electron distribution, a phenomenon analogous to the Brownian motion. The uneven distribution gives rise to a small voltage. While the time average of the voltage is zero (because displacement is equally likely in all directions), the time average of the square of the voltage is not, and is given by the Nyqvist equation

$$d(\bar{v}^2) = 4kT \operatorname{Re} [Z(f)] df \quad (2.6)$$

where $\operatorname{Re} [Z(f)]$ is the real part of the complex impedance $Z(f)$, a function of the frequency f , k is Boltzmann's constant (R/N_0), T is the absolute temperature, and $d(\bar{v}^2)$ is the contribution to $\bar{v}^2$ of the frequency range of width df at f . The total noise is obtained by integrating over the frequency range.

Hogue (see Campbell, "High Temperature Technology", p.377) has devised a simple circuit consisting of a parallel combination of a resistance and a capacitance. When two such circuits are equated, it can be shown that the ratio of the integrals

$$\int_0^{\infty} \operatorname{Re}[Z(f)] df$$

is equal to the ratios of the resistances. Thus, if the noise levels in the two circuits are equal, the temperatures

of the two resistors are inversely proportional to their resistances.

Fig. 2.2 shows a device based on this principle. The resistance R_1 and the capacitances C_1 , C_2 can be adjusted until the noise level is equal for the two circuits at two different frequencies. The temperature of R_2 can then be obtained.

In this particular instrument, the resistor R_2 is a platinum wire welded to platinum leads, and shielded by a platinum sheet. There appears to be no reason, however, why a higher melting metal could not be used.

The use of this instrument depends, of course, on the elimination of all parasitic voltages and sources of non-random noise. Thermoelectric junctions, grid currents, and net thermionic emission must be eliminated. In the present case, considerable interference may be expected due to radiation effects. Since electron displacements due to gamma-radiation are large, it would seem that even a moderate dose rate would have a disproportionately great effect on the average of the squares of the displacements. The dose rate dependence of the noise could be obtained theoretically, so that the use of the noise thermometer cannot be eliminated on this basis alone.

Accuracies obtained under laboratory conditions are of the order of 0.3 - 0.5% at 700°C. Response time is not good, as a time of the order of 500 seconds is required to attain good balance.

Even under optimum conditions, use of this method requires the insertion of a resistor wire with shielding of the same material into the instrument hole. The resistance must stay constant. Thus we again have a dependence on dimensional stability. Thus, even after development, the noise method is not expected to be completely satisfactory.

2.12. Resistance Thermometry

2.12.1. Metals

As the temperature rises, the resistance of metallic materials also rises. The main factor causing this rise is the increased interaction of electrons with atoms that are displaced from their positions in the metal lattice, resulting in a shorter "mean free path" for the electrons. The rise in resistance is rather small and fairly linear. Values of high temperature resistivities of metals will be found in Chapter III. All resistivities tend to converge to

Fig. 2.2 Noise thermometer basic diagram.

values around $1 - 2 \times 10^{-4}$ ohm-cm at high temperatures.

Resistance thermometers, based on the temperature dependence of the resistivity, are widely and increasingly used at lower temperatures. In the range -183°C to 630°C , indeed, the platinum resistance thermometer is the international standard.

The circuit required for determination of the resistance is simple, and consists essentially of a Wheatstone bridge or the equivalent AC bridge circuit. Automatically adjusting null instruments are available.

Commercial resistance thermometers are made of copper (range -140°C to $+120^{\circ}\text{C}$), nickel (-180 to $+320^{\circ}\text{C}$) or platinum (-180 to $+540^{\circ}\text{C}$). The range can be extended upward (especially for Pt). Careful choice of insulation (high-sintered or fused alumina) is said to allow the use of Pt resistance thermometers to temperatures not far below the melting point (1650°C). Readings are expected to become irreproducible if the sintering point is reached or if any other irreversible changes occur in the metal.

From the above it will be clear that while there is no reason in principle why a metal resistance thermometer (using tungsten, for instance) should not be used, this is not a first choice because dimensional stability is necessary for its operation, while it shares with all electrical methods the problems of chemical corrosion and electrical insulation. Moreover, the temperature measured is an average over the length of the resistance, rather than a point temperature.

2.12.2. Semiconductors

In semiconductors the temperature coefficient of resistance is negative, and the rate of change (absolute value) is generally much greater than in metals. The effect is due to the greater relative numbers of electrons which are promoted into the conduction bands at higher temperatures. The number of conductivity electrons is smaller than in the case of metals (where it is substantially independent of temperature) and therefore the resistance, even at the upper limit of the useful temperature range, is several orders of magnitude higher than in metals.

Thermistors are semiconductors which can be brought to a highly reproducible resistance temperature curve. They are comparatively insensitive to impurities. Mixtures of transition metals (Mn to Ni) oxides with or without the addition of spinels (Mg chromite or aluminate) can be used. The top operating temperature of thermistors is about $300-350^{\circ}\text{C}$.

Since the temperature coefficient of the resistivity of some oxides at very high temperatures is also large and negative, it is possible to conceive of high temperature thermistors. Thermal deformation due to sintering, fracture due to thermal shock, changes in the resistance due to impurities and dislocations resulting from radiation damage, and chemical reaction with carbon are the adverse mechanisms which are believed to apply to such a temperature measuring device.

2.13. Hot Wire Techniques

This is an extension of the resistance thermometer. A heated wire loses heat to the surroundings. The rate of heat loss is related to the temperature of the surroundings, and is measured by the energy input necessary to keep the temperature (and resistance) of the wire constant.

Since the wire must be hotter than the surroundings, it would have to be very hot indeed in our case. All mechanical problems applying to the resistance thermometer would thus be aggravated.

2.14. Pneumatic Apparatus

The volume flow rate of a gas through a nozzle (above a certain critical value) is proportional to the square root of the temperature. By comparing flow rates through two successive nozzles, the second being at a known temperature, the temperature at the first nozzle can be estimated.

This method, of course, is already in use in the reactor; but it is not suitable for the measurement of temperature in small volumes, which is the problem we are discussing.

2.15. Thin Metallic Layers (less than 1000 Å)

These exhibit resistivity properties similar to those of semiconductors at liquid hydrogen and helium temperatures. Of course they are not stable at temperatures at which the vapor pressure becomes appreciable.

2.16. Variation of Dielectric Constants

The dielectric constants of insulators show a marked temperature dependence, since the orientation polarization which is due to the dipole moment of the molecule is inversely proportional to the temperature:

$$\frac{D-1}{D+2} = \frac{\rho}{M} (P_D + P_O) \quad (2.7)$$

$$P_O = 4\pi N/3 \quad (\mu^2/3kT) \quad (2.8)$$

where D is the dielectric constant, ρ the density, M the molecular weight, P_D the distortion polarization, P_O the orientation polarization, N is Avogadro's number, μ the dipole moment, k is Boltzmann's constant and T the absolute temperature.

This method has been used for measuring temperatures, but is especially applicable to materials of high dipole moment at low temperatures. At high temperatures P_O becomes relatively insignificant compared with P_D ; moreover, most insulators fail and become conductors.

2.17. Diffusion Methods

The diffusion of gases through orifices and the diffusion of solutes through semi-porous membranes are temperature dependent. For high temperatures, the former method is the one that is applicable.

The number of molecules of an ideal gas hitting a surface of area dA per second is:

$$dn = \frac{3}{13} \bar{u} \rho dA \quad (2.9)$$

where $\bar{u}$ is the root mean square velocity and ρ the number of molecules per unit volume.

Substituting $\bar{u} = \sqrt{3PN_O/M\rho}$ and $\rho = PN_O/RT$, we get:

$$dn = \frac{3}{13} PN_O \sqrt{3/RT} dA \quad (2.10)$$

(N_O is Avogadro's number, P - the pressure, R - the gas constant, T - the absolute temperature, M - the molecular weight.)

Thus, at constant pressure, dn is inversely proportional to the square root of the temperature.

A temperature probe utilizing the diffusion principle might be constructed as follows:

A long U-tube of a high melting material such as tungsten would be inserted into the reactor. At the point at which the temperature is to be measured, there is a partition across the tube. A diffusion pinhole is made in the partition. The gas pressure is maintained at a constant level on one side of the partition and is pumped down to a near-zero value on the other side. The steady-state volume of air pumped through then is an index of the temperature.

Let us say we wish to obtain 10^{-4} moles/sec of gas (2.24 ml at STP) per second, for $P = 20$ atm., $M = 40$ (argon), $T = 2500^\circ\text{K}$. Putting all quantities in cgs units, we get for ΔA :

$$\Delta A = \frac{13 \sqrt{MRT} n}{P N_0 \sqrt{27}} = \frac{13 \times 6 \times 10^{19} \sqrt{40 \times 8.3 \times 10^7} \times 2.5 \times 10^3}{20 \times 10^6 \times 6 \times 10^{23} \times 5.2}$$

$$= 3.6 \times 10^{-5} \text{ cm}^2 \text{ or } 0.0036 \text{ mm}^2 \quad (2.11)$$

A larger area will give a larger volume of gas, e.g., if the area of the pinhole is 0.36 mm^2 , the volume of gas pumped through will be 224 ml/sec at STP. Under such conditions, the pumping efficiency might be the limiting factor. For small hole area, however, the instability of the contour of the hole at high temperatures is obviously the limiting factor, especially since a small change in effective hole area can simulate a very large change in temperature (e.g., a 10% enlargement of the hole will simulate a 475° drop in temperature).

The method does not appear too promising but could be considered as a last resort.

2.18. Thermionic Emission

The thermionic emission current from the surface of a hot metal is highly temperature-dependent:

$$I = AT^2 e^{-B/T}$$

Also the electrical signal is built in. Unfortunately, the method requires a good vacuum and this cannot be attained in an all-hot system.

In the presence of appreciable quantities of vapors, the emitting surface is poisoned and the electron path is no longer collision-free.

2.19. Pyrometric Cones

Pyrometric cones are ceramic compositions with specific melting behavior. The melting point is not quite fixed, but varies somewhat with the rate of heating. Each cone can be used only once. Essentially this is a kind of fixed point method, adapted specifically for ceramic use.

2.20. Light Guides

A novel method of optical pyrometry has been developed by the Linde Air Products Company. It is intended for inaccessible regions and is therefore of considerable interest. A light path is provided for emitted light by means of a sapphire (fused aluminum oxide) light guide. The light guide consists of a monocrystalline rod, which can be bent to fit the geometry of the design. The rod is fire polished and can presumably be passed through a pressure seal. Ordinary rod lengths are up to 18 inches, but larger lengths can be fabricated on order. Thicknesses of the rods can be up to 1/4 inch.

Artificial "sapphire" is colorless and has better light transmission than lucite. Its melting point is about 2000°C. At 1500°C, it is very resistant to chemical attack, though silicon produces a haze effect on the surface after long exposure (months). Thermal-shock resistance is reported to be sufficiently good to allow fire-polishing with a naked hydrocarbon-oxygen flame.

Both absolute brightness and color temperature can be measured. The light can also be directed to a thermopile.

CHAPTER III

BEHAVIOR OF MATTER AT HIGH TEMPERATURES

3.1. General

It is a commonplace that the number of possible construction materials dwindles as the temperature goes up because many of them melt; but this phase change is not the only, nor perhaps the most important phenomenon which makes a material unusable. At high temperatures the cohesive forces, which hold materials together, weaken; mechanical and chemical stabilities are decreased.

Let us examine what happens to three materials when the temperature is raised to 2500°C. We shall take tungsten as a typical metal; silicon carbide as a typical covalent "giant molecule"; and magnesium oxide as a typical ionic (electrovalent) crystal.

In silicon carbide the cohesive forces are very strong at ordinary temperatures, as there are four full electron-pair bonds between each atom and its four nearest neighbors. The breaking of each of these bonds requires about 100 kilocalories per mole. At 300°K there is a chance of only 10^{-12} ($e^{-E/RT}$) that a molecule will have this energy; at 3000°K the chance has risen to the order of 10^{-1} . This means that the rate of bond breaking has become appreciable. In fact, silicon carbide undergoes two changes at high temperature below its melting point. At about 2100°C it begins to undergo a phase transition from the cubic beta to the hexagonal alpha form. At 2400°C it decomposes. Similarly, the very hard diamond form of carbon undergoes a phase transition to graphite at 1600-1900°C. The increased energy of the molecules makes it relatively easy to have enough energy concentrated in one bond to break it; therefore, structures which are metastable at lower temperatures do not endure at these higher ones.

Magnesium oxide is an ionic crystal, and electrostatic forces hold it together. As a result of thermal expansion, the average distance between ions grows and the cohesive forces become weaker. More important, the disruptive forces due to thermal motion and vibration of the ions increase greatly. Crystals rearrange into more stable and less deformed states (sintering). Free electrons and holes become more common, and the electrical resistivity drops continuously with rising temperature. Deformation of the crystals becomes easier and almost all the mechanical strength is lost. Thermal

conductivity remains low, so that the thermal shock properties of the material are poor. Eventually (at 2200°C) the vapor pressure becomes appreciable; since the vapor is composed of MgO molecules, this indicates a breakdown of the ionic crystal structure. The melting point is 2620°C .

The mechanical phenomena in tungsten are more complex than in magnesium oxide, but the basic principle here too is the rearrangement of molecules to more stable forms. Powder metallurgy techniques rely on crystal growth, occurring well below the melting point, for the transformation of tungsten powder to bar tungsten. Actual tungsten materials, such as bars and wires, have been swaged and drawn after annealing, and the crystals have been broken up. Hence, exposure of tungsten wire, for example, to temperatures of the order of 2500°C , causes extensive recrystallization. Grain boundaries, which were previously aligned parallel with the axis of the wire as a result of the drawing operation, now can be found running in a transverse direction; the strength of the wire (so exceptional before heating) is greatly reduced (see Fig. 3.1). After cooling, the frozen-in grain boundaries cause great brittleness. "Non-sag" wires have been perfected, in which an additive retards or directs the grain growth. In addition to mechanical transformation, the chemical reactivity of tungsten is greatly increased at high temperatures. Reaction with oxygen is instantaneous and violent. Tungsten will also react with carbon at temperatures more than 1000°C below its melting point. It is unstable in the presence of water vapor, molten oxidizing salts and other oxidizing media.

From this preliminary survey we see that all specifications must be greatly relaxed at high temperatures. For the building of a temperature measuring device designed to operate inside a nuclear reactor, we do not expect to require extreme values of tensile strength, electrical resistivity, chemical inertness etc. However, it will be of interest to investigate some material properties at high temperatures.

Fig. 3. 1. Diagrammatic presentation of "off-setting" or sagging process in pure tungsten wire heated above recrystallization temperature (according to Smithells): A, fiber structure of swaged and hard drawn wire; B, equiaxed grain structure after recrystallization during heating to high temperature; C, excessive grain growth during prolonged heating at high temperature; and D, "off-setting" of crystals in suspended wire.

3.2. List of High Temperature Materials and Their Melting Points (Over 2400°C)*

3.2.1. Elements

	<u>°C</u>
Carbon (graphite)	3650 (sublimes)
Iridium	2443
Molybdenum	2625
Niobium	2400
Osmium	2700
Rhenium	3170
Ruthenium	2450
Tantalum	2995
Tungsten	3380

3.2.2. Oxides

Beryllia	2550
Calcia	2600
Ceria	over 2600
Hafnia	2780
Magnesia	2800
Strontia	2415
Thoria	3300
Yttria	2410
Zirconia	2680
BaO . ZrO ₂	2700
3BeO . 2ZrO ₂	2535
SrO . ZrO ₂	over 2700
ThO ₂ . ZrO ₂	over 2800
ZrO ₂ . SiO ₂	2420

3.2.3. Carbides

B ₄ C	2450
Al ₄ C ₃	2800
HfC	3890

* Data mostly from Campbell, "High Temperature Technology", Wiley, N.Y., 1956.

<u>Carbides (cont'd)</u>	<u>°C</u>
Mo ₂ C	2690
NbC	3500
TaC	3880
ThC ₂	2655
TiC	3250
UC	2475
VC	2830
W ₂ C, WC	2860
ZrC	3175

3.2.4. Borides - have been omitted

3.2.5. Silicides

TaSi ₂	2400
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3.2.6. Nitrides

ScN	2650
TiN	2950
ZrN	2980
HfN	3310
Ta ₂ N	3090
ThN	2630
UN	2650

3.2.7. Sulfides

CeS	2450
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It should be said that not all these melting points are equally reliable, and sometimes quite a spread can be found in the literature (e.g., for Mo₂C, Friederich and Sittig (Z. anorg. Chemie 144, 169 (1925) give 2310°C; for W₂C, values range from 2700° to 2880°; for WC from 2600° to 2880°C). The compositions of the carbides and nitrides may vary, since they are more nearly interstitial-solution alloys than ordinary chemical compounds.

3.2.8. Types of Bonding

All elements except carbon, all carbides except B₄C, TaSi₂, CeS and the nitrides show metallic structure.

Graphite and B_4C have semi-conductor properties and show covalent bonding.

The oxides are ionic crystals.

3.2.9. Alloys

In addition to these materials, alloys are known. Tungsten and molybdenum form a continuous series of solid solutions with melting points between those of the pure elements. Tungsten-rhenium alloys exist, with a eutectic temperature of 2800°C at a 33% W composition. Platinum-rhenium alloys with high melting points are also known.

Alloys of carbides include $TiC - ZrC$, $TiC - VC$, $TiC - NbC$, $TiC - TaC$, $TiC - Mo_2C$, $TiC - WC$ (m.p. for alloy with 80.7 mol-% WC is 2540°C , Schwartzkopf & Kieffer, "Refractory Hard Metals", Macmillan, N.Y., 1953, p. 195), $ZrC - NbC$, $ZrC - TaC$, $HfC - TaC$ (this system has gained some fame because the melting point of 3930°C (80% TaC) is the highest known), $VC - TaC$, $VC - WC$, $NbC - TaC$ (melting points between those of the pure substances), $TaC - W_2C$ (minimum m.p. at 2760°C , 10 mol-% W_2C) and $Mo_2C - W_2C$. There are also ternary and higher-order alloys.

Also known are alloys $TiN - ZrN$, $TiN - VN$, $TiN - NbN$, $VN - NbN$, $TiN - TiC$, $ZrN - TiC$, $TiN - NbC$, $VN - VC$, $ZrN - ZrC$, $VC - NbN$, $UN - UC$ and many others. In general, interstitial-alloy "hard metals" form solid solutions if the metal atomic radii differ by less than 15%.

3.3 Mechanical Properties

3.3.1. Tensile Strength

The tensile strength of metals has been measured at high temperatures and invariably is seen to be less than at low ones. For tungsten we find:

	Temperature, $^\circ\text{C}$	Tensile strength in psi	Source
<u>0.024-inch wire</u>	20	250,000	Reactor Handbook, (AECD-3647) Vol. 3, Sec. 1, p. 376
	400	190,000	
	800	130,000	
	1200	71,000	
	1800	28,000	

	Temperature, °C	Tensile strength in psi	Source
<u>Single crystals</u>	1500	10,700	Campbell, "High Temper- ature Tech- nology" Wiley, N.Y., 1956, p. 23
	1750	8,250	
	2000	5,800	
	2250	3,400	

Espe and Knoll, "Werkstoffe der Hochvakuumtechnik" (quoted in Goetzel, "Treatise on Powder Metallurgy", Interscience, N.Y., 1950, Vol. II, p. 26) give the following tensile strengths for tungsten wire with additives:

	psi at 2400°C	psi at 2700°C
Non-sag wire	5,700	3,700
0.75% ThO ₂	7,100	2,600
Single crystal wire, 2% ThO ₂	>20,000	13,000

Molybdenum: For 1/4-inch bar

Temperature, °C	Ultimate tensile strength in psi	Source
Room	91,400	Reactor Hand- book, Vol. 3, Sec. 1, p. 216
982	30,500	
1316	18,500	

One-quarter inch plate shows fairly similar strengths. The tensile strength is below that of tungsten and may be expected to remain so at all temperatures.

Tungsten - molybdenum alloy (27 - 80% W)	Ultimate tensile strength
5 mm swaged rod	
1000°C	74,000 - 78,000 psi
1400°	21,000 - 36,000

(from Goetzel, "Treatise on Powder Metallurgy", Vol. II, p. 58)

Oxides: The tensile strength of some oxides at temperatures up to 1460°C is shown in Fig. 3.2.

Carbides: Titanium carbide (binder-free)

980° C	15,850 - 17,200 psi
1200°C	8,000 - 9,400 psi

TABLE 6. TENSILE STRENGTH OF SOME REFRACTORY OXIDES, psi

Temperature, °C	Al ₂ O ₃ ^{***}	BeO ^{***}	MgO ^{†††} (11% porosity)	ZrO ₂ ^{†††} (4% porosity)	MgO·Al ₂ O ₃ ^{***}	ZrO ₂ ·SiO ₂ ^{‡‡‡}
20	37,700	—	14,000	20,000	19,200	—
200	—	—	14,200	16,600	—	—
300	33,600	—	—	—	—	—
400	—	—	15,200	17,500	—	—
500	—	11,100	—	—	—	—
550	—	—	—	—	13,700	—
600	—	—	—	17,600	—	—
800	31,200	—	16,000	16,000	—	—
900	—	7,000	—	—	10,800	—
1000	—	—	11,500	14,800	—	—
1050	33,900	—	—	—	—	8,700
1100	—	—	10,000	13,500	—	—
1130	31,400	—	—	—	—	—
1140	—	2,000	—	—	—	—
1160	—	—	—	—	6,100	—
1200	18,500	—	8,000	12,100	—	3,600
1300	6,400 ‡	600	6,000	10,200 ‡	1,100	—
1400	4,300	—	—	—	—	—
1460	1,500	—	—	—	—	—

* Circular rods pulled in tension. Rods of small diameters gave higher specific strengths than rods of large diameters.

† Rectangular rods made by slip casting. ZrO₂ stabilized with 4% CaO. Tensile strengths determined by transverse loading.

‡ Specimens hot-pressed, machined, and pulled in tension.

§ Stavrolakis ¹⁰² calculated tensile strengths of 11,000 psi for Al₂O₃ and 20,000 psi for ZrO₂ from torsion measurements at 1300°C.

Fig. 3.2. Tensile Strength of Some Refractory Oxides, psi.

Zirconium carbide (binder-free)

980°C	11,700 - 14,450 psi
1200°C	12,950 - 15,850 psi

These are short-time tensile strengths reported by Gangler, J. Am. Ceram. Soc. 33, 367 (1950) (quoted in Schwarzkopf and Kieffer, "Refractory Hard Metals", p. 375).

3.3.2. Hardness: Tungsten

<u>Temperature, °C</u>	<u>Brinell hardness</u>
20	262
1150	62
1627	40

(Reactor Handbook, Vol. III, Sec. 1, p. 376)

3.3.3. Other Mechanical Properties

Perhaps the most striking of these is "creep" - change of dimensions under stress due to recrystallization and annealing phenomena. While few data are available, creep is relatively low for tungsten. Molybdenum shows creep rates up to 1% per hour under 12,500 psi at 2000°F and fails in 0.9 hours under loads of 15,000 psi at that temperature.

Zirconia becomes plastic above about 1300°C. Compressive strength of oxides lessens at different rates, so that above 1600°C BeO is reported to be superior to alumina. Magnesia has a very low creep rate at 1100°C (0.7×10^{-6} hr⁻¹ as compared to 435×10^{-6} for zircon), and remains among the most superior materials at high temperatures, though it, too, develops serious plasticity. Creep resistance and stress-rupture strength are generally high among carbides at elevated temperatures.

Many materials which have been subjected to high temperatures are brittle at room temperature. This is easily understood, since the large grains formed by sintering provide easy fracture planes along their boundaries, but this brittleness does not persist on reheating. Tungsten and molybdenum become softer and less brittle when heated; oxides are also easier to deform plastically.

While failure mechanisms are generally similar at high and low temperatures, one specific high temperature failure mechanism is the separation of grain boundaries; these may creep apart and the resulting cracks may eventually spread over many grains, so that a separation can develop in an

initially homogeneous piece of material. This mechanism applies primarily to metallic materials.

3.4. Thermal Properties

3.4.1 Thermal Conductivity

Few data are available for metals, as low thermal conductivity apparently has never been a critical factor. For tungsten, however, a value of $0.354 \text{ cal sec}^{-1} \text{ cm}^{-1} \text{ }^{\circ}\text{C}^{-1}$ is given for 2227°C . This compares with 0.383 at 0°C , and indicates relative temperature independence of this property. Reactor Handbook (Vol. III, Sec. 1, p. 374) gives 0.28 at 1250°C for W and 0.17 at 2173°C for Mo (0.32 at 0°C) (p. 193). Thermal conductivity data for oxides are given in Figs. 3.3 and 3.4. Thermal conductivities for TiC, ZrC, NbC, TaC at room temperature run from 3.4 to $5.3 \times 10^{-2} \text{ cal sec}^{-1} \text{ cm}^{-1} \text{ }^{\circ}\text{C}^{-1}$.

3.4.2. Thermal Expansion

The coefficient of linear thermal expansion for tungsten is $7.26 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ at 2027°C as compared with 4.44×10^{-6} at room temperature. Values for molybdenum are 7.2×10^{-6} at 2000°C and 5.1×10^{-6} at 27°C . Room temperature values for other elements (in units of $10^{-6} \text{ }^{\circ}\text{C}^{-1}$) are: Ir - 6.5, Nb - 6.5, Os - 6.1, Ta - 7.1, Ru - 9.1, C (graphite) - 3 (rises to 5 to 11 at 1500°C). It is not expected that values at high temperatures are qualitatively different.

For oxides the cumulative thermal expansion is usually given. Some values are (from room temperature to given temperature in %): MgO - 1800°C - 2.6, BeO - 1800°C - 1.9, ThO₂ - 1800°C - 1.8; ZrO₂ (stabilized) - 1535°C - 1.3.

For carbides we have coefficients of expansion: B₄C - $4.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, TaC - 8.2×10^{-6} , TiC - 7.4×10^{-6} , W₂C - 6.0×10^{-6} , WC - 6.2×10^{-6} , ZrC - 6.7×10^{-6} . All these are for the range $0 - 800^{\circ}\text{C}$.

3.4.3. Thermal Shock Properties

These have been summarized by Buessem (Campbell, pp. 460 - 476). They depend on thermal expansion, elastic modulus, tensile strength and thermal conductivity. Buessem defines two thermal shock resistance factors. R measures shock resistance for sudden heating, while R' measures shock

Fig. 3.3. Thermal Conductivity of Polycrystalline Oxides Corrected to Theoretical Density (High Range).

Fig. 3.4. Thermal Conductivity of Polycrystalline Oxides Corrected to Theoretical Density (Low Range).

resistance for slow, steady heating. The higher the factor, the better the resistance.

Elements	$\bar{R}$	$\bar{R}'$
Graphite	735 - 780	109 (1000°C)
Tungsten	2300	1100 (100°C)

Oxides

BeO	53	2.6
MgO	34	0.58
ThO ₂	62 - 75	0.5
ZrO ₂ (stabilized)	93 - 106	0.51
ZrO ₂ . SiO ₂	196 - 210	2.1
TiO ₂ (dense)	63	0.50

3.4.4. Vapor Pressure and Evaporation Rate

Elements Brewer (in Quill, "Chemistry and Metallurgy of Miscellaneous Materials", McGraw-Hill, N.Y., 1950, pp. 30 - 31) lists temperatures at which the elements reach various vapor pressures. An extract from this table follows (temperatures in °K).

Element	P = 10 ⁻⁶ atm	10 ⁻⁵ atm	10 ⁻⁴ atm	10 ⁻³ atm	10 ⁻² atm	1 atm
C*	2650	2855	3090	3370	3705	4540
Ir	2580	2800 (liq)	3040	3350	3700	4800
Mo	2530	2740	3000 (liq)	3330	3750	5077
Nb	2820 (liq)	3050	3340	3700	4120	5400
Os	2700	2900	3160 (liq)	3470	3850	4900
Re	2900	3150	3450 (liq)	3850	4300	5800
Ru	2480	2670	2900 (liq)	3180	3500	4500
Ta	3300 (liq)	3600	3900	4300	4800	6300
W	3230	3490	3780 (liq)	4150	4625	5950

These values are largely calculated, and probably none too reliable. They indicate that none of the refractory metals has a vapor pressure as high as 1 mm Hg much below its melting point. Dushman ("Vacuum Technique", quoted in Campbell, p. 20) gives evaporation rates in g-cm⁻²-sec⁻¹ as shown in Fig. 3.5.

* These data disagree with those quoted in the Reactor Handbook (Vol. III, Sec. 1, p. 138) from Udy and Boulger, BMI-T-35 (1950).

Metal	Vapor Pressure, mm Hg	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	Melting Point, °C	Vapor Pressure at Melting Point, mm Hg
Tungsten	$t, ^\circ\text{C}$	2554	2767	3016	3289	—	—	—
	$W, \text{g/cm}^2/\text{sec}$	1.47×10^{-7}	1.46×10^{-4}	1.45×10^{-3}	1.43×10^{-1}	—	3410	1.75×10^{-1}
Rhenium *	$t, ^\circ\text{C}$	2380	2564	2776	3022	3368	—	—
	$W, \text{g/cm}^2/\text{sec}$	1.55×10^{-7}	1.50×10^{-4}	1.44×10^{-3}	1.39×10^{-1}	1.34×10^{-1}	3180	2.45×10^{-2}
Tantalum	$t, ^\circ\text{C}$	2407	2599	2820	—	—	2996	5×10^{-1}
	$W, \text{g/cm}^2/\text{sec}$	1.55×10^{-7}	1.48×10^{-4}	1.41×10^{-3}	—	—	—	—
Osmium	$t, ^\circ\text{C}$	2101	2264	2451	2667	2920	—	1.35×10^{-1}
	$W, \text{g/cm}^2/\text{sec}$	1.65×10^{-7}	1.60×10^{-4}	1.54×10^{-3}	1.48×10^{-1}	1.42×10^{-1}	2700	—
Molybdenum	$t, ^\circ\text{C}$	1923	2095	2295	2533	—	2623	2.2×10^{-2}
	$W, \text{g/cm}^2/\text{sec}$	1.29×10^{-7}	1.18×10^{-4}	1.12×10^{-3}	1.13×10^{-1}	—	—	—
Ruthenium	$t, ^\circ\text{C}$	1913	2038	2230	2431	2666	2500	9.8×10^{-3}
	$W, \text{g/cm}^2/\text{sec}$	1.26×10^{-7}	1.22×10^{-4}	1.18×10^{-3}	1.13×10^{-1}	1.08×10^{-1}	—	—
Iridium	$t, ^\circ\text{C}$	1993	2154	2340	2536	2811	2454	3.55×10^{-2}
	$W, \text{g/cm}^2/\text{sec}$	1.70×10^{-7}	1.65×10^{-4}	1.59×10^{-3}	1.52×10^{-1}	1.46×10^{-1}	—	—
Niobium	$t, ^\circ\text{C}$	2194	2355	2539	—	—	2415	6×10^{-4}
	$W, \text{g/cm}^2/\text{sec}$	1.16×10^{-7}	1.08×10^{-4}	1.06×10^{-3}	—	—	—	—
Hafnium	—	—	—	—	—	—	2110	—
Rhodium	$t, ^\circ\text{C}$	1681	1815	1971	2149	2358	1966	1×10^{-3}
	$W, \text{g/cm}^2/\text{sec}$	1.34×10^{-7}	1.29×10^{-4}	1.25×10^{-3}	1.20×10^{-1}	1.15×10^{-1}	—	—
Chromium	$t, ^\circ\text{C}$	907	992	1090	1205	1342	1800	63.5
	$W, \text{g/cm}^2/\text{sec}$	1.22×10^{-7}	1.18×10^{-4}	1.14×10^{-3}	1.09×10^{-1}	1.05×10^{-1}	—	—
Zirconium	$t, ^\circ\text{C}$	1527	1660	1816	2001	2212	1830	1.4×10^{-3}
	$W, \text{g/cm}^2/\text{sec}$	1.3×10^{-7}	1.27×10^{-4}	1.22×10^{-3}	1.17×10^{-1}	1.12×10^{-1}	—	—
Thorium	$t, ^\circ\text{C}$	1685	1831	1999	2196	2431	1827	9.3×10^{-4}
	$W, \text{g/cm}^2/\text{sec}$	2.01×10^{-7}	1.94×10^{-4}	1.86×10^{-3}	1.79×10^{-1}	1.71×10^{-1}	—	—
Platinum	$t, ^\circ\text{C}$	1606	1744	1904	2080	2313	1774	1.6×10^{-4}
	$W, \text{g/cm}^2/\text{sec}$	1.88×10^{-7}	1.81×10^{-4}	1.75×10^{-3}	1.68×10^{-1}	1.60×10^{-1}	—	—
Vanadium	$t, ^\circ\text{C}$	1465	1586	1725	1888	2079	1735	1.2×10^{-4}
	$W, \text{g/cm}^2/\text{sec}$	1.0×10^{-7}	9.3×10^{-4}	8.9×10^{-3}	8.6×10^{-1}	8.2×10^{-1}	—	—
Titanium	$t, ^\circ\text{C}$	1134	1249	1384	1546	1742	1725	8.43×10^{-5}
	$W, \text{g/cm}^2/\text{sec}$	1.08×10^{-7}	1.04×10^{-4}	9.92×10^{-4}	9.47×10^{-2}	9.00×10^{-2}	—	—

* Vapor-pressure data obtained from work by Battelle Memorial Institute on Air Force Contract AF 33-616-232

Fig. 3.5. Vapor Pressure and Rate of Evaporation of High-Melting Metals as a Function of Temperature.

He also estimates a temperature for each metal at which weight loss by evaporation will not exceed 1% in 100 hours: V - 2560°C, Ta - 2400, Re - 2350, Nb - 2230, Os - 2110, Ir - 1990, Mo - 1910, Ru - 1900. These data apply to 1 cm cubes heated in high vacuum.

In considering vapor losses in compounds we must consider not only the vapor pressure but also the dissociation pressure. The common refractory oxides, however, do not dissociate markedly (e.g., P_{O_2} over BeO is of the order of 10^{-25} atm at

1500°C (Brace, J. Electrochem. Soc. 94 (4), 170 (1948); Campbell, p. 43). Vapor pressures at 2000°K are as follows:

Oxide	P (mm Hg)
ThO ₂	1×10^{-7} (extrapolated)
BeO	7×10^{-6} (extrapolated)
CaO	1.9×10^{-4} (extrapolated)
SrO	6×10^{-3} (extrapolated)
HgO	3×10^{-1}

Carbides Boiling points of refractory carbides are all above 4000°C, except VC, which is given as 3900°C. Brewer (Quill, p. 49) states that carbides of tantalum, zirconium, titanium, hafnium, thorium, niobium, molybdenum and tungsten volatilize quite slowly in high vacuum at 2500°K. At 2000°K all of these, plus carbides of uranium, yttrium, vanadium and silicon are non-volatile. This means that vapor pressures of the first named carbides at 2500°K are of the order of 10^{-4} mm Hg or less.

Nitrides. In the case of nitrides, dissociation takes place at much lower temperatures than evaporation. Therefore, the degree of dissociation depends on the partial pressure of nitrogen. The subject of high temperature equilibria will be discussed more fully under "Chemical Properties", Section 3.5. Dissociation pressures of nitrides at elevated temperatures have been calculated by Brewer, Bromley, Gilles and Lofgren (Quill, p. 50). They have frequently been referred to, sometimes under the name "vapor pressures" (e.g., Schwarzkopf & Kieffer, p. 259), but all data rest on the same calculation. At 2500°K, the pressures are: ZrN, HfN - 10^{-5} atm; UN - 10^{-4} - 10^{-5} ; Th₃N₄ - over 10^{-5} ; TiN - 10^{-3} ; NbN - over 10^{-3} atm.

Sulfides. In the same place, CeS is described as "rapidly volatile" in high vacuum at 2500°K (i.e., vapor or dissociation pressure is over 10^{-6} atm).

1.4. Electrical Properties

1.4.1. Conductivity (Resistivity)

A short way to describe the dependence of conductivity on temperature is as follows: For metallic substances, the conductivity drops with temperature, but not by many orders of magnitude. For semi-conductors and insulators, the conductivity rises much faster, and eventually all insulating properties break down.

The rising resistance in metals is due to increased interaction of electrons with the lattice of positive ions, as the latter is increasingly disturbed by thermal motion. The "mean free path" of the electron drops, and so does its mobility.

In non-metals, there are only a very few electrons in the conduction bands. Promotion of electrons to these bands requires an activation energy. Therefore, the entry of electrons into these bands requires an activation energy E , and the expression for the number of conduction electrons includes a term $e^{-E/kT}$. Thus, when the temperature rises, the number of conduction electrons increases rapidly, and in some temperature range there will be a rather sharp drop in the resistance. When E is relatively low (SiC , ZrO_2), the drop will come in the moderate temperature range. Such substances can be used as resistors in electric furnaces if preheated to a temperature at which they are no longer good insulators. Other materials (MgO) have high E and do not break down completely even at much higher temperatures.

Because of chemical and other surface processes, much of the increased conductivity of substances like MgO at high temperatures is surface conductivity. Therefore, conductivity tends to increase with increasing porosity.

Impurities can also greatly increase conductivity. There are at least two mechanisms for this. First, impurity atoms may furnish excess electrons to the conducting bands. In this way, very small amounts of impurities may greatly lower the resistance. Second, small amounts of impurities may form a surface electrolytic zone if they react chemically with the substrate. This effect can be seen if an acid oxide, such as SiO_2 , is added to a basic oxide, such as MgO .

Since many high temperature materials contain impurities, sometimes added deliberately to improve mechanical properties, reported conductivities (or resistivities) vary greatly.

For metals, some values are (in microhm-cm)

<u>Tungsten</u>	20°C - 5.5	<u>TiN</u>	20°C - 21.7
	1200° - 40		2950° - 340
	2400° - 85	<u>ZrN</u>	20° - 13.6
	2730° - 99		2980° - 160
	3240° - 118	<u>VN</u>	20° - 86
<u>Molybdenum</u>	20° - 5.1		
	1200° - 33	<u>Ta₂N</u>	2030° - 850 (?)
	2000° - 60		20° - 135
	2330° - 72		1480° - 104
	2620° - 81		2840° - 116
<u>Tantalum</u>	20° - 15	<u>W₂C</u>	20° - 80
	1130° - 61		2000° - 125
	1730° - 80		
<u>Platinum</u>	0° - 11		
	1600° - 63		

Room temperature resistivities (microhm-cm)

Iridium	6.1	HfC	109
Niobium	13.2	VC	150
Osmium	9	NbC	74
Ruthenium	10	TaC	30
Rhenium	20	Mo ₂ C	97
TiC	68	WC	53
ZrC	63	CeS	400

A general rule of thumb is that electrical resistivities of metallic substances tend to approach values around 200×10^{-6} ohm-cm at high temperatures.

Oxides. The resistivities of oxides are shown as a function of temperature in Fig. 3.6. Fig. 3.7 shows effect of sintering on high temperature resistance of alumina. High-sintered materials, with less surface area, are seen to have better insulating properties. Note the inconsistencies in Fig. 3.6, probably due to varying amounts of impurities as well as different histories of the material samples. Note also that in Fig. 3.7 log R is linear with $1/T$, in line with the activation energy concept.

Fig. 3.6. Electrical Resistivity of Refractory Oxides.

Fig. 3.7. Electrical Resistance of Sintered Alumina: A, 1800°C, 1/4 hr. B, 1650°C, 1 hr. C, 1500°C, 7-hr. D, 1000°C, 10 hr.

3.4.2. Thermionic Emission - milliamperes cm⁻²

Tungsten

1800°K	-	.045
2000	-	1.00
2200	-	13.3
2400	-	116
2600	-	716
2800	-	3540
3000	-	14200
3200	-	47800

Tantalum

1500	-	.0047
2000	-	19.5

Molybdenum

1900	-	1.0
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The thermionic emission of carbides is less than that of the corresponding metals.

D. L. Goldwater and F. H. Morgan (J. Appl. Phys. 22, 70 (1951)) have measured thermionic emission currents as follows:

<u>Material</u>	<u>I at: 1800°K</u>	<u>2000°K</u>
ThO ₂	2.6	11
ZrC	0.9	4.0
TiC	0.03	0.30
TaC	0.04	0.32
ThC ₂	0.35	(4)
ZrN		0.05
BN		0.04
TiN		0.05

3.5. Chemical Properties

3.5.1. General

Since the more complicated molecules dissociate at comparatively low temperatures, only the relatively simple compounds survive at very high temperatures, and the chemical reactions which need to be taken into consideration are also few. Essentially they are: combinations of the elements with oxygen, nitrogen, carbon, hydrogen, and some

other elements which we shall not consider (P, Si, B, S); the converse reactions of dissociation of oxides, carbides, nitrides and hydrides; and substitution reactions of the type $MA + B = MB + A$. Since the carbides, nitrides and some of the other compounds are essentially interstitial solid solutions, we can include here also the solution process and the formation of eutectics.

When considering chemical reactions, we are interested in two things: what is the equilibrium situation, and how fast is it attained? The first question can be answered from a consideration of thermodynamic data; the second needs kinetic data. Kinetics of high temperature processes are very little known; and we can say next to nothing about reaction rates. Reactions with activation energies of 100 - 150 kcal/mole attain measurable velocities at temperatures above 2000°C. These energies are equal to most bond strengths and this is why covalent molecules generally dissociate in this range. An approximate rate for reactions can be predicted if the bond strength is taken to be the same as the activation energy and the steric factor is taken as unity:

$$K = \sum e^{-E_B/RT} \quad (E_B = \text{bond strength})$$

If the steric factor is considerably lower, this may be an over-estimate; but if the activation energy is less than the bond strength (as is the case with most room-temperature reactions), this may be a serious underestimate of the rate.

Sometimes an estimate of a reaction rate may be made if a simple step (such as a diffusion) is rate-determining. This may be an overestimate of the rate because there may be another, slower step which actually determines the overall rate.

In general, however, a priori rate calculations cannot be expected to help much in predicting high temperature chemical behavior of materials.

Thermodynamic calculations, on the other hand, can be most helpful, and are limited only by our incomplete knowledge of the thermodynamic functions. In essence, we usually wish to predict an equilibrium constant K , linked to the free energy change ΔF by

$$\Delta F = - RT \ln K$$

To obtain ΔF at high temperatures we must know ΔH , the heat absorbed during the reaction, since

$$\frac{\partial (\Delta F/T)}{\partial T} = -\frac{\Delta H}{T^2}$$

and ΔH can be obtained as a function of temperatures if the specific heats (at constant pressure) of reactants and products are known, since

$$\frac{\partial (\Delta H)}{\partial T} = \Delta C_p$$

Use of this method involves an integration, often a graphical integration; also the specific heat functions required are not always available. Therefore some shorter methods have been proposed.

Perhaps one should mention the method recommended by Brewer and coworkers, which is undoubtedly the simplest. (Quill, "Chemistry and Metallurgy of Miscellaneous Materials", McGraw-Hill, N.Y., 1950, p. 41.)

Since: $\Delta F = \Delta H - T\Delta S$ at 25°C, they use the approximation

$$\Delta F_T = \Delta H_{298} - T \Delta S_{298},$$

thus treating ΔH and ΔS as invariant. Sometimes this gives fair results.

Example: Find decomposition temperature of barium nitride (Ba_3N_2)

Since substances in pure condensed phase are taken to have concentration 1,

$$K = P_{\text{N}_2}^{1/2} \quad (\text{in atmospheres})$$

At the decomposition point $P_{\text{N}_2} = 1$, $K = 1$, $\Delta F = -RT \ln K = 0$,

$$0 = \Delta H_{298} - T \Delta S_{298},$$

$$T = \frac{\Delta H_{298}}{\Delta S_{298}}$$

In the same article ΔH_{298} is given as - 45300 cal/mole and ΔS_{298} as - 28.7 cal mol⁻¹ °K⁻¹

$$T = \frac{45300}{28.7} = 1579^\circ\text{K}$$

Observed decomposition temperature 1270°K.

On the other hand some results are wildly erroneous.

Margrave (J. Chem. Ed. 32, 530 (1955); "High Temperature - A Tool for the Future", Stanford Research Institute, 1956, p. 87) has outlined a second fast method which is more nearly accurate. It involves the use of the "free energy function" (fef), defined as:

$$\frac{1}{T} (F_T - H_{298}) \quad (\text{for condensed phases})$$

or $\frac{1}{T} (F_T - H_0) \quad \text{for gases}$

Then $\Delta F_T = \Delta H_{298} \text{ (or } \Delta H_0) + T\Delta \text{ (fef)}_T = - RT \ln K_T$

Conversion to one reference temperature is easy if $(H_{298} - H_0)$ is known. Many fef's can be calculated from partition functions. But what makes use of this function particularly favorable is that fef's which cannot be calculated can be estimated quite accurately. Tables and nomographs are given, which enable us to estimate equilibrium constants far better than can be done by Brewer's method. For examples, see "High Temperature - a Tool for the Future", p. 91.

Margrave observes that high temperature data are both incomplete and inaccurate. The data obtained from classical thermodynamics require heat capacity measurements, while those obtained via statistical mechanics require a correct interpretation and analysis of spectra. In both cases only incomplete data are available for elements and only very fragmentary data for compounds. At high temperatures there is the additional problem of writing the correct equation. Many new chemical species are totally unexpected (see, for example, Brewer & Searcy in "Annual Review of Physical Chemistry", Vol. VII, 1956, p. 259). In such cases, calculations are useless.

Let us now summarize some of the known data on chemical reactions.

3.5.2. Oxygen

Carbon, molybdenum, tungsten, tantalum, rhenium, and all carbides and nitrides will react with oxygen at elevated temperature. The rate of oxidation depends on the nature of the oxide. If the oxide forms a coherent layer over the surface of the material, the rate-determining step is diffusion of oxygen through the oxide layer, and the amount of oxide formed will be proportional to the square root of the time. If the oxide is volatile (MoO_3 , WO_3) or forms a discontinuous layer (e.g., if its volume is smaller than that of the unoxidized material from which it is formed), the oxygen always has access to the metal surface and the amount of oxide formed is proportional to the time.

There is also a volume - diffusion mechanism which leads to formation of metallic interstitial suboxides such as Mo_3O . This will be discussed under "nitrogen" in the next paragraph.

3.5.3. Nitrogen

The formation of nitrides is due to the solid solution of nitrogen atoms. Two processes are therefore necessary: the catalyzed dissociation of nitrogen at the surface,

and the diffusion of atoms from one interstitial position to another, deeper one. The former may be expected to go to an equilibrium, so that the concentration of nitrogen atoms is expected to be proportional to the square root of the partial pressure of nitrogen. The rate of the latter process is governed by an activation energy (see Fig. 3.8). At 2500°K , the activation energy factors $e^{-E/RT}$ vary from 1.2×10^{-4} for beta titanium to 1.1×10^{-2} for thorium. Allowing for $10^{10} - 10^{13}$ effective vibrations per second, it can be seen that the transport rate of N atoms will be rapid and will approach a straight diffusion process.

The nitrides of Ti, Zr, Hf, Th, V, Nb, and Ta are stable up to high temperatures (see p. 35 for dissociation pressures). The nitrides of molybdenum and tungsten, on the other hand, do not appear to be stable at high temperatures (Blocher, in Campbell, p. 171; Brewer et al., in Quill, p. 42).

Metal	Nitrogen	Oxygen	Hydrogen
Ti alpha	33.8	48	12.4
Ti beta	45.2		6.6
Zr alpha	-		11.4
Zr beta	30.7		
Th	22.5		
Fe	34.0		
Ni	-		8.7

Fig. 3.8. Activation Energies for Diffusion of Nonmetals in Metals.

3.5.4. Hydrogen

It will be seen from Fig. 3.8 that activation energies for the diffusion of hydrogen through transition group metals are very low. Hydride formation should therefore occur easily at higher temperatures. Hydrides are very brittle and can be pulverized easily.

Metal oxides are hydrogen sensitive, and rough calculations (Brewer method) indicate that MgO and BeO will have very appreciable dissociation pressures of metal vapor and H₂O gas in the presence of 1-20 atm of hydrogen at 2000 - 2500°K.

3.5.5. Carbon

Rates of carburization are not known. It is stated, however, (Quill, p. 51) that carburization of Mo and W is slow in the solid phase at temperatures under 2700°C. Tantalum can be carburized in relatively thin layers.

Phase Relationships. Most metals form single eutectics with their carbides. The eutectic temperatures are:

Ti - TiC	-	1750°C	(Schwarzkopf & Kieffer, p.83)
Zr - ZrC	-	ca.1800°	(" " , p.95)
V - VC	-	ca.1700°	(" " , p.104)
Nb - NbC	-	ca.1875°	(" " , p.109)
Ta - Ta ₂ C	-	2800°	(" " , p.118)
C - TaC	-	3300°	(" " , p.118)
Mo - Mo ₂ C	-	2200°	(" " , p.132)
W - W ₂ C	-	2475°	(" " , p.157)
W ₂ C - WC	-	2525°	(do.; see Fig. 3.9)
WC - TiC	-	2490°	(Schwarzkopf & Kieffer, p.195)
W ₂ C - TaC	-	ca.2760°	(" " , p.208)
Ta ₂ Si - Ta	-	2110°	(" " , p.332)

Obviously we have given here only a very brief introduction into the chemistry of materials at high temperatures, with special attention to properties of solids, and those reactions which might lead to failure of structural elements of a temperature probe.

Fig. 3.9. Phase Diagram of the System W-C.

CHAPTER IV

EFFECTS OF REACTOR ENVIRONMENT ON TEMPERATURE MEASURING DEVICES

4.1. Introduction

The external environment in which any, and especially any high temperature, measuring device will be used may impose more severe limitations on the device than the technique employed. In the case of a rocket reactor operating at high temperatures, a number of other effects must be considered in addition to the chemical and physical changes due to the high temperatures. These are radiation-induced changes in the characteristics of the device, radiation-induced spurious signals or changes in the effective output signals, chemically created spurious signals, vibration, erosion and corrosion effects, special high-temperature electrical effects, etc.

In the following sections we shall discuss these phenomena. The discussion will be applied in the main to thermocouples, but the extension to other temperature measuring methods will be fairly obvious.

4.2. Particle Radiation Effects

4.2.1. Radiation Damage

This section is intended to review radiation damage mechanisms only insofar as they affect the properties of the thermocouple, its insulators, or protective sheaths. Since "damage" is a qualitative expression we should, for reference, fix on a given radiation dosage for which we want to discuss effects on materials. We shall take the radiation environment, in which our thermocouple is to be immersed, as a mixture of equal fluxes of thermal neutrons, fast neutrons, and gamma rays each of 10^{11} particles per square centimeter per second. We shall not consider the effects of fission fragments which are assumed absent in the instrument holes of the reactor. If we take ten hours as a satisfactory lifetime for our thermocouple, the total particle dosage for each of the three types of radiation mentioned above will be about 4×10^{15} particles/cm². Radiation damage effects have been discussed in J.C. Slater, J. App. Phys. 22, 237 (1951); G.J. Dienes, Ann. Rev. Nuc. Sci., 2, 187 (1953); C.E. Weber, "High Temperature, a Tool for the Future", Stanford Research Institute, 1956, p. 136; a series of review articles in Nucleonics (Sept. 1956); and A.S. Thompson and O.E. Rodgers, "Thermal Power from Nuclear Reactors", Wiley, 1956, p. 153.

The materials of which a thermocouple will be composed are taken to be metals, refractory metalloids (interstitial type metallic compounds), group III or alkaline earth oxides as insulation and, in some cases, covalent nonmetallic compounds such as silicon carbide or boron carbide.

Our principal concern in evaluating radiation damage effects is to determine whether the calibration of the thermocouple will be affected. Factors influencing the signal out of a thermocouple (as will be seen in Chapter VI) are: the mean free path for an electron in the element of the couple, the distribution of electronic energy-level states, the electrical leakage paths between the thermocouple elements, variation in surface compositions of thermocouple wires, and spurious effects of a chemical or electrical nature. Particle radiation may be expected to influence at least the first three of these. The extent to which such damage may be tolerated and the extent of the damage itself are, however, difficult to assess, and can only be described qualitatively.

A high energy particle passing through solid matter may collide or interact with atoms of the solid material. This slows the particle, the energy of interaction being transferred to the atoms. These atoms in turn transmit energy by vibration to their neighbors. Thus a region of high temperature material is left in the track of the particle, the so-called "thermal spike", which may disrupt the lattice locally. Many atoms of the material may be permanently displaced from their normal positions in the lattice and come to rest at new positions, giving rise to "holes" and "interstitials". Electrons are detached from a parent atom and are captured by other atoms creating ionizations. Neutrons may be captured, forming new isotopes which are "impurities". Obviously these phenomena will affect the macroscopic properties of the medium. Thus the effects of radiation (in addition to bulk heating effects) are the production of vacancies, interstitials, impurity atoms, and high local temperatures.

These effects can be roughly grouped into displacement effects and ionization. In a good conductor, ionization effects rapidly disappear since electrons may migrate relatively freely. In insulators the ionization effects disappear much more slowly, the rates being, of course, temperature dependent. Displacement of atoms will result in changes in the mechanical properties of all materials and especially affect the energy level configurations in semi-conductors.

The macroscopic properties most often measured as a function of radiation dosage are electrical conductivity, thermal conductivity, and hardness. The reason for measuring

conductivity, which generally decreases with increasing dosage in metals, is to obtain a measure of the number of additional electron scattering centers introduced into the medium (shortening of the mean free path). The thermal conductivity is also affected similarly. The hardness of a material is usually a measure of the number of dislocations and the interference among dislocations existing in a medium (strain hardening).

Fig. 4.1 gives a rough summary of the effects of neutron irradiation on various engineering materials. At high temperatures many of the effects mentioned above will "anneal" out. That is, the increased mobility of atoms and electrons helps to restore order to the crystal lattices. Thus an equilibrium may be reached, at which the rate of creation of imperfections is equal to the rate of annealing.

As far as thermocouples are concerned we see from Fig. 4.1 that at a dosage of 10^{15} n/cm² metals, refractory metal compounds, and insulators are little affected. However the thermoelectric power of any couple which depends upon SiC, B₄C, or C for one of its elements may be seriously affected. These materials have many of the attributes of semiconductors, and we would expect their electronic properties to be more seriously changed by radiation damage. The experimental evidence here, however, is not at all clear cut.

4.2. Radiation Induced Signals

4.2.1. Radiation Heating

In the thermocouple the junction and wires might be heated by the absorbed radiation at a rate different from that of the surrounding carbon. If this is so then the actual temperature of the junction may be higher or lower than the bulk temperature of the medium. This type of heating is in addition to the normal methods of heat transfer to the couple.

Let us use a flux of 10^{12} gamma-rays/cm²-sec. For tungsten the absorption coefficient is about 0.8 cm^{-1} . Per cubic centimeter of material there will be 8×10^{11} collisions. We assume (upper limiting) an energy loss of one mev per event, degraded into heat. This yields 8×10^{11} mev/sec-cm³, or 1.3×10^6 ergs/sec-cm³, or 0.13 watts/cm³. Heating due to fast neutrons may bring this figure up to about 0.2 watts/cm³, or about 0.05 cal/sec/cm³. At high temperatures the heat capacity of tungsten is about 1.0 calorie/cm³-°C.

Fig. 4. 1. Sensitivity of engineering properties to radiation. There is wide variation in effect of irradiation on various materials. Levels indicated are approximate and subject to variation. Irradiation dose is in epithermal neutrons. Indicated changes are in most cases at least 10%.

Thus the rate of heating is 0.05°C/sec , which is obviously negligible compared with heating rates in the body of the reactor.

In other words the normal mechanisms of heat transfer will control the junction temperature, rather than particle radiation heating.

4.2.2. Differential Compton Currents

A spurious signal may be generated in the thermocouple leads if charge is lost differentially in the two wires of which the thermocouple is composed. We consider here only the effect of gamma rays, since neutrons enter here principally by interacting with heavy charged particles, which have very short paths, resulting in very little charge loss from the medium.

The limiting case for this calculation is that in which one lead is completely transparent to gamma rays, so that charge is lost only from the other lead. If we make the upper limiting assumption of one electron lost from the wire per gamma interaction we obtain (from 4.2.1 above)

8×10^{11} electrons escaping per cm^3 of material. For a wire 0.3 mm in diameter and 52 inches active length, we have a volume of $9 \times 10^{-2} \text{ cm}^3$, or a current of 7.2×10^{10} electrons per sec, or 1.2×10^{-8} amperes. If the resistance of the thermocouple circuit is 100 ohms (a high value) the emf error introduced is about one microvolt, a maximum error of a fraction of a degree for all practical thermocouples.

4.2.3. Ionization Chamber Effects

The passage of ionizing radiation through the gas space surrounding the wires of a thermocouple will produce free electrons and ions. If these electrons and ions are free to move they may migrate to the wires and their movement then corresponds to a current between the wires, tending to shunt the signal from reaching an outside indicator. If we again take the resistance of the thermocouple circuit to be 100 ohms in the active region, we would like the resistance of all effective leakage paths to be greater than 10^4 ohms.

We take our gamma flux to be 10^{12} gamma-rays/ $\text{cm}^2\text{-sec}$ and the effective absorption coefficient for the gas to be $1.5 \times 10^{-5} \text{ cm}^{-1}$, resulting in 1.5×10^7 interactions per cm^3

per sec. We assume 3×10^4 ion pairs produced per interaction, or a total of 4.5×10^{11} ion pairs produced per second. An alternative method of deriving the number of ion pairs is to use the fact that in air the flux of 10^{12} gammas/cm²-sec is roughly equivalent to $\frac{10^{12}}{2 \times 10^9} = 500$

roentgens/sec. One roentgen per second liberates one esu of plus and minus charge or $\frac{500}{4.8 \times 10^{-10}} \approx 10^{12}$ ion pairs/sec

produced. Let us take this higher value. The equilibrium value of electron density in the instrument hole may be obtained by assuming a negligible loss of electrons by collection in the wires. (This is justified if our final collection rate is low.) Electrons are then lost mainly by recombination (and also by striking the walls of the chamber). Then the rate of change of the electron density at equilibrium (which is zero) is equal to the rate of production of electrons minus the rate of recombination, as

$$\frac{dn}{dt} = 0 = 10^{12} - \beta n^2$$

The recombination coefficient β for electrons is taken as 10^{-10} from Rossi & Staub, "Ionization Chambers and Counters" McGraw-Hill, N.Y., 1949, yielding

$$n = 10^{11} \text{ electrons/cm}^3$$

as the equilibrium electron density. The electron drift velocity is taken as of the order of one centimeter per second for a ratio of E/p of 10 millivolts over 0.5 cm at 20 atmospheres in nitrogen. The total current due to ionization is then:

$$I = nev = 10^{11} \times 1.6 \times 10^{-19} \times 1 = 1.6 \times 10^{-8} \text{ amperes/cm}^2$$

For a total surface area for the wires of 2.5 cm^2 this amounts to about 4×10^{-8} amperes. If the resistance of the circuit is 100 ohms (high by about a factor of 20) the voltage change would then be 4 microvolts, or less than a one-degree error. (We assume a high resistance because thin spots may develop in the wires.)

The above calculation can be seen to be very much dependent upon accurate values for the drift velocity and recombination coefficient, both of which are very poorly determined.

4.3. Other Spurious Signals

4.3.1. Thermionic Emission

It is conceivable that at these high temperatures there will be a differential thermionic emission from the two materials of which the thermocouple is composed. Very little data is available on the thermionic emission of metals under high gas pressure conditions. With no accelerating fields present we may assume that the effect is very much reduced. However, since surface conditions and environment strongly influence thermionic emission we prefer only to note that this effect is common to thermocouples operating in other high temperature environments and this has apparently not caused noticeable errors in readings.

4.3.2. Water Cycle

When water vapor is present, a complicated series of chemical reactions with the metals and insulators can be expected to occur at high temperatures. The net result is oxidation of the metal surface. The oxide then volatilizes and is reduced at a cooler surface, freeing the metal. From our standpoint, this series of reactions, besides perhaps inducing electrochemical potentials, would increase the circuit lead resistance, thus enhancing other spurious signals, and perhaps introduce shunt leakage paths across insulators.

4.3.3. Electrostatic Effects

The reactor body will be subjected to rather large frictional and erosive forces which may tend to create large local electrostatic potentials. These may be induced into the thermocouple wires and perhaps cause "ground currents", etc., which are only important here because of the necessity of transmitting a rather small emf over a large distance to an indicator.

4.3.4. Chemical Effects

As an example of a drift effect introduced by chemical action we recall that carbon will react with tungsten to form a carbide on the surface of the tungsten wire, and that the carbide is a metallic conductor. If this occurs at the thermocouple junction we find that we have a new thermocouple consisting of the carbide in parallel with the main tungsten wire. The emf of the Mo/W₂C junction is undoubtedly different from that of the Mo/W junction, so that shunting effects may occur, leading to drift in the thermocouple output.

Moreover, if the continuity of the tungsten wire is interrupted because carbide is formed all the way through the wire, we may not be measuring the emf of the original thermocouple at all.

4.3.5. Vibration

Vibration effects will be mainly important because the materials of which any sensing unit is made will be fairly plastic at very high temperatures. Vibration, assisted by gravity, may then deform or distort the thermocouple materials so that they might short out, or move to undesired configurations.

Local flexure inasmuch as it effects strain hardening, fatigue, or local heat generation, is not expected to be of serious concern at these temperatures because all effects are soon annealed out.

CHAPTER V

EXPERIENCE WITH HIGH TEMPERATURE MEASUREMENTS

5.1. Non-thermoelectric

In Chapter II it was seen that most methods of temperature measurement are not suitable for use in the reactor. For this reason, no extensive literature search has been made, for instance, on optical methods for measuring high temperatures. References for the various optical methods are:

"Temperature - Its Measurement and Control in Science and Industry" - Reinhold Publishing Co., N.Y., 1941, pp. 1115 - 1226.

Includes 10 papers on optical methods and pyrometers.

Ibid., Vol. 2, Reinhold Publishing Co., N.Y., 1955, pp. 312 - 318 (engineering applications), pp. 265 - 286 (flames and gases)

"High Temperature Technology", I. E. Campbell, Ed., Wiley, N.Y., 1956, pp. 335 - 357 (by Paul H. Dike)

A comprehensive review, with emphasis on emissivity problems.

"Physical Measurements in Gas Dynamics and Combustion", Princeton University Press, Princeton, N.J., 1954, pp. 343 - 364 (by F.P. Bundy and H.M. Strong) (flame temperatures)

Pneumatic methods are reviewed in the last-named book, pp. 369 - 376 (includes sound velocity method). A gas density method related to the pneumatic is described by J. A. Clark and W. M. Rohsenow, ASME Transactions 74, 219 (1952).

An ingenious thermochemical method is described by R. B. Regier in U. S. Patent 2,739,035 (March 20, 1956). In this apparatus a solid which decomposes at a high temperature to give one solid and one gaseous product is put into a tubular probe. From phase rule considerations it can be seen that the dissociation pressure of the gaseous product is a function of the temperature only, if the two solid phases remain separate. The tube is divided into two portions

by a porous septum along its length. One of the portions is filled with the ordinary compound (example: Ca CO_3) while the other is filled with a labelled compound which will give rise to a labelled gas (e.g., $\text{Ca C}^{14}\text{O}_3$). When the probe is exposed to high temperatures, some of the radioactive gas will migrate through the septum, and by determining the relative counting rates in the two sections after cooling, the temperature to which the probe has been exposed can be determined.

Another non-thermoelectric method for determining high temperatures has recently been patented by A. Mathisen (U. S. Patent 2,731,532, Jan. 17, 1956). Here a probe is constructed from two bars of a refractory metal embedded in a refractory ceramic. No metallic connection exists. The failure of the ceramic's insulating properties makes it possible to utilize this set-up as a resistance thermometer at high temperatures.

Of these two new methods, the former is not applicable because we want continuous recording (quite apart from other objections such as interference by induced radioactivity). The second seems, at first sight, more plausible and is apparently intended for moderately high temperatures (1000-1500°C). However, it can be seen that it, too, depends on the constancy of physical dimensions such as the distance between the two metal rods.

5.2. Thermoelectric

5.2.1. General

For high temperature applications for which optical methods are unsuitable, the tendency has been to use thermocouples.

Advantages and disadvantages of the thermocouple are listed in Chapter VI. At high temperatures perhaps the chief advantages of the thermocouple are: that its output is independent of any given dimension of the instrument; that its output does not vary when corrosion, erosion, etc., are held below a certain threshold level; and that the signal is directly obtained in electrical form, so that there is no difficulty in transmitting it from the high- to the low-temperature region.

The fact that only metallic conductors can be used as materials of construction limits the high-temperature use of the thermocouple somewhat; but in the present case this is a

favorable circumstance, since metals are most resistant to radiation damage.

The attempts to measure high temperatures by means of thermocouples can be naturally divided into three lines of endeavor:

- a) Noble metals
- b) Refractory metals
- c) Non-metals

5.2.2. Noble Metals

Noble metals (which, at high temperatures, means metals of the platinum group - Ru, Rh, Pd, Os, Ir, Pt) have the very great advantage that they are oxidation-resistant and can therefore be used in the presence of air. Since Le Chatelier in the late 19th century made and calibrated the Pt vs. 90 Pt - 10Rh thermocouple, noble metal thermocouples have been standards. The Le Chatelier couple has an absolute upper limit at 1769°C, the melting point of platinum. For higher temperatures, new alloys are necessary. Because of the cost of these metals, these thermocouple alloys must have long life.

A systematic investigation of noble metal alloys was made by Goedecke ("Festschrift der Platinschmelze Siebert", Hanau, Germany, 1931, p. 72). He plotted the thermoelectric emf of the following alloys against platinum as a function of composition: Cu-Pt, Co-Pt, Rh-Pt, Ir-Pt, Cr-Pt, Ru-Pt, Fe-Pt, Ta-Pt, V-Pt, Os-Pt, W-Pt, Mo-Pt and Re-Pt. The last four are especially favorable. Among alloys containing 94% Pt and 6% of the named metal, potentials against Pt at 1200°C are: Os - 19 mv, W - 22.5 mv, Mo - 29 mv, and Re - 24 mv. An 8 Re - 92 Pt alloy has the following emf's against Pt: 300°C - 6 mv, 600°C - 13 mv, 900°C - 23 mv, 1200°C - 31.5 mv. Its emf against a 90 Pt - 10 Rh alloy can be obtained by subtracting the corresponding values for the Le Chatelier couple.

For protracted use above 1600°C, Goedecke recommends a couple Rh vs. 92 Pt - 8 Re. This gives about 12 mv at 1200°C and 17.5 mv at 1500°C, and can be used to 1800°C in a gastight alumina tube. Its stability in air is not too good because of the rhenium content.

Goedecke also recommends a couple Rh vs. 92 Rh - 8 Re which can be used to about 1900°C, at which temperature it has an emf of 7.5 mv. Recrystallization at high temperatures, however, greatly impairs its mechanical stability.

It should be noted that most platinum-group alloys are solid solutions and that no eutectics are formed.

As early as 1909, F. Hofmann (Ber. Ver. Fabr. feuerfest. Prod. 29, 45 (1909)) used an Ir vs. 90 Ir - 10 Ru thermocouple. It was unsatisfactory in many ways. The emf at 1600°C was 3.87 mv and at 1900°C, 4.19 mv, so that the thermoelectric power over this interval was only 1 microvolt per degree. It was also very brittle and its calibration changed because of evaporation and oxidation of ruthenium. However, temperatures up to 2300°C appear to have been reached and measured. By using an 90 Ir - 10 Rh vs. 90 Ir - 10 Ru couple, Hofmann was able to raise the emf to 10.26 mv at 1800°C and the thermoelectric power (TEP) to about 4.5 microvolts per degree.

O. Feussner (Elektrotechn. Zeitschr. 54, 155 (1933)) constructed a thermocouple of Ir vs. 60 Rh - 40 Ir. The advantage of this thermocouple is that both these materials can be worked well and that they do not differ much in melting point. Volatility is claimed to be low up to 2000°C. At that temperature the emf is 10.85 mv and the TEP about 5 microvolt/degree. This couple is available commercially from W. C. Heraeus, Hanau, Germany.

The high-melting elements Os and Ru are not well suited for high temperature use because of their appreciable volatility and because they tend to form the volatile (and, incidentally, poisonous) oxides OsO_4 and RuO_4 .

A good summary of early work on high temperature noble-metal thermocouples can be found in A. Schulze, "Metallische Werkstoffe für Thermoelemente", Berlin, 1940 (lithoprinted by Edwards, Ann Arbor, Mich., 1946), pp. 47 - 56. An English summary of this work can be found in J. Inst. Fuel 12, 3 39 (1939).

More recently, work has been resumed to some extent on noble-metal thermocouples. R. C. Jewell, E. G. Knowles and T. Land (Metal Industry 87, 217 (1955)) have explored the alloys of platinum and rhodium. They found that the solidus point of a 40 Rh - 60 Pt alloy was 1950°C, only 10°C less than the melting point of pure Rh, so that it was not profitable to use alloys richer in rhodium, which are harder to work. (However, if price is a factor, rhodium is often cheaper than platinum on a volume basis.) A 20 Rh - 80 Pt alloy has a liquidus point of 1884°C. It was found that 0.5 mm wire of the two alloys could be prepared, through precautions had to be taken in the case of the 40% Rh alloy (frequent annealing, cold work only, moderate size reduction per drawing). Temperature up to 1850°C were readily measured

with this couple (20 Rh - 80 Pt vs. 40 Rh - 60 Pt). The absolute upper limit is 1884°C. The maximum error is believed to be $\pm 10^\circ\text{C}$ at 1800°C. Recrystallized alumina is satisfactory as a sheath if thermal shock is not excessive.

This couple has apparently found a good deal of use in Britain for a number of laboratory and metallurgical applications. It is covered by British Patent 697,919 and Canadian Patent 507,429. (U. S. Patent has been applied for.) Lifetimes up to 250 hours above 1700°C have been recorded. Failure is due mostly to a) chemical attack, especially by silicon, which causes extensive recrystallization, apparently accompanied by silicide formation, and b) mechanical strain at gaps between lengths of sheath, where expansion and contraction result in formation of narrowed "necks".

Calibration is carried out in an argon atmosphere. A sheath should be used to prevent contamination by metal vapors from the heating element. Values of the emf are:

<u>T°C</u>	<u>emf, mv</u>	<u>T°C</u>	<u>emf, mv</u>
0	0.000	1000	1.378
100	0.040	1100	1.680
200	0.090	1200	2.015
300	0.155	1300	2.380
400	0.240	1400	2.780
500	0.352	1500	3.190
600	0.492	1600	3.625
700	0.664	1700	4.070
800	0.866	1800	4.525
900	1.104	1884	4.900

It will be seen that the emf is fairly low, but that the TEP reaches 4 - 4.5 microvolts/degree in the high temperature range. Because of the very low TEP at room temperature, errors due to cold junction compensation are almost eliminated. Stability of emf is high except in the presence of silicon. Ductility is good and brittleness is low, with the same exception.

It seems probable that this is one of the best thermocouples available for the range 1600 - 1850°C.

Lacroix (Rev. metaux 53, 48 (1956)) has confirmed that recrystallization of platinum-rhodium alloys upon aging decreases in importance as the Rh content increases. He also discusses contamination by oxides used as refractory insulators, and finds that thoria is the least objectionable material. (However, the high temperature resistivity of thoria is low.)

A. A. Rudnitskii and I. I. Tyurin (Zhur. Neorg. Khim. 1, 1074 (1956)) have also discussed high-temperature noble-metal thermocouples. They investigated elements of pure Rh, Rh - Pt alloys up to 40% Rh, and ternary alloys: Pt - Rh - Re and Pt - Rh - W. At 1350°C, a couple Rh vs. 80 Pt - 20 Rh was stable for 588 hours, but at 1550°C it was stable for only 7 hours. Rhenium-containing alloys especially grow less stable in air at higher temperatures. At the platinum melting point (1773°C) they found that the best stability characteristics were exhibited by a couple (70 Pt - 20 Rh - 10 W) vs. (80 Pt - 20 Rh). But in presence of corundum insulators, Rh vs. (80 Pt - 20 Rh) is preferred. The influence of carbon compounds and metallic vapors is discussed. The calibration shift is given as 0.66°C/hour. (Chem. Abstr. 50, 15138c (1956).)

In concluding our discussion of noble metals, we should say that iridium-containing alloys are generally reported to be more brittle than other platinum metals, and that embrittlement by hydrogen, severe for platinum metals, is especially severe for iridium.

H. J. Svec (AECU - 1804) reports that volatility of rhodium causes calibration drift at temperatures as low as 1500°C when the Pt vs. (90 Pt - 10 Rh) couple is employed in vacuum of 50 microns or better.

Thermal neutron cross sections of the platinum metals are:

<u>Metal</u>	<u>Barns/atom</u>	<u>cm²/g</u>
Ru	2.46	.0146
Rh	150	.88
Pd	8.0	.045
Os	14.7	.047
Ir	440	1.37
Pt	8.1	.025

5.2.3. Refractory Metals

In order to measure temperatures above 2000°C with thermocouples, refractory metals have been used. These all react vigorously with oxygen and, therefore, require neutral atmospheres.

The greatest amount of published literature concerns the tungsten-molybdenum thermocouple:

S. Mbrugina, Z. techn. Phys. 7, 486 (1926)

- B. Osann and E. Schroeder, Arch. Eisenhüttenwesen 7, 89 (1933)
- R. D. Potter and N. J. Grant, Iron Age 163, 65 (1949)
- F. H. Morgan and W. E. Danforth, J. Appl. Phys. 21, 112 (1950)
- H. T. Greenaway, S. T. M. Johnstone and M. K. McQuillan, J. Inst. Metals 80, 109 (1951)
- J. P. Simons, C. G. Hamstead and E. J. Burton, J. Iron & Steel Inst. 175, 402 (1953)
- H. A. Wilhelm, H. J. Svec, A. I. Snow and A. H. Danne, AECD - 3275, June 29, 1948
- R. K. McGeary, WAPD-58, August 18, 1952
- P. O. Budnikov and G. S. Tresvyatskii, Ogneupory 20, 156 (1955)
- W. C. Troy and G. Steven, Trans. A. S. M. 42, 1131 (1950)
- A. Schulze, Z. Metallkunde 24, 206 (1932)

From these references, the following picture emerges:

The tungsten-molybdenum thermocouple is made from easily available materials. The wires should be about 0.3 mm thick (Simons), as thicker wire is too rigid for easy manipulation and thinner wire is too fragile when heated, (but other authors have used thicker wires). The hot junction need not be welded, but can be made by winding the more ductile molybdenum around the tungsten. (Potter, McGeary) However, welds can be made easily in an inert gas atmosphere by closing a circuit against a tungsten rod, 100 V DC being used (Simons). The weld may be brittle (Troy).

The emf of the couple is generally low. All observers agree that it reverses polarity in the 1000 - 1500°C range; that the curve is roughly parabolic; that the emf reaches a minimum in the vicinity of 600°C; and that the emf reaches only 3 - 5 mv at 1700 - 2000°C. However, details vary:

Minimum: - 1.4 mv at 620°C (Simons); - 1.82 at 630°C (Potter); - 1.36 mv at 630°C (Potter); - 1.40 at 640°C (McGeary); - 1.84 mv at 660°C (Schulze); - 1.7 mv, 700°C (Wilhelm).

emf = 0: 1310°C (Wilhelm), 1160°C (Potter), 1310°C (Potter), 1220°C (McGeary), 1200°C (Morgan), 1260°C (Troy), 1230°C (Schulze), 1220°C (Simons).

emf = 3 mv: 1710°C (Morgan), 1700°C (Wilhelm), 1700°C (McQuillan), 1725°C (Osann), 1760°C (Potter), 1650°C (Potter), 1710°C (Schulze), 1670 - 1740°C (Simons).

It will be evident from this that there is no single calibration curve for the W - Mo thermocouple. Potter and Grant got especially large variations when using different lots of wire. They reported temperature differences as high as 150°C for the same emf.

Simons has reported differences up to 90°C. Evidently the wires are not always the same and small amounts of impurities affect the emf considerably (though the TEP appears to be less affected).

Simons made a special comparison of the emf's of wires obtained from different suppliers. He found fairly wide variation as between suppliers; fairly good reproducibility as between different batches of wire from the same supplier, acquired a few months apart (in most cases within 10°C, but in one case a difference of 55°C); and good reproducibility of results from different thermocouples made from the same batch of wire.

Potter and Grant reported that aging effects caused instability of the thermal emf output of the tungsten-molybdenum couple unless it was annealed before use. They recommended annealing in hydrogen or nitrogen with 7% hydrogen. Simons, on the other hand, found no difference in behavior between annealed and unannealed wire and no aging effect; nor was there any change after cooling and re-heating.

Contamination by carbon, oxygen and silicon may be expected; but in an inert atmosphere the emf is very stable. McGeary reports that in a vacuum furnace in which the calibration of a Ta - W couple varied by 160°C, the variation for W - Mo was only 10°C. Simons reports that there was no difference between calibration in nitrogen and calibration in argon; also, that the emf was not affected by embedding the couple in alumina. On the other hand, in the presence of graphite changes in calibration did take place at 1700°C, amounting to a +25°C change in calibration in 15 minutes.

Because of the recrystallization of tungsten, the W wire becomes quite brittle after heating, and in general the thermocouple cannot be moved after use without breaking (Wilhelm and others).

The W - Mo couple has been used successfully for thermal analysis up to 2200°C (Budnikov; Greenaway) and is used fairly routinely as a pyrometer for steel. For this purpose, no attempt is made to preserve the couple; after each reading, the junction is sacrificed and new wire is drawn down from a reservoir and joined by clamping or welding. Hamstead and Burton found that temperatures measured with a W - Mo couple agree (within 10°C in most cases) with temperatures measured with a Le Chatelier thermocouple (below 1750°) or an optical pyrometer.

Silica and alumina sheaths were used and no protective atmosphere was supplied. Neither sheath material proved fully satisfactory.

The Mo - W couple, then, is cheap and easy to prepare. By using only one batch of wire, calibration troubles can be overcome. Corrosion and embrittlement are no more severe than with other tungsten-containing thermocouples. The emf is low, but at high temperatures the TEP is comparable to that of the Le Chatelier thermocouple. Errors due to spurious signals may become serious. Burton and Weeks (J. Inst. Fuel 26, 260 (1953)) recommend an upper temperature limit of 2000°C for steady use and 2500°C for intermittent measurement. The melting point of molybdenum is 2620°C, and this is the absolute upper limit for use of this combination.

In order to improve the emf characteristics and increase the maximum temperature, tungsten-molybdenum alloys have been substituted for molybdenum and used in thermocouples against tungsten. Apparently the first such couple was constructed by M. Pirani and G. van Wengenhein (Z. techn. Physik 6, 358 (1925)). They used a 75W - 25Mo alloy, which has a melting point of about 3010°C (Goetzel, "Treatise on Powder Metallurgy", Interscience, N.Y., 1950, Vol. II, p. 59) and reported that the resulting thermocouple could be raised to 3000°C. The emf of this couple apparently behaved very much like that of the W vs. Mo couple. A minimum of minus 0.8 to minus 1.0 mv is reached at 500 - 700°C. Zero emf is reached at 1200°C and there is a steady rise to the melting point of Mo (2620°C), at which point the emf is 5.8 mv. Above 2700°C there were some irregularities in the emf, which reached 6 mv at 3000°C.

Pirani and von Wengenhein did not attain exact reproducibility of the calibration of different thermocouples. Both fixed points and optical methods were used for calibration.

A systematic investigation by W. Goedecke (Chem. Fabrik 5, 361 (1932)) revealed that in general the emf of W - Mo alloys against Mo is extremely small and that, therefore, only small changes in emf result when W - Mo alloys take the place of Mo in the W vs. Mo thermocouple. However, Goedecke was able to effect far greater changes in the emf by adding iron to the molybdenum. A W vs. 99 Mo - 1 Fe thermocouple reaches zero emf already at 400°C and the emf reaches 16 mv at 2000°C. A (69W - 30 Mo - 1Fe) alloy can also be used, giving much the same effect as the Mo - Fe alloy; but the resulting thermocouple can be used to 3000°C. Of course a protective atmosphere is necessary, and in the presence of oxygen, a gastight sheath is required. Goedecke recommends Al_2O_3 below and BeO above 2000°C for the sheath, and hydrogen as the protective atmosphere. Alloys were prepared from metal powders and sintered near their melting points.

Because of sheath failure above 2400°C, Goedecke set this temperature as the upper limit of his thermocouple in oxidizing atmosphere. He does not discuss what would happen in total absence of oxygen, nor does he consider the possible effect of the volatility of iron.

In line with the results of Pirani and Wangenheim, F. H. Morgan and W. E. Danforth calibrated a (50 Mo - 50 W) vs. W thermocouple and found it very similar to the W vs. Mo couple. (J. Appl. Phys. 21, 112 (1950)). Two and five mil wires of the alloy were spotwelded to 30 mil tungsten wire and heated in a 10^{-5} mm vacuum. Calibration was by optical pyrometer with an assumed emissivity of 0.43 for tungsten. The highest temperature reached was 2900°C.

Morgan and Danforth (ibid.) also calibrated thermocouples of Ta vs. W. and Ta vs. Mo. A rising curve is obtained for Ta - W, from about 11 mv at 800°C to 22.9 mv at 2000°C. Above 2000°, however, the TEP passes through zero and the emf curve starts to drop. The Ta - W thermocouple is not suitable for temperatures above 2000°C because of the ambiguity involved. Results above 2000° showed discrepancies which were due to a malfunction of the optical pyrometer. The trend of the emf, however, was quite clear. The Ta - Mo curve is close to the Ta - W curve. The two emf curves are separated by the amount of the W - Mo emf, and cross at 1200°C, as they should (emf of W - Mo is zero at 1200°C). Additivity of the three curves is good.

If the vacuum is not as good as this (10^{-5} mm), the "getter" properties of tantalum become evident. R. K. McGeary (WAPD - 58) found a 1.5 mv drop in emf for a 10^{-4} mm vacuum compared to a 10^{-5} mm vacuum at 1500°C. Values by Schulze (Z. Metallkunde 24, 206 (1932)) and Troy and Steven (Trans.

ASM, 42, 1131 (1950)) fall in between the two curves obtained by McGearry.

Both nitrogen and hydrogen effectively contaminate the tantalum, so that this thermocouple will not be useful under any but high vacuum conditions.

Use of the niobium-tungsten thermocouple is recommended by Wilhelm, Svec, Snow and Danne at the Ames Laboratory (AECD-3275), who also calibrated the Ta - W couple. They found emf's of 25.3 mv for Ta vs. W and 28.1 mv for Nb vs. W at 2000°C. The two curves are within 3 mv of each other over the entire range 700 - 2000°C, crossing at 1260°C. (Incidentally, this indicates that an Nb vs. Ta couple would not be suitable.) Different lots of wire differed in calibration by as much as 100°C, but within each lot of wire the calibration was constant to $\pm 25^\circ\text{C}$. Welds were omitted and twisted junctions used. (See Fig. 5.3)

The Nb vs. W thermocouple appears to have been used extensively in the Ames Laboratory for vacuum furnace operation. Nb is expected to have "getter" properties similar to those of Ta when used at higher pressures, according to Steven (Campbell, pp. 361 - 3).

In 1948 - 50, Steven was unable to obtain rhenium wire. Recently, 10 and 20 mil wire has become available and C. T. Sims (Metal Industry 87, 381 (1955)) quotes "recent work" to the effect that "tungsten-rhenium or molybdenum-rhenium thermocouples produce emf's five to ten times as great as those of the well-known tungsten-molybdenum thermocouple." The Re vs. W combination appears most promising because, among metallic elements, these two materials have the highest melting points.

Work done at Battelle Memorial Institute indicates that rhenium is free from many of the drawbacks of tungsten for high temperature applications. In particular, it does not form carbides, and it retains its ductility after thermal cycling to a much greater extent than tungsten. The very attractive possibility exists of making a thermocouple from rhenium and its alloys which will not have tungsten as an element. The main drawback is the high thermal neutron cross section of rhenium.

W. C. Troy and G. Steven have patented a tungsten-iridium thermocouple which has several desirable properties (U. S. Patent 2,588, 998; March 11, 1952). The behavior of the emf is particularly favorable. The TEP is high and nearly constant at high temperatures but almost exactly zero near room temperature. Therefore, the emf is linear

and the cold junction compensation is zero. The emf from 1000° to 2100°C is given by:

$$\text{emf (mv)} = -6.98 + 0.0195T + 1.71 \times 10^{-6}T^2$$

T is temperature in degrees Centigrade. Lifetime is given as 120 hours in a helium atmosphere, with stable emf. (See Fig. 5.1)

However, Steven states that oxygen and hydrogen containing atmospheres both attack the thermocouple. Oxygen, of course, attacks the tungsten; hydrogen atmosphere results in progressive embrittlement and eventually mechanical failure of the iridium. The W vs. Ir couple is also quite sensitive to contamination by carbon.

This couple has many advantages for the range 1800° to 2100°C. It is not, however, too well adapted for the reactor, even for nitrogen atmosphere, because of the high neutron cross section of iridium.

The following table shows thermal neutron cross sections for refractory metals:

	Barns/atom	cm ² /g
Ti	5.6	0.070
Zr	0.18	0.00119
Hf	115	0.39
V	4.7	0.055
Nb	1.1	0.0071
Ta	21.3	0.071
Cr	2.9	0.033
Mo	2.4	0.0151
W	19.2	0.063
Mn	12.6	0.139
Re	84.	0.27
C	0.0045	0.00022

5.2.4. Non-metals

In recent years, a number of thermocouples have been used in which non-metals constitute one or both elements. The prototype for these is the graphite-silicon carbide thermocouple of G. R. Fitterer (AIME Transactions 105, 290 (1933); 120, 189 (1936); "Temperature - Its Measurement and Control", Vol. I, Reinhold, N.Y., 1941, p. 946) which is in extensive use in pyrometers for liquid irons and steels. Fig. 5.2 shows an assembled thermocouple, showing its rugged construction. The outside diameter is 1.75 inches. No welded junction exists in this couple. Instead,

Fig. 5.1. Calibration Curve of Tungsten-Iridium Thermocouple (from U. S. Patent 2, 588, 998).

Fig. 5.2. Sectional view of C-SiC thermocouple assembly. 1-Silicon carbide rod. 2-Graphite tip. 3-Graphite sleeve. 4-Graphite main section. 5-Graphite head nipple. 6-Fused silica insulator (1-3/8" x 1-1/8" x 8"). 7-Fused silica insulators (25/32" x 5/8" x 5"). 8-Porcelain insulator. 9-Copper cooling coil for SiC. 10-Copper cooling coil for graphite.

the interior silicon carbide rod is rammed down into the outer graphite sheath. The sheath is considered expendable, and dissolves in the molten steel in the course of a number of readings. One couple may have a lifetime of about 18 hours.

Fused silica is used as an insulator in the vicinity of the hot junction. The other end of the couple is water-cooled.

The TEP of the couple is much greater than that of metal-metal couples. Fitterer gives it as 0.3 mv per °C in the range of interest. Thus, potentials of the order of 0.5 volts are obtained in liquid steels.

The high TEP is to be attributed to the silicon carbide, since the TEP of a tungsten-graphite thermocouple is within the normal range (H. L. Watson and H. Abrams, Trans. Am. Electrochem. Soc. 19, 54 (1928); Campbell, "High Temperature Technology", p. 376). This is, of course, connected with the semi-conductor structure of the silicon carbide. The number of electrons in the conduction bands increases sharply with temperature, so that the potential needed for withdrawing an electron is strongly temperature-dependent.

Because of this intimate connection of the TEP to the properties of the semiconductor, we would expect the TEP to be very sensitive to radiation damage.

As for the graphite, its properties are believed to be highly sensitive to contaminants and especially to small amounts of moisture. E. E. Loebner (Phys. Rev. 102, 46 (1956)) has demonstrated a considerable dependence of resistance and TEP on sample history for carbon, graphite and intermediate stages.

In addition to the graphite vs. SiC and graphite vs. W thermocouples, a graphite vs. boron carbide thermocouple has also been constructed (R. R. Ridgway, U. S. Patent 2,152,153, March 28, 1939). This couple is probably subject to the same objections as the SiC-graphite thermocouple, and is also objectionable due to the high neutron cross section of natural boron.

Fig. 5.3. (From Wilhelm, Svec, Snow and Danne, AECD-3275)
("Cb" is Nb).

Fig. 5.4. Upper: Characteristic Curves of High-Temperature Thermocouples with Low Emf.
Lower: Characteristic Curves of High-Temperature Thermocouples with High Emf.
Letters Refer to Atmosphere: N-neutral, O-oxidizing, R-reducing, V-vacuum.

CHAPTER VI

THERMOELECTRICITY - THEORY AND PRACTICE

6.1. The Thermocouple

The relative advantages of the thermocouple as a temperature measuring device over almost all other schemes are very evident. In temperature regions and environments in which they can be employed, thermocouples reign almost supreme. Some of the advantages of the thermocouple are:

- 1) Stability
- 2) Lack of hysteretic effects in general
- 3) Small physical sampling size
- 4) Electrical signal generation
- 5) Flexibility as to physical size, orientation, positioning
- 6) Wide range of operation
- 7) Adaptability for measuring gas, liquid or solid temperatures
- 8) Insignificance of correction to readings
- 9) Resistance to corrosion, erosion etc. Readings not effected until phase changes are essentially complete in the materials of which it is composed (for pure material couples)
- 10) Ease of application
- 11) Low cost of material generally
- 12) Large body of experimental technique exists

Among the disadvantages of the thermocouple should be stated the need for electrical measuring apparatus, purely empirical calibration curves, cold junction corrections, special materials used in composition (such as alloys) which make drift of readings possible on change of composition, relatively small d.c. electrical signal outputs and the need in general for potentiometric reading.

Thermocouples retain many of their advantages even at very high temperatures, especially their stability under corrosive influences, as compared with most other techniques of temperature measurement techniques. Therefore they appear to be most attractive high temperature measuring devices and

they have been investigated in some detail in this study.

6.2. The Thermoelectric Effect

The thermoelectric effects existing in metals and semiconductors have been used extensively for about a century for measuring temperature. In general usage these devices are, at best, used as semi-empirical "gadgets", deriving their usefulness from the observed stability of a measured calibration curve.

For about the last twenty-five years, however, because of the advances in solid state physics and improved understanding of the electron structure of matter, serious attempts have been made to formulate theories of the thermoelectric effect. These theories are based on various more or less realistic models of the structure of solids, and for the first time predictions of the thermoelectric effects are possible. Unfortunately, the detailed predictions have not been accurate enough as yet for engineering usage. On the contrary, the measurements of thermoelectric effects have yielded valuable data both for normalizing calculations and for suggesting improvements in the theory. In general we may say that "while the theory of the thermoelectric circuit can be worked out on thermodynamic principles, and while the phenomena involved can be qualitatively deduced from the electron theory of metals, the relationship between a material's composition or structure and its thermoelectric characteristics is not in general established." (P.H. Dike, "Thermoelectric Thermometry", Leeds and Northrup, Philadelphia, 1955, p. 4.)

The theory of the thermoelectric effect is described briefly in the following section. The use of thermocouples is described in the following section, and finally comment is made about the high temperature aspect of the problem.

6.3. Theory of Thermoelectric Effects

6.3.1. Nature of Effects

Three thermoelectric experimental effects, namely the Seebeck, Peltier and Thomson effects, must be considered by any theory of thermoelectricity. For thermocouples the Seebeck effect is of primary concern. As is shown below, however, the division of the three effects is actually historical and arbitrary rather than fundamental.

The Seebeck effect is the experimentally observed electrical current that flows in a circuit composed of two dissimilar metals when the two junctions are maintained at

different temperatures. Peltier discovered that a current flowing across a junction of two dissimilar metals will give rise to an absorption or a liberation of heat, and that the effect is reversible. Sir William Thomson (Lord Kelvin) found reversible heat effects in a single current-carrying conductor in which there was a temperature gradient along the direction of current flow.

6.3.2. Thermodynamic Derivation

We let $\pi_{12} = \frac{Q_{12}}{I_{12}}$ be the Peltier coefficient, where Q_{12} is the reversible heat flow to a junction of dissimilar metals in unit time and I_{12} is the current flowing from conductor (1) to conductor (2). We also let $\sigma = \frac{1}{I} \frac{dQ}{dT}$ be the Thomson coefficient, where I is the current flowing in a conductor and dQ is the heat which is imparted to an element of the conductor with temperature rise dT .

For a closed circuit of two dissimilar metals with the junctions at temperatures T and T' we may write

$$Q = I[\pi_{12} - \pi'_{12} + \int_{T'}^T (\sigma_1 - \sigma_2) dT] \quad (6.1)$$

where Q is the total heat imparted to the system per unit time to maintain a stationary current I . If E is the electromotive force of the circuit, then

$$E = \pi_{12} - \pi'_{12} + \int_{T'}^T (\sigma_1 - \sigma_2) dT \quad (6.2)$$

is the expression of the first law of thermodynamics. As T approaches T' , we may write

$$\frac{dE}{dT} = \frac{d\pi_{12}}{dT} + \sigma_1 - \sigma_2 \quad (6.3)$$

Since the processes discussed above are reversible the total cyclic entropy change around the circuit is zero.

$$\oint dS = \oint \frac{dQ}{T} = 0 \quad (6.4)$$

or

$$\frac{\pi_{12}}{T} - \frac{\pi'_{12}}{T'} + \int_{T'}^T \frac{\sigma_1 - \sigma_2}{T} dT = 0 \quad (6.5)$$

and as T approaches T' , $(T - T')$ becomes dT ,

$$\text{or } \frac{d(\pi_{12}/T)}{dT} = \frac{\sigma_2 - \sigma_1}{T} \quad (6.6)$$

From the above equations it follows that

$$\frac{dE}{dT} = \frac{\pi_{12}}{T} \quad (6.7)$$

a quantity which is known as the thermoelectric power, and that

$$\sigma_2 - \sigma_1 = T \frac{d}{dT} \left(\frac{\pi_{12}}{T} \right) = T \frac{d^2 E}{dT^2} \quad (6.8)$$

which are two consequences of the second law of thermodynamics.

Finally since $\frac{\pi_{12}}{T}$ is the change of entropy for an electron in passing across the junction, Nernst's postulate states that

$$\lim_{T \rightarrow 0} \left(\frac{\pi_{12}}{T} \right) = 0 \quad (6.9)$$

so that integrating equation 6.7 we obtain

$$\pi_{12} = T \int_0^T \frac{\sigma_2 - \sigma_1}{T} dT \quad (6.10)$$

and since the integral must converge

$$\lim_{T \rightarrow 0} (\sigma_2 - \sigma_1) = 0 \quad (6.11)$$

In fact, in the limit, σ_2 and σ_1 must vanish individually.

We see that the three thermoelectric effects are intimately related. In practice, the Peltier and Thomson effects can be completely neglected, as the heat produced by them is too small by several orders of magnitude to effect a measurable change in the temperature of any actual system.

6.3.3. Derivation from Electron Theory

The existence of thermoelectric effects may be deduced on quite general grounds, given any reasonable model for the solid state—say the free electron model of Sommerfeld. At junctions these effects arise as contact potentials due to the tendency of electrons in one metal to escape to a contiguous metal by virtue of the difference in electronic energy levels in the two metals.

The derivation of such effects will only be sketched here, and follows the treatments of Mott and Jones, and Seitz. A semi-qualitative treatment is given by Wright.*

For heat accumulating into a unit volume of metal which is carrying electrical and thermal currents in the x direction, the following relation holds:

$$\frac{dH}{dT} = I_x E_x - \frac{\partial C_x}{\partial x} \quad (6.12)$$

Here $\frac{dH}{dT}$ is the rate of heat accumulation, $I_x E_x$ is the electrical work done, and $-\frac{\partial C_x}{\partial x}$ is the divergence of the heat current C .

The expressions for E_x and C_x may be derived from the electron theory of matter as follows: An expression for the velocity distribution function for the electrons in the material is developed using the Boltzmann equation of state. External electric and magnetic fields result in a perturbation of the distribution function, and a new distribution function is calculated as a series expansion in powers of the applied fields, usually retaining only first powers. Using the new terms, an expression is written for the mean free path of the electron in the material. Using this expression, electrical and thermal conductivity may be calculated. For example:

$$I_x = - \int e v_x f_n d\sigma \quad (6.13)$$

$$C_x = \frac{1}{2} \int v_x m v^2 f_n d\sigma \quad (6.14)$$

where f_n is the distribution function. For a metal with no external fields applied

$$f_n^0 = \frac{2\pi^3}{h^3} f(\epsilon), \quad \text{where} \quad (6.15)$$

$$f(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon^0)/kT} + 1} \quad (6.16)$$

* N.F. Mott and H. Jones, "Theory of the Properties of Metals and Alloys", Oxford, 1936. F. Seitz, "The Modern Theory of Solids", McGraw-Hill, New York, 1940, pp. 178 - 181. D.A. Wright, "Semiconductors", Wiley, New York, 1955. H. Jones, "Handbuch der Physik", Vol. 19, Springer, Berlin, 1956, p. 271 ff.

which is the Fermi-Dirac distribution function for metals, ξ^* being the Fermi energy.

If, on the other hand, we allow a perturbation of f_n by external fields, we arrive at the following expression for I_x and C_x , for the case in which we allow an electric field and thermal gradient in the x direction:

$$I_x = \frac{4\pi e}{3} \int_0^\infty v^3 l \left(\frac{\partial f_n^*}{\partial x} - e E_x \frac{\partial f_n^*}{\partial \xi} \right) dv \quad (6.17)$$

and

$$C_x = -\frac{4\pi m}{6} \int_0^\infty v^5 l \left(\frac{\partial f_n^*}{\partial x} - e E_x \frac{\partial f_n^*}{\partial \xi} \right) dv \quad (6.18)$$

where ξ is the energy coordinate, $l(\xi)$ is the mean free path and f_n^* is the zeroth order term in the expansion of the distribution function. Writing $\frac{\partial f_n^*}{\partial x}$ in terms of E and a thermal gradient $\frac{dT}{dx}$, we obtain (Seitz, p. 177)

$$I_x = -\frac{e}{3} \sqrt{\frac{2}{m}} \left\{ K_1 \left[e E_x + T \frac{d}{dT} \left(\frac{E'}{T} \right) \frac{dT}{dx} \right] + \frac{K_2}{T} \frac{dT}{dx} \right\} \quad (6.19)$$

$$C_x = \frac{1}{3} \sqrt{\frac{2}{m}} \left\{ K_2 \left[e E_x + T \frac{d}{dT} \left(\frac{E'}{T} \right) \frac{dT}{dx} \right] + \frac{K_3}{T} \frac{dT}{dx} \right\} \quad (6.20)$$

where

$$K_i = \frac{4\pi(2m)^{3/2}}{h^3} \int_0^\infty \xi^i l \frac{df_n^*}{d\xi} d\xi \quad (6.21)$$

Solving for E_x we obtain

$$E_x = -\frac{1}{e} \sqrt{\frac{m}{2}} \frac{1}{K_1} I_x - \frac{T}{e} \frac{d}{dT} \left(\frac{E'}{T} \right) \frac{dT}{dx} - \frac{K_2}{K_1} \frac{1}{eT} \frac{dT}{dx} \quad (6.22)$$

From (6.20) and (6.22),

$$C_x = -\frac{K_2}{K_1} \frac{1}{e} I_x + \frac{1}{3} \sqrt{\frac{2}{m}} \left(\frac{K_2 K_1 - K_3^2}{T K_1} \right) \frac{dT}{dx} \quad (6.23)$$

When $I_x = 0$ the thermal conductivity is

$$K = \frac{C_x}{dT/dx} = -\frac{1}{3} \sqrt{\frac{2}{m}} \left(\frac{K_2 K_1 - K_3^2}{T K_1} \right) \quad (6.24)$$

When $\frac{dT}{dx} = 0$ and at ordinary temperatures ($\epsilon' \approx \epsilon_0 = \frac{h^2}{2m} \left(\frac{3n_0}{8\pi} \right)^{2/3}$),

$$I_x = -E_x \frac{e^2}{3} \frac{C}{V} \sqrt{\frac{2}{m}} \int_0^\infty \epsilon \ell \frac{\partial f(\epsilon)}{\partial \epsilon} d\epsilon \quad (6.25)$$

where

$$\frac{C}{V} = \frac{4\pi(2m)^{3/2}}{h^3} = \frac{3n_0}{2\epsilon_0^{3/2}} \quad (6.26)$$

and n_0 = number of electrons per unit volume. Now, it can be shown^o (Seitz pp. 147-148) that

$$\int_0^\infty \epsilon \ell \frac{\partial f(\epsilon)}{\partial \epsilon} d\epsilon \approx -\epsilon_0' \ell(\epsilon_0') \quad (6.27)$$

where ϵ_0' is the Fermi energy in the absence of external fields.

Therefore the electrical conductivity

$$\sigma = \frac{I_x}{E_x} = \frac{e^2}{3} \frac{C}{V} \sqrt{\frac{2}{m}} \epsilon_0' \ell(\epsilon_0') = \sqrt{\frac{2}{m}} \frac{e^2 n_0 \ell(\epsilon_0')}{2 \epsilon_0'^{3/2}} \quad (6.28)$$

If we now recall the formula for the heat balance in the wire, namely

$$\frac{dH}{dt} = I_x E_x - \frac{\partial C_x}{\partial x} \quad (6.12)$$

and substitute in the values for E_x and C_x derived above, we obtain (after some manipulation)

$$\frac{dH}{dT} = \frac{I_x^2}{\sigma} - \frac{I_x}{e} T \frac{d}{dx} \left(\frac{K_x}{TK_x} - \frac{\epsilon'}{T} \right) + \frac{d}{dx} \left(k \frac{dT}{dx} \right) \quad (6.29)$$

where σ and k are the electrical and thermal conductivity given above.

The first term is the Joule heat and the third is that arising from the ordinary flow of heat. These terms are independent of the relative directions of the electrical current and the thermal gradient. The second term does depend upon both the direction of electrical current flow and the direction of the temperature gradient. This term then embodies the thermoelectric effects which will now be discussed.

6.3.3.1. Thomson Effect

Consider a wire in which $\frac{dT}{dx}$ is constant and which carries current I_x . Then, according to the second term above (not considering the Joule heat), heat is produced at the rate

$$\frac{dH}{dt} = - \frac{I_x}{e} T \frac{d}{dT} \left(\frac{K_2}{TK_1} - \frac{\xi'}{T} \right) \frac{dT}{dx} \quad (6.30)$$

which is known as the Thomson heat. Now the Thomson coefficient is defined as

$$\sigma_T = - \frac{dH/dT}{I_x \frac{dT}{dx}} \quad (6.31)$$

so that

$$\sigma_T = - \frac{T}{e} \frac{d}{dT} \left(\frac{K_2}{TK_1} - \frac{\xi'}{T} \right) \quad (6.32)$$

In terms of mean free path the coefficient turns out to be

$$\sigma_T = - \frac{k^2 T}{e} \frac{\pi^2}{3} \left[\frac{1}{L_1} + \frac{\xi'(L_1)}{\xi(L_1)} \right] \quad (6.33)$$

The values of the K factors must be determined from a theory of the mean free path, but in general the contrary procedure is more useful. Experimental results are used for σ_T , and from equation (6.33), we derive the mean free paths which must then be matched by the theory. For the alkali metals σ_T is in general negative, showing that the electrons carry heat from hot to cold regions of the metal.

6.3.3.2. Peltier Effect

As described previously, the Peltier coefficient is defined by

$$\Pi_{12} = - \frac{1}{I_x} \frac{dH}{dt} \quad (6.34)$$

where $\frac{dH}{dt}$ is the heat evolved at a junction of two metals at the same temperature due to a current I_x flowing from metal 1 to metal 2. From the second term of our heat balance equation

$$\begin{aligned}\pi_{12} &= -\frac{T}{e} \int_1^2 \frac{d}{dx} \left(\frac{\kappa_2}{T} - \frac{\xi'}{T} \right) dx \\ &= -\frac{T}{e} \left[\left(\frac{\kappa_2}{T} - \frac{\xi'}{T} \right)_2 - \left(\frac{\kappa_2}{T} - \frac{\xi'}{T} \right)_1 \right] \quad (6.35)\end{aligned}$$

Comparing this with the expression for the Thomson coefficient we see that

$$\frac{d}{dT} \left(\frac{\pi_{12}}{T} \right) = \frac{\sigma_{T2} - \sigma_{T1}}{T} \quad (6.36)$$

We see again that the value of π_{12} depends upon the values of the Thomson coefficients.

6.3.3.3. Seebeck Effect

The Seebeck emf E_s is defined as the total force acting around a closed loop of two dissimilar metals with junctions at T' and T'' when the current is zero.

We may obtain this emf by integrating the value for E_x previously given around the closed circuit for $I_x = 0$

$$\begin{aligned}E_s &= -\oint E_x dx = \frac{1}{e} \oint \left[T \frac{d}{dx} \left(\frac{\xi'}{T} \right) + \frac{\kappa_2}{\kappa_1 T} \frac{dT}{dx} \right] dx \\ &= \frac{1}{e} \oint \left(-\frac{\xi'}{T} \frac{dT}{dx} + \frac{\kappa_2}{\kappa_1 T} \frac{dT}{dx} \right) dx \quad (6.37)\end{aligned}$$

Changing the variable of integration from x to T and dividing the integral into integrals over each metal we obtain

$$E_s = -\frac{1}{e} \int_{T'}^{T''} \left[\left(\frac{\kappa_2}{T} - \frac{\xi'}{T} \right)_2 - \left(\frac{\kappa_2}{T} - \frac{\xi'}{T} \right)_1 \right] dT \quad (6.38)$$

or

$$E_s = \int_{T'}^{T''} \frac{\pi_{12}}{T} dT \quad (6.39)$$

Hence the thermoelectric power $\frac{dE_s}{dT}$ is

$$\frac{dE_s}{dT} = \frac{\pi_{12}}{T} \quad (6.40)$$

We see that the results agree with the thermodynamic derivation. Predictions based on this calculational scheme must rest upon the nature of the detailed model assumed and

none of these predictions are as yet accurate enough to be quantitatively useful.

Typically in the free electron approximation the expression for the thermoelectric power is

$$\frac{dE_i}{dT} = \frac{\pi^2}{3} \frac{k_B^2}{e} T \left\{ \frac{d}{dE} [\log \rho(E)] \right\}_{E_F} \quad (6.41)$$

where e is the electronic charge, k_B Boltzmann's constant, T the absolute temperature, $\rho(E)$ the resistivity for electrons of energy E , and E_F is the Fermi energy.

One more point should be mentioned. The thermoelectric emf is the net effect of the difference in contact potentials at two junctions maintained at different temperatures. In metals the differences in electronic energy levels which determine the contact potentials are governed by the Fermi distribution so that relatively few of the electrons are involved in the higher energy states. In semiconductors, on the other hand, small changes in temperature can lift relatively many electrons into conduction bands. These effects are reflected in the much larger observed thermoelectric powers for semiconductor-metal thermocouples over the metal-to-metal types. (See Wright p. 75)

6.4. Thermocouple Practice

This section will deal with the practical aspects of utilizing thermocouples as temperature-sensing devices, and especially with the high temperature aspects of thermocouple thermometry.

6.4.1. Thermoelectric "Laws".

Experiment and experience have led to the formulation of practical thermoelectric "laws".

a. The Law of the Homogeneous Circuit

An electric current cannot be sustained in a circuit of a single homogeneous metal, however varying in cross section, by the application of heat alone. Observed deviations from this law have proved to be due to inhomogeneities in the wires used. This law is especially important for high temperature work, where large thermal gradients are anticipated, since it shows that if great care is taken to insure homogeneity, the lead wires will not affect the emf of the couple.

b. Law of Intermediate Metals

The algebraic sum of the electromotive forces in a circuit composed of any number of dissimilar metals is zero, if all of the circuit is at a uniform temperature. This law ensures (esp. at high temperatures) that any chemical action at the junction, short of breaking the junction of the couple, will not affect the emf output of the couple if all of the affected region is at the same temperature. It also makes possible the use of extension leads.

c. Law of Successive or Intermediate Temperatures.

The thermal emf developed by any thermocouple of homogeneous metals with its junctions at any two temperatures T_1 and T_3 is the algebraic sum of the emf of the thermocouple with one junction at T_1 and the other at any temperature T_2 and the emf of an identical thermocouple with its junctions at T_2 and T_3 .

The above laws are summarized as follows: The algebraic sum of the thermoelectric forces generated in any given circuit containing any number of dissimilar homogeneous metals is a function only of the temperatures of the junctions.

6.4.2. Thermoelectric Thermometry

The definite reproducible relationship between the difference of temperatures of the junctions of a thermoelectric circuit and the emf of the circuit makes the use of a thermocouple circuit suitable for thermometry. An emf measuring device such as a potentiometer or a millivoltmeter, combined with the circuit, makes up a pyrometer. The temperature difference between a junction at an unknown temperature and a junction maintained at a known temperature (usually 0°C) can be easily determined by a reading of the emf of the circuit and a calibration curve of emf vs. temperature (with the "cold" junction at the reference temperature). In practice, the "cold" junction is often replaced by an automatic reference junction compensator which may be either mechanical or electrical in its mode of operation. In the case of some thermocouples (e.g., W versus Ir) the emf output at low temperatures is so small that no cold junction compensation is necessary.

6.4.3. Materials

In this section we shall discuss materials used commonly for thermocouples in the range of -200°C to $+1700^\circ\text{C}$. Materials for high temperature thermocouples are discussed

separately in Chapter V.

The criteria which must be satisfied by the materials used for thermocouples are as follows:

a. The thermal emf increases continuously with increasing temperature over the temperature range in which the thermocouple is to be used.

b. The thermal emf is great enough to be measured with reasonable accuracy.

c. The thermoelectric characteristics are not appreciably altered either by calibration or use in the intended environment.

d. Oxidation, corrosion, erosion, etc., do not destroy the material.

e. The melting points, or any phase transition points of the materials used, must be above any temperature at which the thermocouple is to be used.

f. The materials are reproducible and readily obtained in uniform quality.

It should be noted, as was pointed out in Section 6.3, that the thermoelectric power for all materials tends to zero as the temperature approaches zero. Although thermocouples have been used for measurements below 10°K , a practical lower limit for thermocouple thermometry is about 20°K . Thermocouples made of semiconducting materials might perhaps have the required sensitivity at low temperatures, but would probably not be as reliable as other available techniques.

Almost all pure metals and a large variety of alloys have been used as thermocouple elements. Experience has however reduced the number of choices to the list that follows. The period of usefulness of a thermocouple is a function of the temperature, diameter of wires, accuracy required, environment, etc.

6.4.4. Types of Thermocouples and Useful Temperature Ranges

Type of Thermocouple	Usual Temperature Range °C	Maximum Temperature °C
Platinum vs. 90 Pt - 10 Rh (Le Chatelier)	0 to 1450	1700
Chromel P vs. Alumel	-200 to 1200	1350
Iron vs. Constantan	-200 to 750	1000
Copper vs. Constantan	-200 to 350	600

Fig. 6.1 gives a plot of the thermoelectric powers of various metals against platinum.

The emf of any metal used as thermocouple element against any other may be obtained by integration of the thermoelectric powers of the two metals. Table 6.4.4.1 is a listing of metals, so arranged that each item in the list is thermoelectrically negative with respect to all those below it.

6.4.4.1. Thermoelectric Series of Selected Metals and Alloys

100°C	500°C	900°C
Antimony	Chromel-P	Chromel-P
Chromel-P (90Ni-10Cr)	Nichrome	Nichrome
Iron	Copper	Silver
Nichrome	Silver	Gold
Copper	Gold	Iron
Silver	Iron	90Pt-10Rh
90Pt-10Rh	90Pt-10Rh	Platinum
Platinum	Platinum	Cobalt
Palladium	Cobalt	Alumel
Cobalt	Palladium	Nickel
Alumel (94Ni-3Mn-2Al-1Si)	Alumel	Palladium
Nickel	Nickel	Constantan
Constantan (57Cu-43Ni)	Constantan	
Copel	Copel	
Bismuth		

6.4.5. Fabrication

The fabrication of thermocouples has been accomplished by almost as many techniques as are known for bonding metals together. Some of the techniques used have been soldering, brazing, welding, forging, electroplating, vapor deposition, swaging, friction, etc. Concentric tube and wire or rod arrangements have been used where mechanical stability was imperative. Surface temperature measurements have been made

Fig. 6. 1. Thermoelectric Powers of Common Thermocouple Elements Against Platinum.

by plating or tamping thermocouples into surfaces. In at least one case, a thermocouple has been made without junction, by dipping two dissimilar rods into a molten metal.

In most cases precautions must be taken to prevent the oxidation of the joint and to exclude foreign materials which would weaken the mechanical properties of the joint.

In measuring high gas temperatures care must be taken to prevent radiation losses from the thermocouple. This is usually accomplished by encasing the hot junction in porous metallic shields of low emissivity. Elaborate schemes have sometimes been used to ensure the smallest radiation losses, such as installing heating elements in the radiation shields to maintain the shield and couple at the same temperature.

For high temperatures the couple elements should be so constructed as to offer less resistance to corrosion at the junction than along the elements themselves. This is to ensure that corrosion effects along the length of the couple elements will not result in parasitic emf's.

6.4.6. Installation

The installation of thermocouples must be done with some care, in order to make sure that the junction is maintained at the same temperature as the material whose temperature is being measured. Heat losses by conduction of the thermocouple leads and radiation losses to colder surroundings must be minimized. The heat capacity of the thermocouple and its appurtenances must be small enough to allow the junction to follow temperature changes in the medium at a satisfactory rate.

In addition the thermocouple assembly should be composed of materials, which will resist physical or chemical effects that would change its calibration or actually incapacitate the element.

In order to meet the foregoing requirements a large body of experiential art has been developed for common industrial usage. H. D. Baker, "Manual on Thermometry", United Aircraft Co., E. Hartford, Conn., 1950, has given an excellent review of many of these techniques. However, under unusual conditions each problem must be solved by re-considering the fundamentals of the situation, and usually compromising.

At very high temperatures the problem of physical and chemical corrosion becomes of paramount importance. Most metals experience recrystallization and become embrittled.

Phase changes are experienced, and chemical reaction rates increase exponentially. Protection tubes or wells to insulate the thermocouple from the environment are usually necessary. The thermocouple cannot be physically removed after installation and operation at high temperatures without injury to the components. If possible, the thermocouple should be operated in an inert atmosphere such as argon, although even argon or helium may cause embrittlement of certain metals (e.g., tantalum).

Caution should be observed in the selection of insulators to space the couple elements. Even if a material is satisfactory at high temperatures for its insulating properties, it may still react with the thermocouple elements at high temperatures. Typically some of the oxides will react to oxidize the couple elements while freeing metallic vapors. These vapors may ultimately short out the insulators.

For leading the signal from a thermocouple wire to a measuring instrument extension wires are often used. These are wires of the same composition as the thermocouple wires, but are usually of smaller diameter. The composition of thermocouple material and extension lead wire must be the same if spurious emf's are not to be introduced into the circuit. For high temperature applications, the cold junction is usually maintained at the point of exit from the hot region by artificial cooling so that ordinary wires suffice for leading the signal to the measuring instrument.

6.4.7. Measurement of Emf

Any of the standard techniques for the measurement of emf may be used as long as they have the requisite accuracy. However, at high temperatures those schemes which require drawing a current from the circuit should be avoided. This is because progressive resistance changes of the thermocouple and leads due to physical and chemical aging or corrosion must be expected. If a multiple channel recorder is to be employed it should be of the potentiometric type.

Dike gives a resume of Leeds and Northrup type instruments. They are fairly characteristic of what is commercially available.

6.4.8. Standardization and Calibration

Calibration of a thermocouple is usually accomplished by comparison with a standardized thermocouple in the moderate temperature ranges and against an optical pyrometer in the higher ranges. Calibration must be carried out under environmental conditions as close as possible to those of the

application, allowing the couples to come to equilibrium. Standard couples may be certified by the National Bureau of Standards and are usually standardized by taking a number of freezing point curves of selected chemical elements.

In using the optical pyrometer as a standard, the usual precautions concerning intervening vapors, emissivities, and collimation must be considered.

Roeser and Wensel ("Temperature, Its Measurement and Control", Reinhold, N.Y., 1941, Vol. 1, p. 284); Forsythe (ibid., p. 1115) and Weber ("Temperature Measurement and Control", Blakiston, Philadelphia, 1941) have summarized calibration procedures and the precautions which must be observed.

6.4.9. Limitations of Thermocouples

Disregarding the element of cost, there are still applications for which other methods of temperature measurement are preferable to thermocouples. For example the resistance thermometer may be much more accurate in measuring temperatures in the low to moderate temperature range, and the complexity of its recording equipment may be less. In situations where they are applicable, the radiation and optical pyrometers compete favorably with the thermocouple, and in fact are the standard of temperature measurement above 1063°C.

The main limitations on the use of thermocouples at high temperatures involve the useful lifetime of the sensing element and the rate of contamination or change of calibration. Each application and environmental condition will dictate the useful lifetime, and the accuracy desired will determine the allowable drift. Acceptable lifetimes may vary from seconds to years. For example, in measuring liquid metal temperatures it may be sufficient to read a temperature by a "dip" test, whereas in furnace applications thermocouples may have to be installed in inaccessible locations.

In the main it may be said that raising the operating temperature of a couple will shorten its life at a progressively greater rate. Generally, operating the thermocouple in a non-corrosive atmosphere (at any temperature) will increase its life greatly.

CHAPTER VII

RECOMMENDATIONS

7.1. Temperatures to 1800°C

It is now appropriate, in the light of the data assembled in Chapters II - VI, to consider a solution to the problem of temperature measurement in the reactor.

In view of the great range of temperatures to be found in it, it seems reasonable to divide the reactor into zones on the basis of anticipated maximum temperature. In each zone we will endeavor to install a temperature measuring device which will a) register temperatures up to the anticipated maximum temperature and somewhat above it, b) will have an adequate lifetime at the anticipated maximum temperature, and c) will register temperatures through a considerable range below the anticipated maximum temperature.

In view of the preceding discussion, it will be fairly obvious that thermocouples are the best temperature measuring device for the reactor. We therefore propose that consideration of all other devices be postponed until thermocouples have been thoroughly investigated experimentally.

Current practice has been to use thermocouple wires embedded in a ceramic insulator and contained in a swaged stainless steel sheath. For the lower temperatures, we believe that this method is entirely appropriate and may well be continued. For the range from -200°C to 700°C, the iron-constantan thermocouple can be used. From 700°C to 1100°C, chromel-alumel thermocouples can be used. Aluminum oxide is the best insulating material. At 1100°C, we are getting to the upper limit at which stainless steel can be used. Thermo-Electric Co.'s catalog gives 2100°F (1150°C) as the highest rating for any stainless steel (this is for alloy No. 310).

Above 1100°C, the Le Chatelier thermocouple is recommended to about 1500°C. Melting points of stainless steels have been reached or passed, so that if a sheath is desired, a different metal must be used. Zirconium and molybdenum come to mind. Both must be well protected against oxygen and water. Molybdenum is available in swaged or seamless tubes.

The insulator at temperatures up to 1500°C can still be alumina. High-sintered alumina still has a resistivity above 10^5 ohm-cm at that temperature.

Because of the high cost of platinum and rhodium, it may prove necessary to use copper wire for the extensions, from the cold end of the reactor through the pressure shields to the recording device. In that case, a compensating couple will be necessary because of the large temperature difference between the cold portion of the reactor and the instruments.

Above 1500°C, we are getting into the temperature range in which no thermocouple, and few materials in general, can be expected to have unlimited lifetime. Therefore, it is advisable to consider each thermocouple set-up as having an average finite lifetime at each temperature. We therefore envisage an experimental program which is designed to determine the temperature - lifetime relationships of a number of thermocouples, and to select the most suitable for the purposes of the reactor.

For the temperature range 1500 - 1800°C, it is possible to use the thermocouple $Pt_{80}Rh_{20}$ vs. $Pt_{60}Rh_{40}$, developed by Land and Jewell (See Chapter V). This instrument has the advantage of needing little or no protection against nitrogen and carbon, though embrittlement by hydrogen is a possibility. It is commercially available (in England) but expensive. The neutronic properties are better than those of iridium - containing thermocouples. The failure temperature is 1885°C, so that local overheating may cause failure quite easily. It is therefore possible that use of this thermocouple may not be worth while, as it will probably be advantageous to keep the number of types of instruments as low as possible. We recommend use of this thermocouple in the event that other thermocouples, stable to higher temperatures, do not work out as well as expected.

7.2. High Temperature Thermocouple Elements

For the range above 1800°C, it is no longer possible to fall back on previous industrial practice. While (as we have seen) considerable laboratory experience exists, each thermocouple has certain disadvantages. We have not been able, on the basis of a literature survey alone, to come up with a definite decision.

Let us list the properties, and especially the disadvantages, of each type of thermocouple.

Tungsten - Molybdenum

Theoretical top temperature: 2620°C

Emf characteristics: Admittedly the emf and TEP are

low. We do not regard the loss of precision introduced by this as serious, since good potentiometers are available. However, inaccuracies due to various spurious effects would become more important.

Because of the change in polarity at 1200°C, no temperatures lower than this could be measured.

Chemical stability: Fortunately oxygen can be assumed to be absent or present only in very low concentration. Reaction with nitrogen is not expected to be serious, as thermodynamic data indicate that molybdenum and tungsten nitrides are unstable at high temperatures and are formed only very slowly at lower ones. This leaves contamination by carbon. This is a very serious problem because of the effect of carbide formation. Above 2200°C (the eutectic temperature of Mo - Mo₂C) carbide formation may result in failure, but at much lower temperatures the presence of carbon causes emf drift, so that all readings become unreliable. Simons (J. Iron Steel Inst. 175, 402 (1953)) reports a drift of 25°C in 15 min. at 1700°C. This is undoubtedly due to carbide formation. The carbide is also metallic and therefore can also form thermoelectric junctions. If the thermocouple is installed in the reactor, there is no way to tell whether a drift is taking place. Therefore we consider protection from carbon necessary not only for this couple but for any one containing W or Mo.

Actual operating temperature: If protected from carbon, there is no reason why the W vs. Mo couple should not be used up to 2500°C.

Embrittlement: Again this is a trait common to all couples having tungsten as one element. We see no present remedy for embrittlement. "Non-sag" treatment can remove some of the tendency to fail at high temperatures, but the wires will remain brittle after cooling. We believe that it is not possible to avert this embrittlement, and that we had best give up all notions of re-using the same thermocouple over several thermal cycles. We believe that embrittlement before use can be avoided if we a) do not weld the two wires together but twist them and clamp or swage them together under high pressure, and b) do not calibrate each couple but rather calibrate one or more couples for each batch of wire.

Neutronic properties: Good for Mo, fair for W.

Stability of emf: Good in any one wire in absence of carbon. Emf apparently reproducible in any one batch of

wire, but each batch requires calibration.

Wire size: Simons, Hamstead and Burton (J. Iron & Steel Inst. 175, 402 (1953)) recommend that 0.3 mm wires be used, as they are the largest size that can easily be bent and twisted. We should, however, like to try a larger size wire if at all possible, and we believe that with a certain amount of patience it can be twisted and clamped (especially the molybdenum). We saw in Chapter IV that many of the spurious signals, induced by radiation, are directly proportional to the resistance of the couple. Perhaps even more important, shorting of the couple through the failing insulation will be proportional to its resistance. It is therefore important that the resistance be kept low, and therefore we should use the thickest wires compatible with proper design and the neutron balance of the reactor.

Troy and Steven (NEPA - 1580) used W and Mo wires 20 to 35 mils thick (0.5 to 0.8 mm), and we recommend use of similar wires.

Other thermocouples will be viewed in terms of their advantages and disadvantages compared to the W vs. Mo couple.

W-Mo alloy vs. W:

Emf: much the same as W vs. Mo.

Top temperature: Higher if protected from carbon. But in presence of carbon a C-W-Mo eutectic may develop, whose melting point should be lower than that of the eutectic in the C-Mo system.

Temperature of change in polarity: About the same as W vs. Mo.

Chemical stability: Needs protection from carbon just like the W vs. Mo couple.

Embrittlement: The same as W vs. Mo.

Neutronic properties: Somewhat inferior to W vs. Mo.

Chief advantage: Higher melting point (up to 3000°C)

Chief disadvantages: a) Higher cost and lesser availability, b) possibility of differential evaporation from W-Mo element, resulting in a change in composition and emf.

W-Mo-Fe alloy vs. W.

Emf: much higher than W vs. Mo.

Temperature of change in polarity: greatly reduced.

Top temperature: higher if protected from carbon, but again may form eutectics if not protected.

Chemical stability, embrittlement: same as W vs. Mo.

Neutronic properties: slightly poorer than W vs. Mo.

Chief advantages: a) higher emf, b) greater temperature range (lower reversal point and higher melting point).

Chief disadvantages: differential evaporation may change emf. This is especially important since Fe is much more volatile than either W or Mo.

W vs. Ir

Theoretical top temperature: 2440°C. Actual top probably a little lower.

Emf characteristics: excellent.

Embrittlement, chemical attack: still the same as W vs. Mo. Troy and Steven (NEPA - 1580, p. 21) found an emf drift, at 2000°C, of 0.1 millivolt (4.2°C) per minute when this couple was heated in argon in the presence of graphite.

Neutronic properties: poor.

Chief advantage: good emf characteristics.

Chief disadvantages: a) cost, b) very sensitive to hydrogen, c) high thermal neutron cross section.

W vs. Ta and W vs. Nb

Emf characteristics in vacuum are good, but we do not propose to consider these thermocouples because of the high affinity of Ta and Nb for gases. This has been shown (Troy and Steven, NEPA-1580, p. 14) to cause such strong emf drift that they are unusable.

W vs. Re

Theoretical top temperature: 3170°C

Emf characteristics: not known in detail, but reported to be superior to W vs. Mo. (C. T. Sims, Metal Industry, 87, 381(1955))

Embrittlement, chemical attack: Unknown. Certainly not better, and probably not worse, than W vs. Mo.

Neutronic properties: Considerably poorer than W vs. Mo.

Advantages and disadvantages: The properties of this thermocouple are so little known that no estimate can be made.

It would be very interesting to know more about the embrittlement characteristics of rhenium wire and about its resistance to attack by nitrogen, hydrogen and carbon. If these prove superior to tungsten, as seems probable (see Chapter V), it may be possible to construct a thermocouple without tungsten, which will not be subject to the same problems as the tungsten - containing instruments. Such an investigation should definitely be included in any wider experimental program.

Summing up, we say that at our present state of knowledge we see no thermocouple which has a clear advantage over the tungsten vs. molybdenum couple in the range 1800°C to 2400°C. Use of the W vs. Mo couple is contingent upon: a) use of sensitive instruments and elimination of spurious signals; b) protection from carbon; c) maximum avoidance of embrittlement. We believe that an experimental program should emphasize the fulfillment of these conditions.

7.3. Insulators for Thermocouples

Troy and Steven found that sapphire (monocrystalline alumina) was a satisfactory insulator to 1900°C. At higher temperatures only a few oxides retain their insulating properties, and even those only to rudimentary degree: magnesia, beryllia and possibly calcia. Data on calcia are scarce because it reacts so readily at low temperatures with H₂O and CO₂ and at high temperatures reacts with carbon to form calcium acetylide (calcium carbide, CaC₂). Its melting point is extremely high (2800°C). We have found no reference relating to its high temperatures resistivity, but it may be assumed to be high for the pure material with large particle size.

Magnesium oxide is much better known as a high temperature material, and is manufactured into thermocouple tubing by the Norton Company under the trade name "Magnorite". There is considerable disagreement in the literature about

its high temperature resistivity (see Chapter III) and it appears to be highly sensitive to impurities. Unfortunately, Magnorite contains 3 - 5% of impurities, mainly silica, and special high-purity ware may need to be ordered. The melting point of MgO is high (2600 - 2800°C), but its vapor pressure is appreciable above 2300 - 2400°C. Reaction with carbon is rapid at and above 2000°C. The coefficient of expansion of magnesium oxide is rather high, so that its thermal shock resistance is not good. If MgO is sintered at very high temperatures it can be comparatively gas tight, and its resistivity at high temperature is much improved (see Fig. 3.6 for this phenomenon in alumina).

Beryllium oxide (BeO) would seem to be the most eligible insulating material in many ways; it is, however, much more expensive than magnesia and also presents a health hazard. The melting point is 2550°C. The thermal expansion is moderate, and the thermal conductivity quite good; therefore thermal shock resistance is high. Electrical conductivity, on the other hand, is low up to high temperatures. It is believed that refractory bodies of beryllium oxide can be obtained on order. High-density beryllia bodies can be obtained by firing at 2000°C. Vapor pressure is lower than that of MgO. Resistance to reduction by carbon is also good, but water vapor will attack the material. Neutronic properties are excellent. Beryllia becomes fairly plastic above 2000°C, and must not be subjected to any load. Possibly it may not support its own weight for protracted periods.

Suppliers for high purity alkaline-earth oxides: It is believed that the Norton Company can make high-purity refractories on order; but its representative in Los Angeles or even the main office in Worcester, Mass., must be approached on this matter. Degussa Co. in Germany advertises tubing and other ware made to order from 99.5% BeO and from 96 - 97% MgO. They are represented in this country by the Liasson Co. of New York.

Thermal neutron cross-sections of alkaline earths and oxygen:

Element	barns/atom	cm ² /g
Be	0.009	0.0006
Mg	0.059	0.00146
Ca	0.43	0.0065
Sr	1.16	0.0080
Ba	1.17	0.0051
O	under 0.0002	under 7.5×10^{-6}

The shape of the insulator may also be of considerable importance. In view of the greatly lowered electrical resistance of all insulators at 2000°C and over, the contact area between wires and insulation should be held to a minimum. We believe that this can best be achieved by forming beads, of "fish-spine" or diamond shapes, which will touch the wires at a knife-edge only, at first. (Of course, we must expect such edges to become rounded when sintering temperatures are reached.) The diameter of the beads should be slightly over one-half the diameter of the instrumentation cavity, and the beads can be spaced alternately on the wires. Upper and lower surfaces of the beads should be at different angles from the horizontal, so as to prevent intimate contact between them.

7.4. Protective tube

In view of the high temperature sensitivity to carbon of tungsten and molybdenum, as well as the alkaline earth oxides, it appears quite essential to us that the thermocouple be protected from contact with carbon, carbon vapor, and carbides. Four methods of doing so suggest themselves:

- a) Embedding the wires in a refractory insulator.
- b) Coating the wires with a protective material.
- c) Containing the entire couple in a protective tube.
- d) Coating the walls of the instrumentation cavity.

Of these methods, we can immediately discard a), because the resistance between the thermocouple wires would be inadequate. Method b) was tried and rejected by Troy and Steven (NEPA-1580, p.23), who found that silicon monoxide did not provide adequate protection against oxygen. Any compound used for coating the wires should not have metallic conductivity, as this would create one or more new thermocouples. This greatly restricts possible coatings. Moreover, to date all high-temperature coatings have had quite high porosity. Method c) appears more promising. A protective tube might be made of an insulator, such as beryllium oxide, or of a metallic refractory, such as zirconium nitride. Fabrication difficulties would probably be less with the former. On the other hand, a beryllium oxide tube would probably have more residual porosity than a zirconium nitride tube. We believe that a protective tube would not be the best solution. A long and narrow tube, extending from a hot to a cold region, would undergo great thermal stress and would be almost sure to crack. But in this case (unlike that of the usual thermocouple twin bore

tube) effective functioning depends on the integrity of the tube. We therefore favor method d), the coating of the walls of the instrumentation cavity. For this purpose we favor zirconium nitride, which can be deposited in situ. The carbon surface is to be heated to about 2000°C in an atmosphere containing zirconium chloride vapor and ammonia or nitrogen and hydrogen. Instructions for this are given by K. Moers (Z. anorg. allgem. Chemie 198, 243 (1931)) and by I. E. Campbell, C. F. Powell, D. H. Nowicki and B. W. Gosser (J. Electrochem. Soc. 96, 318 (1949)). Zirconium nitride is the most stable of the nitrides at high temperatures and also has admirable neutronic properties. We suggest that the deposition of ZrN can be carried out on each of the ten layers in the reactor separately. If this proves impractical, zirconium carbide coating may be used instead; but it is a poor second, since it is a source of carbon only slightly inferior to carbon itself.

7.5. Summary of Recommendations for High Temperature

- 1) The high temperature measuring device should be a thermocouple.
- 2) Tungsten and molybdenum elements are recommended initially, but an investigation of other elements is appropriate.
- 3) Calibration of one or two sets of wires is to hold for an entire batch, if uniformity within the batch is established.
- 4) Wires are to be twisted together and clamped under high pressure, to avoid making a weld. Recommended wire thickness is 0.5 - 0.8 mm.
- 5) Insulation is to consist of beads, of beryllia or pure magnesia, diamond or fish-spine shape, made under high compacting pressure and fired at 2000°C or higher, spaced alternately.
- 6) To protect wires and insulation from attack by carbon, the instrumentation cavities are to be coated with zirconium nitride, deposited from a mixture of $ZrCl_4$, N_2 and H_2 .

7.6. Recommendations for Experimental Program

The first task of an experimental program must be to construct and test a thermocouple according to the above specifications. The second task is to find methods of improving it.

For the first aim, it is necessary to draw up specifications and to order the wires and beads. Suppliers must be located, and it will probably be wise to interview them in person. Then, a furnace and related facilities must be built and tested. The deposition of zirconium nitride on carbon is to be carried out and studied. Tungsten-molybdenum thermocouples are to be made and calibrated. Calibration should be with an optical pyrometer which is reliable to high temperatures. Constancy of the calibration in any given batch of wire must be checked. Properties of the insulating material at high temperature should be determined. Lifetime tests of the thermocouple at different temperatures and environments must be run. Constancy of emf in presence of insulator and coated and uncoated carbon tubes must be examined. Other coatings can be examined.

After this, the functioning of our original thermocouple will be fairly well known, and other metal combinations can be studied. We believe that tungsten-molybdenum - iron alloys and rhenium offer outstanding possibilities.

7.7. The "Minimum Thermocouple"

In order to accelerate the experimental program, we had considered the possibility of examining, at first, a "minimum thermocouple", which is to be constructed of commercially available materials only. It would have consisted of tungsten and molybdenum wires and double-bore Magnorite tubing, and would have been unprotected against carbon. Further study, however, has convinced us that protection against carbon is absolutely necessary, and that Magnorite probably will not be a satisfactory insulator. However, if we add a beryllia protective tube, available on order from Degussa in Hanau, Germany, we may have an adequate "minimum thermocouple". An experimental program which includes the "minimum thermocouple" will be somewhat more expensive, but would be expected to give at least an interim result rather quickly.

Addendum

After completion of this report, we received some additional data on the properties of rhenium metal, through the courtesy of Mr. C. T. Sims of the Battelle Memorial Institute. Figure 7.1 shows calibration curves for the tungsten-rhenium and molybdenum-rhenium thermocouples, with formulas of the empirical curves fitted to the data. Mr. Sims confirms that rhenium remains relatively ductile after exposure to high temperatures. The breaking stress at 2000°C is given as 1100 psi, with rupture occurring after 12.3 hours and an elongation of 4.4% when oxidation was prevented. The 100-hours rupture stress is estimated as 800 psi at 2000°C. The work hardening rate is high, especially after swaging and wire drawing. Rhenium is very little attacked by molten copper at 1180°C.

The electromotive force of a platinum-rhenium thermocouple to 1600°C is given by the empirical equation

$$E = 1.56 - 0.90 \times 10^{-2} T + 1.29 \times 10^{-5} T^2$$

where E is in millivolts and T in degrees Kelvin.

Further references: Journal of Metals, August 1956, p. 1, Trans. AIME 203, 168 (1955).

Fig. 7.1. Experimental Data and Matching Curves for Tungsten-Thenium and Molybdenum-Rhenium Thermocouples.

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