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TEMPERATURE MEASUREMENTS IN CRYOGENICS

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TEMPERATURE MEASUREMENTS IN CRYOGENICS *

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I. INTRODUCTION

The word cryogen is derived from the two Greek words kryos- and -gen, meaning literally "the production of icey-cold". More simply, a cryogen is a refrigerant. Cryogenic is the adjective form of the noun, and signifies physical phenomena below -150°C (123°K). This is the approximate temperature at which physical properties of many substances begin to show significant variation with temperature (1).

Of natural importance to research, engineering design and operation at the low temperatures is the measurement of the temperature itself. The purpose of this paper is to discuss this question in a reasonably broad context within the framework of the 1968 state-of-the-art.

The selection of a suitable temperature sensing element depends on a number of important considerations. Perhaps most fundamental of all is the accuracy required in the measurement. Entirely different techniques will be employed, for example, if

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*Prepared for Measurement Techniques in Heat Transfer, AGARD Publication, Edited by Professor E. R. G. Eckert, 1969.

an accuracy of $0.001^{\circ}K$ is necessary or if $1.0^{\circ}K$ is sufficient. Other significant factors include the influence of transient effects, sensitivity, type of readout, nature of signal, availability or desirability of recording and control, durability, stability and ruggedness of the sensing element, and of course, replacement, interchangeability and cost.

As of this writing (1968) no internationally accepted standard for temperature measurement exists below the defining fixed point temperature for oxygen ($90.18^{\circ}K$, $-182.97^{\circ}C$)*. This situation is expected soon to be resolved, however, with the adoption of a uniform scale sometime during 1968 or 1969 which will extend the range of the present international scale to $13.8^{\circ}K$ (4). Below this temperature no international scale will exist for some time although convenient and practical methods for measurement of temperatures to $0.2^{\circ}K$ and lower have been developed during the past decade. These will be included in this discussion.

This paper will cover the following topics: the concept of temperature, the absolute thermodynamic temperature scale, the gas thermometer, the International Practical Temperature Scale, temperature scales below $90^{\circ}K$, thermocouples, resistance thermometry, and magnetic thermometry or adiabatic demagnetization. The basic principles as well as practical considerations of measurement will be presented.

It will probably be of value at the outset if the principal sources of reference for cryogenic temperature measurement are listed. Most of these will be cited from time to time in the body of this paper and hence are also included among the references. However, in view of their value it is important to have them conveniently listed, as follows:

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*In 1960, the 11th General Conference on Weights and Measures dropped the notation "Fundamental" and "Primary" fixed points and adopted instead the terms "defining fixed points" and "secondary reference points" for the various two-phase reference states for temperature calibration (2, 3).

1. Temperature, Its Measurement and Control in Science and Industry, Reinhold Publishing Co., American Institute of Physics.
   - (i) Vol. I, 1941, 1343 pages.
   - (ii) Vol. II, Edited by Hugh C. Wolfe, 1955, 451 pages.
   - (iii) Vol. III, Charles M. Hertzfeld, Editor-in-Chief, 1962.
     - a. Part I, "Basic Concepts, Standards and Methods", F. G. Brickwedde, Editor, 838 pages, 1962.
     - b. Part II, "Applied Methods and Instruments", A. I. Dahl, Editor, 1087 pages, 1962.
     - c. Part III, "Biology and Medicine", J. D. Hardy, Editor.

2. R. B. Scott, Cryogenic Engineering, Van Nostrand Co., 1959.

3. R. W. Vance and W. M. Duke, Editors, Applied Cryogenic Engineering, John Wiley & Sons, 1962.

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5. Encyclopedia of Physics, Edited by S. Flügge, Vol. XV, Low Temperature Physics II. "Adiabatic Demagnetization", by Dirk De Klerk.

6. Journal of Research, NBS, Section A (Physics and Chemistry); Section C, (Engineering and Instrumentation).

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9. Metrologia, Vol. 1-4, 1964-68 (to date), Published under the auspices of the International Committee of Weights and Measures.

10. The International Temperature Scale (ITS)
    - a. 1927 ITS
      G. F. Burgess, "International Temperature Scale", J. Research NBS, Vol. 1, p. 635-37, 1925.
      See also, Temperature, Vol. 1, 1941, p. 21-23.
    - b. 1948 ITS
      - (i) J. A. Hall, Temperature, Vol. 2, 1955, p. 115-141.
      - (ii) H. F. Stimson, "The International Temperature Scale of 1948", J. Research NBS, Vol. 42, p. 209, 1949.
    - c. 1960 Text Revisions of the 1948 ITS
      H. F. Stimson, "International Practical Temperature Scale of 1948. Text Revision of 1960", J. Research, NBS, Vol. 65A, No. 3, 1961. See also, H. F. Stimson, "The Text Revision of the International Temperature Scale of 1948", Temperature, Vol. 3, Part I, 1962, p. 59-67.

II THE CONCEPT OF TEMPERATURE

The concept of temperature is old and doubtless stems from the desire to attach definite numerical quantities to a feeling of hotness or coldness. Galileo (1600) was one of the earliest to experiment with the design of an instrument to which a scale was attached for the purpose of indicating a numerical temperature. These early instruments were called "Thermoscopes" and were said to have measured "degrees of heat". Today, 370 years later, we find the art of temperature measurement highly developed but under continued study. The basic standard instrument presently employed is the Gas Thermometer in some respects similar to the first of Galileo, but registering in degrees of absolute temperature, not in degrees of heat. This distinction was made only after the discovery of latent heats by Joseph Black and James Watt (1764) and the enunciation of the Second Law of Thermodynamics (about 1850).

A sensation of warmth or cold is of little value to the physical world when measurement and reproducibility of temperature is required. While it is of small value in measurement, the subjective sense might be used to indicate an equivalent "hotness" or "coldness" of two separate bodies. It is common experience, for example, that two blocks of iron, one taken from an ice bath, and the other from a furnace, will approach the same feeling of warmth if they are brought into thermal contact with one another. Of course, great doubt might reasonably be raised concerning the validity of the conclusion of equal "hotness" if the indications were taken by touching the blocks with the skin of the hands. However, other schemes could be used which are less subjective and would produce the same result. One might not use the hands but use, for instance, a small rod of silver and place it in intimate thermal contact with each iron block. The increase or decrease in the length of the silver rod could then serve as an indicating device since by experience it is known that this dimension will change as the rod is heated or cooled; also, when the heating or cooling ceases the changes in length also cease. Hence, after some period of time following the bringing of the two blocks together very careful observations of the length (say with a powerful microscope) would show no subsequent change in length of the rod when it was placed successively in contact with each block. Furthermore, if the block and the silver rod were mutually in thermal contact with each other and with nothing else, the length of the rod would be the same when it was attached to each block.

This would define the measureable state known as the Equality of Temperature. The silver rod might also be called a temperature meter or, more simply, a thermometer. The process just described has led to a generalization, or law, called the Zeroth Law of Thermodynamics. This law, which is the logical basis of all temperature measurement, may be stated as follows:

> Two bodies (the iron blocks) at the state of equality of temperature with a third body (the silver rod) are in a state of equality of temperature with each other.

Returning to the silver rod, which has been called a thermometer, one might be led to attempt to assign a sort of numerical scale to its length so as to convert its elongation or contraction into some definite, reproducible scale of temperature. It is apparent that this could be done with no particular mechanical difficulty, although some amplification of the changes in the length might be necessary for convenience in use. The selection of the type and magnitude of the units on this scale is wholly arbitrary. It is known that when the rod is placed into a bath of ice and liquid water or in a bath of saturated steam at constant pressure and allowed to reach a state of equality of temperature with the bath in each instance, it does not change in length, but has a greater length in the steam than in the ice. Because the length

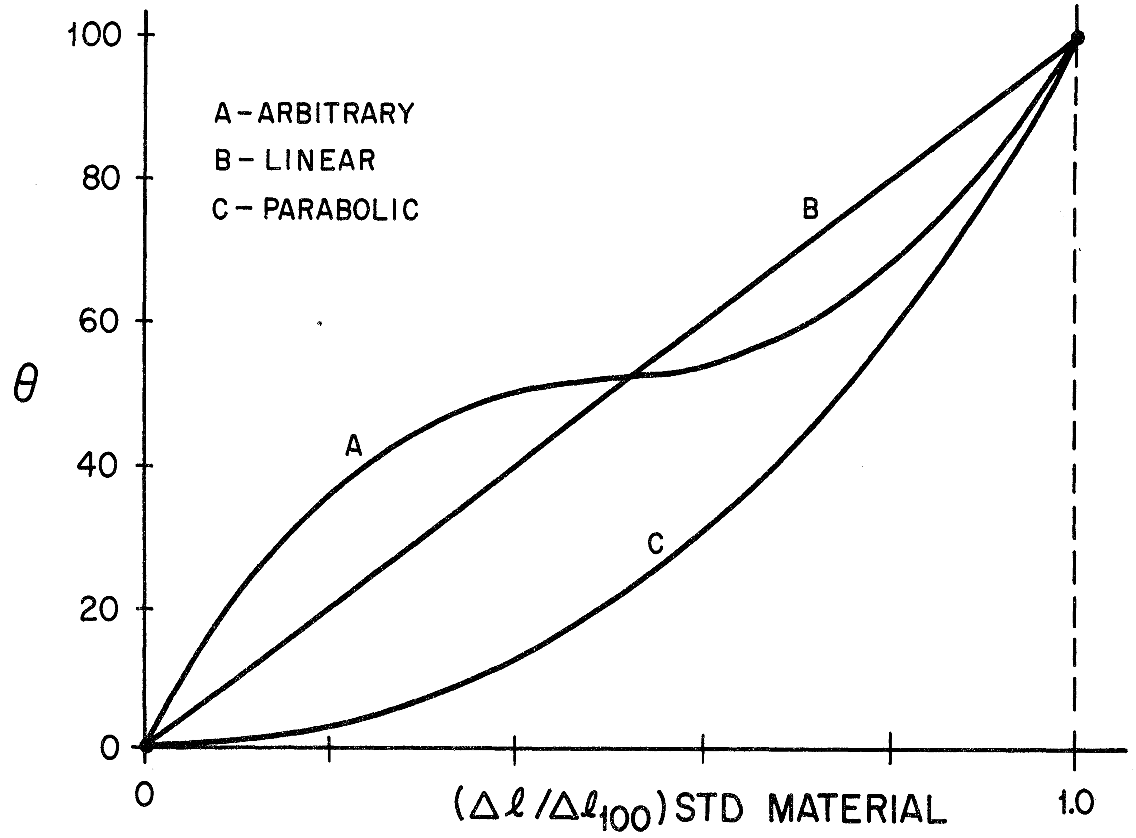

Figure 1. Arbitrary Scales of Temperature.

is greatest in the steam bath, it would seem reasonable to assign it the greatest level of temperature, although this is arbitrary and the reverse has been done, as in the Celsius Scale (1740). The temperature of the ice bath, for convenience, then could be established as zero, while that of the steam bath could be taken as 100. This would define a difference of 100 degrees of temperature between these two fixed points. The final decision to be made in the construction of a temperature scale is the selection of an interpolation device to be employed to obtain the level of temperature and the magnitude of the unit degree of temperature in this interval from observations of the length of the rod. Freedom of choice is to be had in this selection also. That is, any curve connecting the 0 and 100 degree points in Figure 1 may be chosen as the interpolation device.* Some curves obviously are more convenient than others. One would find a multivalued curve quite inconvenient to use, for example.

Three curves or interpolating devices are shown in Figure 1. The abcissa is the ratio Δl, the difference between the length of the rod at intermediate levels of temperature and at the ice bath temperature to Δl_{100}, the difference between its length in the steam bath and the ice bath. Clearly, there are an infinite number of different scales one could select. One could take curve B which is a straight line joining the fixed points of temperature, and have a linear scale which, if the silver rod were used as the thermometer, could be called the linear silver scale of temperature. Denoting this as the θ scale, the relationship between length changes and θ is the simple one:

$$\frac{\Delta l,}{\Delta l_{100}'} = \frac{\theta}{100}$$

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*The ordinate in Figure 1 is divided arbitrarily into 100 equal divisions between 0 and 100. A scale of temperature is established both by the curves and the scale of the ordinate, as is evident, but freedom of choice is preserved if one fixes the scale of the ordinate and allows the curves to have an arbitrary shape.

A question which might be raised now is this: Is this θ scale fundamental or if only the material in the rod is changed, will a different scale result? It turns out that this scale, indeed, is not fundamental and different temperatures would be obtained with, say a linear copper scale. This important consequence of physics may be demonstrated as follows.

Consider that a linear silver scale has been adopted for reference with the silver rod being selected as the primary standard thermometer. All temperatures will be referred to this scale which we have called θ. We may take any property of matter which is measureable and which changes with heating and cooling as the indicating quantity. Changes in such properties may be called $\Delta p = p - p_0$ where p_0 is the magnitude of the property p at the level of temperature of the ice bath. In a rod of any other material the temperature coefficient of p based on the linear silver scale of temperature is defined as:

$$\alpha = \frac{\partial p}{\partial \theta} \quad . \tag{1}$$

Hence,

$$\Delta p = \int_0^{\theta} \alpha d\theta \quad , \tag{2}$$

Also,

$$\Delta p_{100} = \int_0^{100} \alpha d\theta \quad , \tag{3}$$

so,

$$\frac{\Delta p}{\Delta p_{100}} = \frac{\int_0^{\theta} \alpha d\theta}{\int_0^{100} \alpha d\theta} \quad , \tag{4}$$

Each of the integrals in equations (2) and (3) may be expressed as follows:

$$\int_0^\theta \alpha \, d\theta = \bar{\alpha}_\theta \cdot \theta ,$$

$$\int_0^{100} \alpha \, d\theta = \bar{\alpha}_{100} \cdot 100 ,$$

where $\bar{\alpha}$ is the average value of α in a range of temperature.

Equation (4) is then written:

$$\frac{\Delta p}{\Delta p_{100}} = \left(\frac{\bar{\alpha}_\theta}{\bar{\alpha}_{100}}\right) \frac{\theta}{100} \tag{5}$$

It is a matter of experience that any property which changes with heating or cooling (such as length) does not do so at a constant rate of change in terms of the temperature of the scale of temperature employed to measure it. The exception, of course, is the property of the material used to define the linear scale of a selected standard temperature scale. But this is trivial.

A linear scale based on $\frac{\Delta p}{\Delta p_{100}}$ of any other material would be written:

$$\frac{\Delta p}{\Delta p_{100}} = \frac{t}{100} , \tag{6}$$

where t is the temperature on the linear scale pertaining to this other material. Combining equations (5) and (6) we have:

$$\frac{\bar{\alpha}_\theta}{\bar{\alpha}_{100}} \left(\frac{\theta}{100}\right) = \frac{t}{100}$$

or

$$\frac{\theta}{t} = \frac{\bar{\alpha}_{100}}{\bar{\alpha}_\theta} \tag{7}$$

Equation (7) is the expression relating the linear scales of temperature (θ and t) of two different materials.

We find therefore, except in that rather improbable instance of $\bar{\alpha}_{100}/\bar{\alpha}_{\theta}$ being universally unity for all materials, a fundamental difference must be expected between scales of temperature defined in the manner outlined here. It is only for the case of a constant value of the temperature coefficient of change of a temperature dependent property that would produce a value of $\bar{\alpha}_{100}/\bar{\alpha}_{\theta}$ of unity and exact agreement between all linear scales of temperature. This circumstance cannot reasonably be expected in nature.

We conclude from these arguments that thermometers constructed after the fashion described, while useful as operational tools to measure and reproduce levels of "temperature", would each produce different values of temperature when used to measure the state of a given system. This is roughly the present state of thermometry for temperatures below 90°K. In this range there presently exists no accepted standard thermometer nor scale although many working groups have defined their own "wire" scales (5). However, these scales all differ from each other. This is demonstrated by Hust (6) in Figure 2, where temperature scales from several different laboratories in the U.S., Canada and Europe are compared with a scale created by the National Bureau of Standards (NBS-55) in the range 10°K to 90°K. This scale is formed by lowering all temperatures on a previous scale (NBS-39), references 7 and 8, by 0.01°K.

III THE ABSOLUTE (THERMODYNAMIC) TEMPERATURE SCALE

In 1848 Kelvin extended the reasoning of Carnot and demonstrated the existence of a scale of temperature which, unlike those shown in Figure 1, would be completely independent of a thermometric substance. Hence, such a scale is called an "absolute" scale and being deduced from the laws of thermodynamics only, it is known as the

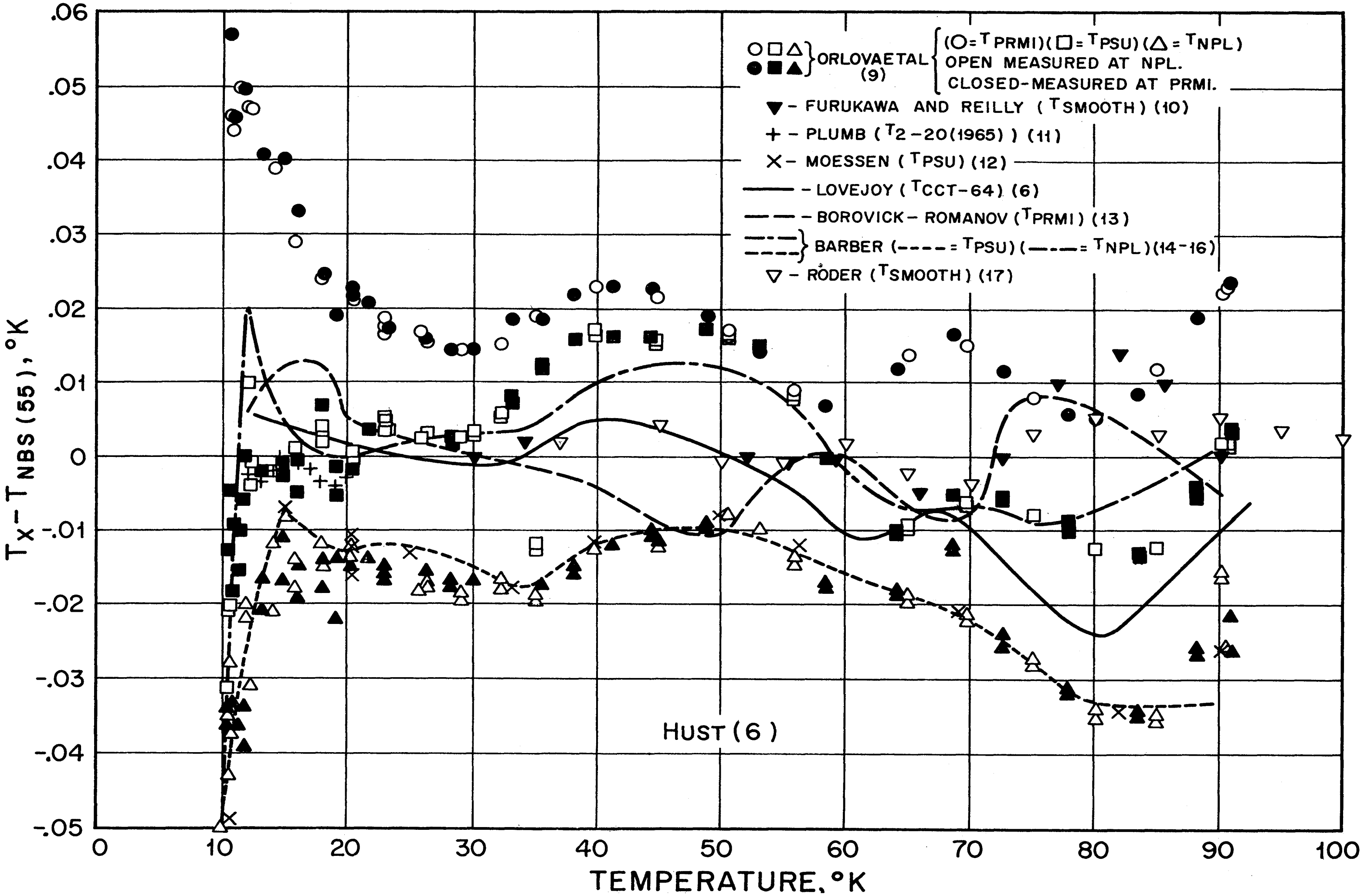

Figure 2. Comparison of Low Temperature Scales (10 to 90°K), Including PSU, NPL, PRMI, CCT-64, and NBS(2-20) 1965, with Respect to NBS(55) Scale. PSU = Pennsylvania State University; NPL = National Physical Laboratory (England); PRMI = USSR; CCT = Advisory Committee on Thermometry, International Committee on Weights and Measures; NBS = National Bureau of Standards (USA).

Absolute Thermodynamic Temperature Scale. Actually, there are an infinite number of such scales of temperature possible, the final one selected being a matter of convenience. The scale we employ today is not the first scale Kelvin proposed but rather his second proposed scale. His first scale had $+\infty$ and $-\infty$ as the upper and lower bounds of temperature, which is inconvenient, but his second scale remedied this having bounds at 0 and $+\infty$.

From the Second Law of Thermodynamics, Kelvin was able to show that the ratio of the heat quantities from a cyclicly operating reversible heat engine could be written:

$$\frac{Q_1}{Q_0} = \frac{f(t_1)}{f(t_0)} , \qquad (8)$$

where f(t) denotes an unknown but arbitrary function of temperature alone. The form of this function is specified by the scale of temperature chosen and can therefore have an infinite number of possible forms. When a specific form is chosen a scale of temperature is then defined which is independent in its definition of any thermometric substance. The reversible engine becomes the thermometer but the nature of such a device, as well as the ratio of its heat quantities, is quite independent of the fluid - the thermometric substance - employed to operature the engine. Kelvin selected as his second scale the simple function $f(t) = T$, where T is called the Absolute Thermodynamic Temperature and is given in degrees Kelvin. Hence equation (8) becomes

$$\frac{Q_1}{Q_0} = \frac{T_1}{T_0} , \qquad (9)$$

where T_1 and T_0 are the Kelvin temperatures of the heat source and the heat sink, respectively.

The complete definition of the Kelvin scale, including the establishment of the size of the degree, is dependent on a single arbitrary constant. Originally this was accomplished by defining the difference between the steam and ice points as 100 degrees Kelvin, exactly. The absolute temperature of the ice point was then determined experimentally using a gas thermometer. Since 1954, however, the arbitrary constant selected for defining the scale has been the temperature of the triple point of water, taken to be 273.16°K exactly* (2, 3). The size of the degree in the interval between the ice and steam points now must be determined experimentally. This interval will certainly not be exactly 100°K but will probably be within 0.001°K or less of this value.

The dependence of the Kelvin scale on a single arbitrary constant may be shown by a simple argument. For fixed thermal states at, say, T_1 (steam point) and T_0 (ice point) the ratio of the heat quantities in equation (9) is established by the constraints of nature. Thus,

$$\frac{Q_1}{Q_0} = r = \frac{T_1}{T_0} = \text{constant.} \tag{10}$$

If we define ΔT_{01} as $T_1 - T_0$, then the temperature of the ice point T_0 may be expressed in terms of ΔT_{01} as,

$$T_0 = \frac{\Delta T_{01}}{r - 1} \, . \tag{11}$$

Hence, since r is fixed by the thermal states (T_0, T_1 whose numerical temperatures may be yet unknown), T_0 is determined by the value of ΔT_{01} or ΔT_{01} is determined

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*In 1854, one hundred years earlier, Kelvin had stated that the triple point of water "must be adopted ultimately" as a defining fixed point (3). The triple point has been adopted to replace the ice point owing to a greater reliability in establishing its temperature experimentally and the fact that the triple point temperature is not pressure sensitive as are two-phase states.

by the value of T_0. Thus, one constant only, either T_0 or ΔT_{01}, is sufficient to define the scale. Prior to 1954 ΔT_{01} was chosen as 100°K and T_0 determined by the gas thermometer. Since 1954 the reverse procedure has been adopted and T_0 is <u>defined</u> as the triple point of water at 273.16°K*. Now, the thermodynamic temperatures of all defining fixed points and secondary reference points must be determined by the gas thermometer.

IV THE ABSOLUTE (GAS) TEMPERATURE SCALE

The practical use of the Kelvin scale would require the operation of reversible engines. This, of course, is quite impossible and it is necessary to find an approximation to the Absolute Thermodynamic Scale. This is found from the properties of an ideal gas** for if such a fluid is employed in a reversible engine it may be shown that:

$$\frac{Q_1}{Q_0} = \frac{\theta_1}{\theta_0} , \qquad (12)$$

where θ is a "temperature" on a new scale called the Absolute (Gas) Temperature Scale and would be determined from pressure and volume measurements on the gas, as:

$$\theta = \frac{pv}{R} . \qquad (13)$$

Further, if the difference $\theta_1 - \theta_0$ or θ_0 are defined to be identically the same as $T_1 - T_0$ or T_0, respectively, then it follows from equations (9) and (10) that:

$$\begin{aligned} \theta_1 &= T_1 \\ \theta_0 &= T_0 \qquad (14) \\ \text{or,} \quad \theta &= T \quad . \end{aligned}$$

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*The triple point of water is <u>defined</u> by the International Practical Temperature Scale as +0.01°C (°C being degrees Celsius) which gives the ice point an absolute temperature of 273.15°K (3).

**An ideal gas is defined as a substance having an internal energy (u) which is a function only of temperature and an equation of state written as $pv = R\theta$.

In words, the Absolute (Gas) Temperature Scale is identical with the Absolute (Thermodynamic) Temperature Scale if an ideal gas is employed in a reversible engine or any other device permitting the measurement of p and v. Such a device (which now replaces the reversible engine) is known as a gas thermometer and is the primary standard thermometer used to determine and establish the absolute thermodynamic temperature scale. Beattie (18) and Barber (19) describe the gas thermometer and the techniques of its use. Gas thermometers are either of constant pressure or constant volume. Although both types give essentially identical results independent of the type of gas used, the constant volume type appears to be the more widely used. The M.I.T. thermometer used by Beattie (18,20,21) is of the constant volume type and uses nitrogen gas in a very pure state as the thermometric substance. Gas thermometry also, has used H_2, He, Ne, A and Air as thermometric substances.

It was found by equation (14) that the requirement of a reversible engine as a thermometer was unnecessary to realize the Kelvin scale, if one could substitute a gas thermometer using an ideal gas. However, owing to the departure of the properties of a real gas from conditions of ideality, it becomes necessary to emperically correct the readings taken from a gas thermometer in order to determine the absolute temperature. Such temperatures are not Kelvin temperatures, actually, but owing to the necessary corrections must be looked upon as approximations. They are called Absolute (Gas) Temperatures and represent the closest approximations to the absolute scale of Kelvin. The nature of these corrections is well established and is outlined by Keyes (22). However, it will be appropriate to indicate the nature of the result for a constant-volume gas thermometer. From thermodynamic theory and the properties of real gases it may be shown that for $V^* = V$

$$\frac{p - p^*}{(T-T^*)p^*} = \frac{1}{T^*} + \frac{T}{(T-T^*)p^*} \int_{T^*}^{T} C_v \left(\frac{\partial T}{\partial v}\right)_u d\left(\frac{1}{T}\right) \tag{15}$$

The integral is the gas scale correction and is evaluated from measurements of the properties of real gases. Having once obtained the absolute temperature T^* of the triple point of water, for example, by definition at 273.16°K, then equation (15) can be used to obtain the absolute temperature T on the gas scale of any other thermodynamic state from gas thermometer measurements of p and p^* and the real properties of the gas.

A simple constant-volume gas thermometer for cryogenic application is illustrated by Barber (19) and shown in Figure 3. This gas thermometer is used for the calibration of platinum resistance thermometers in the liquid hydrogen temperature range. A typical gas bulb with platinum thermometer receptacles and auxiliary apparatus is shown in detail in Figure 4 taken from Moessen, et al (12). Figure 5 shows temperature scale corrections for the non-ideality of the helium gas scale and the absolute temperature scale. This indicates that gas thermometer temperatures from various laboratories may differ from each other in the cryogenic temperature range by as much as 0.03°K. These differences are attributed to the various methods used to account for gas imperfectability and do not include the influence of dead space volume, gravity and other deviations from ideal measuring conditions.

A negative absolute temperature may seem to be a suitable subject for a discussion of cryogenic temperatures. The concept of a negative absolute temperature is presented by Ramsey (24) and Hertzfeld (25). Such a condition may be described whenever the population of an energy state of higher energy is greater than the population of a lower energy state (25) under conditions which permit a statistical mechanical interpretation of thermodynamics. Hertzfeld (25) lists these conditions as: "(1) The system must be fairly well isolated from its surroundings, but must come to internal equilibrium rapidly; (2) the states of the system must be quantized; and (3) the system must have a highest state in the same sense that a system has a

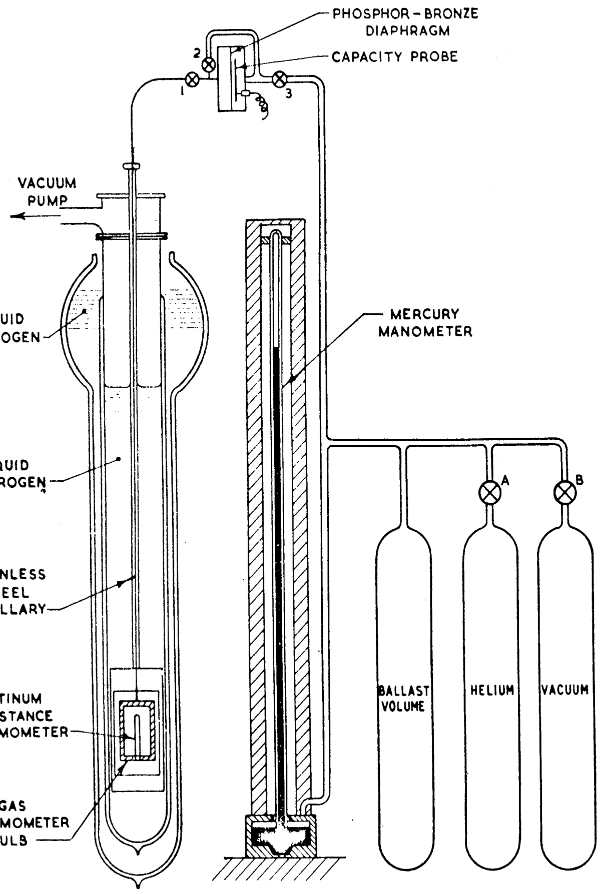

Figure 3. Constant Volume Gas Thermometer Used for Calibration of a Platinum Resistance Thermometer.(19)

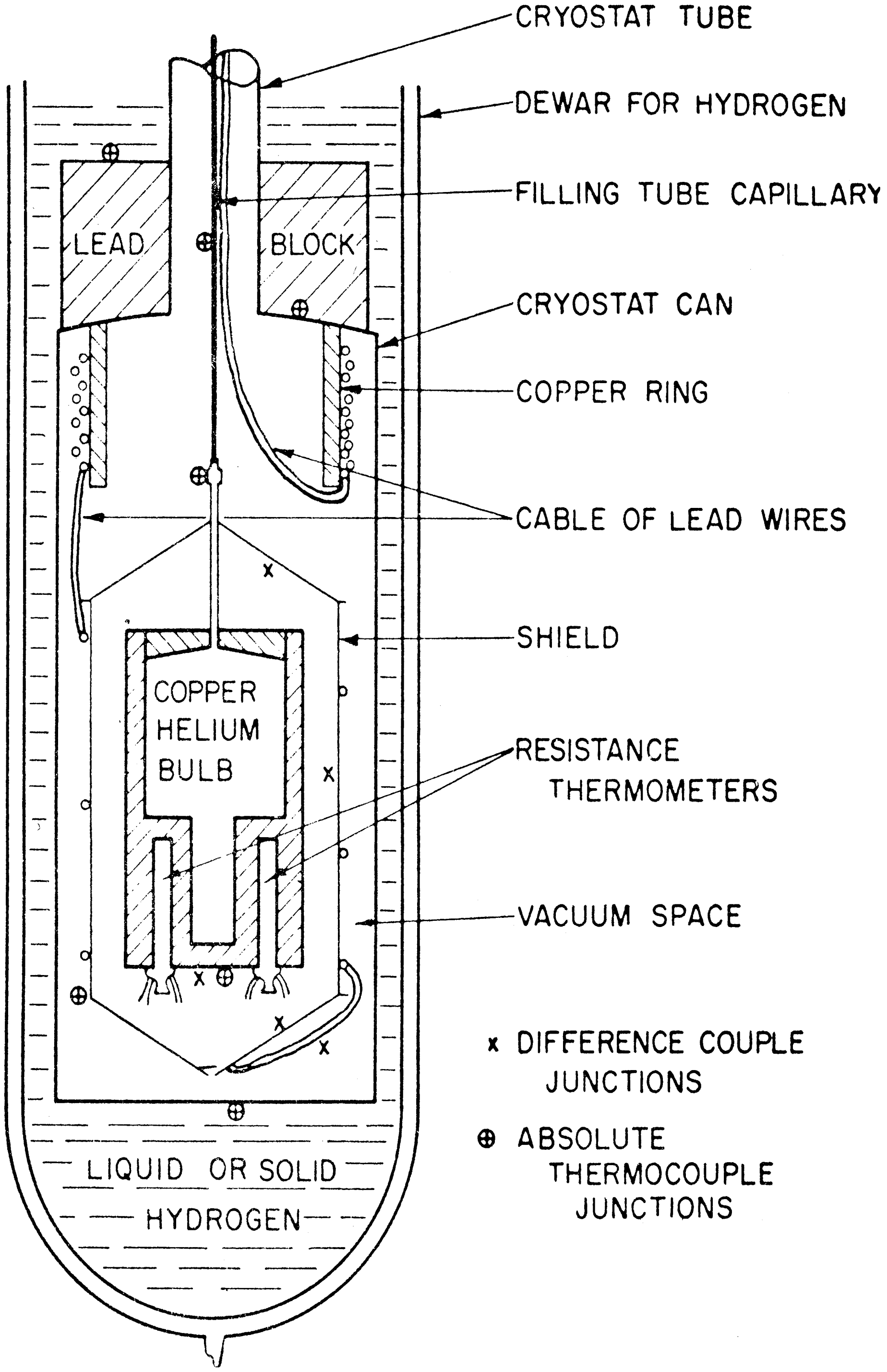

Figure 4. Thermometer Bulb, Shields, and Cryostat.(12)

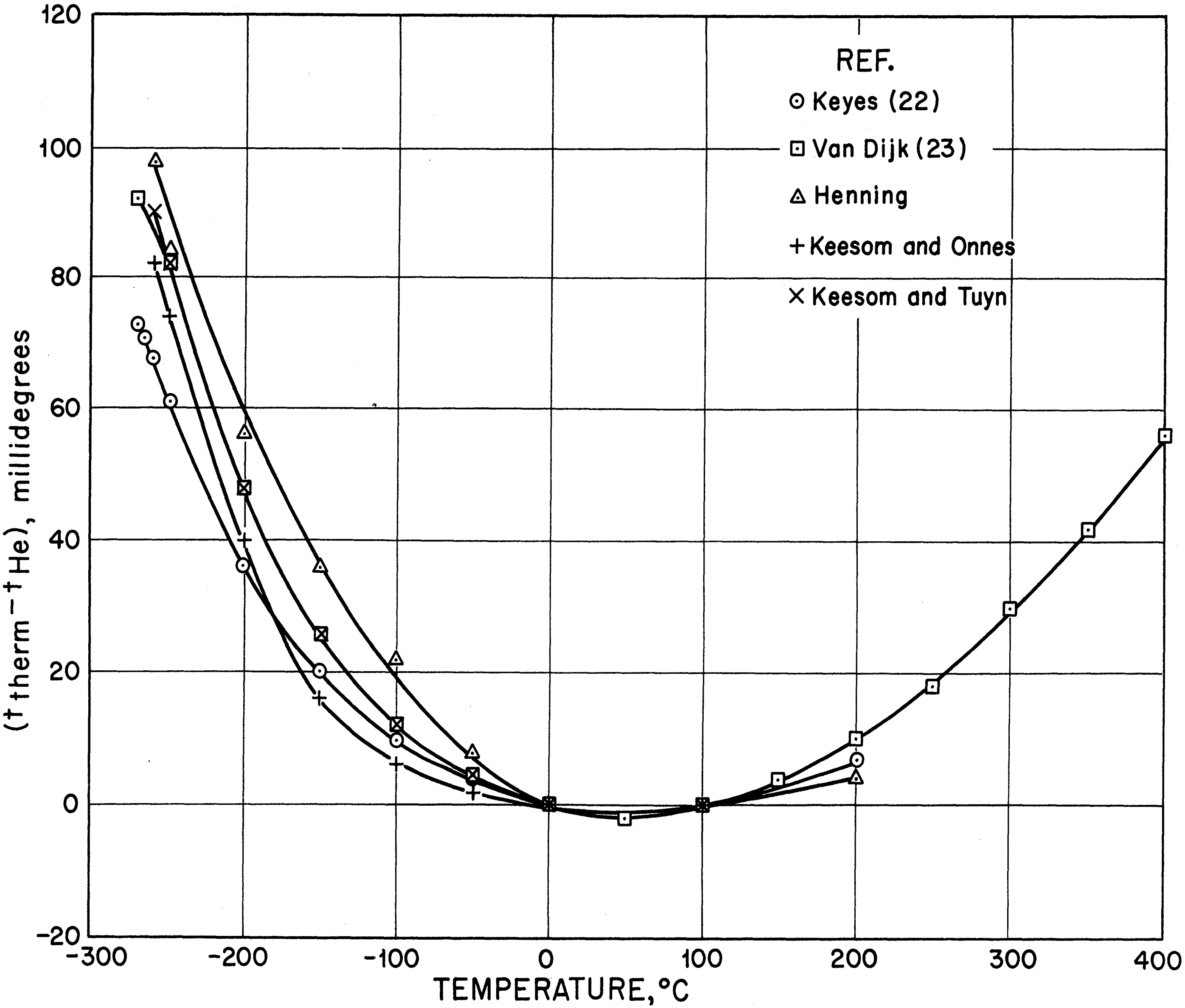

Figure 5. Gas Imperfection Corrections for Constant Volume Helium Gas Thermometer.(6)

lowest state." Examples of such systems are the nuclear magnetic moments of the constituents of certain crystals. No violation of the principles of thermodynamics is envisioned in this phenomenon. Interestingly, states at negative absolute temperatures are "hotter" than those at infinite temperature. This results from the fact that at T equal to ∞ all states are equally populated. However, if higher energy states have larger populations than lower energy states the system must be "hotter" than those states having a temperature of infinity. This naturally removes the discussion from the cryogenic range!

V THE INTERNATIONAL TEMPERATURE SCALE (ITS)

Owing to its size and complexity the gas thermometer is impractical to use for laboratory or industrial measurement of temperature. Most gas thermometers occupy a room-sized space and require elaborate and time consuming preparations for their use. For these reasons a simple, reproducible and convenient secondary temperature standard is required even for precise laboratory measurements. The gas thermometer remains, of course, the primary standard and is employed to determine the gas scale absolute temperature of the various defining fixed points and to calibrate precision laboratory secondary standard thermometers.

The definition of the secondary standard thermometers is established by international agreement by the General Conference on Weights and Measures, a body consisting of scientific representatives from 36 nations which meets every six years. This parent body is assisted by a smaller executive group known as the International Committee on Weights and Measures which consists of 18 elected members from the various nations and normally meets every two years. It is this group that supervises the International Bureau of Weights and Measures at Sévres, near Paris, France. This committee also oversees the publication of Metrologia*, a journal devoted to original papers on research "directed towards the significant improvement of fundamental measurements in any field of physics". An Advisory Committee on Thermometry (Comité Consultatif de Thermométrie), the CCT, actively assists the International Committee on Weights and Measures in all matters relating to temperature measurement.

International Temperature Scales (ITS) have been adopted in 1927 (26) and in 1948 (27,28). In 1960 a textual revision of the 1948 scale was made (2,3). This revision did not significantly affect the numerical values on the scale. The principal changes were:

a. Replace the ice-point with the triple point of water (0.01°C, exactly).

b. Use zinc point (pressure insensitive) instead of the sulphur point (pressure sensitive).

c. Change the name to the International Practical Temperature Scale (IPTS).

The ITS (1927 and 1948) is a Celsius (°C, 1948) scale and no mention was made in the text of an International Practical Kelvin Temperature Scale (IPKTS). However, in practice this conversion was made on the basis of the accepted value of T_0, the Kelvin scale temperature of the ice-point. The 1960 revision of the ITS (1948) specifically mentions the IPKTS and relates it to the IPTS by

$$T^{o}K(\mathrm{IPKTS}) = t^{o}C(\mathrm{IPTS}) + T_0, \qquad (16)$$

where T_0 is now defined to be 273.15°K. This was done so that the IPKTS will have the same value (273.16°K) for the triple point of water as the Kelvin Absolute Tem-

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*A publication of Springer-Verlag.

perature Scale. The IPTS and the Celsius scale both are defined to have a value of 0.01°C as the triple point of water. Stimson (2) observes that for precision no greater than 0.001°C, the zero on the 1948 Celsius scale (ITS 1948) may be realized with an ice bath as described in the 1948 ITS.

The International Practical Temperature Scale (IPTS) specifies four things: (a) the gas scale temperatures of reproducible defining fixed points and the secondary reference points at which instruments are calibrated, (b) the types of instruments to be used in realizing the scale, (c) the equations to be used for interpolating or extrapolating from the fixed points, and (d) the experimental procedures recommended for both measurement and calibration. A summary of the IPTS and a comparison of the 1927, 1948 and the 1960 revision of the 1948 scale are given in Tables I, II and III, taken from Hust (6). The complete range of temperatures from -182.97°C to 1063°C is included for completeness. Twenty-two secondary reference points from -78.5°C to 3380°C including their vapor temperature-pressure relations are given by Stimson (3).

The relationship between the International Practical Temperature Scale (1948) and the thermodynamic scale is shown in Table IV (2).

Because of the polynomial form of the interpolating equations used to describe the International Practical Temperature Scale (IPTS) between the defining fixed points, an inherent difference exists between the IPTS and the thermodynamic temperature scale (TTS). This difference is determined by comparing gas thermometer readings with those from standard thermometers as prescribed by the IPTS. Hust (6) reports the data of several investigators who examined the differences between the TTS and the IPTS in the range -190°C to 0°C. These results are shown in Figure 6. As may be noted, fairly large discrepancies exist between these various results probably because of differences in the gas thermometers measurements as suggested

TABLE I

Defining Fixed Points for the International Temperature Scales. Hust (6)

Description (all at 1 atm) except triple point of water	°C (Int 1927) ITS	°C (Int 1948) ITS	°C (Int 1948) 1960 text rev. IPTS
Oxygen point: Equilibrium between liquid and gaseous oxygen	-182.97	-182.97	-182.97
Ice point: Equilibrium between ice and air saturated liquid water	0.000	0.000	
Triple point of water: Equilibrium between ice liquid water and gaseous water			0.010
Steam point: Equilibrium between liquid and gaseous water	100.00	100.000	100.000
Sulfur point: Equilibrium between liquid and gaseous sulfur	444.60	444.60	(444.60)
Zinc point: Equilibrium between solid and liquid zinc			419.505*
Silver point: Equilibrium between solid and liquid silver	960.5	960.8	960.8
Gold point: Equilibrium between solid and liquid gold	1063.0	1063.0	1063.0

*Recommended to replace the sulfur point

TABLE II

Official Interpolation Procedures for the 1927 and 1948 International Temperature Scales. Hust (6)
(t in °C; T in °K; T_0 is temperature of ice point, $T_0 = 273.15°K$)

1927 Scale	1948 Scale
-190 to 0°C platinum resistance thermometer $R_t = R_0 \left[1 + At + Bt^2 + C(t - 100)\ t^3\right]$ calibrate at O_2, ice, steam, S-points	-182.97 to 0°C platinum resistance thermometer $R_t = R_0 \left[1 + At + Bt^2 + C(t - 100)\ t^3\right]$ calibrate at O_2, ice, steam, S-points
0 to 660°C $R_t = R_0\ (1 + At + Bt^2)$ $R_{100}/R_0 \geqslant 1.390$; $R_{444.6}/R_0 \geqslant 2.645$ calibrate at ice, steam, S-points	0 to 630.5°C $R_t = R_0\ (1 + At = Bt^2)$ $R_{100}/R_0 > 1.3920$ calibrate at ice, steam, S-points
660 to 1063°C Pt-Pt 10% Rh thermocouple $e = a + bt + ct^2$ calibrate at Sb, Ag, Au-points	630.5 to 1063°C Pt-Pt 10% Rh thermocouple $e = a + bt + ct^2$ calibrate at Sb, Ag, Au-points
above 1063°C monochromatic optical pyrometer $\log \frac{J_t}{J_{Au}} = \frac{c_2}{\lambda} \left[\frac{1}{1336} - \frac{1}{t + T_0} \right]$ with $c_2 = 1.432$ cm deg	above 1063°C monochromatic optical pyrometer $\log \frac{J_t}{J_{Au}} = \frac{\exp \frac{c_2}{(tAu + T_0)} - 1}{\exp \frac{c_2}{(t + T_0)} - 1}$ $c_2 = 1.438$ cm deg

TABLE III

Differences Between ITS (1927) and IPTS (1948). Hust (6)

Platinum Thermometer Range

The temperature differences in this range are negligible. The changes were made primarily to make the scale more reproducible and definite. Note that the range on the 1948 scale is restricted to -182.97 to 630.5°C instead of -190 to 660°C.

Standard Thermocouple Range

t, $^{\circ}$C (Int) 1948	t $^{\circ}$C (Int) 1948 - $^{\circ}$C (Int) 1927
630.5	0.00*
650	.08*
700	.24
750	.35
800	.42
850	.43
900	.40
950	.32
1000	.20
1050	.05
1063	.00

---

* These values are uncertain since platinum thermometers are defined only up to 630.5°C on 1948 scale (see Corruccini (29).

Radiation Law Range

It is difficult to determine exact differences of the ITS and IPTS in this range because of the variability of λ ; the wavelength of the radiation on the 1927 scale is restricted only to the visible spectrum and is not restricted at all on the 1948 scale. The following table contains the differences calculated at $\lambda_1=0.4738\times10^{-4}$cm and $\lambda_2=0.65\times10^{-4}$cm according to Corruccini (29).

t	Δ_t	
$^{\circ}$C (Int) 1948	$^{\circ}$C (Int) 1948 - $^{\circ}$C (Int) 1927	
	λ_1	λ_2
1063	0	0
1500	- 2	- 2
2000	- 6	- 6
2500	-12	-12
3000	-19	-20
3500	-28	-30
4000	-38	-43

TABLE IV

Relation Between the International Practical Scale and the Thermodynamic Scale*

International Practical Scales

	Celsius	Absolute
Names	International Practical Temperature →	International Practical Kelvin Temperature
Symbols	t_{int}	$T_{int} = t_{int} + T_0$
Designations	°C (Int. 1948) degrees Celsius international practical 1948	°K (Int. 1948) degrees Kelvin international practical 1948

Thermodynamic Scales

	Celsius	Absolute
Names	Thermodynamic Celsius temperature	← Thermodynamic Kelvin temperature
Symbols	$t = T - T_0$	T
Designations	°C (therm.) degrees Celsius thermodynamic	°K degrees Kelvin

($T_0 = 273.15^\circ$)

NOTE: For the international practical temperature, the subscript "int" after t may be omitted if there is no possibility of confusion.

* Adopted 11th General Conference on Weights and Measures, October 1960.

by the data in Figure 5. In order to examine and define these differences systematically, Preston-Thomas and Kirby (35) redetermined part of the TTS, in terms of platinum resistance thermometer readings, by means of a constant volume helium gas thermometer of reasonably high accuracy. These authors expect to extend similar measurement to -219°C, the triple point of oxygen. Their measurements in the range -183°C to 100°C are given in Figure 7. As may be seen by the data in Figures 6 and 7, the IPTS and the TTS differ by a maximum of about 0.04°C in the cryogenic range.

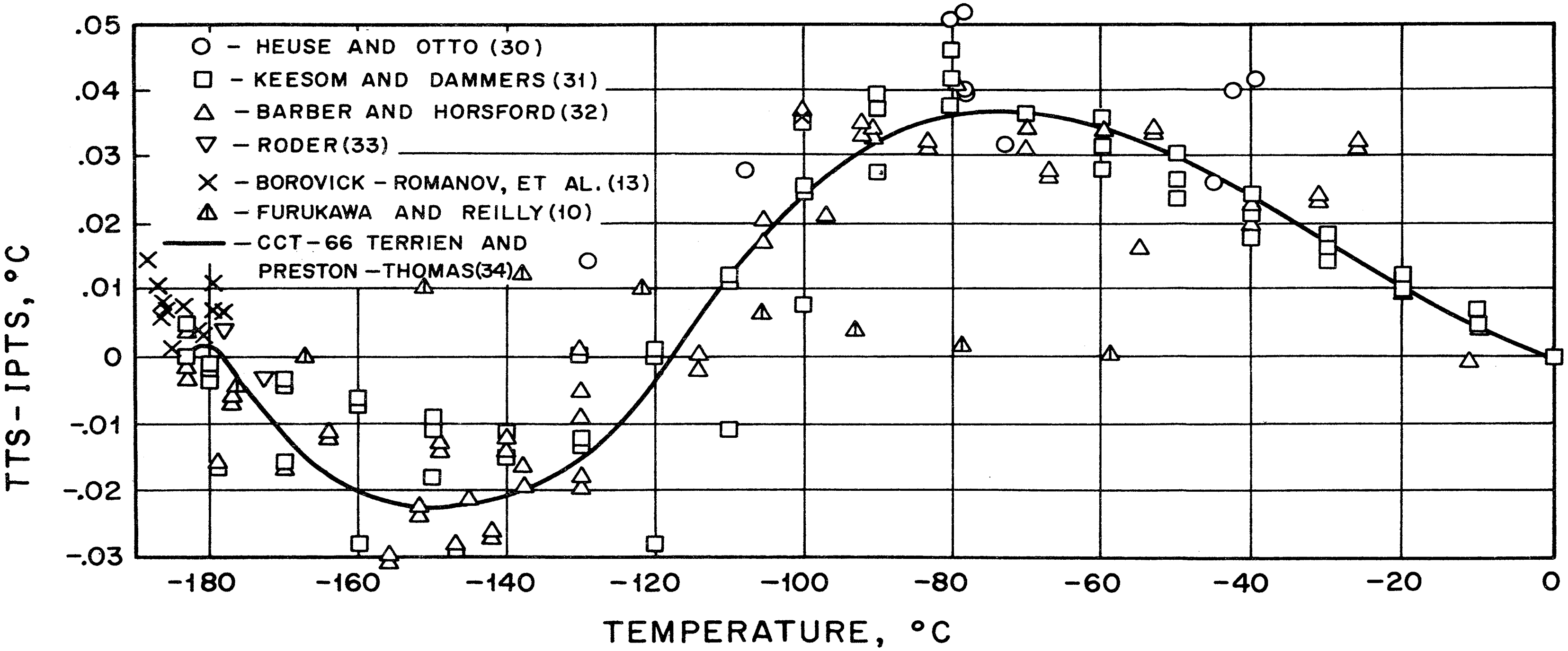


Figure 6. Temperature Differences Between Thermodynamic and International Temperature Scales.(6)

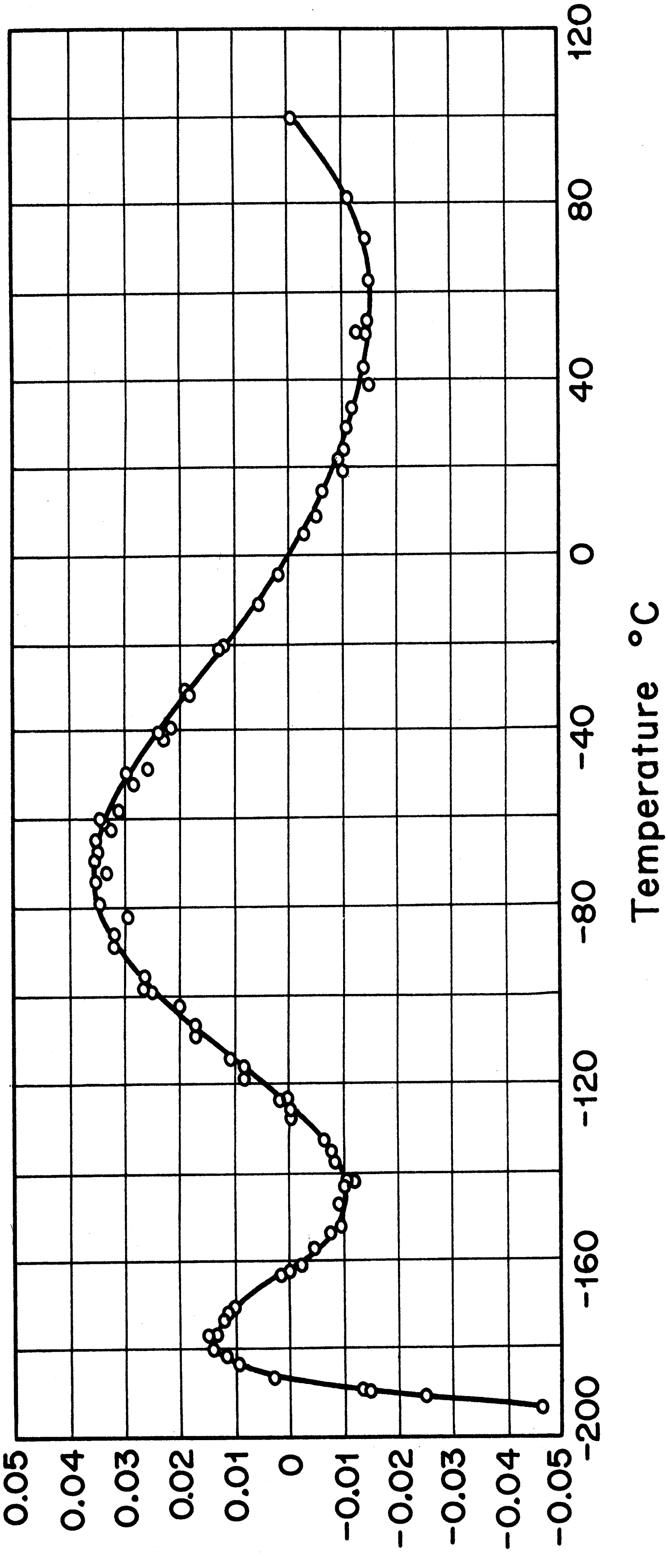


Figure 7. Comparison of Measurements of TTS - IPTS.(35)

VI TEMPERATURE SCALES BELOW 90°K

Below the oxygen point (-182.97°C, 90.18°K) no International Temperature Scale presently exists. During the past few years, however, a great deal of study has been devoted to this problem by the CCT and a number of proposals for extending the IPTS to 13.8°K, the triple point of equilibrium hydrogen, have been made. It now seems probable that the IPTS in force since 1948 will be abandoned and replaced with a new scale (4,5). This new scale, which may take effect as early as late 1968 or perhaps during 1969, will conform to the best experimental values of the thermodynamic temperatures now available. If these events transpire as expected, it will mark a period of 20 years between the new scale and the 1948 scale which itself replaced the 1927 scale after about a similar 20 year tenure. This will, of course, leave the important range below 13.8°K undefined by an international standard. Since this includes the entire region of He^4 and He^3 it can only be hoped that similar efforts by the CCT will bring about a standard scale at these very low temperatures.

Because of the absence of an international standard below 90°K several "national" or "laboratory" scales have been developed. Each of these is different from the others and from the thermodynamic scale. They are based on the resistance characteristics of platinum calibrated against a gas thermometer. Several of these scales were compared in Figure 2. Scott (36) compares several other scales as indicated in Figure 8. The NBS (1939) scale has been superseded by the NBS (1955) scale formed by lowering all temperatures on the NBS (1939) scale by 0.01°C. These scales have been the basis for all NBS calibrations in the interval 12° to 90°K since 1939. The agreement of the NBS (1939) scale with the thermodynamic scale was $\pm$ 0.02°C in the range 12° to 90°K. It is interesting to note that the scale identified as "Calif (1927)" in Figure 8 is formulated on the basis of a copper-constantan thermocouple which was stable over a period of 3 years having an estimated accuracy of 0.05°K in the range 12° to 90°K (37).

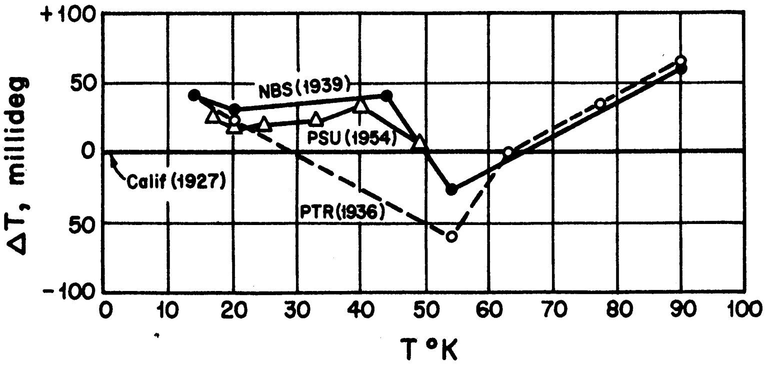


Figure 8. Comparison of Temperature Scales.(36)
Calif--University of California(37)
NBS --National Bureau of Standards(7,8)
PSU --Pennsylvania State University(12)
PTR --Physikalische Technische Reichsanstalt(36)

In 1964 the CCT established a provisional temperature scale to be considered as a replacement for the IPTS below 273.15°K. This scale, in the form of a resistance-temperature table for platinum thermometers, is referred to as CCT-64 and extends from 10°K to 273.15°K. The derivation for the range 90°K to 273.15°K is given by Barber and Hayes (38). Certain modifications currently are being considered in this scale prior to its recommendation as an international scale (5). However, any modification in CCT-64 will doubtless be small and the low temperature part is assumed (6) to be the best approximation to the thermodynamic scale in this region.

Calibration of thermometers below 90°K may be accomplished using a number of multi-phase equilibrium states, called fixed points. Timmerhaus (39) lists several of these states which are given here in Table V. These are not presently "secondary reference points" as prescribed by an International Temperature Scale, but represent the best literature values. An equilibrium cell or vapor pressure thermometer is employed to determine these states and would be similar to the oxygen vapor-pressure thermometer described by Timmerhaus (40) shown in Figure 9.

For precise calibration of thermometers in the range 0.20°K to 5.2°K the vapor pressure scales of He^4 and its light isotope He^3 are available. For temperatures between 1°K and 5.2°K the International Committee on Weights and Measures in October 1958 recommended for international use a scale based on equilibrium between He^4 liquid and its vapor now known as the "1958 He^4 scale of temperatures". This scale is described by Brickwedde, et al (41) where the vapor pressure of He^4 is tabulated for intervals of 0.001°K from 0.50°K to 5.22°K. Clement (42) concludes that the He^4 1958 scale is accurate within 0.001 to 0.002°K with a roughness less than 0.0001°K. Values of the vapor pressure of He^4 in microns (10^{-3} mm Hg) for intervals of 0.01°K are given in Table VI, taken from reference 41.

TABLE V

Fixed Points Below 90°K (39)

Point	Temp., °K
Lambda point of helium	2.173
Boiling point of helium (1 atm)	4.215
Triple point of equilibrium hydrogen	13.81
Triple point of normal hydrogen	13.95
Boiling point of equilibrium hydrogen (1 atm)	20.27
Boiling point of normal hydrogen (1 atm)	20.39
Triple point of neon	24.57
Boiling point of neon (1 atm)	27.17
Triple point of oxygen	54.36
Triple point of nitrogen	63.14
Boiling point of nitrogen (1 atm)	77.35

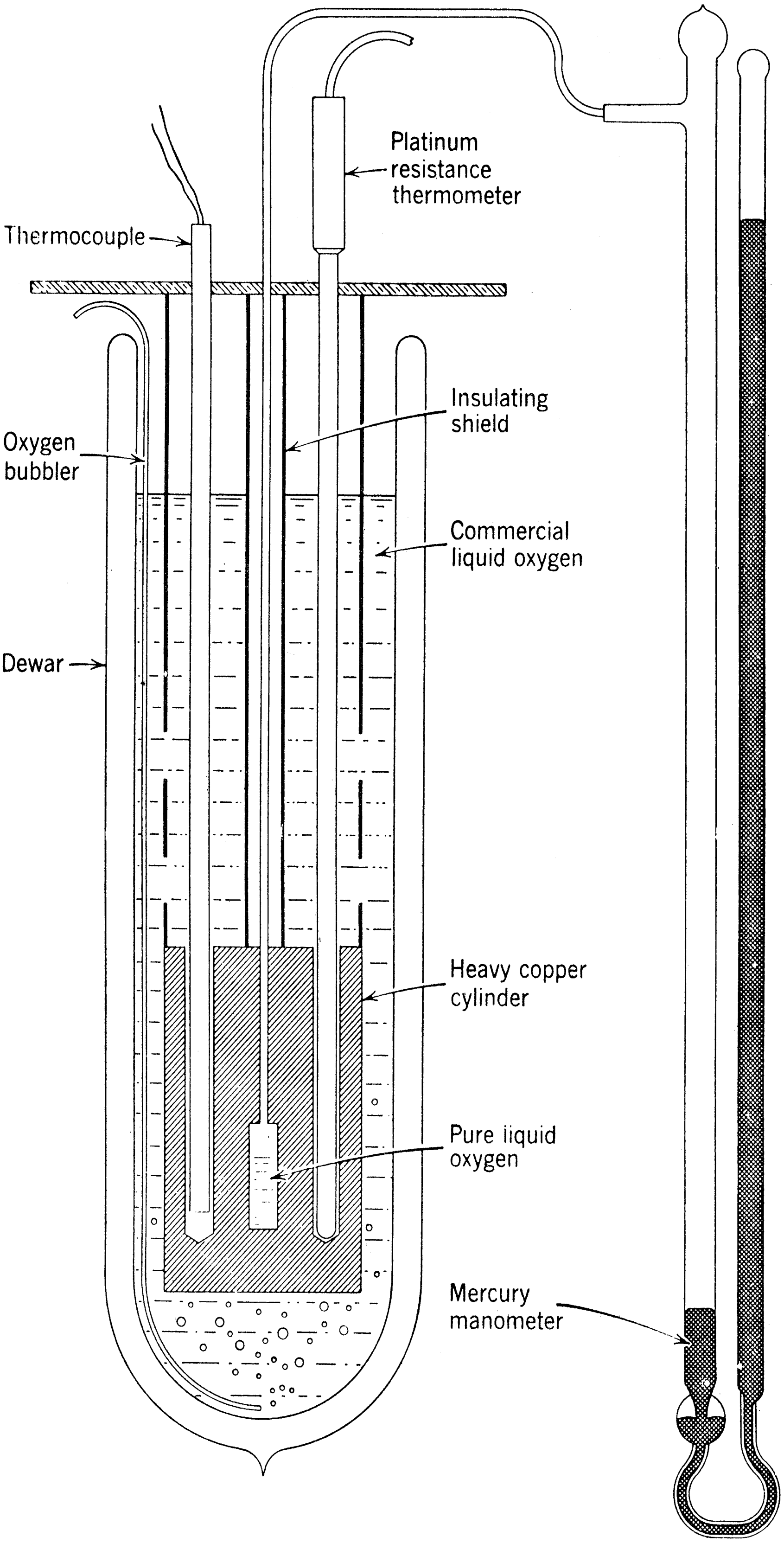


Figure 9. Oxygen Vapor-pressure Thermometer for Calibrating Working Thermometers.(40)

A comparison of the 1958 He^4 scale with previous scales is shown in Figure 11, taken from Hust (6). The identification of the various scales is given by Brickwedde, et al (41). The acoustical thermometer of Plumb and Cataland (11) provides an interesting comparison with the results of the vapor pressure scale.

The phase diagram for He^4 is shown in Figure 10. Below the λ-point at 2.172°K liquid helium experiences a transition to its superfluid state. The tendency of superfluid helium to flow makes vapor pressure measurements difficult below the λ-point. Furthermore, below 1°K the vapor pressure of He^4 is less than 120 microns which adds additional problems in measurement. To overcome both of these drawbacks the vapor pressure of the light isotope He^3 was determined and developed into the He^3 scale. A comparison of the vapor pressures of He^3 and He^4 is given in Figure 12, taken from Arp and Kropschot (43). For comparison it will be noted that the vapor pressure of He^3 at 1°K is 8,842 microns and that of He^4 at the same temperature is only 120 microns.

The International Committee on Weights and Measures in 1962 recommended the use of the He^3 vapor pressure temperature data for international use. This scale, which is known as the "1962 He^3 scale of temperatures", is tabulated in intervals of 0.001°K from 0.20°K to 3.324°K by Sherman, et al (44). Vapor pressure data in intervals of 0.01°K for He^3 are given in Table VII, taken from the summary table of Sydoriak, et al (45).

Preston-Thomas and Bedford (5) have examined the reproducibilities of various actual and postulated temperature scales in the range 1°K to 1063°K. Their results are given in Figure 13 indicating a general reproducibility of 10^{-2} to 10^{-3} over the full range.

TABLE VI

Brickwedde, et. al. (41)

Vapor pressure of He^{4} (1958 scale) in microns (10^{-3} mm) mercury at 0^{o}C and standard gravity (980.665 cm/sec^{2})

T^{o}K	Microns	T^{o}K	Microns	T^{o}K	Microns	T^{o}K	Microns	T^{o}K	Microns	T^{o}K	Microns	T^{o}K	Microns
0.50	0.016342	1.30	1208.51	2.00	23767.4	2.70	112175	3.40	314697	4.10	680740	4.80	1263212
.51	.022745	1.31	1284.81	2.01	24470.9	2.71	114145	3.41	318659	4.11	687399	4.81	1273414
.52	.031287	1.32	1364.83	2.02	25188.1	2.72	116139	3.42	322654	4.12	694103	4.82	1283673
.53	.042561	1.33	1448.73	2.03	25919.2	2.73	118156	3.43	326684	4.13	700851	4.83	1293991
.54	.057292	1.34	1536.61	2.04	26664.2	2.74	120198	3.44	330747	4.14	707643	4.84	1304367
.55	.076356	1.35	1628.62	2.05	27423.3	2.75	122263	3.45	334845	4.15	714479	4.85	1314802
.56	.10081	1.36	1724.91	2.06	28196.3	2.76	124353	3.46	338976	4.16	721360	4.86	1325297
.57	.13190	1.37	1825.58	2.07	28983.2	2.77	126465	3.47	343141	4.17	728285	4.87	1335850
.58	.17112	1.38	1930.79	2.08	29784.2	2.78	128603	3.48	347341	4.18	735255	4.88	1346462
.59	.22021	1.39	2040.67	2.09	30599.1	2.79	130765	3.49	351575	4.19	742269	4.89	1357136
0.60	0.28121	1.40	2155.35	2.10	31428.1	2.80	132952	3.50	355844	4.20	749328	4.90	1367870
.61	.35649	1.41	2274.99	2.11	32271.1	2.81	135164	3.51	360147	4.21	756431	4.91	1378662
.62	.44877	1.42	2399.73	2.12	33128.0	2.82	137401	3.52	364485	4.22	763579	4.92	1389516
.63	.56118	1.43	2529.72	2.13	33998.6	2.83	139663	3.53	368860	4.23	770772	4.93	1400429
.64	.69729	1.44	2665.09	2.14	34882.8	2.84	141949	3.54	373269	4.24	778010	4.94	1411404
.65	.86116	1.45	2805.99	2.15	35780.3	2.85	144260	3.55	377714	4.25	785294	4.95	1422438
.66	1.0574	1.46	2952.60	2.16	36690.9	2.86	146597	3.56	382194	4.26	792623	4.96	1433533
.67	1.2911	1.47	3105.04	2.17	37614.3	2.87	148961	3.57	386710	4.27	799999	4.97	1444690
.68	1.5682	1.48	3263.48	2.18	38550.2	2.88	151349	3.58	391262	4.28	807422	4.98	1455911
.69	1.8949	1.49	3428.07	2.19	39500.3	2.89	153763	3.59	395849	4.29	814893	4.99	1467191
.70	2.2787	1.50	3598.97	2.20	40465.6	2.90	156204	3.60	400471	4.30	822411	5.00	1478535
.71	2.7272	1.51	3776.32	2.21	41446.6	2.91	158671	3.61	405130	4.31	829978	5.01	1489940
.72	3.2494	1.52	3960.32	2.22	42443.5	2.92	161164	3.62	409825	4.32	837592	5.02	1501409
.73	3.8549	1.53	4151.07	2.23	43456.5	2.93	163684	3.63	414556	4.33	845255	5.03	1512940

TABLE VI (cont.)

$T^{o}K$	Microns	$T^{o}K$	Microns	$T^{o}K$	Microns	$T^{o}K$	Microns	$T^{o}K$	Microns	$T^{o}K$	Microns	$T^{o}K$	Microns
.74	4.5543	1.54	4348.79	2.24	44485.7	2.94	166230	3.64	419324	4.34	852966	5.04	1524535
.75	5.3591	1.55	4553.58	2.25	45531.3	2.95	168802	3.65	424128	4.35	860725	5.05	1536192
.76	6.2820	1.56	4765.68	2.26	46593.5	2.96	171402	3.66	428968	4.36	868533	5.06	1547912
.77	7.3365	1.57	4985.18	2.27	47672.5	2.97	174028	3.67	438846	4.37	876390	5.07	1559698
.78	8.5376	1.58	5212.26	2.28	48768.6	2.98	176682	3.68	438760	4.38	884296	5.08	1571546
.79	9.9013	1.59	5447.11	2.29	49881.8	2.99	179364	3.69	443713	4.39	892252	5.09	1583458
.80	11.445	1.60	5689.88	2.30	51012.3	3.00	182073	3.70	448702	4.40	900258	5.10	1595437
.81	13.187	1.61	5940.76	2.31	52160.2	3.01	184810	3.71	453729	4.41	908313	5.11	1607481
.82	15.147	1.62	6199.90	2.32	53325.8	3.02	187574	3.72	458794	4.42	916418	5.12	1619589
.83	17.348	1.63	6467.42	2.33	54509.2	3.03	190366	3.73	463897	4.43	924573	5.13	1631761
.84	19.811	1.64	6743.57	2.34	55710.5	3.04	193187	3.74	469038	4.44	932778	5.14	1644000
.85	22.561	1.65	7028.47	2.35	56930.0	3.05	196037	3.75	474218	4.45	941033	5.15	1656305
.86	25.624	1.66	7322.31	2.36	58167.8	3.06	198914	3.76	479435	4.46	949338	5.16	1668673
.87	29.027	1.67	7625.21	2.37	59423.8	3.07	201820	3.77	484691	4.47	957693	5.17	1681108
.88	32.800	1.68	7937.40	2.38	60698.8	3.08	204755	3.78	489985	4.48	966099	5.18	1693612
.89	36.974	1.69	8259.02	2.39	61992.0	3.09	207719	3.79	495317	4.49	974556	5.19	1706180
.90	41.581	1.70	8590.22	2.40	63304.3	3.10	210711	3.80	500688	4.50	983066	5.20	1718817
.91	46.656	1.71	8931.18	2.41	64635.2	3.11	213732	3.81	506098	4.51	991628	5.21	1731521
.92	52.234	1.72	9282.06	2.42	65985.4	3.12	216783	3.82	511547	4.52	1000239	5.22	1744290
.93	58.355	1.73	9643.02	2.43	67354.8	3.13	219864	3.83	517036	4.53	1008905		
.94	65.059	1.74	10014.3	2.44	68743.5	3.14	222975	3.84	522564	4.54	1017621		
.95	72.386	1.75	10395.9	2.45	70152.0	3.15	226115	3.85	528132	4.55	1026390		
.96	80.382	1.76	10788.2	2.46	71580.2	3.16	229285	3.86	533739	4.56	1035213		
.97	89.093	1.77	11191.2	2.47	73028.1	3.17	232484	3.87	539387	4.57	1044087		
.98	98.567	1.78	11605.1	2.48	74496.0	3.18	235714	3.88	545075	4.58	1053014		
.99	108.853	1.79	12030.1	2.49	75984.2	3.19	238974	3.89	550805	4.59	1061995		
1.00	120.000	1.80	12466.1	2.50	77493.1	3.20	242266	3.90	556574	4.60	1071029		

TABLE VI (cont.)

T^oK	Microns	T^oK	Microns	T^oK	Microns	T^oK	Microns	T^oK	Microns	T^oK	Microns	T^oK	Microns
1.01	132.070	1.81	12913.7	2.51	79022.2	3.21	245587	3.91	562383	4.61	1080114		
1.02	145.116	1.82	13372.8	2.52	80572.2	3.22	248939	3.92	568234	4.62	1089254		
1.03	159.198	1.83	13843.6	2.53	82142.9	3.23	252322	3.93	574126	4.63	1098449		
1.04	174.375	1.84	14326.1	2.54	83734.6	3.24	255736	3.94	580059	4.64	1107699		
1.05	190.711	1.85	14820.7	2.55	85347.2	3.25	259182	3.95	586034	4.65	1117002		
1.06	208.274	1.86	15327.3	2.56	86981.2	3.26	262658	3.96	592051	4.66	1126359		
1.07	227.132	1.87	15846.3	2.57	88636.7	3.27	266166	3.97	598110	4.67	1135772		
1.08	247.350	1.88	16377.7	2.58	90313.8	3.28	269706	3.98	604210	4.68	1145239		
1.09	269.006	1.89	16921.7	2.59	92012.6	3.29	273278	3.99	610352	4.69	1154761		
1.10	292.169	1.90	17478.2	2.60	93733.4	3.30	276880	4.00	616537	4.70	1164339		
1.11	316.923	1.91	18047.7	2.61	95476.0	3.31	280516	4.01	622764	4.71	1173972		
1.12	343.341	1.92	18630.1	2.62	97240.8	3.32	284183	4.02	629033	4.72	1183662		
1.13	371.512	1.93	19225.5	2.63	99028.2	3.33	287883	4.03	635345	4.73	1193407		
1.14	401.514	1.94	19834.1	2.64	100838	3.34	291615	4.04	641700	4.74	1203209		
1.15	433.437	1.95	20455.9	2.65	102669	3.35	295380	4.05	648099	4.75	1213066		
1.16	467.365	1.96	21091.1	2.66	104525	3.36	299178	4.06	654541	4.76	1222981		
1.17	503.396	1.97	21739.7	2.67	106403	3.37	303008	4.07	661026	4.77	1232955		
1.18	541.617	1.98	22402.0	2.68	108304	3.38	306871	4.08	667554	4.78	1242983		
1.19	582.129	1.99	23077.9	2.69	110228	3.39	310768	4.09	674125	4.79	1253069		
1.20	625.025												
1.21	670.411												
1.22	718.386												
1.23	769.057												
1.24	822.527												
1.25	878.916												
1.26	938.330												
1.27	1000.87												
1.28	1066.67												
1.29	1135.85												

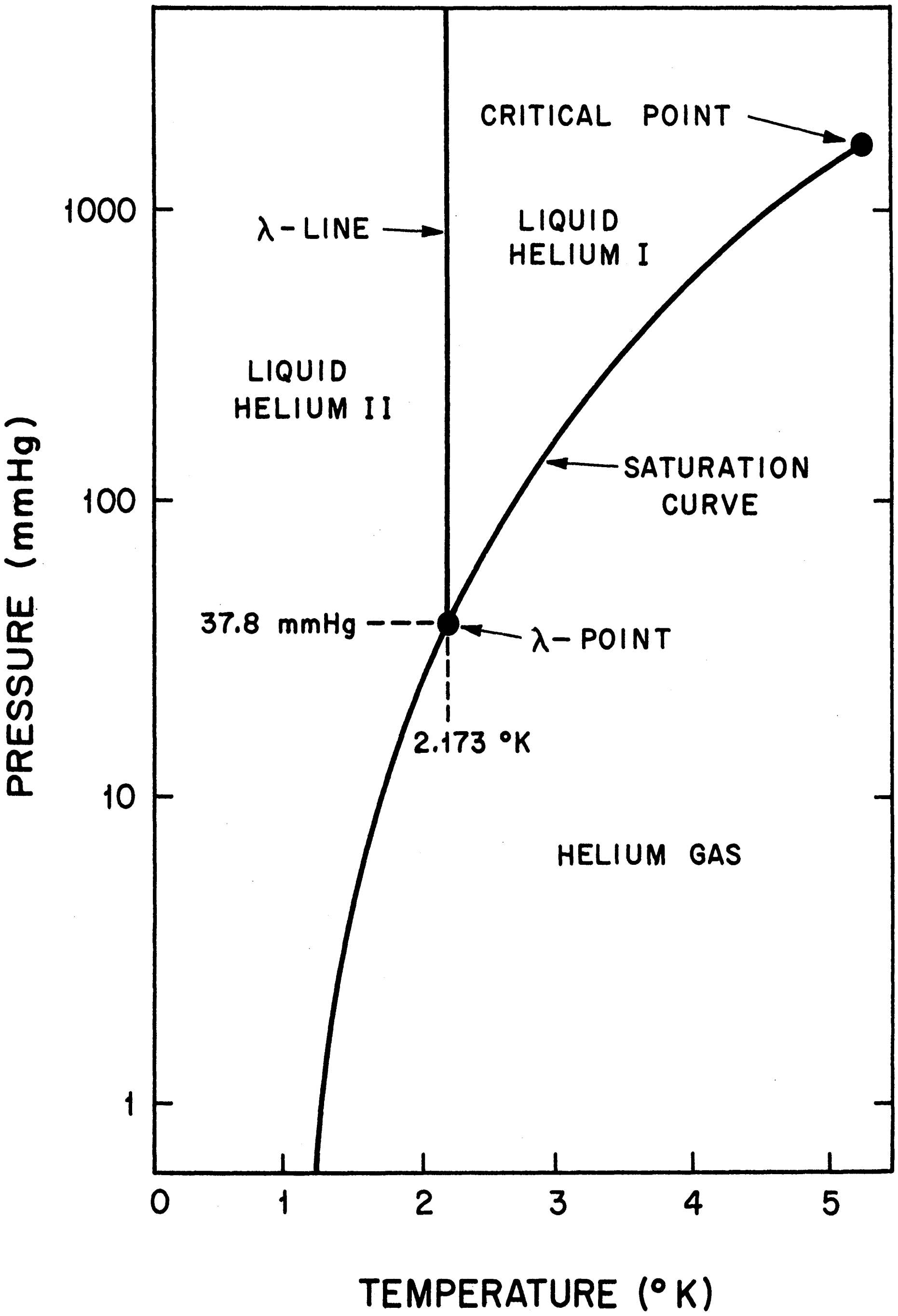


Figure 10. Phase Diagram for Helium.

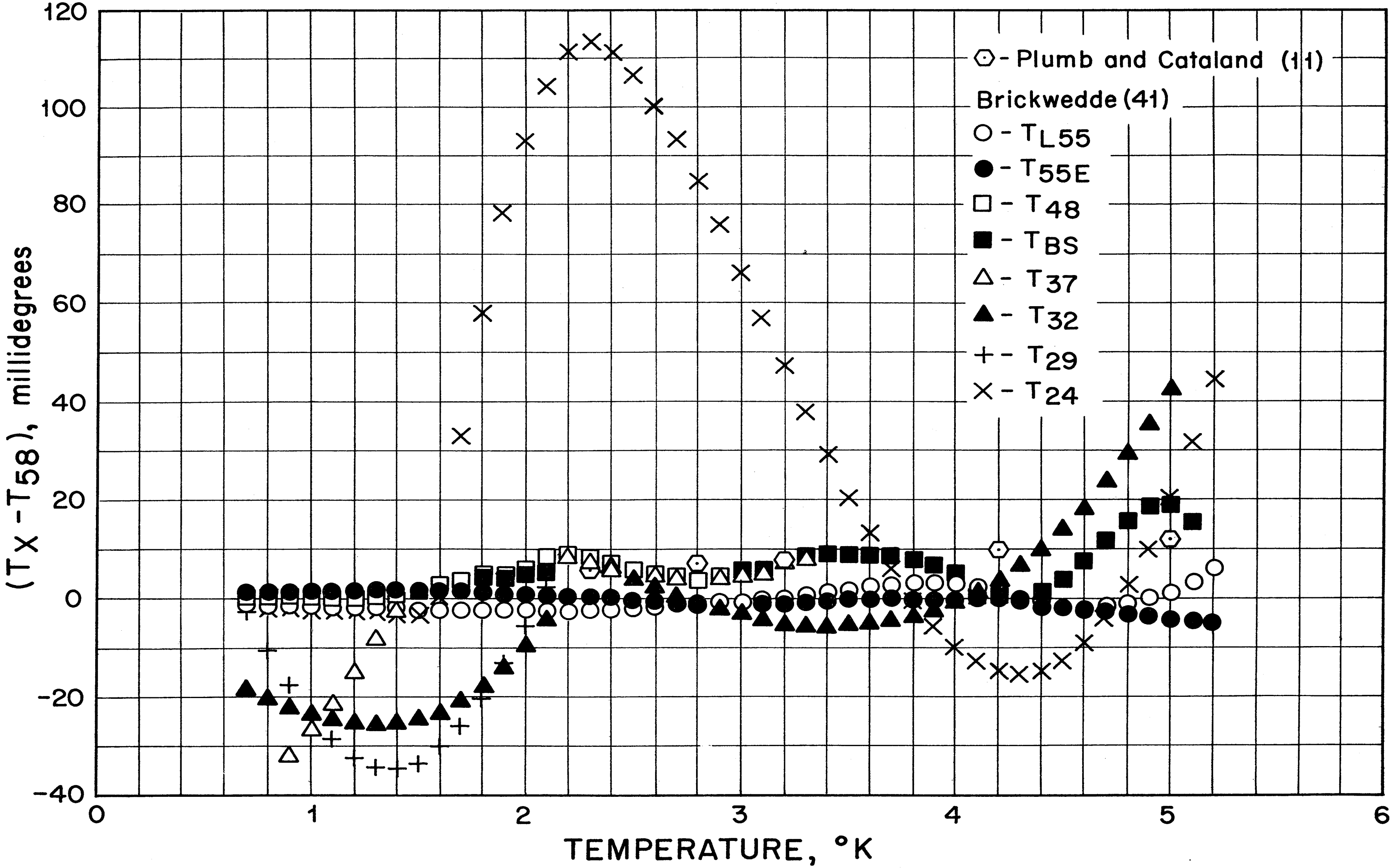


Figure 11. Deviation of Earlier Helium Vapor Pressure Scales from the 1958 He^4 Scale.(6)

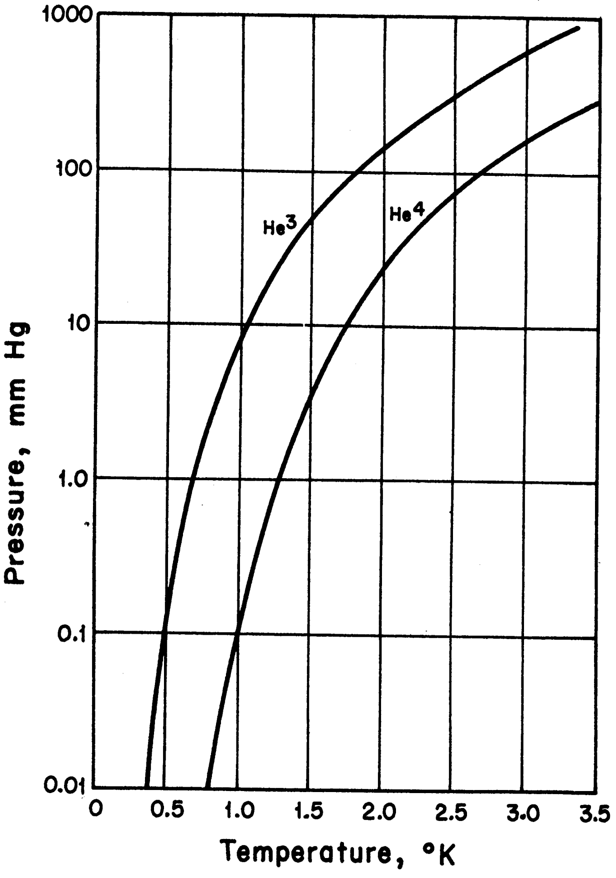


Figure 12. Vapor-pressures of He^3 and He^4.(43)

TABLE VII*

He^3 vapor pressures on the 1962 He^3 scale at 0^oC and standard gravity, 980.665 cm/sec^2

The units of pressure are microns (10^{-3} mm) of mercury below 1^oK and millimeters of mercury at higher temperatures

T	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.20	0.012	0.024	0.046	0.084	0.144	0.239	0.382	0.592	0.891	1.308
0.30	1.877	2.636	3.633	4.921	6.561	8.619	11.173	14.304	18.105	22.673
0.40	28.11	34.54	42.08	50.86	61.01	72.68	86.02	101.17	118.31	137.61
0.50	159.2	183.3	210.1	239.8	272.5	308.5	347.9	391.1	438.0	489.1
0.60	544.4	604.3	668.9	738.4	813.0	893.0	978.7	1070.1	1167.6	1271.4
0.70	1381	1498	1622	1753	1892	2038	2192	2355	2525	2704
0.80	2892	3089	3295	3511	3736	3971	4216	4472	4739	5016
0.90	5304	5603	5914	6237	6572	6918	7277	7649	8034	8431
1.00	8.842	9.267	9.704	10.156	10.622	11.102	11.597	12.106	12.631	13.170
1.10	13.725	14.295	14.881	15.484	16.102	16.737	17.388	18.056	18.741	19.443
1.20	20.163	20.900	21.655	22.428	23.220	24.029	24.857	25.704	26.571	27.456
1.30	28.360	29.285	30.229	31.193	32.177	33.181	34.206	35.252	36.319	37.407
1.40	38.516	39.646	40.799	41.973	43.169	44.388	45.629	46.893	48.179	49.489
1.50	50.822	52.178	53.558	54.961	56.389	57.840	59.316	60.817	62.342	63.892
1.60	65.467	67.068	68.694	70.345	72.022	73.726	75.455	77.211	78.993	80.802
1.70	82.638	84.501	86.391	88.309	90.254	92.228	94.229	96.258	98.315	100.402
1.80	102.516	104.660	106.833	109.035	111.266	113.527	115.818	118.138	120.489	122.870
1.90	125.282	127.724	130.197	132.701	135.236	137.803	140.401	143.031	145.692	148.386
2.00	151.112	153.870	156.661	159.485	162.342	165.232	168.155	171.112	174.102	177.126
2.10	180.184	183.276	186.403	189.564	192.760	195.990	199.256	202.557	205.894	209.266
2.20	212.673	216.117	219.597	223.113	226.665	230.255	233.881	237.544	241.244	244.982
2.30	248.757	252.570	256.420	260.309	264.236	268.202	272.206	276.249	280.331	284.452
2.40	288.613	292.813	297.053	301.333	305.653	310.013	314.414	318.855	323.337	327.861
2.50	332.425	337.031	341.679	346.368	351.100	355.874	360.690	365.549	370.450	375.395
2.60	380.383	385.414	390.489	395.608	400.771	405.978	411.230	416.526	421.868	427.254
2.70	432.686	438.164	443.687	449.256	454.872	460.534	466.242	471.998	477.801	483.651
2.80	489.549	495.495	501.488	507.531	513.622	519.762	525.951	532.189	538.477	544.815
2.90	551.203	557.642	564.131	570.672	577.264	583.907	590.602	597.349	604.149	611.002

TABLE VII* (cont.)

T	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
3.00	617.907	624.866	631.879	638.945	646.066	653.241	660.472	667.757	675.098	682.496
3.10	689.949	697.459	705.026	712.650	720.332	728.072	735.871	743.728	751.644	759.620
3.20	767.656	775.753	783.910	792.128	800.408	808.750	817.155	825.622	834.153	842.747
3.30	851.406	860.130	868.918	877.773						

*From Sydoriak, et al. (45)

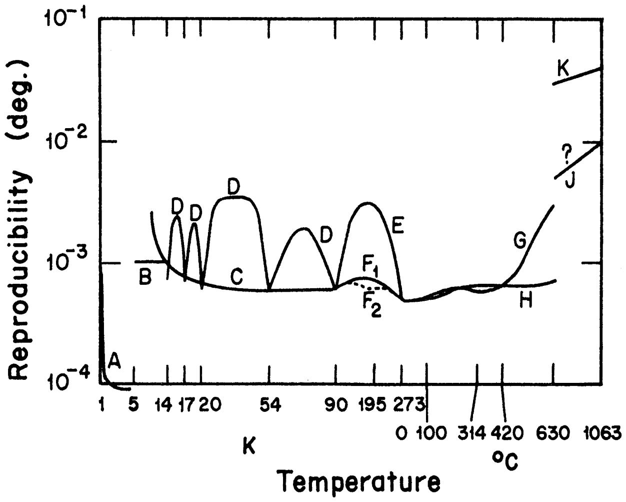


Figure 13. Estimated Reproducibilities of Various Actual and Postulated Temperature Scales.(5)

A. Vapour Pressure Measurement. 1958 He- Scale;

B. Estimated Reproducibility of a Ge Resistance Thermometer "Wire Scale";

C. Estimated Reproducibility of Any of the Pt Resistance Thermometer "National" Scales;

D. Reproducibility of the Barber van Dijk Scale(46) on the (Optimistic) Assumption of the Fixed Points being Realisable to 0.2 Millikelvin;

E. IPTS in the 90 K to 273 K Range Assuming the Indeterminacy Shown by Barber(32);

F. IPTS in the 90 K to 273 K Range Assuming the Indeterminacy Shown by Lovejoy(47)(F_1) or Alternatively the Use of an Additional Fixed Point (CO_2 Point) in a Modification of the IPTS (F_2);

G. IPTS in the Range 0°C to 630°C;

H. Reproducibility of a Modification of the IPTS in the Manner Suggested by McLaren(48);

J. Estimated Reproducibility of a Pt Resistance Thermometer Scale in the 630°C to 1063°C Range;

K. Reproducibility of the IPTS (Using Pt 10 Rh/Pt Thermocouples) in the 630°C to 1063°C Range.

VII. Thermometers for Cryogenic Temperatures

The remaining sections of this paper will consider the principal devices which are employed to measure cryogenic temperatures. These will include thermoelectric, electrical resistance and magnetic thermometers. A survey of available low temperature thermometers is illustrated in Figure 14 for the temperature range 0.05°K to 300°K. This is an extension of a similar chart presented by Timmerhaus (40).

A comparison of the performance of several of these devices has been prepared by Corruccini (63) in a survey of temperature measurements at cryogenic temperatures. His results are given in Table VIII.

TABLE VIII

Comparison of Cryogenic Temperature Measuring Devices

Type	Range,°K	Best Reproducibility,°K	Best Accuracy,°K
1. Platinum Resistance	10-900	10^{-3} to 10^{-4}	10^{-2} to 10^{-4}
2. Carbon	1-30	10^{-2} to 10^{-3}	10^{-2} to 10^{-3}
3. Germanium	1-100	10^{-3} to 10^{-4}	10^{-2} to 10^{-3}
4. Gold-Cobalt vs Copper Thermocouple	4-300	10^{-1} to 10^{-2}	0.10

VIII. Thermocouples

The familiar thermo-electric circuit - the thermocouple - in which an EMF is produced by subjecting the junctions of dissimiliar metallic combinations to different temperatures is commonly used in the cryogenic temperature range. In circumstances where measurement accuracy is from 0.50 to 1.0°F a thermocouple may even be the preferred temperature sensing element. There are several reasons for this. A thermocouple is easily made, is small and can be mounted relatively simply in remote and fairly inaccessible locations, requires only standard laboratory or industrial measuring instruments, can be made rugged and relatively insensitive to environmental disturbances, and is inexpensive. Other desirable characteristics that can be obtained using thermocouples are: a large net thermal EMF, a monotonic or linear EMF-temperature characteristic, a stable EMF-temperature characteristic, resistance to chemical corrosion, including the effects of both oxidizing and reducing atmospheres, uniformity of the wire material in large batches and high thermal response. The influence of the environment often must be reduced by the use of protection tubes. The common thermo-electric elements in use today at temperatures from 4°K to 300°K are the gold-cobalt vs copper and the constantan vs copper junctions. These will be described below. Measurements made at the liquid nitrogen, liquid oxygen and liquid hydrogen temperatures probably have used the constantan vs copper thermocouple with greater frequency than any other single combination. As was mentioned earlier, the "Calif (1927)" scale in Figure 8 was formulated on the basis of a copper-constantan thermocouple (37). This particular thermocouple was found to be stable for a period of 3 years in the temperature range 12°K to 90°K with an accuracy of 0.05°K.

Although thermocouples are commonly used at temperatures below 300°K the International Practical Temperature Scale is not specified in terms of thermo-electric systems in the cryogenic range of temperatures. The principal reasons for this are accuracy and reproducibility as compared with the platinum resistance thermometers.

The general principles of thermo-electric thermometry and the various thermo-electric circuits and instrumentation are, of course, important to design for the installation of thermocouples. In view of space limitations here and the generally wide availability of this kind of information, it will not be

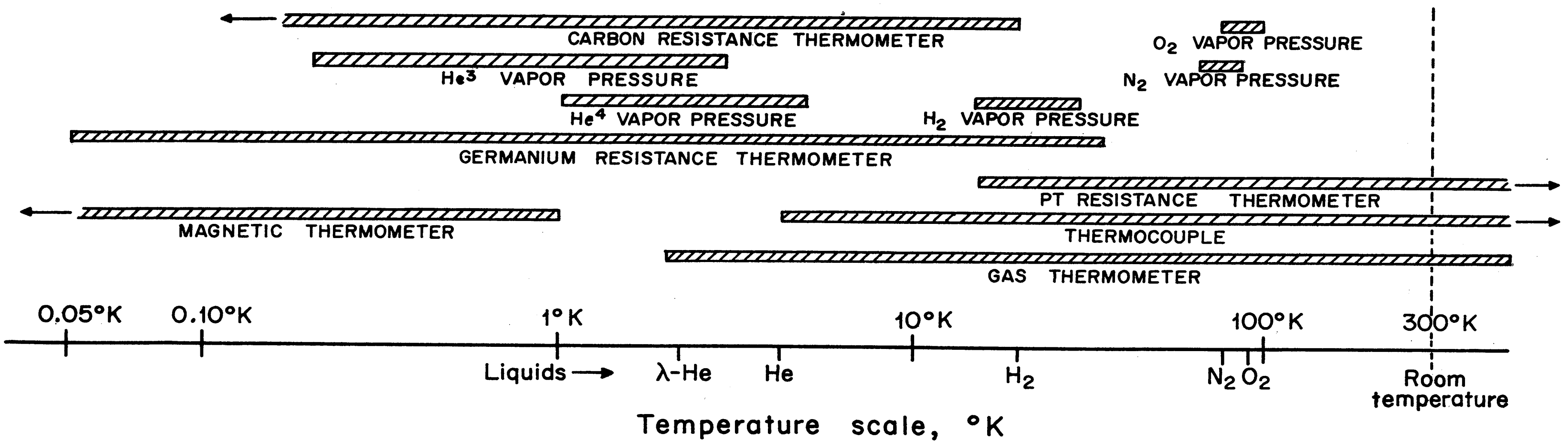


Figure 14. Temperature Ranges Normally Associated With Various Low Temperature Thermometers.

included in this discussion. Finch (49) has given a thorough presentation of the principles of thermoelectricity. Some improved reference tables for iron-constantan, chromel-alumel, copper-constantan and chromel-constantan thermocouples are presented by Benedict and Ashby (50). Caldwell (51) discusses the properties of various materials that could be used as thermocouple elements at temperatures above 0°C. The use of thermocouples in engineering measurements and their circuits are given by Weber (52), Baker, et al (53) and Dike (54), among others.

The behavior of a thermocouple element is usually characterized by its thermoelectric potential or EMF, E, and its thermoelectric power, dE/dT. Its EMF, E, is always related to an arbitrarily selected reference temperature. At cryogenic temperatures the common thermoelectric combinations are gold-cobalt (Au + 2.11 atomic percent Co) vs copper, copper vs constantan (60% Cu and 40% Ni), gold-cobalt vs normal silver (Ag + 0.37 atomic percent Au), Iron vs constantan and chromel-P (90% Ni and 10% Cr) vs Alumel (95% Ni and 5% (Al, Si, Mn)). The most frequently used thermocouples, however, are the gold-cobalt vs copper and the copper vs constantan combinations. These thermocouples have been used to temperatures as low as 0.2°K. Their best accuracy in the temperature range 4 to 300°K is 0.10°K for gold-cobalt vs copper and 0.50°K for copper vs constantan.

The thermoelectric potential differences for these 5 thermocouples is given in Table IX, taken from Powell, et al (55).

TABLE IX

Thermoelectric Potential Differences in Microvolts for Several Thermocouple Combinations (55)

Thermocouple Combination

Temp. °K	Constantan vs. Copper	Gold-Cobalt vs. Copper	Normal Silver vs Copper	Iron vs. Constantan	Chromel P vs. Alumel
4-20	57.8	171.4	0.2	59	41
20-76	646.9	1562.5	37.9	805	616
76-273	5545.6	8123.2	133.7	8252	6182

The principal advantage of the use of the gold-cobalt vs. copper combination is evident from these data as it has a significantly higher thermal EMF. However, owing to inhomogeneities in its chemical constituency this combination produces irregular EMF's that are uncompensated for in its calibration. This, of course, gives rise to measurement errors. In fact, this lack of homogeneity in composition is the single greatest defect in the Au-Co vs. Cu thermocouple. When the chemical metallurgy of the Au-Co wires can produce a product having a constant, controllable and stable composition this thermocouple will come into much wider use at very low temperatures. The effects of inhomogeneity are usually greatest when the measuring and reference junctions are at widely different temperatures. In such cases the thermocouple lead wires are subjected to steep temperature gradients and at the points of greatest temperature change in the wire chemical inhomogeneity will produce an EMF. Thus, the Au-Co vs. Cu combination is best used where temperature differences to be measured are small. A convenient and practical application is the use of the Au-Co vs. Cu combination as a differential thermocouple in an installation where the temperature differences are small or zero, as in constant temperature baths, cryostats and equilibrium cells for temperature calibration.

The Fe vs. Con and Ch vs. Al thermocouples are infrequently used at low temperatures principally because of voltage uncertainties resulting from inhomogeneities in the wires.

An estimate of the inhomogeneity of thermoelectrical voltages obtained by placing one section of a wire sample in a cryogen while the two ends of the wire are attached to a potentiometer is reported by Powell, et al (56) and shown in Table X.

TABLE X

Inhomogeneity of Thermoelectric Voltages
Obtained from Dip Tests (50)

Samples*	Bath temperatures			
	4-300°K		76-300°K	
	Voltage (uV)		Voltage (uV)	
	Maximum	Average	Maximum	Average
(1) Cu	4.5	2.5	2.0	0.8
(2) Cu	1.8	0.7	1.0	0.3
(3) Constantan	0.5	0.2	0.5	0.2
(4) Au-Co	5.0	3.0	4.0	2.5
(5) Au-Co	5.5	3.5	4.0	2.5
(6) Ag-Au	2.2	1.2	1.2	0.8

*Samples were: (1) Instrument grade copper, 32 A.W.G.; (2) Thermocouple grade copper, 36 A.W.G.; (3) Thermocouple grade constantan, 36 A.w.g.; (4) Gold-cobalt, Bar 9, 36 A.w.g. (1960); (5) Gold-cobalt, Bar 5, 36 A.w.g. (1958); (6) 'Normal' silver, 36 A.w.g.

As is evident from this sampling, the gold-cobalt wire is subject to the greatest voltage uncertainty. Thermocouple grade copper and constantan exhibit the least voltage uncertainty owing to inhomogeneity.

Powell, et al (55, 56) have studied the thermoelectric characteristics of several thermocouple combinations in the temperature range 4°K to 300°K. A summary of their results for the Au-Co vs. Cu and Cu vs. Con thermocouples is given in Table XI for a 0°K reference temperature. An extensive tabulation of the thermoelectric potentials and thermoelectric power in 1°K intervals for these combinations from 0°K to 300°K is found in reference 56. These results represent the best average or smoothed data for a family of thermocouple combinations. Thus, they may be used as the standard reference data for each thermocouple. Such data are of great value in thermocouple calibration, as is discussed later.

TABLE XI

Thermoelectric Potential Differences in Microvolts for Gold-Cobalt and Constantan vs. Copper Thermocouples (56)

Temp., °K	Au-Co	Constantan
0	0.00	0.00
2	2.09	0.66
4	8.22	2.62
6	18.20	5.83
8	31.83	10.26
10	48.93	15.88
12	69.30	22.64
14	92.75	30.50
16	119.1	39.43
18	148.1	49.40
20	179.6	60.40
25	269.1	92.31
30	372.5	130.3
35	488.0	173.9
40	614.2	222.9
45	749.9	276.8
50	893.9	335.6
55	1045.2	398.8
60	1202.9	466.2
65	1366.2	537.5
70	1534.5	612.7
75	1707.1	691.2
80	1883.5	773.0
85	2063.4	858.1
90	2246.8	946.7
95	2433.3	1038.5
100	2622.6	1133.7
110	3008.5	1333.7
120	3402.8	1546.4
130	3804.1	1771.7
140	4211.2	2009.5
150	4623.2	2260.0
160	5039.1	2522.7
170	5458.4	2797.1
180	5880.4	3083.1
190	6304.6	3380.3
200	6730.6	3688.6
210	7158.0	4007.7
220	7586.4	4337.4
230	8015.7	4677.5
240	8445.5	5027.8
250	8875.6	5388.0
260	9305.9	5757.9
270	9736.2	6137.3
280	10166.3	6526.0
290	10596.1	6923.7
300	11025.5	7330.2

The thermoelectric power, dE/dT, in microvolts per degree Kelvin for the five thermocouple combinations in Table IX is given in Figure 15 as a function of temperature. At temperatures from 4°K to about 200°K, the Au-Co vs. Cu thermocouple is clearly the superior combination from the standpoint of thermoelectric power. Below about 40°K the Fe vs. Con, Ch vs. Al and Cu vs. Con thermocouples have about the same thermoelectric power. Normal silver vs. copper produces an almost insignificant thermoelectric power at low temperatures.

The thermoelectric power, dE/dT, in Figure 15 may be used to give an indication of the sensitivity of temperature measurement when it is related to the measurement sensitivity of the potentiometer ΔE^* in microvolts, used to measure the thermal EMF of the thermocouple. That is, the uncertainty in temperature indication, ΔT^*, may be written

$$\Delta T^* = \frac{\Delta E^*}{(dE/dT)} \tag{17}$$

Thus, thermocouples having large thermoelectric power will enable smaller measurement uncertainty for a given measuring instrument.

The calibration of a thermocouple is conveniently done by establishing its deviation characteristic as compared with "Standard" thermocouple EMF. Standard thermocouple potentials at cryogenic temperatures are given in Table XI in summary form for Au-Co vs. Cu and Cu vs. Con and may be found in much greater detail in reference 56. The thermocouple "Deviation" is defined as

$$\Delta E_{DEV} = E_{STD} - E_{OBS} , \tag{18}$$

where E_{STD} is the standard EMF corresponding to the temperature of the thermocouple for which E_{OBS} is its "observed" EMF. A deviation plot is usually constructed by obtaining several corresponding values of ΔE_{DEV} and E_{OBS} over a range of temperatures. Generally, when these data are plotted as ΔE_{DEV} vs. E_{OBS} a smooth, frequently almost linear, curve may be used to join the data points. This is a result of the fact that while each individual thermocouple

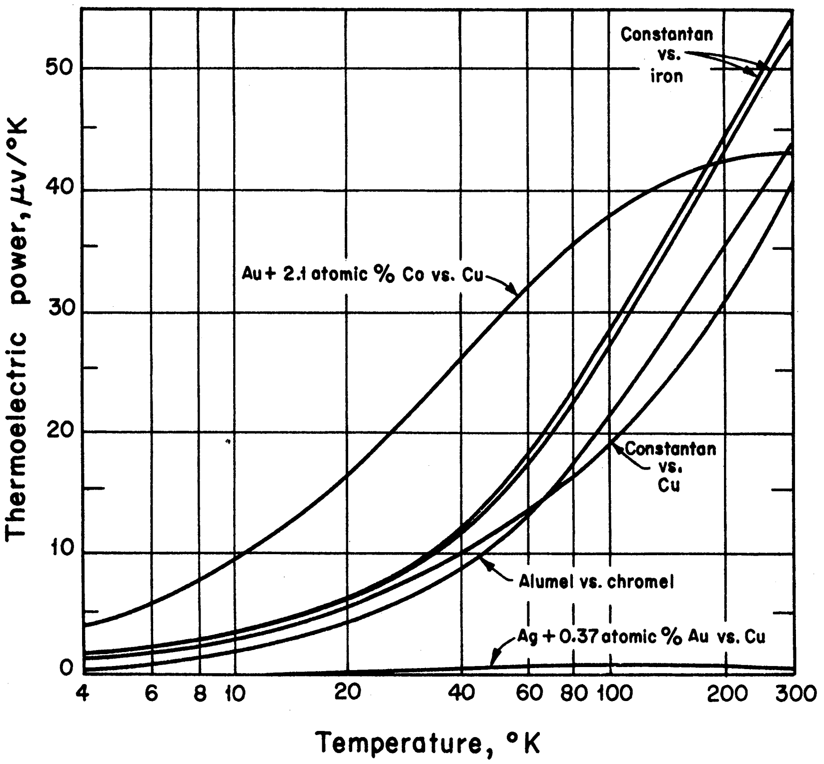


Figure 15. Thermoelectric Power as a Function of Temperature for Various Thermocouple Combinations.(63)

wire combination will differ slightly from others of similar composition, the EMF-temperature characteristics of a "family" of similar wires are essentially parallel. Thus, their "deviations" will be almost linear and exactly zero at a common reference temperature.

The use of a deviation plot provides a very convenient method for making accurate temperature measurements with thermocouples. Owing to the essential linearity of a deviation curve interpolation between a minimum number of calibration points may be done with confidence. The determination of an unknown temperature in measurement is made by computing E_{STD} from Equation (18) using ΔE_{DEV} taken from the deviation plot corresponding to the E_{OBS} for the thermocouple. The unknown temperature is found from the "standard" table of E_{STD} vs. temperature. The "standard" table is usually formulated in great detail and represents the best, smoothed data for a family of thermcouple combinations.

A potentiometer is probably the most satisfactory instrument for precision temperature measurement using thermocouples. These instruments are described in detail elsewhere (52, 53, 57). Instruments presently available by the Leeds and Northrup Co., the K-5 (facility) and K-3 have sensitivities 0.02-0.1 μV and 0.5 μV, respectively. The Wenner potentiometer has a sensitivity of 0.1 μV. A potentiometer manufactured by the Minneapolis Honeywell Co. also has a sensitivity of 0.1 μV. Similar potentiometers are produced by other companies. Comparing these sensitivities with the thermoelectric power of the Au-Co vs. Cu thermocouple, temperature sensitivities will range from 0.002°K to 0.01°K at a level of temperature of 10°K.

X. RESISTANCE THERMOMETRY

The variation of electrical resistance with temperature provides a very convenient, accurate and practical method for temperature measurement. This method is enhanced when the material from which the thermometer is made has a stable and easily reproducible composition. Otherwise, the method becomes impractical owing to inherent instabilities in the resistance-temperature characteristic and consequent uncertainties in the temperature. The basic measurement required is that of electrical resistance and this can be done with great precision using available resistance bridges or potentiometers. Hence, with a stable material and present instrumentation a resistance thermometer can be used to measure temperature to a high degree of accuracy (52, 53, 58-60). For precision measurements the platinum resistance thermometer is the most widely used temperature measuring device in the range 1°K to 300°K. As mentioned in Section V, the International Practical Temperature Scale (1948) is defined in terms of the resistance characteristics of platinum from -183°C to 630.5°C. Undoubtedly, when the new International temperature scale is introduced (4, 5, 6) some time in the period 1968-69, as expected, it also will employ the resistance characteristic of platinum as the standard below 300°K, as well as above that temperature. The reason for this, of course, is the unusually high degree of purity that can be achieved in the production of platinum, the reproducibility of the purity from batch to batch, its monotonic resistance-temperature curve in the strain-free, annealed state, and its inertness to chemical contamination. Its cost is high which may be a factor in its use. Other materials which also are used include copper, nickel, carbon, germanium and certain semi-conductors known as thermstors. These will be discussed later.

The resistance-temperature characteristic of platinum is shown in Figure 16. Above 50°K this relationship is essentially linear. The 1948 IPTS requires that the resistance ratio in Figure 16 be equal to or greater than 1.3920 at 373.15°K (100°C) to insure purity in the platinum wire. The resistance-temperature characteristics of platinum, a platinum film on a non-conducting substrate, nickel, tungsten and copper are shown in Figure 17.

Precision platinum-resistance thermometers are made of a fine coil of highly purified, strain-free platinum wire would around a non-conducting frame. A typical method of construction is shown in Figure 18. The ice-point resistance of these thermometers is commonly set at approximately 25.5 absolute ohms. The platinum thermometer is usually manufactured as a capsule (Figure 18) or as a cane. In each case four lead wires are provided for resistance measurement. Precision resistance is best measured using a Mueller Bridge with a four lead wire thermometer as shown in Figure 19. The accuracy of this bridge circuit is 10^{-5} ohms (39) which would correspond to approximately 0.003°K at 12°K and 0.00009°K at 100°K. Except at very low temperatures accuracies from 0.001°K to 0.0001°K can be obtained using a platinum thermometer and Mueller Bridge. As indicated in Figure 19, the four lead wire circuit provides a means for reversing lead wire connections during a measurement. This technique permits the complete cancellation of lead wire resistance so that the net measured resistance is that of the platinum resistance thermometer wire itself. Potentiometric methods for resistance measurement are summarized by Dauphinee (61).

Calibration of a platinum thermometer can be made using a gas thermometer, another standard thermometer or using the defining fixed-points and a polynomial equation between resistance and temperature, such as the Callendar or Callendar-VanDusen equations (28) which are equivalent to those given in Table II. In the United States calibration is frequently done by the National Bureau of Standards, Institute for Basic Standards. Typical calibration data for a platinum thermometer is given in Table XII. The constants α, δ and β were found from the Callendar-VanDusen formula:

$$t = \frac{R_t - R_o}{\alpha R_o} + \delta\left(\frac{t}{100} - 1\right)\left(\frac{t}{100}\right) + \beta\left(\frac{t}{100} - 1\right)\left(\frac{t}{100}\right)^3 \qquad (19)$$

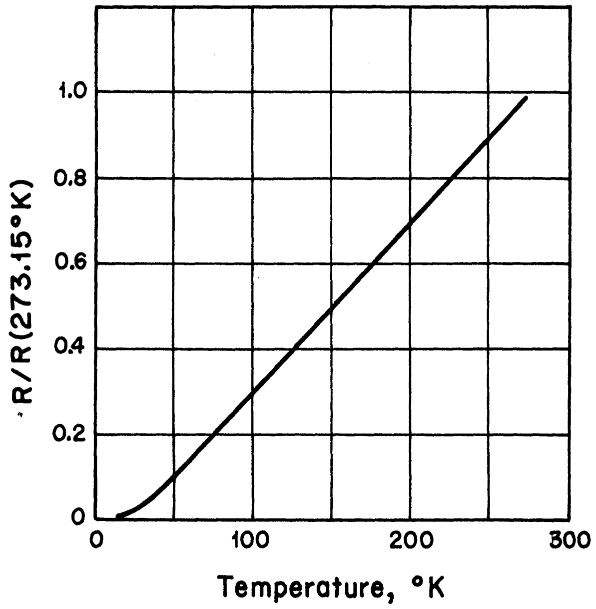


Figure 16. Resistance Ratio of Platinum as a Function of Temperature.

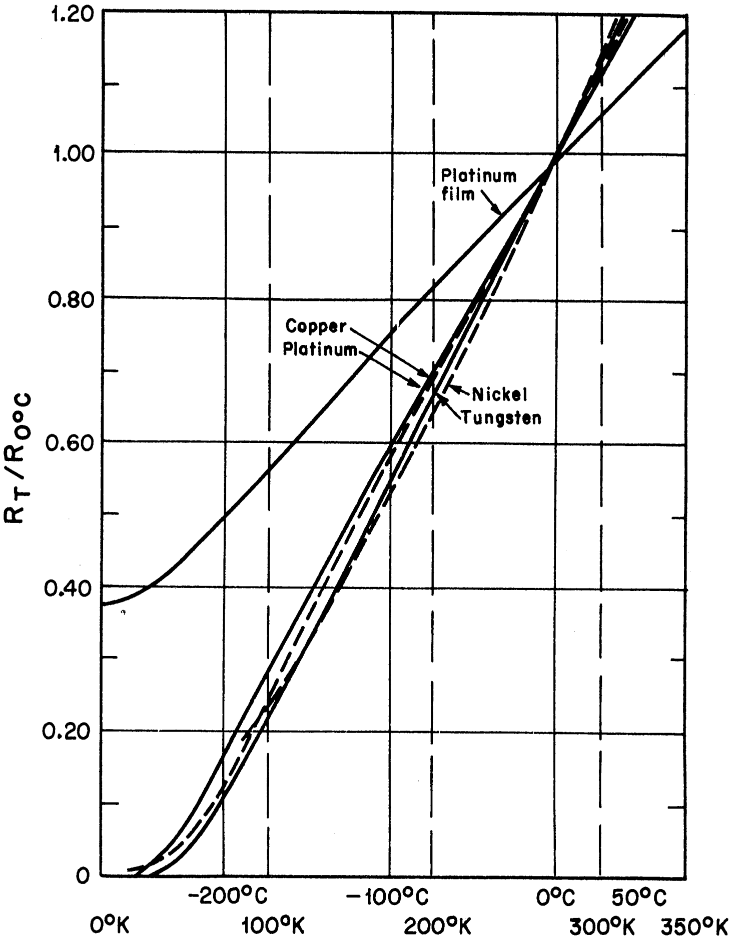


Figure 17. Resistance-temperature Relationship for Various Resistance Type Temperature Sensors-high Range. Sources of Data: Platinum, Mean of NBS Calibration; Tungsten; Copper; and Nickel. (Courtesy of Rosemount Engineering Company.)

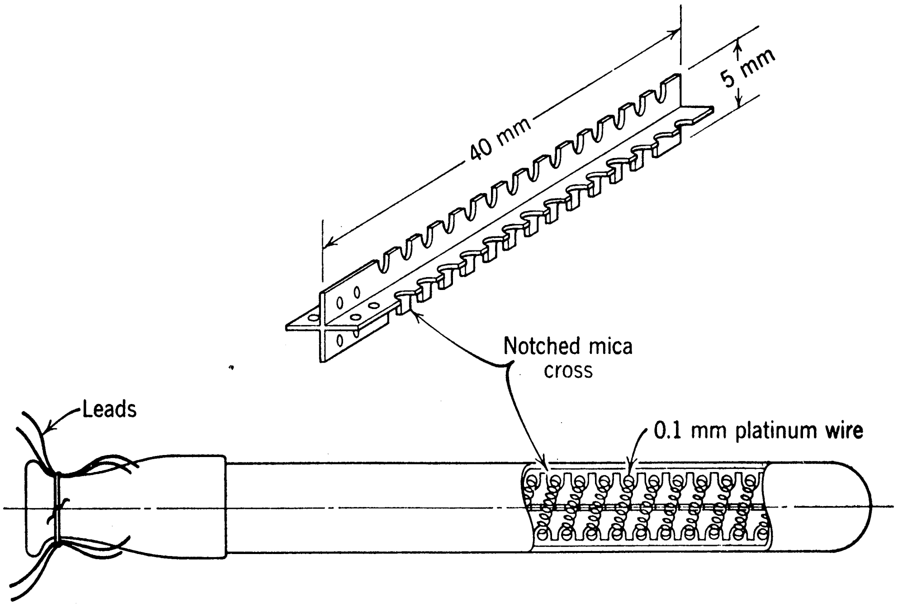


Figure 18. Capsule-type, Strain-free Resistance Thermometer.(40)

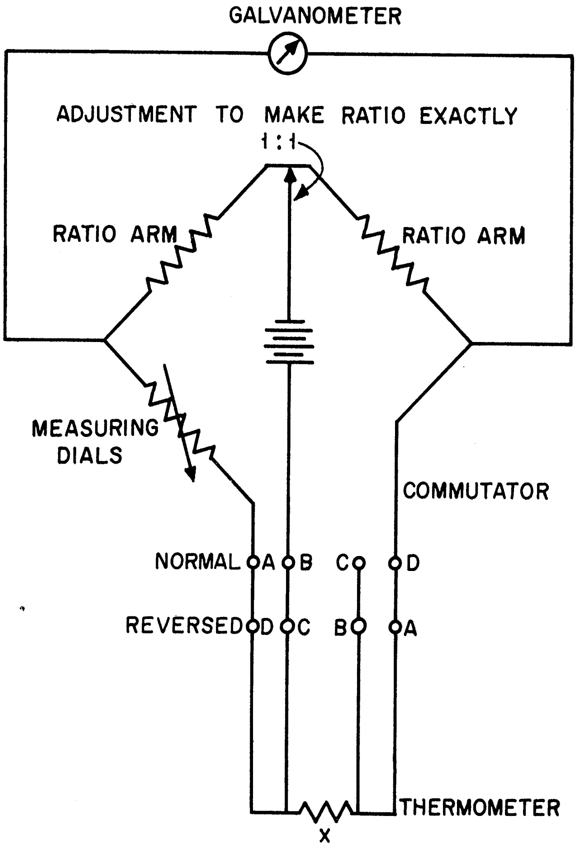


Figure 19. Mueller Bridge with a Four-lead Platinum Resistance Thermometer.

TABLE XII

Report of Calibration of Platinum
Resistance Thermometer, L & N No. 1653433

Submitted by The University of Michigan (62)

Constant	Value
α	0.003925780
δ	1.49168
β	0.11116 (t below 0°C)
β	0 (t above 0°C)
R_o	25.5510 abs. ohms

Additional qualifying information was provided by the NBS for this calibration as follows:

"The value of δ was estimated using the assumption, based on experience with similar thermometers, that the product $\alpha \cdot \delta$ is a constant. The uncertainty in the estimated value of δ is equivalent to an uncertainty at the sulfur point of less than ± 0.01 deg C. The other values given are determined from measurements at the triple point of water, the steam point, and the oxygen point. The uncertainty of the measurements at these points, expressed in temperature, is less than ± 0.0003, ± 0.0015 and ± 0.005 deg C respectively. About one-half of each of these uncertainties is an allowance for systematic errors, including the differences among national laboratories, the remaining part representing the effect of random errors in the measurement process. The effects of these uncertainties on other measured temperatures are discussed in Intercomparison of Platinum Resistance Thermometers between -190 and 445°C, J. Research NBS 28, 217 (1942). During calibration the value of R_o changed by the equivalent of 5×10^{-4} deg C. These results indicate that this thermometer is

Satisfactory for use as a defining standard in accordance with the text of the International Practical Temperature Scale."

Resistance-temperature data on the thermometer described in Table XII are listed in Table XIII for a small range of temperatures above 90°K. These data are computed from the following equation and represent a few of the numerical results abstracted from the original calibration.

$$\frac{R_t}{R_o} = 1 + \alpha t \ [1+\delta(1- \frac{t}{100})10^{-2} + \beta t^2(1- \frac{t}{100})10^{-6}] \ . \tag{20}$$

The first column is the temperature in °K (IPTS 1948), the second column is the thermometer resistance in absolute ohms and the third column gives the inverse (reciprocal) of the difference between each two successive values in the second column. These reciprocal first differences are included to facilitate interpolation. The error introduced by using linear interpolation will be less than 0.0001°C. The third column may also be expressed as dT/dR, °K/ohm, as the tabular difference in the first column is 1.0°K. The thermometer described in Table XII was also calibrated and the results tabulated in 0.1°K intervals from 11°K to 92°K by the NBS using the NBS-1955 temperature scale. This temperature scale was referred to in Section II and Figure 2 and defines the temperature in terms of the electrical resistance of platinum in the range 10°K to 90°K.

An important class of low temperature thermometers are those whose electrical resistance increases with decrease in temperature, rather than the opposite, as is the case with platinum. Below 20°K these thermometers become most practical. This class of thermometers includes carbon, germanium, and the semi-conductors (thermistors) and are the most sensitive resistance elements to temperature changes at low temperatures available. The electrical resistance characteristics of these materials is shown in Figure 20 in comparison with platinum, tungsten and indium.

TABLE XIII

August 1965 Table for Platinum Resistance Thermometer 1653433

TEMP. DEG.K	RESISTANCE ABS OHMS	INVERSE DIFF.
90	6.20974	
91	6.32084	9.001
92	6.43186	9.008
93	6.54279	9.015
94	6.65364	9.022
95	6.76440	9.029
96	6.87507	9.035
97	6.98567	9.042
98	7.09617	9.049
99	7.20660	9.056
100	7.31695	9.063
101	7.42721	9.069
102	7.53739	9.076
103	7.64749	9.083
104	7.75751	9.089
105	7.86745	9.096
106	7.97732	9.102
107	8.08710	9.109
108	8.19681	9.115
109	8.30644	9.122
110	8.41599	9.128
111	8.52546	9.135
112	8.63486	9.141
113	8.74419	9.147
114	8.85343	9.153
115	8.96261	9.160
116	9.07171	9.166
117	9.18074	9.172
118	9.28969	9.178
119	9.39857	9.184
120	9.50738	9.190
121	9.61612	9.196
122	9.72479	9.202
123	9.83338	9.208
124	9.94191	9.214
125	10.05036	9.220
126	10.15875	9.226
127	10.26707	9.232
128	10.37532	9.238
129	10.48350	9.244
130	10.59162	9.249
131	10.69967	9.255
132	10.80765	9.261
133	10.91556	9.267
134	11.02341	9.272
135	11.13120	9.278
136	11.23892	9.283
137	11.34657	9.289
138	11.45417	9.294
139	11.56169	9.300
140	11.66916	9.305
141	11.77656	9.311
142	11.88390	9.316
143	11.99118	9.322
144	12.09840	9.327
145	12.20556	9.332
146	12.31265	9.337
147	12.41969	9.343
148	12.52667	9.348
149	12.63358	9.353
150	12.74044	9.358
151	12.84724	9.363
152	12.95399	9.368
153	13.06067	9.373
154	13.16730	9.379
155	13.27387	9.384
156	13.38038	9.389
157	13.48684	9.393
158	13.59324	9.398
159	13.69959	9.403
160	13.80588	9.408
161	13.91212	9.413
162	14.01830	9.418
163	14.12443	9.423
164	14.23050	9.427
165	14.33653	9.432
166	14.44249	9.437
167	14.54841	9.441
168	14.65428	9.446
169	14.76009	9.451
170	14.86585	9.455
171	14.97156	9.460
172	15.07722	9.464
173	15.18283	9.469
174	15.28839	9.473
175	15.39390	9.478
176	15.49936	9.482
177	15.60477	9.487
178	15.71013	9.491
179	15.81545	9.495
180	15.92071	9.500
181	16.02593	9.504
182	16.13110	9.508
183	16.23623	9.513
184	16.34130	9.517
185	16.44633	9.521
186	16.55132	9.525
187	16.65625	9.529

The most common resistance element which also is readily available and inexpensive, is the conventional carbon radio resistor. In addition to its high thermal sensitivity at low temperatures, the carbon resistor can be made small, is rather insensitive to magnetic fields and has a small heat capacity for rapid thermal response. It is slightly pressure sensitive, having temperature changes of 0.31°K at 20°K and 0.02°K at 4°K for an increase in pressure of 1000 psi (64), and is subject to thermal instabilities or ageing. This lack of reproducibility is particularly significant after the resistor has been exposed to thermal cycling. Carbon in the form of thin graphite coatings has been used as a thermometer (65). This type of thermometer is especially useful where high response is required, as in low temperature (0.1°K) adiabatic demagnetization experiments.

Lindenfeld (66) reports on the use of carbon and germanium thermometers between 0.30°K and 20°K. One problem in the use of carbon radio resistors below 1°K is the difficulty in measuring their high resistance. Maximum power dissipated in these resistors is about 10^{-8} watts for temperatures 1°K and higher. Using a Wheatstone Bridge temperature changes of 10^{-5} to 10^{-6}°K can be detected. The use of the carbon resistor in measurement is greatly aided if a reasonably simple and accurate formula can be written relating resistance to temperature. Clement and Quinnell (67) found that Allen-Bradley Company cylindrical carbon radio resistors has a resistance temperature relationship below 20°K which could be expressed to within ± 1/2% by a semi-empirical expression of the form

$$\log_{10}R + \frac{K}{\log_{10}R} = A + \frac{B}{T} \qquad (21)$$

The constants K, A and B are determined by a calibration of the resistor at a minimum of three known temperatures. Typical resistance-temperature curves for two Allen-Bradley carbon resistors are shown in Figure 21. Schulte (68) calibrated an Allen-Bradley 0.1 W, 270 ohm carbon resistor between 4°K and 296°K and found his

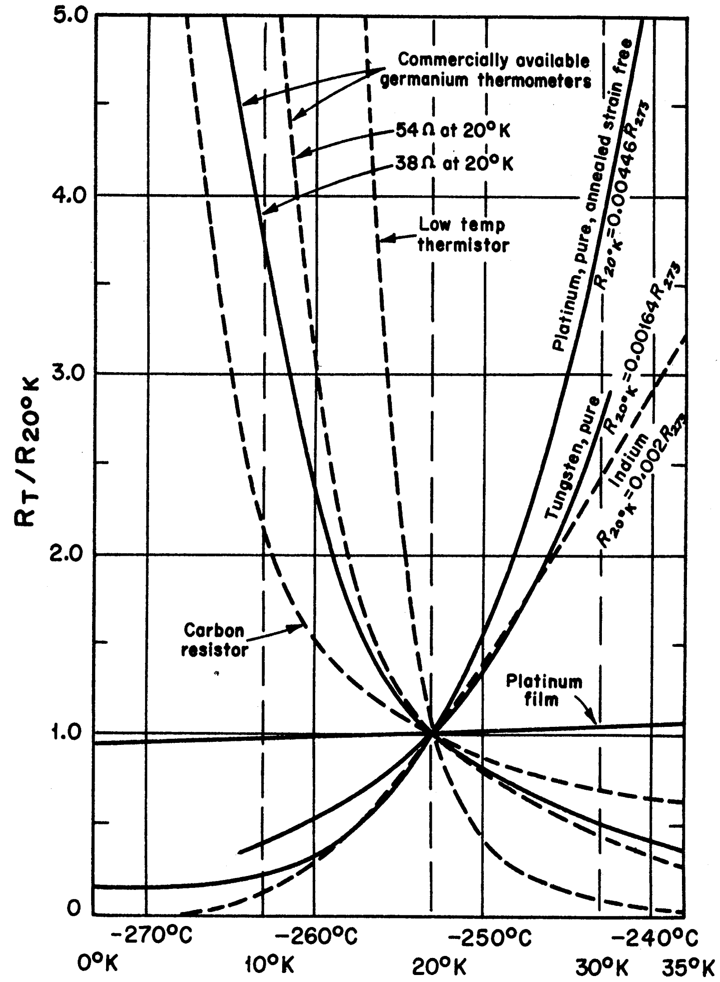


Figure 20. Resistance-temperature Relationship for Various Resistance-type temperature Sensors-low Range. Sources of Data: Platinum, Mean of NBS Calibrations, Carbon Resistor; Germanium Thermometer; Thermistor; Tungsten; and Indium. (Courtesy of Rosemount Engineering Company.)

results to correlate within 7 percent of Equation (21). For a range of temperatures from 2°K to 20°K Mikhailov and Kaganovskii (69) also found that Equation (21) gave satisfactory results for carbon thermometers. In this case the constants in Equation (21) were determined from calibrations at 2°K, 4.2°K and 20.4°K. This permitted temperatures to be calculated with an accuracy of a few hundredths of a degree in the range 2°K to 4.2°K. After 100 heating and cooling cycles between 300°K and 77°K, uncertainty in the temperature measurements in the same 2.2°K interval did not exceed 0.01°K.

Measurement of the resistance of a carbon thermometer may be made with a resistance bridge, as in Figure 19, or with a potentiometer using an accurately calibrated monitoring resistor of known resistance. A schematic diagram of this latter method is shown in Figure 22 as used by Greene (70). He calibrated a carbon resistor having a nominal resistance of 82 ohms with a measuring current of 10 μ-a. The results of this calibration are given in Figure 23 which illustrates the influence of thermal cycling, the reproducibility of the calibration before and after a calibration run and heat conduction along the thermometer lead wires. The ordinate in Figure 23 is the voltage drop across the resistor for a 10 μ-a current. During any one calibration the accuracy amounts to ± 0.02°K and is within the precision of the measurements. Although thermal cycling did produce a shift in the calibration curve, its slope remains constant. Thermal conduction along the lead wires raised the calibration curve by approximately 0.10°K in this instance.

The use of carbon resistors for field measurement where laboratory precision is not demanded has been studied by Herr, et al (71). Allen-Bradley Co. 0.1 watt, 100 ohm (± 5% at 300°K) resistors were found to be reproducible within ± 1% of the absolute temperature in the range 19.5°K to 55.5°K (35°R to 100°R). The measurement of resistance ratio rather than absolute resistance was found to be a more satisfactory method owing to drift in the resistance values of the carbon resistor.

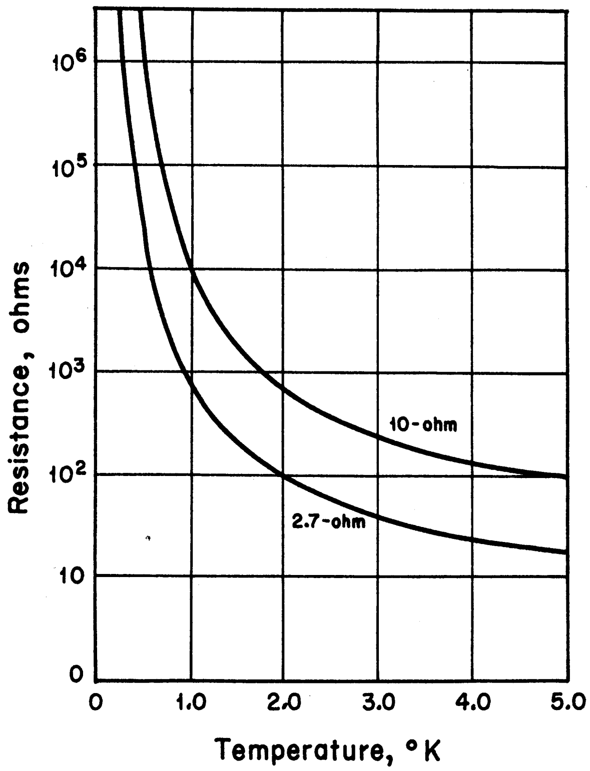


Figure 21. Resistance-temperature Curve for Two Allen-Bradley Carbon Resistors.(39)

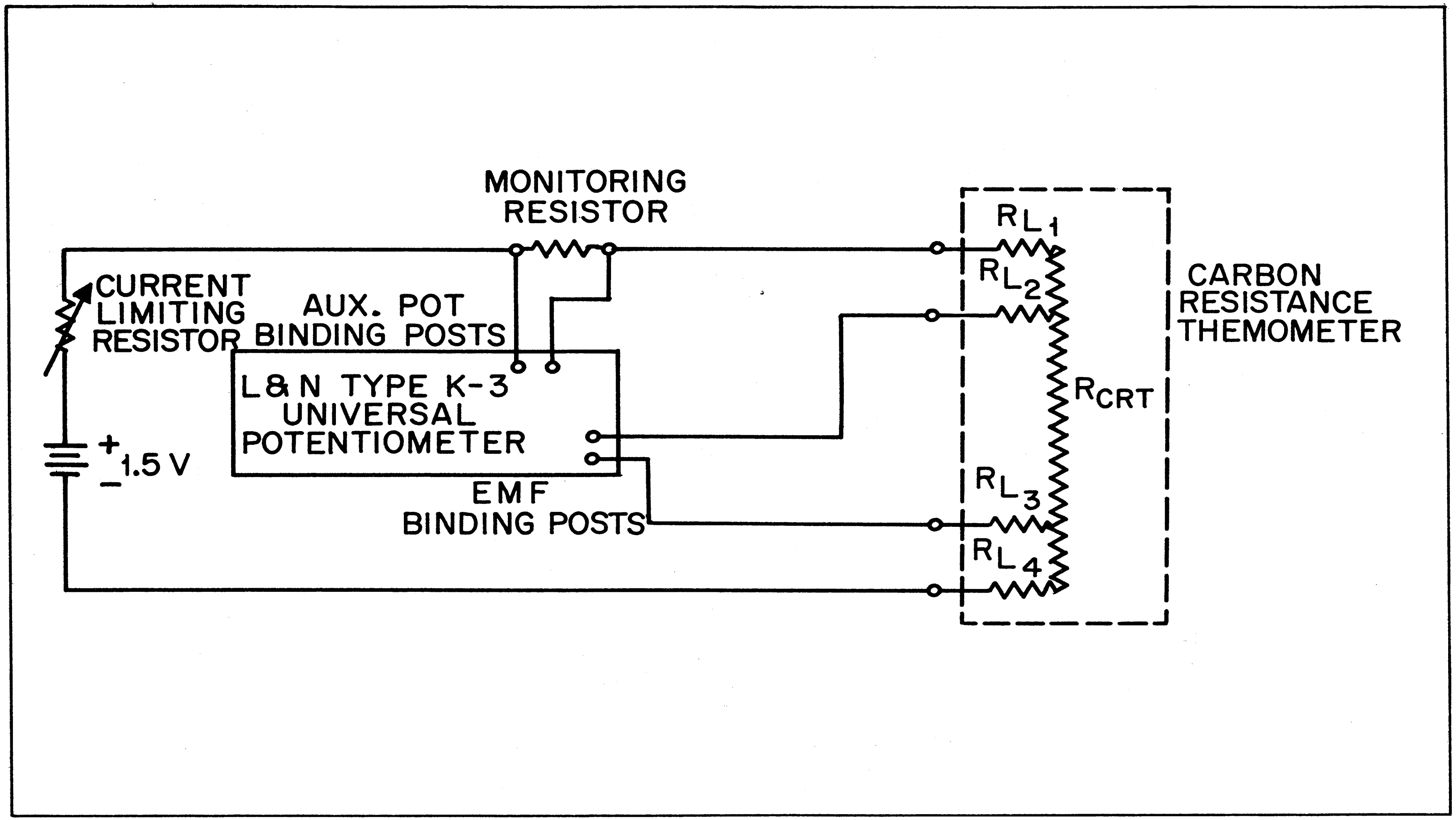


Figure 22. Schematic Diagram of the L&N Type K-3 Universal Potentiometer Circuit.(70)

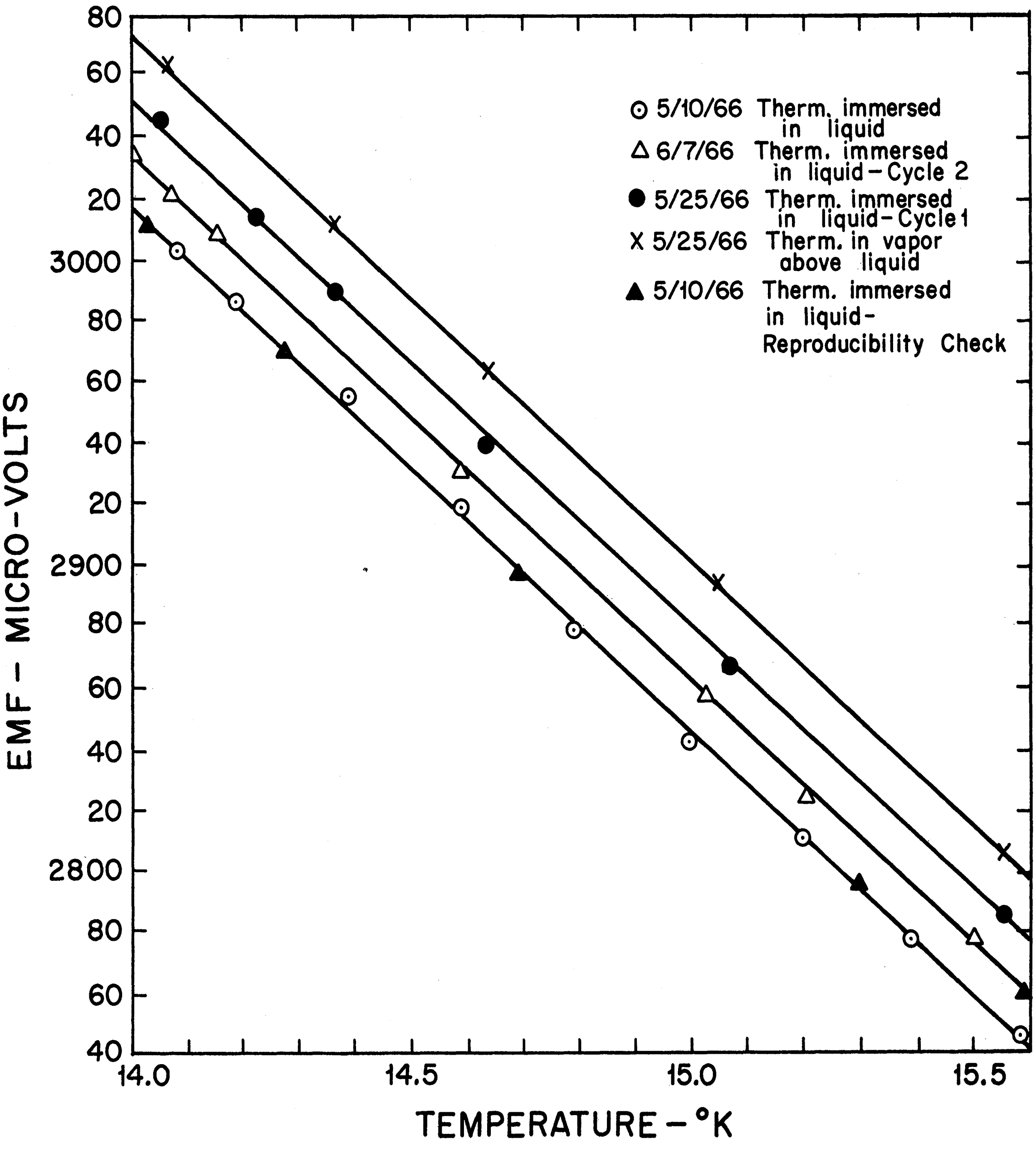


Figure 23. Typical Calibration Curves for Carbon Resistance Thermometer (Nominal Resistance 82 OHMS).(70)

The word "thermistor" is a trade name for a class of semi-conducting solids having a large negative temperature coefficient of electrical resistance. It is a name derived from the word combination thermal-sensitive-resistor. In a physical description these substances are classed as electronic semi-conductors whose characteristics have been given much theoretical and experimental examination since World War II.

Semi-conductors may be classed with those substances having electronic conductivities in the range 10^{-5} to 10^{3} $(\text{ohm-cm})^{-1}$, or resistivities falling between 10^{-3} and 10^{5} ohm-cm (72). This can be compared with the pure metals and metallic alloys whose resistivity (73) are generally less than 10^{-4} ohm-cm or with the electrical insulators, as mica and quartz, having resistivities above 10^{6} ohm-cm at ordinary temperatures. Figure 24 shows these relationships. The important difference between semi-conductors and metals for thermal sensitive uses is not, however, their orders of magnitude of resistivity but the great differences in the change of resistivity with temperature as compared with the metals. This may be illustrated by a typical thermistor which will increase in resistance from 780 to 17,800 ohms for a temperature change from +30 to -30°C. This is a total change of approximately 17,000 ohms or a percentage change of about 2000%. Compared with standard platinum and copper resistance thermometers the corresponding change is about 6 and 100 ohms, respectively, over the same range of temperatures, both changing about 20%. The thermistor, then, undergoes a percentage change in resistivity of about 100 times that of the metals in this range of temperature. Should a greater interval of temperature be examined, as in Figure 24, the percentage change for the thermistor might be as large as 2×10^{6}. Possibly of greater significance in the field of thermal measurements is (dR/DT), the rate of change of resistance with temperature, of this thermistor as a function of temperature. At 25°C, for example, dR/dT is 44 ohms/°C and at -30°C it is 1120 ohms/°C, while for a standard 25-ohm platinum resistance thermometer, dR/dT is about 0.10 ohms/°C in this same range of temperature. This means that if one is able to measure changes in resistance, say, to 0.01 ohm, the temperature change capable of detection with this thermistor is 0.0002°C at 25°C and 0.000009°C at -30°C. Some commercially available thermistors have sensitivities 100 to 1000 times greater than this. The ordinary platinum resistance thermometer would detect a temperature change of 0.1°C under these same circumstances. It is quite generally true that thermistors have greatest sensivitity at lower temperatures. For absolute temperature measurement other considerations, naturally, are necessary, not least among which is the thermal stability of the thermistor element, a property possessed in the highest degree by an annealed, strain free platinum resistance thermometer.

Thermistors are available from the manufacturers in a variety of shapes and sizes: discs, beads, rods, washers, and wafers. The shape selected depends on the use to be made of the element. The sizes range from 0.006 inch to 0.10 inch diameter. For beads, 0.2 to 0.75 inch diameter and 0.040 to 0.500 inch thick for discs, wafers and washers, and for rods from 0.01 to 0.50 inch diameter, 0.25 to 2 inches long. Lead wires of various lengths and diameters consist of platinum, platinum-iridium alloys, or copper which can be butt-soldered, wrapped and soldered or fired in place on the thermistor element. Silver paste contacts are available to which the user can soft-solder lead wired, if desired. Washer type elements have terminals which may be mechanically clamped into place against the faces of the element. Protective coatings are frequently placed over the thermistor to prevent or retard atmospheric attack. These consist of a thin or thick layer of glass or enamel coating. For certain applications the element can be placed in an evacuated or gas-filled bulb.

The recommended maximum temperature for continuous service varies but it can be as high as 300°C, some manufacturers recommend a temperature no greater than 150°C, however. To a large extent this will depend upon such things as accuracy

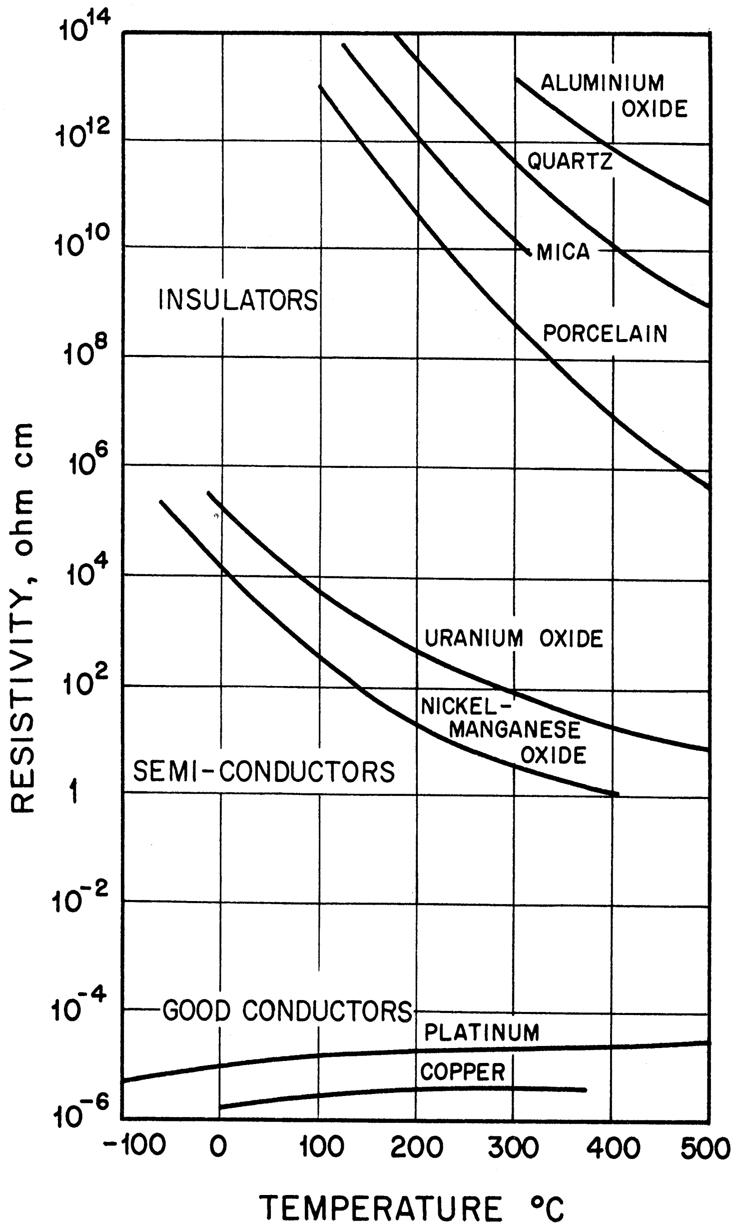


Figure 24. Temperature-resistivity Relationship of Insulators, Semi-conductors and Good Conductors.(84)

required, the atmosphere surrounding the element and the melting point of the solder, if any, used to fasten the lead wires to the element. In any event, the thermistor is used to its greatest advantage, from a thermal-sensitive consideration , at lower temperatures.

Most thermal-sensitive semi-conductors (thermistors) are manufactured by sintering various mixtures and combinations of metallic-oxides, the common materials being the oxides of manganese, nickel, cobalt, copper, uranium, iron, zinc, titanium, and magnesium. For the commercial thermistors the oxides of manganese, nickel and cobalt, however, are the most commonly used substances for the mixtures. The result of this type of manufacturing process is a hard, dense ceramic type of material.

Other materials (72, 74) which may be classed with the semi-conductors and which possess a large negative temperature coefficient of electrical resistance include chlorides such as NaCl, some sulphides like Ag_2S, CuS, PbS, CaS and some iodides, bromides, and nitrides. Lead sulfide has been used as a detector of infra-red radiation in a radiation pyrometer and is marketed commercially. Its response is high (10,000 cps) and can detect temperatures as low as-300°F. The uses of thermistors in a radiation-type pick-up is reported (77) for measurement of sub-zero temperatures.

Some pure materials such as silicon, tellurium, germanium and selenium (74) which are monatomic become semi-conductors in the presence of certain impurities. This effect is shown qualitatively in Figures 25 and 26 for silicon containing an unknown impurity and for cuprous oxide with varying amounts of oxygen in excess of the stoichiometric. Figure 25 taken from Becker, et al (75), shows a 10^7 increase in the conductivity of pure silicon by the addition of a foreign impurity. A similar large increase in conductivity is seen in the case of cuprous oxide, Figure 26, also taken from reference (75) where the increase is due to an excess

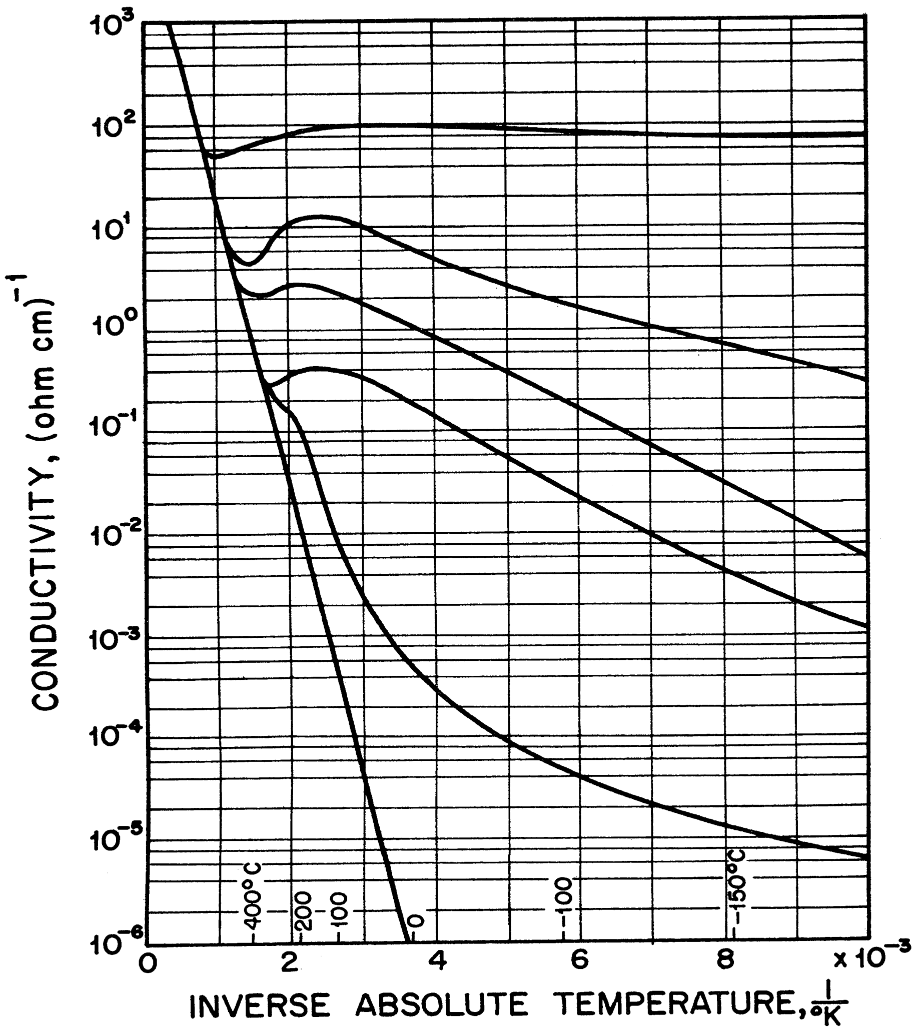


Figure 25. Logarithm of the Conductivity of Various Specimens of Silicon as a Function of Inverse Absolute Temperature.(84)

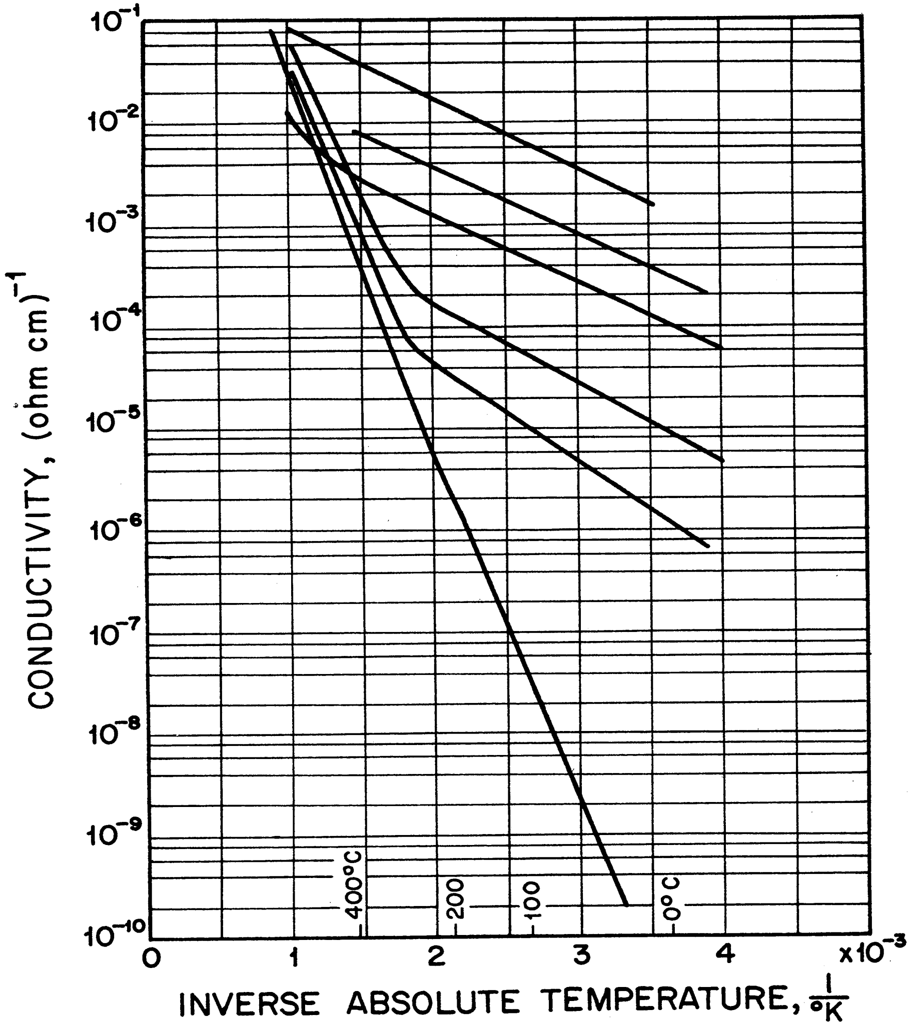


Figure 26. Logarithm of the Conductivity of Various Specimens of Cuprous Oxide as a Function of Inverse Absolute Temperature.(84)

of oxygen up to 1%. These effects vary greatly with the type of impurity, its amount, its dispersion within the solid, and the heat treatment of the solid.

Generally speaking, a thermistor can be considered for use in any application requiring a thermal sensitive electrical resistance element. The obvious and perhaps most widely employed application is that of temperature measurement. As was pointed out earlier, it is possible to detect very minute changes in temperature with a thermistor owing to the large change in its electrical resistance with temperature. Brown (76) employed a Western Electric 17A thermistor to measure small changes in air temperature. The device was used in a bridge circuit, the output of which was amplified and fed into a recording oscillograph. During the initial measurements it was found that the thermistor was so sensitive that it recorded with fidelity the fluctuations in air temperature resulting from atmosperic turbulence. Figure 27 taken from this work shows a typical oscillograph record. Changes in temperature could be measured to an estimated 0.0007°C.

Theoretical work of Wilson (78, 80) and others has lead to the following expression for the electronic conductivity of a semi-conductor

$$\sigma = Ae^{-B/T} \tag{22}$$

Since the conductivity σ is the reciprocal of the resistivity ρ we may write

$$\rho = Ce^{B/T}$$

or,

$$\rho = \rho_o e^{B\left(\frac{1}{T} - \frac{1}{T_o}\right)} \quad . \tag{23}$$

Also, since the electrical resistance is a geometric extension of the resistivity Equation (23) may be written

$$R = R_o e^{B\left(\frac{1}{T} - \frac{1}{T_o}\right)} \tag{24}$$

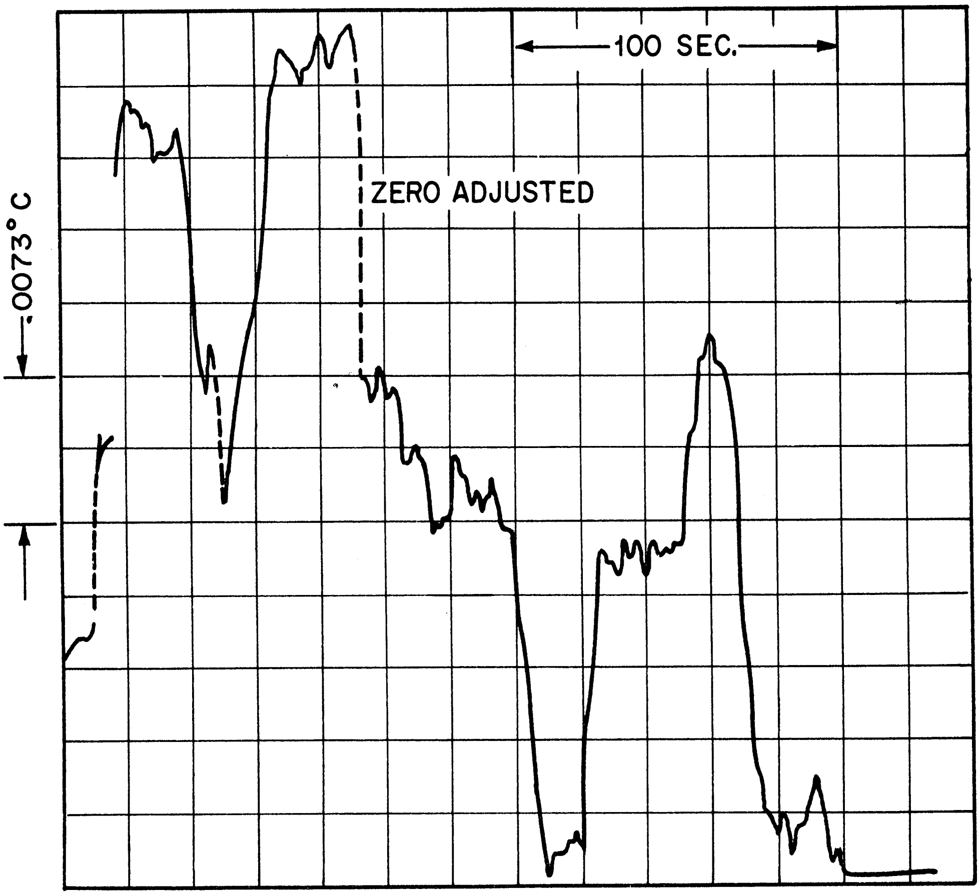


Figure 27. Thermistor Response to Room Temperature Variations.(84)

Because of the form of Equations (23) and (24), the logarithm of the resistivity or resistance is frequently plotted against the reciprocal of the absolute temperature, as shown in Figure 28, in order to demonstrate the electrical characteristics of a thermistor and to compare it with others. These data are experimental and are taken from Becker, et al (75).

The experimental curves in Figure 28 are almost straight, as required by Equation (23). However, close inspection will disclose a slight curvature which may be shown to increase linearly with increase in level of temperature (75). Hence, the equation is sometimes modified as

$$\rho = ET^{-c} e^{D/T} , \tag{25}$$

where C is a small number compared with D or B and may be positive, negative or zero depending on the material (75). For our present purpose we shall employ Equation (24), since if the interval $T - T_o$ is not too great this equation will adequately represent the data and it is somewhat easier to handle mathematically.

As was mentioned above the relationship of resistance to absolute temperature, given by Equation (24), has the same shape as the curve shown in Figure 28. From such a curve several important characteristics may be obtained relative to the suitability of a thermistor as a temperature sensing element. A curve of R vs. 1/T is also a convenient chart for comparing several different thermistors for use in temperature measurement. By taking logarithms and differentiating Equation (24) the following equations are obtained:

$$\frac{dR}{R} = - \frac{B}{T^2} \, dT , \tag{26}$$

or,

$$\frac{1}{R} \frac{dR}{dT} = - \frac{B}{T^2} , \tag{27}$$

and,

$$\frac{dR}{dT} = - B \frac{R}{T^2} , \tag{28}$$

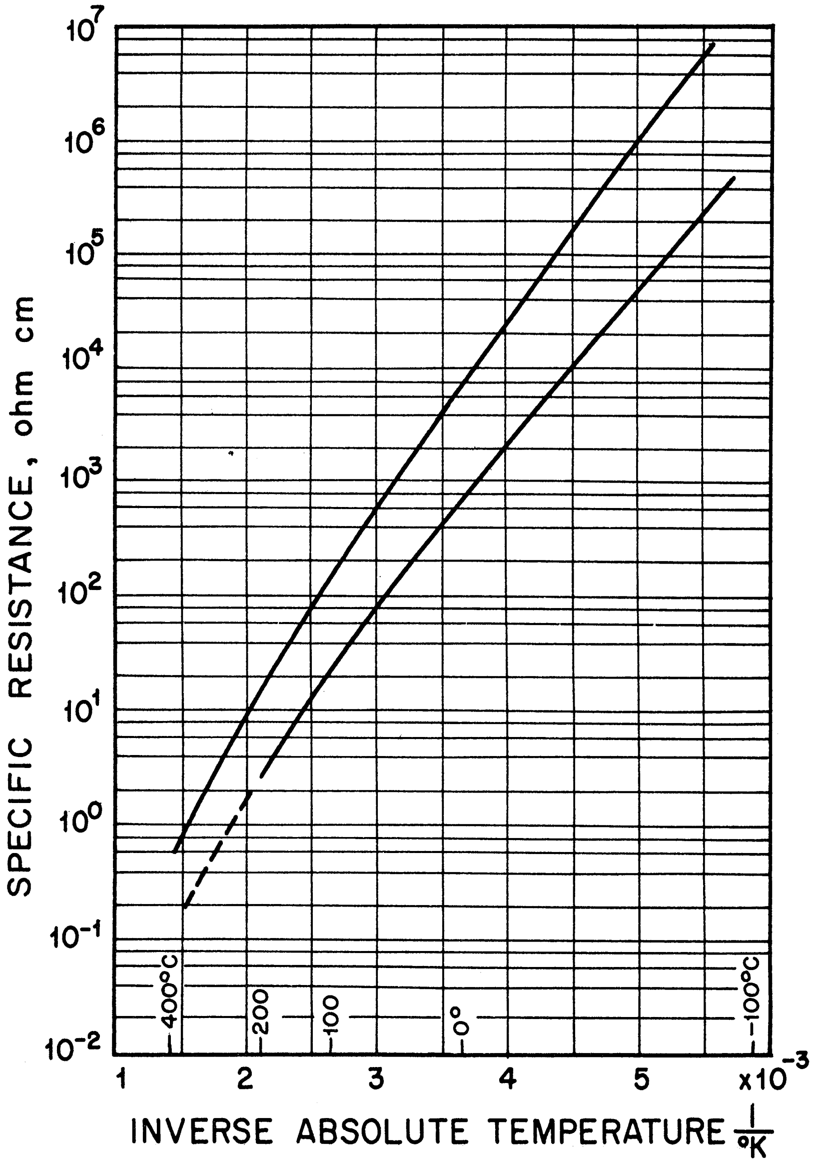


Figure 28. Logarithm of the Specific Resistance of Two Thermistor Materials as a Function of Inverse Absolute Temperature.(84)

Equation (28) may be interpreted in relation to a curve similar to Figure 28 or Log R vs. 1/T. It will be noted that the slope of a curve on such a chart is written

$$\frac{d\ (\mathrm{Log}\ R)}{d(1/T)} = \frac{dR/R}{-dT/T^2} = \text{(slope of Log R - 1/T curve)} \quad . \tag{29}$$

Comparison of Equations (28) and (29) disclosed that the right hand side of Equation (29), the slope of a curve plotted as Log R vs 1/T, is equal to the parameter B in Equation (24). Hence

$$B = \text{(slope of Log R vs. 1/T curve).} \tag{30}$$

Equation (28) is then rearranged to

$$\frac{dR}{dT} = - \text{(slope)} \frac{R}{T^2} \tag{31}$$

Interpretation of Equation (31) is as follows. For use as a temperature sensing element it is desirable that a thermistor have as large a value of dR/dT as possible in order that it be sensitive and capable of detecting small changes in temperature for any given resistance measuring system. From Equation (31) it follows that at any given temperature, that thermistor which has the greatest slope on a Log R vs. 1/T plot and the greatest resistance will also be the most sensitive as a temperature sensing element. In this way, therefore, a series of thermistors can be very rapidly evaluated as to their thermal sensitivity.

Another method for evaluation of thermistors consists of plotting Log R_o vs. B, where B is determined from experimental thermistor data in the region of T_o, which may be taken to be 0°C; R_o is then the resistance of the thermistor at 0°C. Because most thermistors have similar characteristics it will be generally true that a thermistor with superior thermal sensitivity at 0°C will also have superior sensitivity at other temperatures. In any event the resistance-temperature characteristics of the thermistor can be obtained approximately from Equation (24) or from the manufacturer's published data. Equation (24) is approximate owing to the non-linear nature of Log R vs. 1/T, as mentioned above in connection with Equation (25) and Figure 28.

The technical literature does not contain a large body of data on the stability or ageing effects of thermistors. What is reported here are heterogeneous results of a number of observers on a few isolated tests. It may be generally concluded, however, that an ageing effect may be expected which usually is of the nature of an increase with time of the electrical resistance. This increase is not linear but logarithmic, resulting in smaller percentage changes in resistance with increased time. Pre-ageing may be accomplished by heating or by the passage of higher than service current through the thermistor (79). These have the effect also of accelerating the ageing if the temperature is high enough.

The change of electrical resistance is sometimes attributed to a rearrangement in the distribution of the components of the mixture of oxides making up a semiconductor. Heat treatment is believed to play a major role in the dispersion of the components. Hence, ageing and pre-ageing usually involve some kind of heat treatment.

Muller and Stolen (81) tested two Western Electric 14A thermistors at 25°C over a period of six months. They report a decrease in resistance of about 50 ohms out of a total of approximately 100,000 ohms. This corresponds to an ageing effect of about 0.012°C.

Figure 29 shows ageing data (75) taken on three quarter-inch diameter discs of material No. 1 and No. 2 (No. 1 is composed of manganese, nickel oxides; No. 2 is composed of oxides of manganese, nickel and cobalt) with silver contacts and soldered leads. These discs were measured soon after production, were aged in an oven at 105°C and were periodically tested at 24°C. The percentage change in resistance over its initial value is plotted versus the logarithm of the time in the ageing overn. It is to be noted that most of the ageing takes place in the first day or week. If these discs were pre-aged for a week or a month and the subsequent change in resistance referred to the resistance after pre-ageing, they would age only about 0.2 per cent in one year. In a thermistor thermometer, this change in resistance would correspond to a temperature change of 0.05°C. Thermistors mounted in an evacuated tube or coated with a thin layer of glass age even less than those shown in the figure. For some applications such high stability is not essential and it is not necessary to give the thermometers special treatment.

Thermistors have been used at high temperatures with satisfactory ageing characteristics. Extruded rods of material No. 1 have been tested for stability by treating them for two months at a temperature of 300°C and -75°C for a total of 700 temperature cycles, each lasting one-half hour. The resistance of typical units changed by less than one per cent.

In order to determine the life of 1A thermistor, Pearson (82) placed it in a circuit where an off-and-on current of 10 mA. a.c. was repeated 30 seconds over an extended period of time. Resistance measurements were made on the units periodically in order to determine their stability with time. The general trend was a rise in resistance during the first part of its life, after which the resistance became quite constant.

Over a period of 15 months, during which time the thermometer was put through 650,000 heating cycles, the cold resistance did not increase by more than 7%. The resistance of the thermistor when hot was found to be equally stable.

The characteristics of both thermistors and thermocouples shift when exposed to high temperatures for lengthy periods of time (83). For thermistors the resistance change varies logarithmically with time with higher temperatures accelerating the change. This suggests that if thermistors are subjected for several

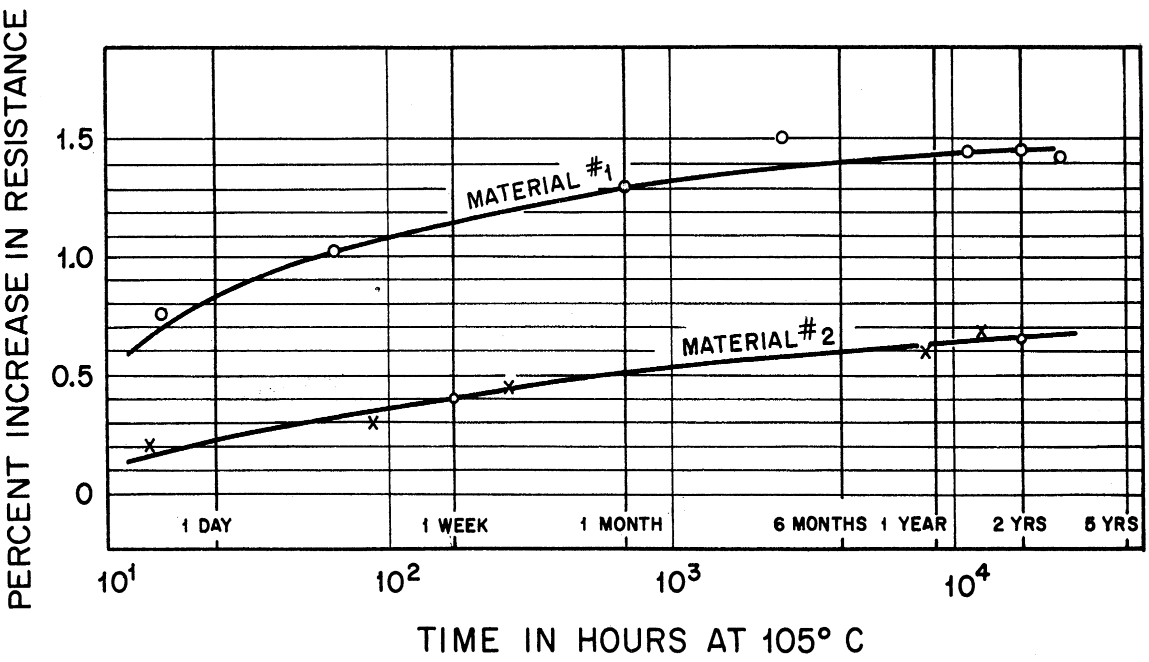


Figure 29. Effect of Aging in 105C Oven on Thermistor Characteristics; Materials 1 and 2.(84)

days or weeks to temperatures somewhat higher than those to be encountered in actual use, the major portion of the change would have occurred. For thermocouples, the change in voltage output becomes greater as the exposure time to high temperature is increased. Over a three month period in which thermistors and thermocouples were exposed to 200°F for about 15 hours, the thermistor shifted a maximum of 0.2°F, while the thermocouple shifted 0.3°F. However, when new elements were tested and aged for 100 hours at 500°F, the thermistors still shifted only 0.2°F while the thermocouples shifted twice as much or 0.6°F.

It was found by Muller and Stolen (81) that if the exciting potential is left impressed across the thermistor, a steady state is reached. This implied a resistance change of less than 1 ohm on daily measurement. The cold resistance of this thermistor at 0°C was 350,000 ohms.

Short range stability of a Western Electric 14A thermistor measured at five minute intervals at 25°C (in ohms) is shown in the table below. The authors (81) used the thermistor to measure small temperature difference in a laboratory experiment.

	Thermistor A		Thermistor B
1.	96,234.0	1.	96,234.7
2.	96,234.6	2.	96,234.6
3.	96,234.2	3.	96,234.9
4.	96,235.0	4.	96,234.4
5.	96,234.8	5.	96,234.4
6.	96,234.8	6.	96,234.8
7.	96,234.7	7.	96,234.2
8.	96,234.8	8.	96,234.7
9.	96,234.6	9.	96,234.0
10.	96,235.0	10.	96,234.6

The conclusion is that no significant change in resistance was detected which could not be attributed to measurement uncertainty.

To obtain a stable thermistor the following steps are generally thought to be necessary (75). By these precautions remarkably good stabilities can be attained.

1. Select only semi-conductors which are pure electronic conductors.
2. Select those which do not change chemically when exposed to the atmosphere at elevated temperatures.
3. Select one which is not sensitive to impurities likely to be encountered in manufacture or in use.
4. Treat it so that the degree of dispersion of the critical impurities is in equilibrium or else that the approach to equilibrium is very slow at operating temperatures.
5. Make a contact which is intimate, sticks tenaciously, has an expansion coefficient compatible with the semi-conductor, and is durable in the atmosphere to which it will be exposed.
6. In some cases, enclose the thermistor in a thin coating of glass or a material impervious to gases and liquids, the coating having a suitable expansion coefficient.
7. Pre-age the unit for several days or weeks at a temperature somewhat higher than that to which it will be subjected.

Clark and Kobayashi (84, 85) have studied the general characteristics of thermistors to be used for temperature measurement. This includes the theory of their conductance properties, the dynamic response and steady-state error of the thermistor temperature-sensing element, their stability and the resistance-temperature characteristics of approximately 300 commercially available thermistors from 8 different manufacturers. Friedberg (79) describes a semi-conducting film of ZnO used as a thermometer at 2°K. This device had an electrical resistance of $5(10^5)$ ohms at liquid helium temperatures and had a sensitivity of approximately $5(10^4)$ ohms per degree K at 2°K.

Germanium, with impurities consisting variously of arsenic, gallium or indium, has become one of the most satisfactory materials for thermal resistance elements in the range 0.2°K to 20°K. This material possesses a negative temperature coefficient of resistance, a moderate level of resistance, high sensitivity of resistance change to temperature change, high reproducibility and stability to thermal cycling and is readily manufactured and fabricated. The impurities are included in the germanium in controlled quantities to influence both the resistance-temperature characteristics and the sensitivity. A typical resistance-temperature curve for germanium "doped" with 0.001 At% indium is shown in Figure 30 for the temperature range 1°K to 5°K. This particular element was found to be highly reproducible over a period of several months. The thermometer was subjected to a number of warming and cooling cycles following which its resistance-temperature characteristic could be reproduced to within ± 0.001°K. The measuring current used was 0.01 ma although the author reports an increase of current to 0.1 ma did not appreciably influence the R-T characteristic (79).

Edlow and Plumb (86, 87) studied the reproducibility and temperature-resistance characteristics of a number of commercially available germanium thermometers. The germanium had either arsenic or gallium as the impurity. Their purpose was to find out if a germanium thermometer was sufficiently stable to be used as a basic secondary standard thermometer. As a consequence of their study the NBS adopted the germanium resistance thermometer as the basis for the NBS scale from 2°K to 20°K and used it for basic temperature calibration in this range. The determination of reproducibility was made by cycling the resistance element from 4.2°K to 300°K and measuring the resistance change at 4.2°K. This change in resistance was then related to the corresponding temperature change. Two typical heating-cooling cycle tests are shown in Figures 31 and 32. In each case the reproducibility is within ± 0.001°K. In the case of resistor D, Figure 32, the reproducibility is within 0.0005°K after 86 cycles. Because of this high degree of stability the resistor of Figure 32 became one of the NBS standard thermometers. This result is quite typical

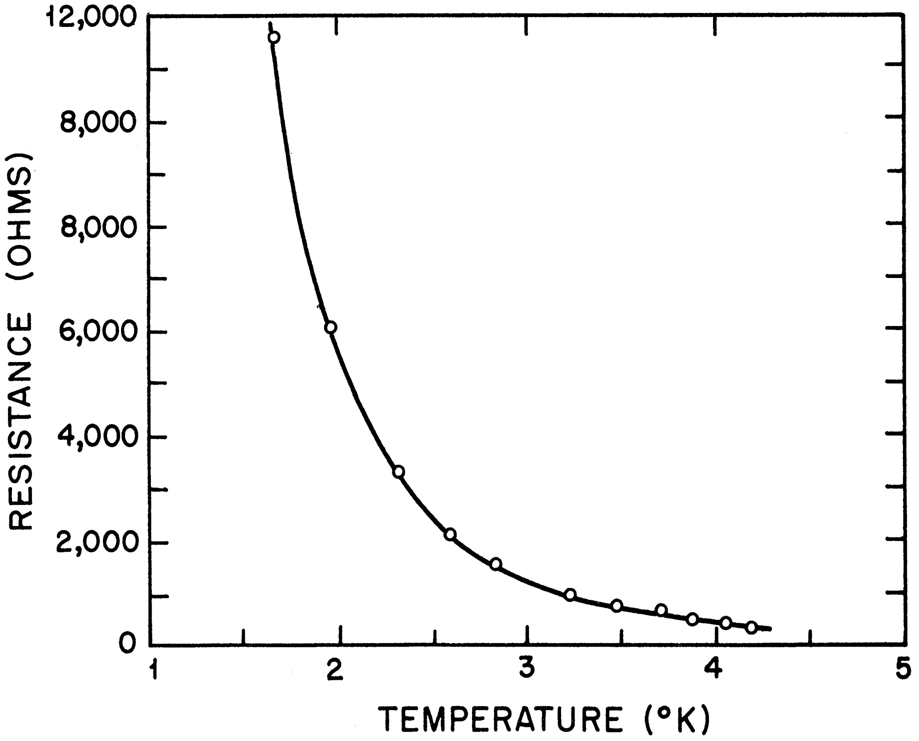


Figure 30. Calibration Curve for A Germanium Thermometer.(79)

of that found by others. Kunzler, et al (88), for example, cycled arsenic "doped" germanium encapsulated in helium-filled thermometers as many as 50 times and found no evidence of calibration change of as much as 0.0001°K. Furthermore, they report two such thermometers in use for 3 years on low temperature experimental apparatus with no observable change in calibration. From results such as these it seems safe to conclude that germanium "doped" with a selected impurity is a suitable material for low temperature thermometers below 20°K.

The resistance-temperature calibration data for a number of encapsulated, hermetically sealed, arsenic "doped" germanium thermometers was determined by Enlow and Plumb (86) in the range 2.1°K to 5.0°K. The resistance was measured at temperature intervals of 0.1°K in a pressure-controlled helium liquid-vapor equilibrium cell. Other measurements were made in a calibration comparator apparatus. The results agreed to within 0.001°K. The basic standard temperature reference was the NBS 1958 He^4 scale, Table VI. Some typical data are given in Figure 33. A polynomial function was derived for each thermometer to represent its resistance-temperature calibration in the range 2.1°K to 5.0°K.

The sensitivity of a germanium thermometer, dR/dT, manufactured by Cryo Cal, Inc. (89), is shown in Figure 34 for the temperature range 2°K to 28°K. At 20°K the sensitivity of this thermometer is 3 ohms per °K which may be compared with a sensitivity of 0.0185 ohms per °K for a platinum thermometer at the same temperature. The very large increase in sensitivity for germanium at temperatures below 20°K is characteristic of this type of resistance thermometer.

The use of arsenic-doped germanium prepared from a single germanium crystal is reported by Kunzler, et al (88). The germanium element is cut into the form of a "bridge" of dimensions 0.06 x 0.05 x 0.52 cm with side arms near each end for electrical connections. An encapsulated thermometer design is illustrated in Figure 35. When covered with a platinum case it is filled with helium gas which limits its lowest useful temperature to about 0.25°K. "Bare" bridges have also

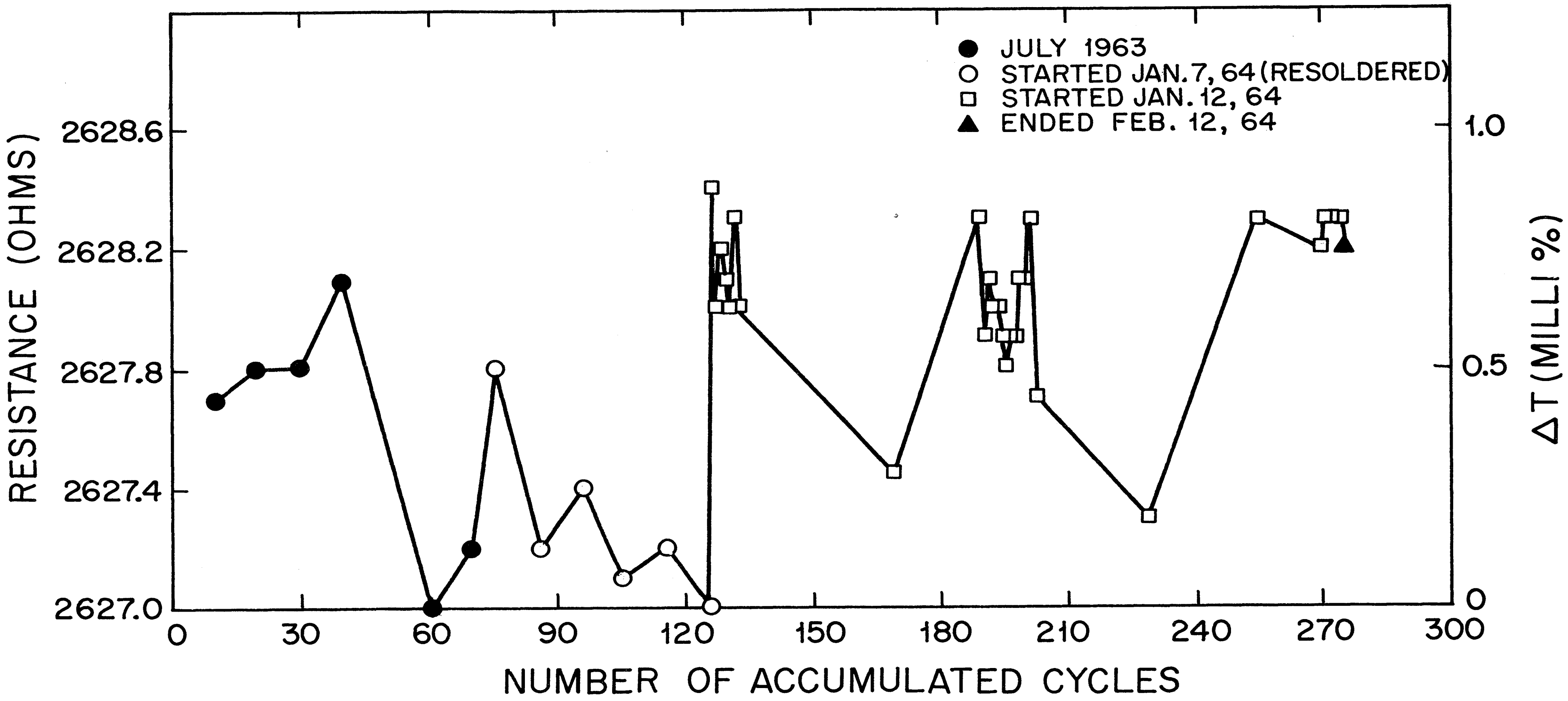


Figure 31. Equilibrium Resistance As A Function of the Number of Accumulated Cycles T = 4.2°K.(87)

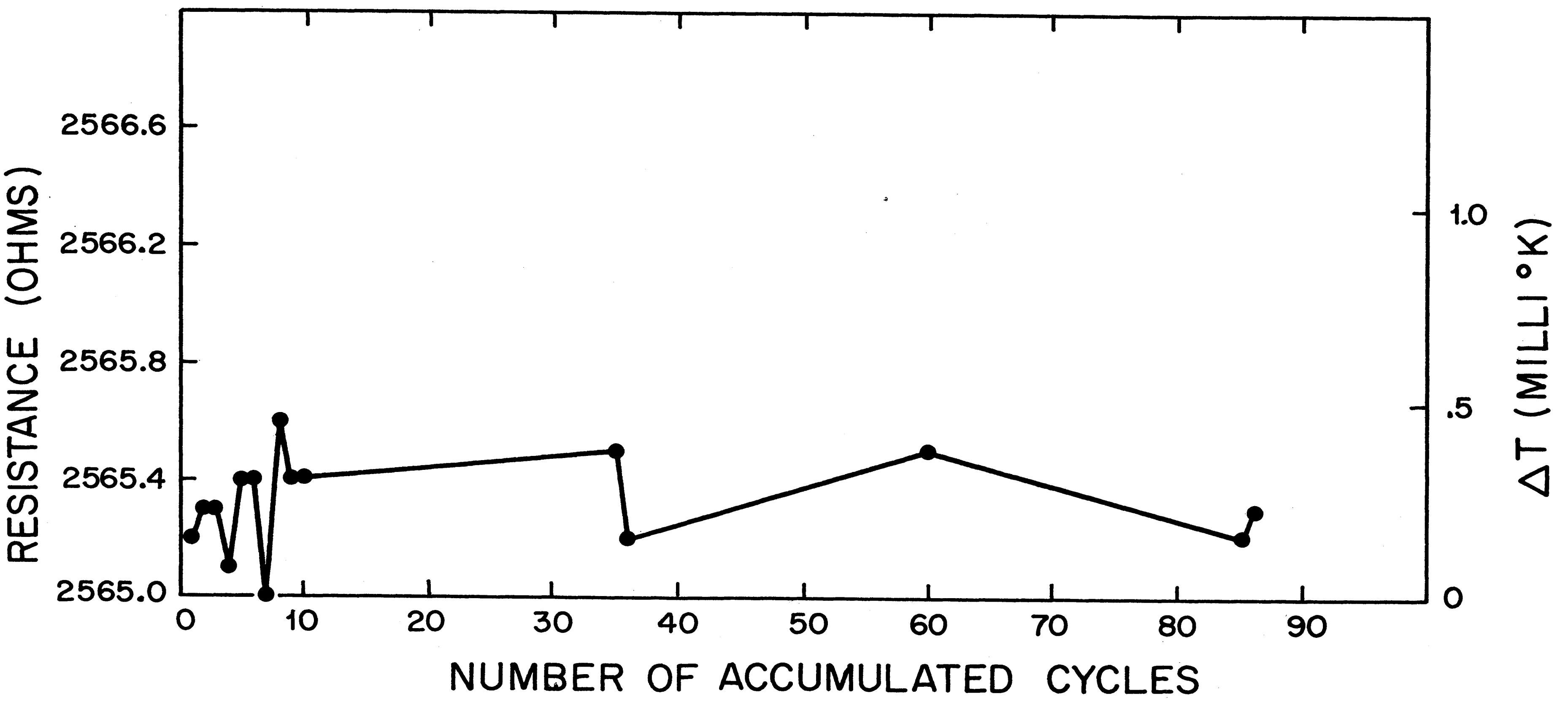


Figure 32. Equilibrium Resistance As A Function of the Number of Accumulated Cycles for Resistor D.(87) T = 4.2°K.

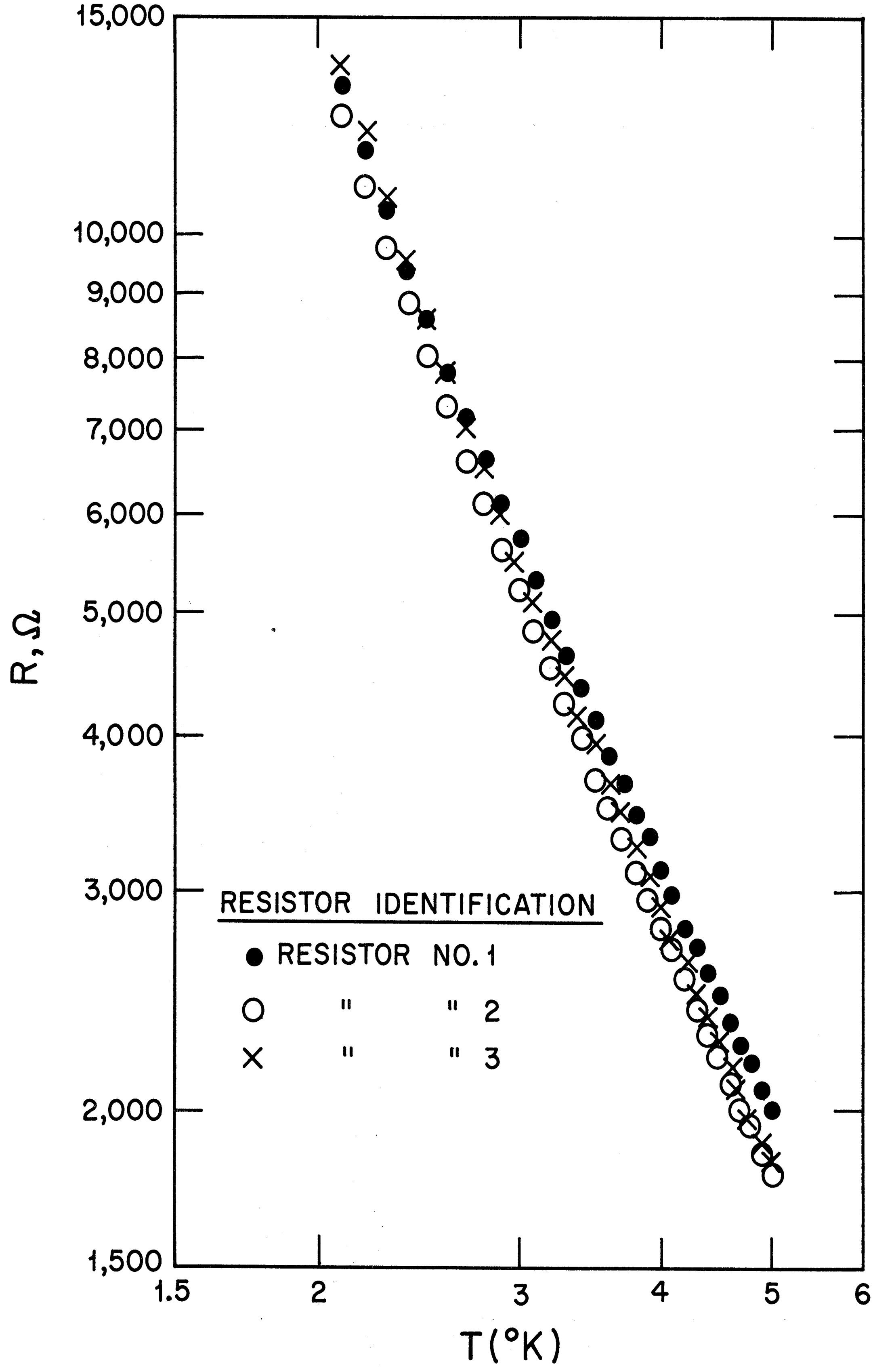


Figure 33. A Plot of the Resistance-temperature Calibration Data for Resistors 1, 2 and 3.(86) Temperatures were Derived from Liquid Helium-4 Vapor Pressures.

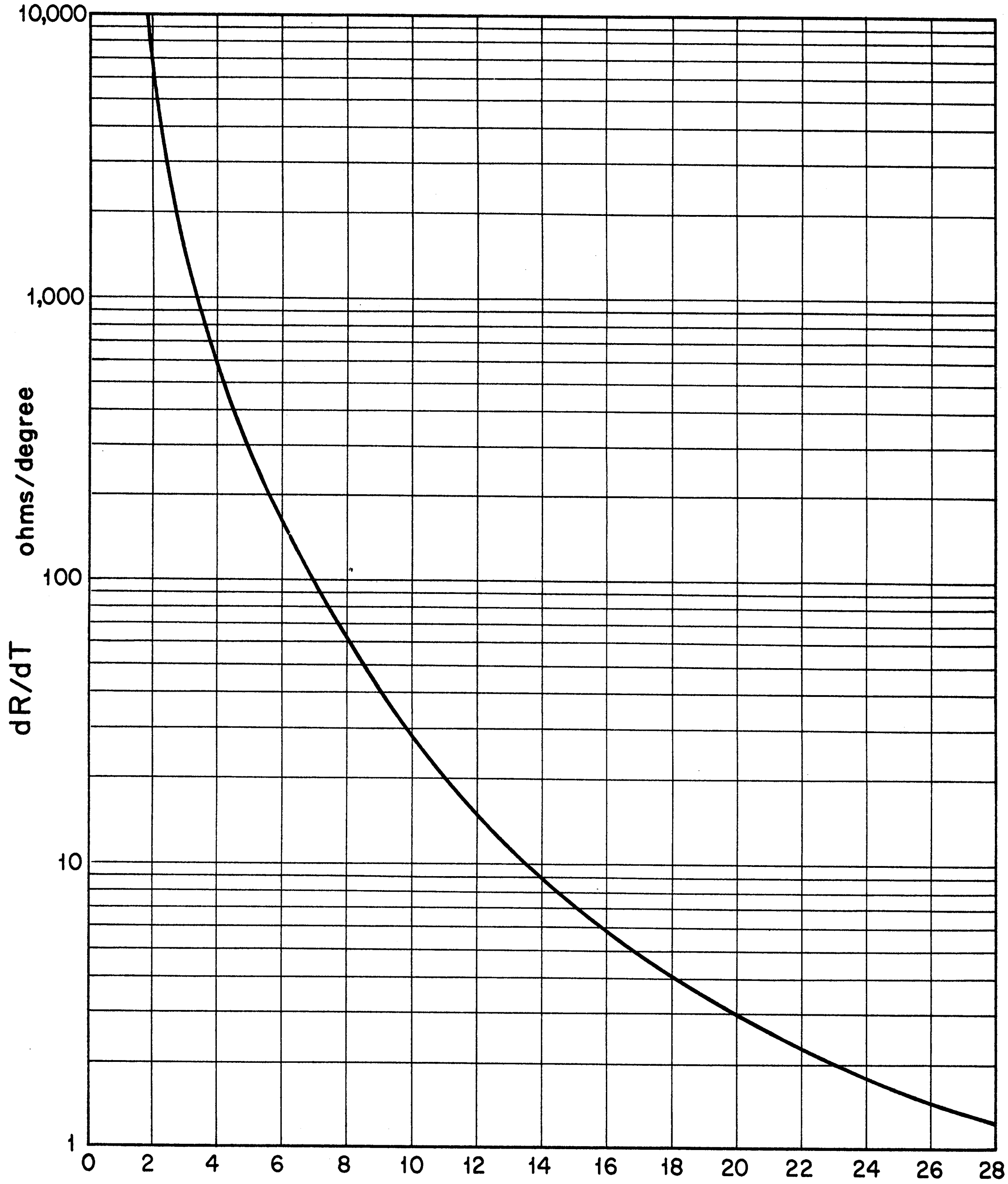


Figure 34. Sensitivity dR/dT Typical Standard Cryo Resistor. (Courtesy Cryo. Cal, Inc.)(89)

been used in applications such as adiabatic demagnetization experiments where a thermometer with minimum heat capacity is required to give high response. In this case a lag time between the thermometer and sample was 0.1 second. Higher currents are permitted with the "bare" bridge than with encapsulated models owing to the improved cooling permitted by the exposed germanium element. The resistance-temperature characteristics of the encapsulated model were found to be unaffected (within ± 0.0001°K) by thermal cycling or aging over a period of several years. Cycling of the "bare" bridge between 4.2°K and 293°K several times produced only a few thousandths of a degree change in its calibration.

The resistance-temperature characteristics of four typical encapsulated thermometers are shown in Table XIV and Figure 36.

TABLE XIV

Resistance-Temperature Characteristics of Germanium Thermometers Fabricated from Arsenic-Doped Crystal VIII-899-N (88)

	Sample no.							
T°K	9-2R		15-2R		21-2R		27-2R	
	R ohms	dR/dT	R	dR/dT	R	dR/dT	R	dR/dT
273	∼1		∼1		∼1		∼1	
77	2.0		1.9		1.8		1.7	
35	4.6	0.16	4.3	0.13	3.9	0.11	3.4	0.07
20	8.0	0.5	7.0	0.3	5.9	0.22	4.9	0.15
15	10.5	0.8	9.0	0.6	7.3	0.4	5.9	0.25
10	18.3	2.8	14.1	1.8	10.7	1.1	8.0	0.67
4.2	101	50	53	15.5	29	7.7	16.7	2.6
2	789	1000	216	200	77	46	29.5	11.2
1.5	2300		450		120		36.5	

The R-T characteristics of a carbon thermometer is shown for comparison. At low temperatures the germanium thermometers have widely different electrical properties because the arsenic impurity concentration is not the same in each sample even though they were cut from the same germanium crystal. This is a good example of the

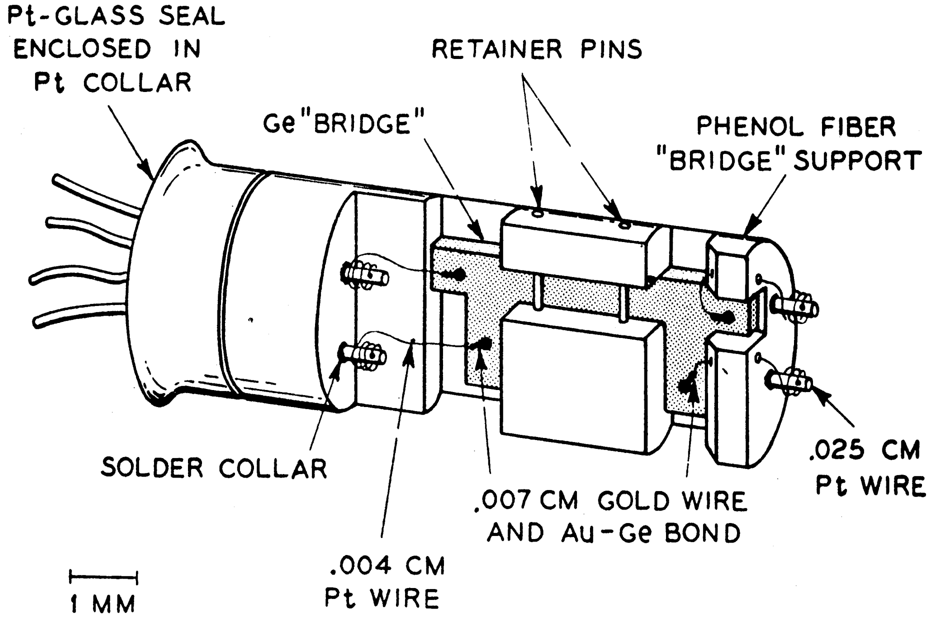


Figure 35. Encapsulated Germanium Thermometer--Model II, with Cover Removed.(88)

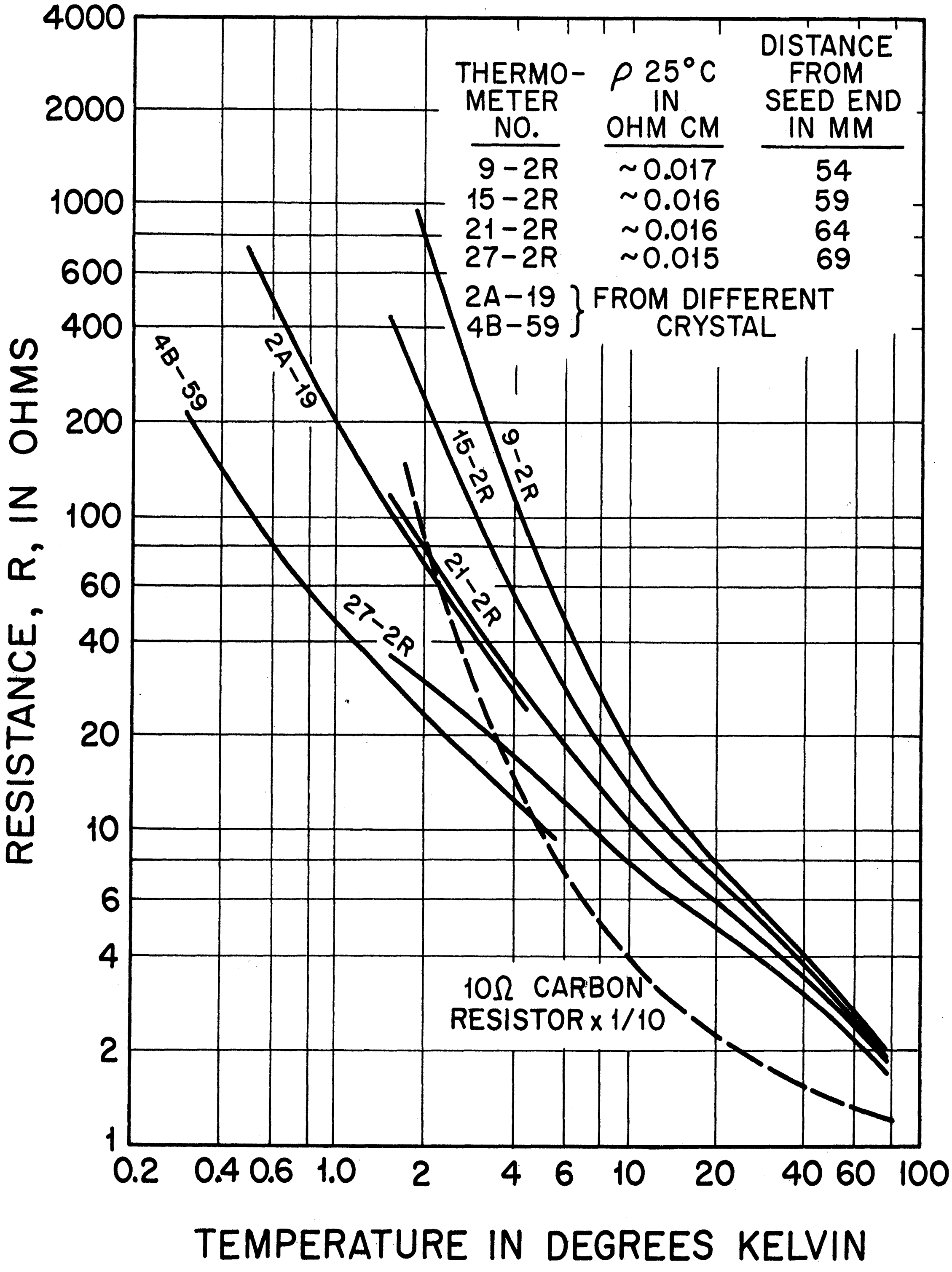
extreme sensitivity of the electrical properties of these resistors to impurity concentration. However, in the range 2°K to 35°K the ratio (dR/R)(dT/T) is of the order of unity for all samples, a result found with germanium bridges cut from other crystals as well. This characteristic is responsible for the tremendous temperature sensitivity of the resistance thermometers. The sensitivity dR/dT at 4.2°K of several thermometers, including those in Table XIV, is shown in Figure 37. An increased sensitivity may be achieved roughly according to $R^{3/2}$, by selecting a thermometer of higher resistance providing the instrumentation is compatible with the selected resistor.

The resistance of germanium is influenced by a magnetic field. The variation of the magnetoresistance with temperature was studied by Kunzler, et al (88) using a germanium bridge having a zero field resistance ($R_{H=0}$) of 200 ohms at 4.2°K The magnetoresistance ($\Delta R/R_{H=0}$) at 18 kilogauss was found to be 0.16 at 4.2°K and gradually increased with decreasing temperature, reaching a maximum value of 0.28 at 1.9°K. Below 1.9°K the magnetoresistance decreased to a value of $\Delta R/R_{H=0}$ of 0.21 at 1.2°K. At 4.2°K the corresponding change in temperature calibration as a result of the magnetic field would be approximately 0.20°K. The magnetoresistance of germanium is also slightly anisoptrpic, being somewhat less than 10% of the total magnetoresistance over 180 angular degrees at 4.2°K and in an 18 kilogauss field.

Other papers treating the germanium resistance thermometers have been published by Low (90) and Orlova, et al (91). Antcliffe, et al (92) report the use of germanium thermometers below 1°K. Their lowest temperature was 0.40°K obtained by a He^3 bath and the range of temperatures investigated was 4.20°K to 0.40°K. Between 4.20°K and 1.20°K the data were fitted to

$$R = CT^{-A} e^{-B/T} , \qquad (32)$$

with representative values of the constants as A = 0.507 - 1.004, -B = 1.245 - 1.399 and C = 71.89 - 112.8 for three resistors calibrated.



THERMOMETER NO.	ρ 25°C IN OHM CM	DISTANCE FROM SEED END IN MM
9-2R	~0.017	54
15-2R	~0.016	59
21-2R	~0.016	64
27-2R	~0.015	69
2A-19 4B-59	FROM DIFFERENT CRYSTAL	

Figure 36. Resistance-temperature Characteristics of Germanium Thermal Sensing Elements. The Curve Extending to Temperatures Below 1°K are for Elements from a Different Crystal than those Extending to the Higher Temperatures. The Characteristics at Low Temperature are Very Sensitive to Arsenic Concentration. However, the Resistivity-temperature Characteristics of an Element are Defined Approximately by its Resistivity at 4.2°K.(88)

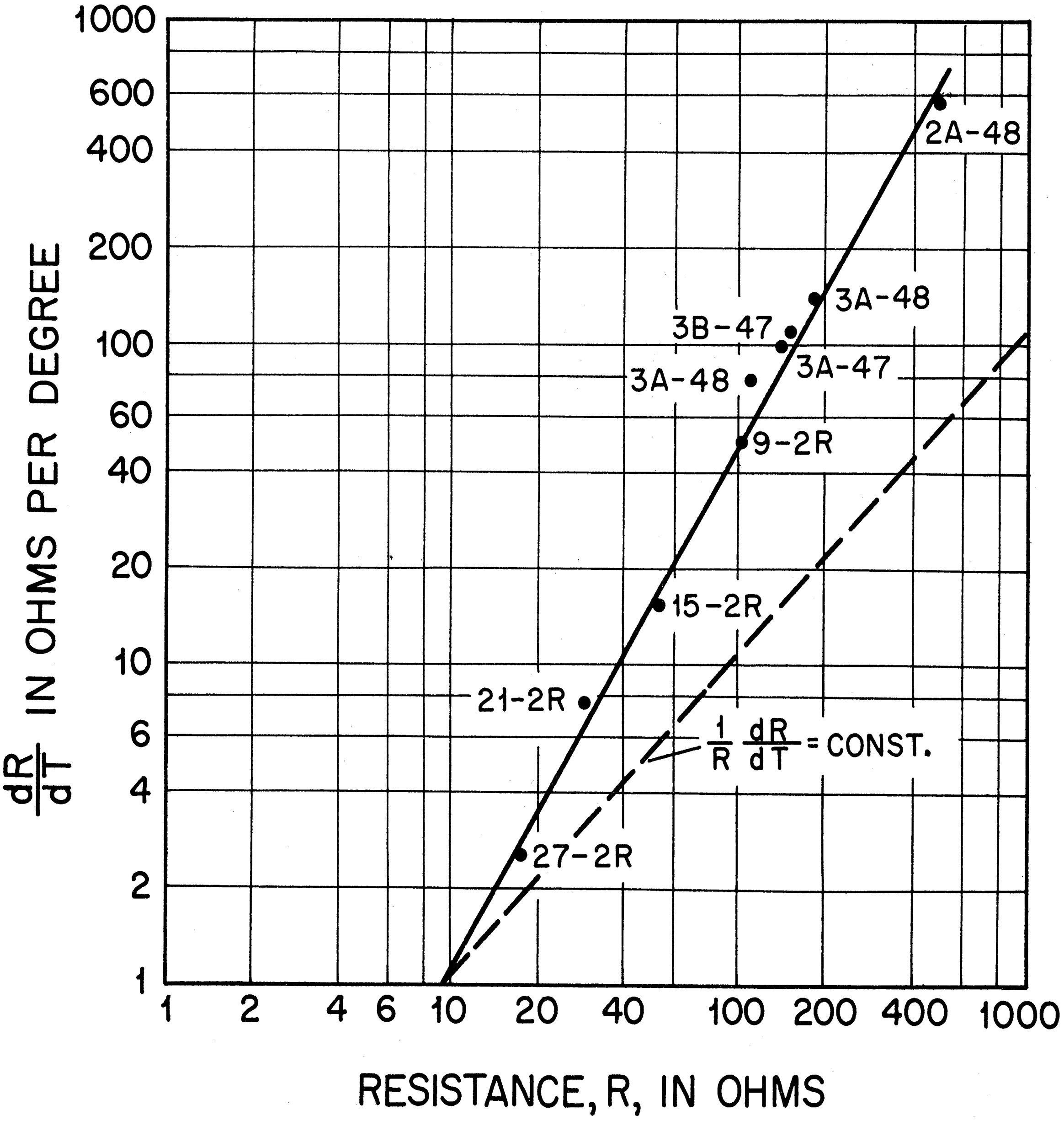


Figure 37. Variation of $\frac{dR}{dT}$ with Resistance at 4.2°K. The variation of the Sensitivity of Thermometers with Their Resistance at 4.2°K is Approximately $\frac{1}{R}\frac{dR}{dT} \sim R^{1/2}$.(88)

X. MAGNETIC THERMOMETRY

The practical minimum temperature which may be produced by pumping helium is about 1°K for He^4 and 0.5°K for He^3. Below these temperatures the vapor pressure is too low to be maintained for most useful experimental purposes. To produce as well as measure temperatures below 0.5°K the properties of paramagnetic substances, usually paramagnetic alums, are used. The low temperatures are achieved by demagnetizing these salts adiabatically from an initial state of a high magnetic field and a temperature of approximately 1°K. The process of adiabatic demagnetization produces a rapid drop in the temperature of the salt owing to a decrease in its energy by the work of demagnetization. This is analogous to the drop in temperature of a compressed gas as it expands isentropically or adiabatically while doing work on its environment. Garrett (93) reports the limit of cooling by this process (electronic) is about 10^{-4}°K but if the energy of nuclear spin is involved a temperature of 10^{-6}°K is thought possible. A two stage demagnetization of a diluted chromium alum has produced a final temperature of 10^{-3} °K with a field of 9000 gauss. To reach this temperature in a single demagnetization from 1°K a field of 25,000 gauss would be required. Temperatures of a few hundredths of a degree absolute can be achieved without exceptional difficulties and those of the order of one-thousandths of a degree can be obtained with somewhat greater effort (94, 95). Table XV, prepared by Zemansky (96), summarizes some results of adiabatic demagnetization experiments and identifies the paramagnetic salts used. Certain properties of commonly used paramagnetic salts are given in Table XVI (96).

TABLE XV

Temperatures Attained by Adiabatic Demagnetization of Various Paramagnetic Salts (96)

Experimenters	Date	Paramagnetic salt	Initial field, oersteds	Initial temp. °K	Final magnetic temp. T^*°K
Giauque and MacDougall	1933	Gadolinium sulfate	8,000	1.5	0.25
De Haas, Wiersma, and Kramers	1933	Cerium fluoride	27,600	1.35	0.13
		Dysprosium ethyl sulfate	19,500	1.35	0.12
		Cerium ethyl sulfate	27,600	1.35	0.085
De Haas and Wiersma	1934	Chromium potassium alum	24,600	1.16	0.031
	1935	Iron ammonium alum	24,075	1.20	0.018
		Alum mixture	24,075	1.29	0.0044
		Cesium titanium alum	24,075	1.31	0.0055
Kurti and Simon	1935	Gadolinium sulfate	5,400	1.15	0.35
		Maganese ammonium sulfate	8,000	1.23	0.09
		Iron ammonium alum	14,100	1.23	0.038
		Iron ammonium alum	8,300	1.23	0.072
		Iron ammonium alum	4,950	1.23	0.114
MacDougall and Giauque	1936	Gadolinium nitrobenzene sulfonate	8,090	0.94	0.098
Kurti, Laine, Rollin, and Simon	1936	Iron ammonium alum	32,000	1.08	0.010
Kurti, Laine, and Simon	1939	Iron ammonium alum	28,800	9.5	0.36
Ashmead	1939	Copper potassium sulfate	35,900	1.17	0.005
DeKlerk (95)	1956	Chromium Potassium alum	--	--	0.0029

Table XVI

Properties of Paramagnetic Salts (96)

Paramagnetic salt	Gram-ionic weight M (gm)	Density, $\frac{gm}{cm^3}$	Curi const., C $\frac{cm^3\ deg}{gm\ ion}$
Cerium magnesium nitrate. $2Ce(NO_3)_3 3Mg(NO_3)_2 24H_2O$	765	--	0.318
Chromium potassium alum. $Cr_2(SO_4)_3K_2SO_4 24H_2O$	499	1.83	1.86
Chromium methylammonium alum. $Cr_2(SO_4)_3CH_3NH_3SO_4 24H_2O$	492	1.645	1.87
Copper potassium sulfate. $CuSO_4K_2SO_4 6H_2O$	442	2.22	0.445
Iron ammonium alum. $Fe_2(SO_4)_3(NH_4)_2SO_4 24H_2O$	482	1.71	4.35
Gadolinium sulfate. $Gd_2(SO_4)_3 8H_2O$	373	3.010	7.85
Manganese ammonium sulfate. $MnSO_4(NH_4)_2SO_4 6H_2O$	391	1.83	4.36
Titanium cesium alum. $Ti_2(SO_4)_3Cs_2SO_4 24H_2O$	589	~ 2	0.118

At liquid helium temperatures the orientation of the magnetic ions in the paramagnetic salts are influenced by a magnetic field in a significant way and contribute to both the energy and the entropy of the salt. Lattice vibrations also have energy and entropy contributions but at the low temperatures ($< 1°K$) associated with adiabatic demagnetization experiments these effects are small. The partial spacial ordering of the paramagnetic ions in the presence of a magnetic field at constant temperature results in a decrease of the system entropy, as would be expected in an isothermal transition from a less-ordered to a greater ordered state. Thus, the effect of an increase in the magnetic field on a paramagnetic salt is exactly analogous to the isothermal compression of a fluid or the isothermal extension of an elastic substance. This is illustrated in Figure 38 which shows the temperature-entropy diagram of a paramagnetic salt for magnetic fields of strength H. States of lower entropy at a given temperature correspond to the magnetic fields of greater strength, i.e., $H_4 > H_3$, etc.

The process of magnetic cooling consists first of cooling a sample of paramagnetic salt to as low a temperature as possible in the absence of any significant magnetic field ($H \cong 0$) shown as state A, Figure 38. This is usually accomplished in a helium cryostat pumped to a temperature T_1 of approximately 1°K. While maintained at this temperature by the helium bath a magnetic field is introduced into the system which causes the entropy to decrease to state B, Figure 38. In state B the paramagnetic salt is removed from the immediate influence of its cooling bath, usually accomplished by pumping away the helium surrounding the salt, and the magnetic field switched off. With the removal of the field the paramagnetic ions are reoriented to a state of greater disorder in a reversible-adiabatic process with a corresponding flow of work to the environment by virtue of the magnetic rearrangement. The consequence of this is an isentropic drop in energy of the salt to a state of zero magnetic field and lower temperature T, shown as state C, Figure 38. A cryostat for doing this is described by DeKlerk and Steenland (97) and shown in Figure 39. The time required to reduce the magnetic field is about 1 second which may be compared with the spin-spin relaxation time of 10^{-9} seconds and the spin-lattice relaxation time of 10^{-3} seconds (93, 98).

The temperature T to which the paramagnetic salt was cooled is computed from "Curie's Law",

$$M = \frac{C}{T} H, \tag{33}$$

or

$$M = \chi H, \tag{34}$$

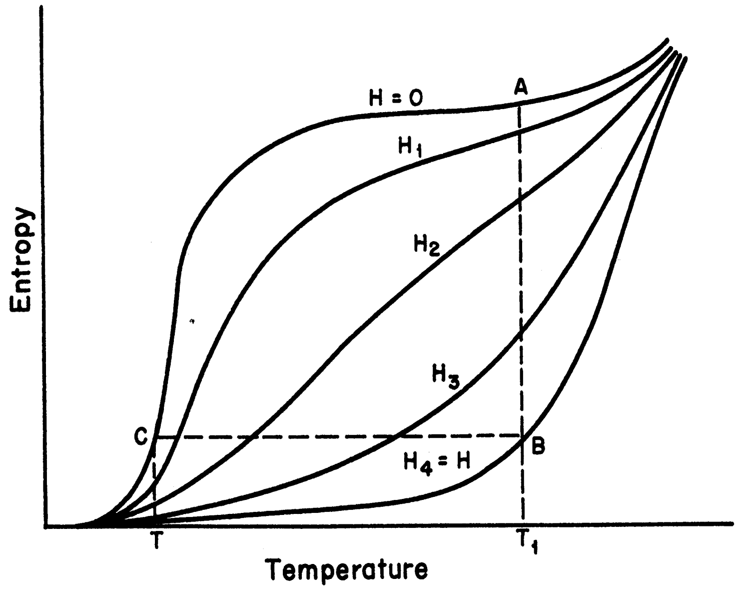


Figure 38. Temperature-entropy Diagram for a Paramagnetic Salt Under the Influence of Different Magnetic Fields.(40)

with

$$\chi = \frac{C}{T} , \tag{35}$$

where M is the magnetization or magnetic moment, C is Curie's constant, H is the magnetic field strength and χ is the magnetic susceptibility. The magnetic susceptibility is related to the permeability, μ, and the magnetic flux intensity, B, by

$$B = \mu H \quad , \tag{36}$$

and

$$4\pi\chi = \mu - 1 . \tag{37}$$

Substances are classified according to the value of χ: diamagnetic for $\chi < 0$, paramagnetic for $\chi > 0$, and ferromagnetic $\chi \gg 0$.

Departures from Curie's Law result from the effects of the shape of the paramagnetic salt and are expressed by the Curie-Weiss Law,

$$\chi = \frac{C}{T-\Delta} , \tag{38}$$

where Δ is the Curie-Weiss constant and is equal to zero for a spherical sample. For this reason spherical samples are used, as in Figure 39, if possible or, if not, the results are corrected to that of a spherical sample. Typical spherical and spheroidal sample tubes are illustrated by DeKlerk (94) in Figure 40. The magnetic temperature computed from Equations (35) or (38) is not a true thermodynamic temperature owing to the emperical constants C and Δ which do not follow from considerations of the second law of thermodynamics. These temperatures will be denoted as T* and will be related to the thermodynamic temperature T later.

For either spherical or spheroidal samples the defined magnetic temperature is written (94) as,

$$T^*_{\text{sphere}} = \frac{C}{\chi_{\text{sphere}}} \tag{39}$$

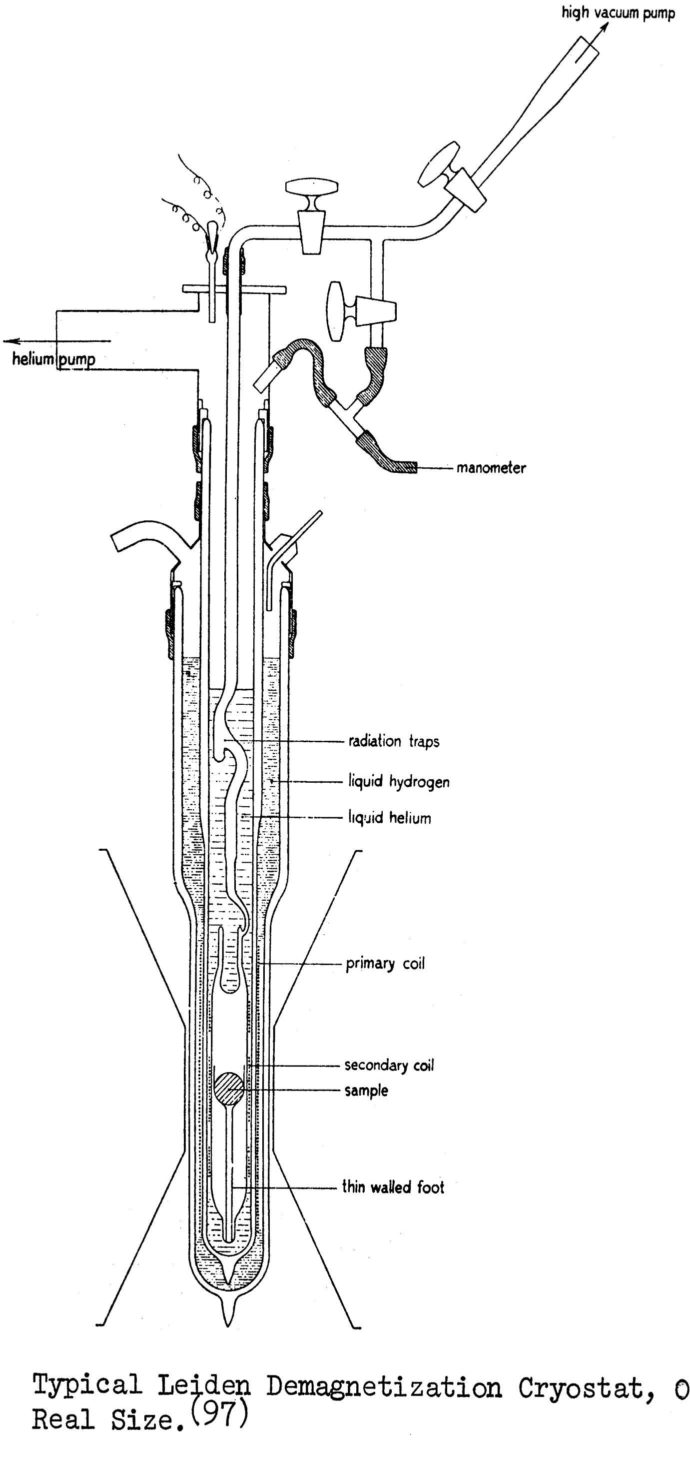


Figure 39. Typical Leiden Demagnetization Cryostat, One Fifth of Real Size.(97)

where

$$\chi_{sphere} = \chi_{spheroid}/[1 + (4\pi/3 - \alpha)\ \chi_{spheroid}] \ , \tag{40}$$

$$\alpha = 4\pi \left(\frac{1-e^2}{e^2}\right) \left[\frac{1}{2e} \log_e \left(\frac{1+e}{1-e}\right) - 1\right] , \tag{41}$$

and

$$e = (1-\epsilon^2)^{1/2} \ , \tag{42}$$

ϵ is defined as the eccentricity of the spheroid as outlined by Maxwell (99).

The magnetic behavior of four paramagnetic salts showing their conformance with Curie's Law at liquid helium temperatures and higher is given in Figures 41 and 42, taken from Kittel (100). At low temperatures saturation effects cause departure from Curie's Law at a certain magnetic field strength, as illustrated in Figure 42.

The determination of T^*_{sphere}, or $T - \Delta$, is made by measuring the magnetic inductance produced by the paramagnetic salt in an electrical measuring circuit, as shown in Figure 43. The magnetic inductance is proportional to the magnetic susceptibility, χ. The magnetic susceptibility of the salt is determined at 1°K and 4°K using the 1958 He^4 scale and then extrapolated to lower temperatures for use during demagnetization experiments. T^*_{sphere} is a good approximation to T for a few tenths of a degree below 1°K. At the lowest temperatures it fails to represent T since for all known salts a maximum in χ has been found which produces a minimum in T^*_{sphere}. Demagnetization from still higher fields results in progressively lower values of χ and higher T^*_{sphere}. In this range T^*_{sphere} and T may differ by an order of magnitude. The final temperature T^*_{sphere} for a chromium potassium alum as a function of magnetic field strength is shown in Figure 44. In this case a minimum T^*_{sphere} is approached asympotically for progressively higher fields.

The thermodynamics of a paramagnetic salt indicate (94) that the entropy S is a

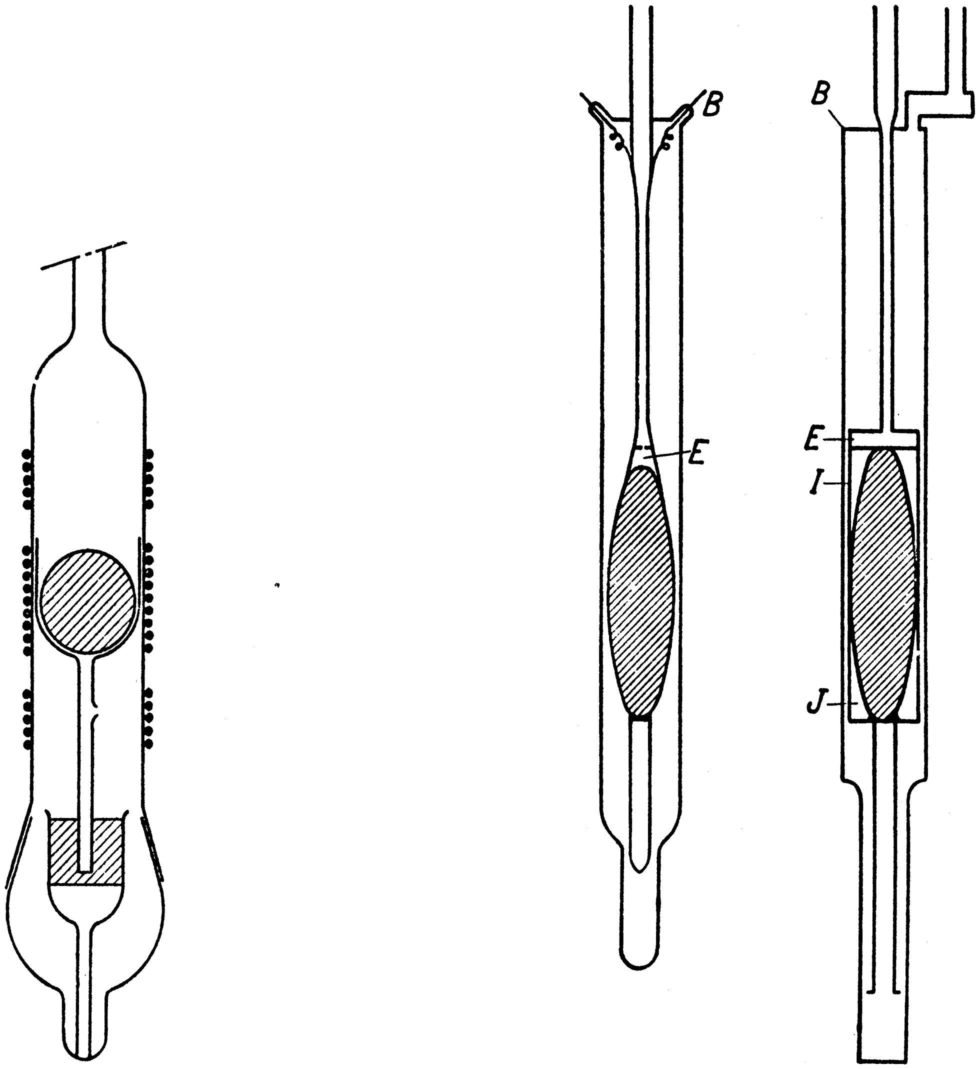


Figure 40. Typical Paramagnetic Salt Samples.(94)

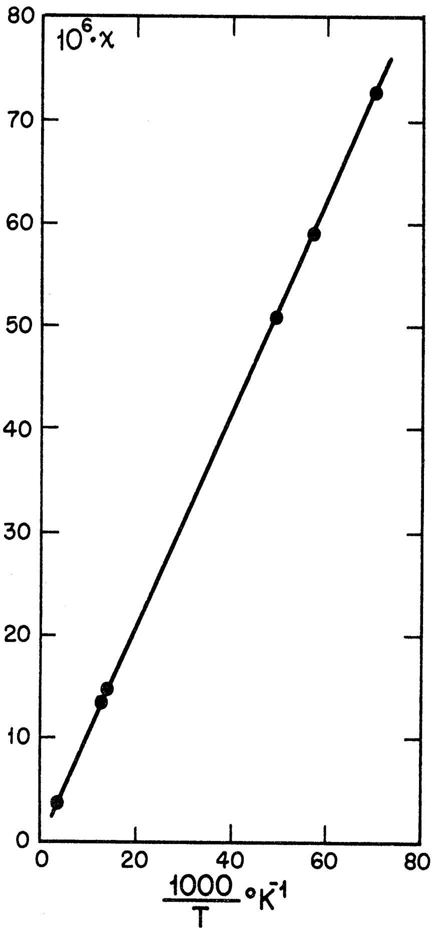


Figure 41. Plot of Susceptibility per gm vs Reciprocal Temperature for Powdered $CuSO_4 \cdot K_2SO_4 \cdot 6H_2O$, Showing the Curie Law Temperature Dependence.(100)

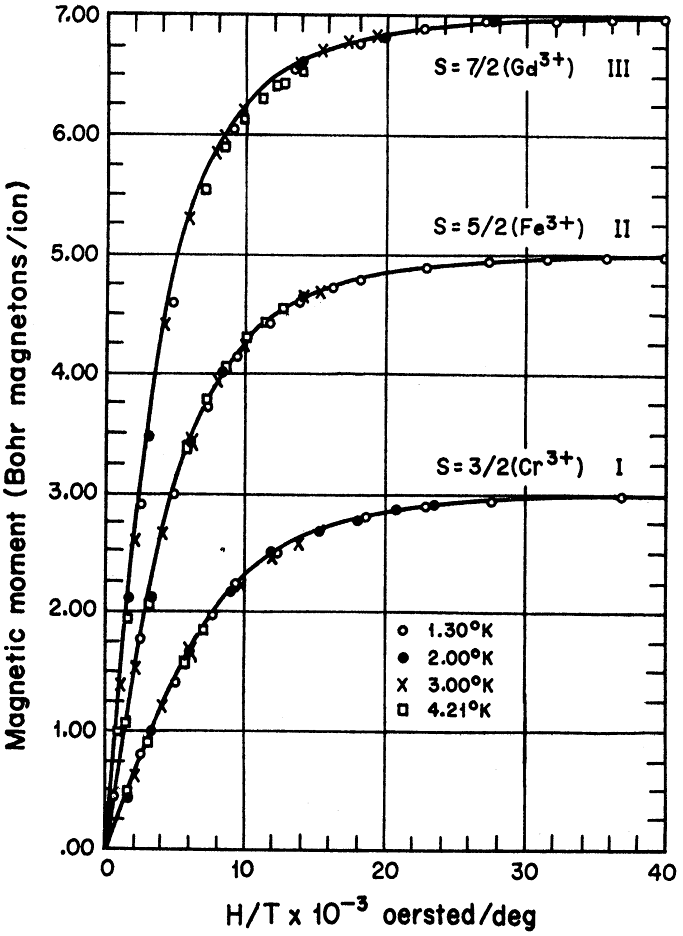


Figure 42. Plot of Magnetic Moment vs H/T for Spherical Samples of (I) Potassium Chrominum Alum, (II) Ferric Ammonium Alum, and (III) Gadolinium Sulfate Octahydrate. Over 99.5% Magnetic Saturation Is Achieved for 1.3°K and About 50,000 Gauss.(100)

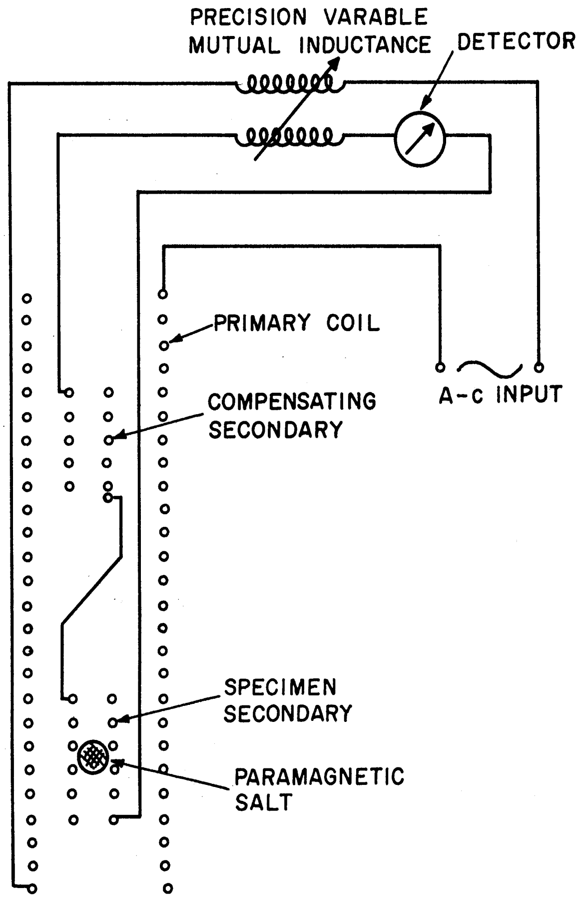


Figure 43. Electrical Circuit for Magnetic Thermometer.(40)

function of T and H. Thus,

$$S = f\ (T,\ H). \tag{43}$$

This may also be written (94)[*]

$$Tds = C_H dT + T\ \left(\frac{\partial M}{\partial T}\right)_H\ dH \tag{44}$$

where

$$C_H = \left(\frac{\partial E}{\partial T}\right)_H = T\ \left(\frac{\partial S}{\partial T}\right)_H \tag{45}$$

For the isentropic demagnetization, state B to C, Figure 38, then equation (44) indicates that

$$T - T_1 = \int_0^{H_4} \frac{T}{C_H} \left(\frac{\partial M}{\partial T}\right)_H dH \tag{46}$$

Since, $(\partial M/\partial T)_H < 0$ by Equation (33), the temperature T will always be less than T_1 for adiabatic demagnetization processes.

The relation between T^*_{sphere} (to be identified as T* hereafter) and the thermodynamic temperature T is determined from the thermodynamic definition

$$T = \left(\frac{dQ}{dS}\right)_{Rev} \tag{47}$$

This may also be written

$$T = \frac{(dQ/dT^*)_{H = 0}}{(dS/dT^*)_{H = 0}} \tag{48}$$

Now (dQ/dT*) may be found from heating experiments in which

$$\left(\frac{dQ}{dT^*}\right)_{H = 0} = m \left(\frac{dh}{dT^*}\right)_{H = 0} , \tag{49}$$

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[*] For a detailed account of the thermodynamic analysis of paramagnetism the work of DeKlerk (94) or Garrett (93) should be consulted.

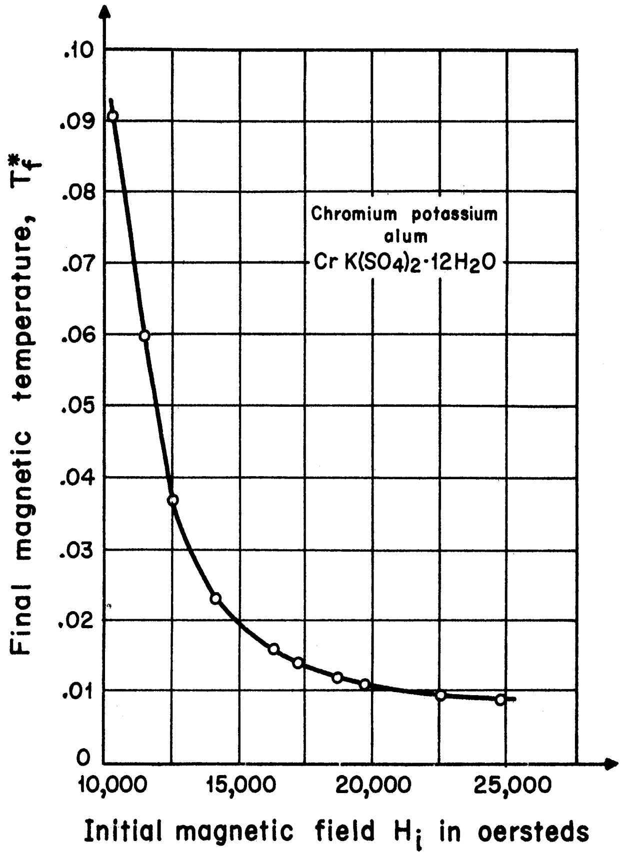

Figure 44. DeKlerk's Results in the Adiabatic Demagnetization of Chromium Potassium Alum. (Initial Temperature = 1.17°K)(96)

in which, m is the mass of a sample of paramagnetic salt and h is its enthalpy per unit mass.

The quantity $(dS/dT^*)_{H=0}$ is determined from a series of demagnetization experiments from T_1, Figure 38, and a number of different magnetic fields such as H_1, H_2, H_3 and H_4. The entropies corresponding to the isotherm T_1 and the various fields is determined from Equation (44) as

$$S(H,T_1) - S(0,T_1) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \, . \tag{50}$$

The corresponding temperatures are then computed from Equation (46). This gives a curve of S vs. T* for a zero field (H = 0). From this the slope (dS/dT*) may be derived and T computed from Equation (48).

The relationship between T and T* for several paramagnetic salts is shown in Figures 45 and 46.

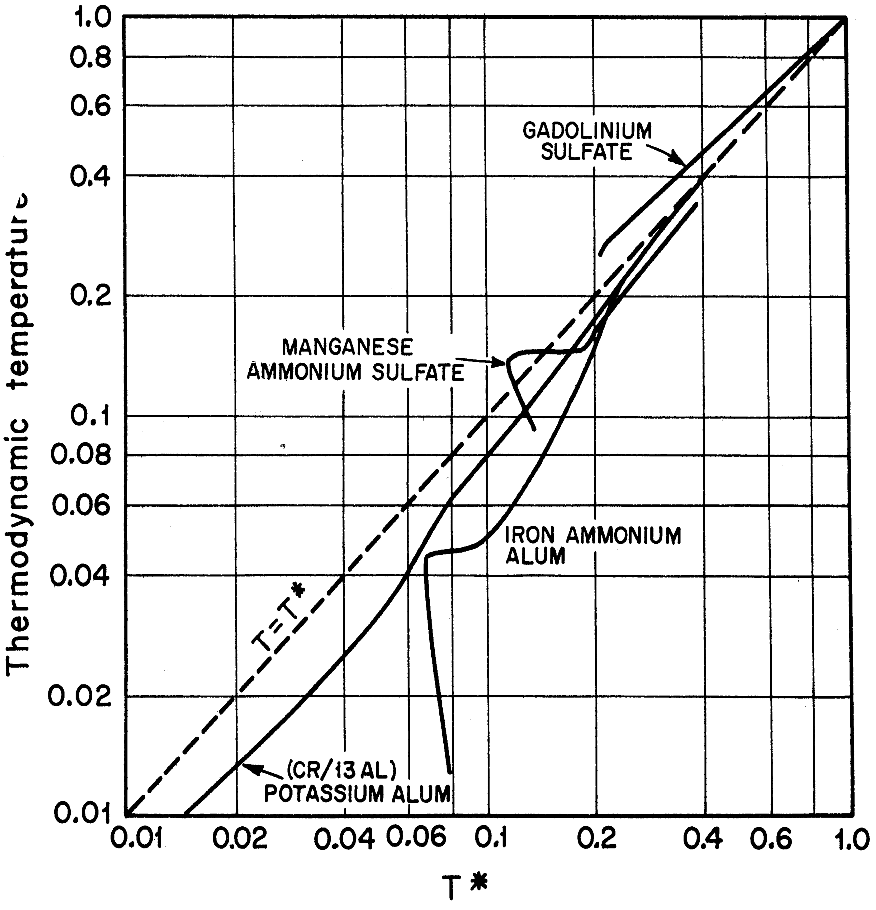

Figure 45. Deviation of Curie Temperature T* from Thermodynamic Temperature for Several Paramagnetic Salts.(40)

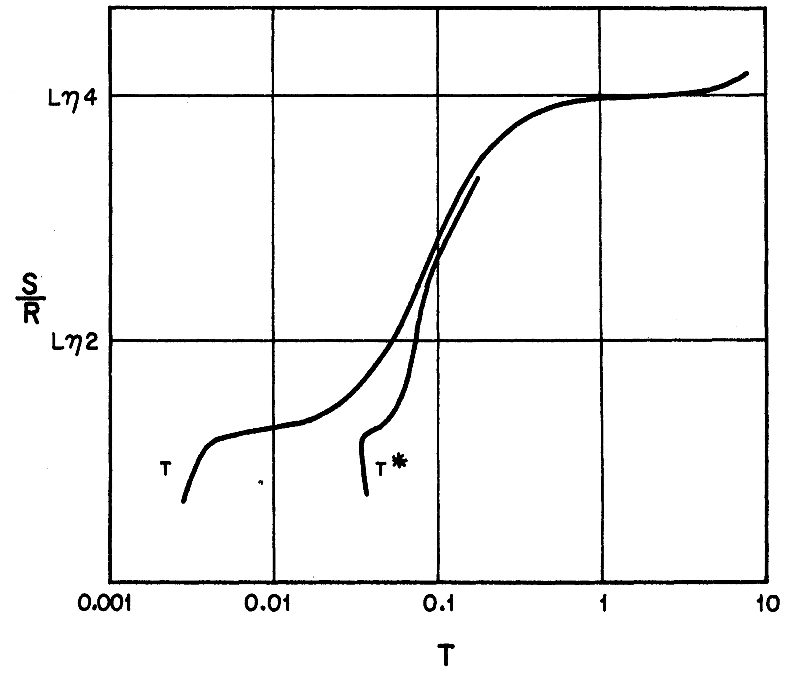

Figure 46. Entropy of Potassium Chrome Alum as a Function of Absolute Temperature and of T*.(93)

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