TEMPERATURE SCALES AND SILICATE RESEARCH

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ABSTRACT. The temperature scale for the range 300° to the melting-point of platinum, used by the Geophysical Laboratory from 1912 to the present, was based on the nitrogen thermometer work of Day and Sosman. The first International Temperature Scale (1927) was a thermodynamic scale, with fixed points a little higher than those of Day and Sosman. The revision of the I.T.S., adopted in 1948, by raising the value of the constant in the Wien-Planck Law of radiation, brings the high-temperature scale nearer to the Geophysical Scale. Curves show the difference between the Geophysical and the I.T.S. of 1927 and 1948.

INTRODUCTION

ONE of the first problems that faced the growing group of students of high-temperature silicates in the early 1900's was the problem of the temperature scale. Precise measurements were beginning to replace the crude melting points of earlier years, but there was no accepted scale to which they could be referred.

Arthur Louis Day had received his Ph.D. at Yale University in 1894 and, after serving there as instructor in physics for a few years, had taken up work on high-temperature gas thermometry at the Physikalisch-Technische Reichsanstalt in Germany. When he became the first Director of the Geophysical Laboratory of the Carnegie Institution of Washington in 1907, it was natural that the first large piece of apparatus installed in the new laboratory should be a gas thermometer, designed for improved accuracy of measurement of the most essential variable in high-temperature research on silicate systems.

In 1908 I had the good fortune to become associated with Day and Allen in the Laboratory's work on high-temperature thermometry, and I assisted in the development of a temperature scale that met the needs of the Laboratory in the range between the melting point of zinc (419° C.) and the melting point of palladium (1549° C.).

This work was completed in 1912, and we turned back to our natural field of work, the mineral oxides, sulfides, and silicates. In the years 1928-1947 I found myself deep in

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pyrometry again, in the Research Laboratory and the plants of the United States Steel Corporation; hence I have never lost interest in the problem of temperature scales.

In what follows I shall have little to say about the instruments of high-temperature thermometry used in silicate research—the thermocouple, the electrical resistance thermometer, and the optical pyrometer—but will concentrate on the vicissitudes of the temperature scale itself during the period 1907-1948.

TEMPERATURE SCALES

Before 1848, science had no universal temperature scale. It had a lot of competing scales, differing one from another at every point except at the freezing and boiling points of water, and there was no good ground for choosing one in preference to another except the convenience of the experimenter. The scale went with the thermometer.

In 1848, William Thomson (later Baron Kelvin) pointed out that a temperature scale independent of the properties of any substance can be defined in terms of the convertibility of heat into other forms of energy. It is only necessary to select two reproducible temperatures, such as the temperature of equilibrium of ice and water in air at one atmosphere (the "ice point"), and the temperature of equilibrium of water and its vapor at a pressure of one atmosphere (the "steam point"), and give an arbitrary quantitative value, say 100°, to the difference between them, just as we do when we say that the distance between two marks on a certain platinum bar shall be called 1 meter; we must then adopt, arbitrarily, some mathematical relationship between temperature and quantity of energy, and the scale is set. Kelvin adopted the relationship \( Q_1/Q_2 = \theta_1/\theta_2 \), in which \( Q_1-Q_2 \) is the amount of heat reversibly converted by a thermodynamic engine into other forms of energy when its temperature falls from \( \theta_1 \) to \( \theta_2 \). The absolute value of any temperature could then be experimentally measured: the temperature of the ice point, for example, turns out to be 273.16°. The steam point, consequently, is 373.16°. These are temperatures on the absolute thermodynamic scale or the Kelvin thermodynamic scale.

By subtracting the experimentally determined value of
273.16° from all temperatures of the Kelvin scale, we create the more familiar *Celsius thermodynamic scale*\(^1\) with its ice point of 0°.

**PRECISE THERMOMETRY**

It is one thing to define an independent scale such as the Kelvin. It is quite another to realize it experimentally in a form that permits high precision of measurement. In principle, any scale whatever can be evaluated in terms of either the Kelvin or the Celsius thermodynamic scale, provided the necessary energy data are available. Actually, only two varieties of temperature scale have met the requirements, which have to do, first, with the precision of the measurement, second, with the definiteness of the thermodynamic relations. They are: the gas thermometer scales, up to temperatures near 1600° C. where materials of construction begin to fail; and the optical pyrometer scale, from about 1000° C. up into indefinitely high temperatures.

Now to return to the matter of precision. Precise thermometry need not wait upon the realization of a thermodynamic scale any more than precise measurements of mass needed to wait upon the determination of the density of water. Precise weighing became possible as soon as a sensitive balance was constructed and a reproducible standard kilogram was accepted, no matter whether it represented accurately the mass of a cubic decimeter of water or not. So precise thermometry in the range −30° to +200° C. followed upon the development of special glasses for the mercury-in-glass thermometer; it spread out to cover the range −180° to +600° C. with the development of the hydrogen and nitrogen gas thermometers employing vitreous silica; reached on up past 1100° C. with the invention of the platinum resistance thermometer; and attained over 1700° C. with the construction by Carl Barus and Henri Le Chatelier of thermocouples made from the platinum-group metals. All these thermometers were capable of precise measurement in varying degree; none gave directly the temperature on the independent thermodynamic scale.

\(^1\)This is the scale commonly known as the centigrade scale, which is a misnomer, because the Kelvin scale is also centigrade; both are based on an arbitrary difference of 100° between ice and steam points.
CALIBRATING A SCALE

Heat is such an imaginary and imponderable thing that temperature standards comparable to the standard meter and kilogram are out of the question. The standard scale has to be defined in terms of a series of fixed and reproducible temperatures combined quantitatively with reproducible phenomena. A million fixed temperatures are readily available, each determined by Gibbs' Phase Rule, which says that in a chemical system in which the number of phases in equilibrium exceeds by 2 the number of components, the temperature and the pressure can have but a single value. If the pressure be arbitrarily set, say at 1 atmosphere, the number of phases needs to exceed the number of components only by 1, in order to fix the temperature. The ice point and the steam point are fixed temperatures of this kind; whether they were the best fixed temperatures to take in defining the fundamental interval is open to question, but the matter is now academic, as they are very unlikely to be abandoned in favor of some other pair. Two points much farther apart in temperature would have been a better choice, from the standpoint of precision.

For fixed points above the fundamental interval, the freezing points of pure metals have been preferred, with boiling points of pure liquids at 1 atmosphere as next most popular choice. For interpolation between fixed points, either the electrical resistance thermometer or the thermoelectric couple is accepted, while at temperatures above the highest fixed point, as well as between the higher points, dependence is placed on the Wien-Planck Law of monochromatic radiation.

THE GAS THERMOMETERS

It was early perceived that the perfect thermometer for the realization of a thermodynamic scale is one that measures either the change of volume or the change of pressure of an ideal gas. The ideal gas is defined as one which (1) obeys Boyle's Law, \((pv) = \text{constant}\), and (2) neither absorbs nor evolves heat when expanding into a vacuum.

Helium comes nearest to meeting these specifications, but helium had not even been discovered in the early decades of temperature standardization. Air, hydrogen, and nitrogen became the preferred thermometric gases.
Temperature Scales and Silicate Research

Private initiative had already made considerable progress with gas thermometry when the national (and international) standardizing institutions began to appear in the field. The first of these was the Bureau International des Poids et Mesures at Sèvres, France, where Chappuis did his pioneering work on the hydrogen thermometer. Next followed the Physikalisch-Technische Reichsanstalt in Germany, where gas thermometry was ultimately carried to 1680° C. The National Physical Laboratory in England worked with air and nitrogen, mainly in the intermediate range of 100°-900° C. At the National Bureau of Standards of the United States, Buckingham in 1906 made the best analysis of the derivation of the thermodynamic scales from the gas scales that had been made up to that date, but the Bureau attempted no experimental gas thermometry at all, confining its interest to the optical pyrometer above 1000° C., so far as high-temperature standardization was concerned.

STATUS OF TEMPERATURE SCALES IN 1907

In 1907, then, the year in which the Geophysical Laboratory was established, there was no international temperature scale possessing the official sanction of the governments which had cooperated in establishing the international meter and kilogram. There was general satisfaction with the hydrogen thermometer scale for temperatures up to about 200° C. For higher temperatures the platinum resistance thermometer with Callendar's formula was accepted by many, while others preferred the platinum-platinrhodium thermocouple using a quadratic formula through 3 calibration points. Standard calibration points had not been agreed upon. The boiling points of water and sulfur and the melting points of ice, zinc, antimony, silver, gold, and copper were the most commonly used standard points.

Above the gold point the platinum alloy thermocouple was being extrapolated to about 1600° C., with some support from gas thermometer measurements in Germany and England. At still higher temperatures every investigator was on his own.

STATUS OF TEMPERATURE SCALES IN 1912

In 1911 the Carnegie Institution of Washington issued Publication 157, "High Temperature Gas Thermometry," by
Day and Sosman, and this was followed in 1912 by their paper on "The Nitrogen Thermometer Scale from 300° to 630°, with a Direct Determination of the Boiling Point of Sulphur," which supplied more accurate data for the lower part of the scale. These papers became the basis for the Geophysical Laboratory's scale of temperature for the range 300° C. to 1755° C.

The original temperatures were on the constant-volume nitrogen scale with initial pressure 200-500 mm. of mercury. Buckingham's calculations, made from a variety of experimental data on thermometric gases, had shown that the corrections to convert the Day and Sosman nitrogen scale to true thermodynamic temperatures are positive, and do not exceed 1° at any temperature up to 1500° C. The corrections increase with the initial pressure of nitrogen and with the temperature, and become more uncertain as the temperature rises. Thermodynamic corrections of 0.1° to 0.2° were applied to the Day and Sosman scale below 650° C., but the higher temperatures were at first left unchanged.

In 1914 L. H. Adams, following up a preliminary note by Johnston and Adams in 1912, reviewed the status of the Geophysical Scale and published comprehensive tables for typical copper-constantan and platinum-platinrhodium thermocouples from 0° to 1755° C., converting all the Day and Sosman fixed calibration points to thermodynamic, and expressing the relation of e.m.f. and temperature by means of formulas having e.m.f. as argument in place of temperature. The principal fixed points were:

<table>
<thead>
<tr>
<th>Substance</th>
<th>b.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>217.95°</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>305.9</td>
</tr>
<tr>
<td>Zinc</td>
<td>419.4</td>
</tr>
<tr>
<td>Sulfur</td>
<td>444.55</td>
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<tr>
<td>Antimony</td>
<td>630.0</td>
</tr>
<tr>
<td>Silver</td>
<td>960.2</td>
</tr>
<tr>
<td>Gold</td>
<td>1062.6</td>
</tr>
<tr>
<td>Copper</td>
<td>1082.8</td>
</tr>
<tr>
<td>Diopside</td>
<td>1391.5</td>
</tr>
<tr>
<td>Palladium</td>
<td>1549.5</td>
</tr>
<tr>
<td>Platinum</td>
<td>1755</td>
</tr>
</tbody>
</table>

This scale is still used by the Geophysical Laboratory.

The nitrogen-thermometer calibration by Day and Sosman had ended at the palladium melting point, 1549.2°. Extension to
the platinum point, taken as $1755^\circ$, was based on optical pyrometer measurements at the Bureau of Standards and the Reichsanstalt, which gave the difference between the palladium and platinum points. The platinum point thus derived was appreciably lower than the value obtained by extrapolating the thermocouple curve, or the value that had been recently obtained in Germany with a small and consequently less precise nitrogen thermometer with an iridium bulb. The value $1755^\circ$ was, however, acceptable to the Bureau of Standards and was used there in the calibration of pyrometers for a number of years.

**THE INTERNATIONAL SCALE OF 1927**

After World War I the international conference finally got around to the matter of a temperature scale. Scheduled to meet every six years, the General Conference on Weights and Measures, representing 33 nations, elects 18 scientists to an International Committee on Weights and Measures, which thereupon meets every two years. Their recommendations as to a temperature scale were adopted by the Seventh General Conference in 1927, and were widely accepted under the designation *International Temperature Scale of 1927*.

![Diagram](image)

**Fig. 1.** Corrections to the Geophysical Laboratory temperature scale of 1912, to convert to International Temperature Scale of 1927 and of 1948.
The fixed points of this scale, in addition to ice and steam, were: oxygen and sulfur boiling points, \(-182.97^\circ\) and \(444.60^\circ\); silver and gold freezing points, \(960.5^\circ\) and \(1063^\circ\). Above the gold point the scale was based on this point and on the Wien formula for the intensity, \(J_\lambda T\), of monochromatic radiation:

\[
J_\lambda T = c_1 \left(\frac{\lambda}{c_2}\right)^5 e^{-c_2/\lambda T}
\]

in which \(T\) is Kelvin temperature, \(\lambda\) is wave-length, \(c_1\) and \(c_2\) are constants, and \(e\) is the base of natural logarithms. Since all temperatures are related to the gold point as a standard, the value of \(c_1\) does not have to be specified, but \(c_2\) has to be known: its value was set at 1.432 cm. degrees.

The International Scale of 1927 made some significant departures from the Geophysical Scale based on the work of Day and Sosman. The silver point was set \(0.3^\circ\) higher, gold \(0.4^\circ\) higher, and palladium \(5.5^\circ\) higher than their value. The most important effect in the high-temperature region was on the freezing point of platinum, which was presently shown by the optical pyrometer measurements of Wensel and Roesser to be unquestionably higher than the extrapolated value previously quoted: the new datum was 1773.

The atlas of four large-scale ternary phase equilibrium diagrams of silica, alumina, lime, and magnesia, prepared by Sosman and Andersen from Geophysical Laboratory data and published by the Research Laboratory of the United States Steel Corporation in 1933, was probably the first publication on silicates to use the I.T.S. of 1927.Investigators at the Geophysical Laboratory continued to use the scale adopted in 1914, so that their temperatures remained consistent. The difference between the Geophysical Scale and the 1927 I.T.S. is shown in figure 1. The rather odd shape of this curve emphasizes the fact that most recorded temperatures up to the freezing point of platinum could be referred to a reliable standard, either the melting point of a silicate or the freezing point of palladium or platinum, and that the really important changes were in the interval \(1550^\circ\) to \(1773^\circ\). Above \(1773^\circ\) the basis of calibration of the silicate and oxide points was, in many cases, too uncertain to make a definite correction feasible, although in most of the Geophysical Laboratory measurements a stated melting point of platinum had been used, so that it became possible to make an approximate cor-
rection of temperatures between 1750° and 2050° C. There
was no good reason for making any change in the very high
and somewhat uncertain melting points of the pure basic
oxides: MgO, 2800°, and CaO, 2570°.

EVIDENCE FROM AN UNANTICIPATED SOURCE

During the 1930’s a new line of evidence, to which the
International Committee of 1927 had given little if any atten-
tion, began to influence physicists concerned with the high-
temperature scale. Since physical measurements can all be
reduced to five elementary concepts—length, mass, time, electric
charge, and temperature (or entropy)—the fundamental con-
stants of physicochemical science must bear certain necessary
relations to one another. Consistency among the constants gives
independent evidence as to the reliability of any one of them.

In 1926 R. T. Birge began a thorough-going intercomparison
among 11 fundamental constants, including the speed of light,
Faraday’s electrochemical constant, Rydberg’s spectroscopic
constant, Avogadro’s number, the volume of a mole of the
ideal gas, the pressure of the standard atmosphere, and the
ice point on the Kelvin scale. Among constants derived from
the foregoing 7 are: the charge of the electron e, the constants
c₁ and c₂ of the Wien-Planck law of monochromatic radiation,
and the constant σ of the Stefan-Boltzmann law of total radia-
tion.

In 1929 the consistency was satisfactory throughout, except
for a disagreement between two methods for determining e. This
was cleared up in 1935. In the meantime a new dis-
crepancy turned up, between Millikan’s value for e by the oil
drop method and the value derived from the grating measure-
ment of X-ray wave lengths. New data correcting Millikan’s
viscosity of air resolved this difference, but immediately
introduced several new discrepancies, of which the worst were
in c₂ and σ.

THE INTERNATIONAL SCALE OF 1948

The conviction spread, among physicists interested in the
subject, that c₂ would have to be raised, for it was evident
that the others would then fall into line. A correction could
and should have been made in 1939, for the newly created
(1937) Advisory Committee on Thermometry was ready with
a report to the International Committee, but World War II interrupted everything international. A new scale (Stimson, 1949) was finally adopted by the Ninth General Conference in October, 1948, and became the International Temperature Scale of 1948.

The two most important changes from the 1927 scale are: (1) the melting point of silver is raised from 960.5° to 960.8°; (2) the value of \( c_2 \) is raised to 1.438. In effect, this latter change nearly restores the Geophysical Scale in the vicinity of 1550° C., for the Day and Sosman gold and palladium points corresponded to \( c_2 = 1.439 \). (Note: an increase of 0.010 in \( c_2 \) at 1550° is equivalent to a decrease of 4.0° in the temperature.) The change from the Wien to the Wien-Planck radiation formula

\[
J_{\lambda T} = c_1 \lambda^{-5} (e^{c_2/\lambda T} - 1)^{-1}
\]

does not appreciably change any temperature below about 3500° C.

On the basis of the 1948 scale, the corrections made by Sosman and Andersen in 1933 at 1550° C. and lower, none of which exceeded \( \pm 5° \) C., are reduced to about 2/3 their former magnitude, and the original Geophysical temperatures can usually be left unchanged without error beyond the experimental uncertainty. Temperatures above 1550°, however, will still have to be proportionately increased, as in figure 1, to bring them into line with the International Scale. The melting point of pure silica as cristobalite, for example, originally 1713°, becomes 1723° C.

It should be emphasized again that the standard calibration points recommended for the International Scales of both 1927 and 1948 are temperatures on the Celsius thermodynamic scale. The two methods recommended for interpolation between these temperatures in the range \(-183°\) to \(1063°\) C., however, are strictly methods of interpolation, and their accuracy is not involved in the choice between the gas thermometer scales (hydrogen, helium, nitrogen), and the thermodynamic scale. Enough intermediate points have been checked with the hydrogen, helium, or nitrogen thermometer to assure that the interpolated temperature is not off the Celsius thermodynamic scale by more than a fraction of a degree. The International Committee does, in fact, give certain secondary fixed points
for calibration purposes; these include the freezing points of lead, 327.3°; zinc, 419.5°; antimony, 630.5°; and aluminum, 660.1°.

Above 1063° the temperatures are per se thermodynamic, because the Wien-Planck law, originally proved by reference to gas-thermometer temperatures, corrected to thermodynamic, between 1000° and 1600°, is now so thoroughly grounded in theory and in measurement as to be virtually a definition.

Calibration points recommended in this region, points between which the platinum-platinrhodium couple with quadratic formula will doubtless continue to be used for interpolation, though not included as a part of the I.T.S., are the freezing points of copper, 1083°; nickel, 1453°; cobalt, 1492°; palladium, 1552°; and platinum, 1769°. In silicate research, particularly when the quenching method is to be used, melting points such as those of diopside (CaMgSi₂O₆) at 1392° C. and anorthite (CaAl₂Si₂O₈) at 1552° C. (both I.T.S., 1948) are more convenient.

THE KELVIN SCALE

An international Kelvin or absolute thermodynamic scale, not yet adopted, except in principle, by the General Conference, would involve an entirely distinct international agreement, such as the proposal made by the Advisory Committee on Thermometry in 1939, that the best value of the ice point is 273.15° K. American scientists have usually used the value 273.16°. Addition of either of these values to a temperature measured on the Celsius thermodynamic scale gives the Kelvin temperature with any desired accuracy to ± 0.01°.

THE FAHRENHEIT SCALE

Nothing has been said in foregoing pages concerning the Fahrenheit scales because they are never used in silicate research. It is unfortunate that two scales with different fundamental intervals have come into general use, when either one would have served the purpose. The only advantage possessed by the Celsius scale is that its zero is at the lower end of the fundamental interval. There is nothing decimal about it, and nothing that has any relation to the meter and kilogram.

If we call the interval between ice and steam points 180° instead of 100°, we will have the Rankine thermodynamic scale
on which the ice point is 491.67°. If now we subtract the figure 459.67 from all temperatures on this scale, we will have a Fahrenheit thermodynamic scale, parallel to the Celsius, but with a zero 32° below the ice point and not defined by any naturally reproducible fixed temperature.²

The persistence of the Fahrenheit scale after the scientific world had adopted the Celsius is, I suspect, the result of economic inertia, first of the British, then of the American instrument manufacturers. Sixty years ago either scale could have been discontinued without much monetary loss, but so many millions of dollars are now invested in thermometers, pyrometers, and temperature control mechanisms that the replacement of either scale by the other is now hopeless, except by the methods used by Genghis Khan and Tamerlane.

REFERENCE


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²Logically, the International Celsius is now no longer different from the Fahrenheit in this respect, for the new definition of the Celsius zero is "the temperature 0.0100 degree below that of the triple point of pure water." This definition was adopted because the invariant point of equilibrium between ice, water, and water vapor is more precisely reproducible than the old ice point.