The Emissivities of Liquid Metals at Their Fusion Temperatures

D. W. Bonnell, J. A. Treverton,* A. J. Valerga

and J. L. Margrave

Department of Chemistry
Rice University
Houston, Texas 77001

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ABSTRACT

A survey of the literature through 1969 shows an almost total lack of experimental emissivity data for metals in the liquid state. The emissivities for several transition metals and various other metals and compounds in the liquid state at their fusion temperatures have been determined in this laboratory. The technique used involves electro-magnetic levitation-induction heating of the materials in an inert atmosphere. The brightness temperature of the liquid phase of the material is measured as the material is heated through fusion. Given a reliable value of the fusion temperature, which is available for most pure substances, one may readily calculate an emissivity for the liquid phase at the fusion temperature. Even in cases where melting points are poorly known, the brightness temperatures are unique parameters, independent of the temperature scale and measured for a chemically defined system at a fixed point. One may recalculate better emissivities as better melting point data become available.

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* Present address: University of Leicester, Chemistry Department, Leicester, England.

Introduction

The use of brightness temperature as a measure of temperature is subject to an evaluation of the surface emissivity of the substance in question. The ability to generate blackbody conditions in most research applications has in the past made brightness temperature a secondary value, normally used only for monitoring purposes. However, when one deals with refractory metals, and wishes thermodynamic quality data concerning the liquid phase, blackbody conditions are no longer easily obtainable, especially if the container problem is also to be avoided. Application of other methods of non-contact temperature measurement, such as two color pyrometry are less convenient and of dubious advantage when good spectral emissivity data are available.

Interest in emissivity measurements has been sporadic, the primary literature sources of data being a review by Burgess and Waltenberg in 1915 (1), and a collection of NBS measurements by Roeser and Wenzel (2).

The recent advent of direct applications of electromagnetic levitation to drop calorimetry (3) and its immediate success have brought the temperature measurement problem to the fore. The primary source of error for property measurements in the 2000 to 3000 K temperature range is now almost exclusively the lack of accuracy in temperature measurements.

For this research, a direct attempt to measure brightness temperatures at a standard wavelength for a variety of liquid metals was undertaken. If the brightness temperature is monitored as a function of time for a substance being heated during levitation, it is observed that at the point of fusion, the brightness temperature remains almost constant for a

relatively long time. Experiments for several substances including copper

were run at various heating rates, varying by nearly an order of magnitude,

and the final value of emissivity showed no correlation with heating rate

in any case. This corresponds well with other observations on substances

subjected to constant heating, i.e., the phase change occurs at constant

temperature. By using a recording pyrometer and noting the brightness

temperature at the end of this plateau, the emissivity for the liquid at

its fusion temperature can be calculated immediately from the Wien equation.

The advantages of levitation as a heating device have been pointed

out (3) previously. In this application the primary advantage is the

ability to use a relatively massive sample, corresponding to sizes of

surfaces normally under consideration in laboratory-scale experiments. With

no container to interfere, the material is unaltered by its surroundings.

Apparatus

The levitation apparatus has been described in detail elsewhere (3).

The primary addition to the experimental arrangement is the Leeds and

Northrup automatic recording pyrometer model 8641-1, serial # 1720818.

The automatic pyrometer operates at an effective wavelength of 6450 Angstroms

with a band width of approximately 350 $\overset{o}{A}$. Basic response time is about

1 sec. for $0.5^\circ C$ resolution at $1063^\circ C$. The automatic pyrometer was

calibrated by comparison against a L & N model 8622-C manual pyrometer

(serial # 1077349, calibrated by L & N by comparison with NBS Test No. 201571 (4)

reference standard, report dated 9 Dec., 1970). Both pyrometers were

sighted alternatively on a G.E. 20A pyrometer lamp. Ten calibration points

across the medium range of the automatic machine were determined individually

by each of two observers and a least squares line fitted to the deviations. The RMS error of the line is less than 2 degrees.

The technique used for measurement was generally the same for all samples. The flask surrounding the levitation coil was flushed for 5 to 10 minutes with pure argon which had been dried by passing through a magnesium perchlorate column and then deoxygenated by passing over a 19" long column of fine copper turnings heated to $350^{o}C$. In cases such as copper and nickel where surface coatings were noticed, the materials were cleaned with 1:1 diluted reagent hydrochloric acid, then rinsed with deionized water and dried with acetone. The sample was then immediately suspended in the coil and power applied. The automatic pyrometer was used to follow the passage through fusion, a process which took more than 10 seconds in all cases. Each measurement was made with a fresh sample and every recovered sample showed a surface at least as bright as the material before levitation.

The samples used were supplied in massive form (either 1/4" rod, platelets, or shot). Table I lists sources and purity. In all cases where more than one source was used, there was no difference in results attributable to source.

Results

The results of this investigation are presented in Table I. The uncertainties given are in terms of precision of measurement. The accuracy of calibration of pyrometers in general can contribute an error of ±5 - 7 K. It is expected that the higher precision of automatic pyrometers will soon allow a much needed improvement in this figure. The fusion temperatures reported are either those of Hultgren, Orr, and Kelley(5), modified to agree

Table I

Normal Spectral Emissivities

Substance	Fusion Temp. (K)	Brightness Temp. of Liq. at Fusion (K)	Emissivity ($\lambda=0.645\mu$)	No. of Determinations
Co[a] (99.95%)	1767[f]	1626 ± 2	0.335 ± .006	6
Cr[a] (99.95%, 99.997%)	2133	1891 ± 3	0.262 ± .005	9
Cu[b] (99.9%)	1357.6[f]	1216 ± 2	0.147 ± .010	7
Fe[a] (99.95%)	1811	1671 ± 1	0.357 ± .003	3
Mo[a] (99.9%)	2895	2510 ± 4	0.306 ± .004	8
Nb[a,c] (99.9%, 99.8%)	2744	2405 ± 2	0.317 ± .002	9
Ni[d] (99.8%)	1728[f]	1597 ± 2	0.346 ± .005	11
Pd[a] (99.95%)	1827[f]	1684 ± 2	0.354 ± .005	5
Ta[a] (99.9%)	3256	2779 ± 3	0.309 ± .003	2
Ti[a] (99.95%)	1946	1814 ± 1	0.434 ± .003	16
V[e] (99.9%)	2178	1973 ± 2	0.343 ± .004	10
Zr[c] (99.9% 99.8%)	2128	1918 ± 2	0.318 ± .004	8

[a] A. D. Mackay, Inc.

[b] Baker and Adamson Reagent Chemicals

[c] Alfa Inorganics, Inc.

[d] J. T. Baker Chemical Co.

[e] Research Organic/Inorganic Chemical Corp.

[f] Secondary reference points on the IPTS-68. The other fusion temperatures are taken from reference 4 by Hultgren, Orr and Kelley and are adjusted to the IPTS-68.

with the International Practical Temperature Scale of 1968 (6) or values
which are secondary reference points of IPTS-68. The brightness temperature
is related to the emissivity through the Wien equation (7). At the temp-
eratures involved in this work, the error introduced by this approximation
to Plank's law is less than 0.1%. Wien's law gives, for a body of emissivity
E_λ, the intensity of radiation at some wavelength λ,

$$J_\lambda = E_\lambda C_1 \lambda^{-5} e^{-C_2/\lambda T}. \tag{1}$$

The relation between brightness temperature, T_B, and true temperature T is
then

$$\frac{1}{T} - \frac{1}{T_B} = \frac{\lambda \ln E_\lambda}{C_2} \tag{2}$$

where C_2 is 1.4388 cm K (IPTS-68) and λ is 6.45×10^{-5} cm. If (2) is
solved for E_λ,

$$E_\lambda = EXP\left(\frac{C_2}{\lambda}\left[\frac{1}{T} - \frac{1}{T_B}\right]\right) \tag{3}$$

is obtained. Taking differentials of both sides yields

$$dE_\lambda = \left\{EXP\left(\frac{C_2}{\lambda}\left[\frac{1}{T} - \frac{1}{T_B}\right]\right)\right\}\left\{-\frac{C_2}{\lambda}\right\}\left\{-\frac{1}{T_B^2}\right\}dT_B. \tag{4}$$

Dividing (4) by (3) gives

$$\frac{dE_\lambda}{E_\lambda} = \frac{C_2}{\lambda T_B}\left(\frac{dT_B}{T_B}\right) \tag{5}$$

where $C_2/\lambda = 22310$ K.

Use of equation (5) shows the extreme sensitivity of emissivity values
to small errors in brightness temperatures. For example, in the neighborhood
of 2000 K, if the brightness temperature is in error by 10 K (a typical
value), and if the nominal emissivity is 0.30, dE_λ = .017, an error of more
than 5%. Thus, the opposite side of the coin to temperature measurement
being relatively insensitive to errors in emissivity is that emissivity

values derived from temperature measurements are very sensitive to inaccuracies in brightness temperature.

Discussion

These data were specifically produced at a known calibration point in order to provide stable reference values independent of the normal problems of temperature stability. For this reason, the reported brightness temperature is the fundamental measurement and is specific to the fusion temperature of the metal under one atmosphere of inert gas.

Reported errors in brightness temperature correspond to less than 0.2 mv deviation in the measured variable recorded on a L & N Speedomax H 6½" chart recorder equipped with Azar universal range and span device. The span used for all measurements was 2 mv full scale and selected points across all ranges at this span were calibrated against a L & N Type K-3 potentiometer. Calibration corrections were of the order of .07 - .10 mv in the ranges of interest and were applied.

The data of Table I are in reasonable agreement with the reported values of emissivity from Burgess and Waltenberg (1) and Roeser and Wenzel (2) with few exceptions. The most notable of these exceptions are titanium and chromium. Reference to oxide emissivity data of Roeser and Wenzel (9) shows the emissivities of the oxides of these metals to be considerably higher than the clean surface. Titanium is very reactive at higher temperatures, showing an ability to oxidize even in the presence of trace amounts of carbon dioxide. Observations of chromium after levitation melting and dropping on a cold plate showed the bulk material to discolor easily in open air, presumably oxidation. The conclusion to be drawn is

that probably the earlier measurements were of a surface slightly contaminated with oxide, resulting in a higher brightness temperature.

The emissivity value from Treverton and Margrave (8) for molybdenum has changed because recalibration of the automatic pyrometer showed a slight but significant deviation from agreement with IPTS-68.

Measurements of niobium and tantalum are at temperatures high enough that questions of equilibrium for the melting point and actual true measured values at other temperatures must be a factor in other measurements (1, 2, 10). The levitation technique allows a reasonable time for equilibration at the melting point.

It is to be noted that for almost all the materials reported on here, no sign of a change in brightness temperature was observed during the melting process. The single exception was copper. Even in the case of copper, however, the observed effect was not a change in emissivity from .10 to .15, as reported earlier. The current observations showed the surface to superheat slightly, settling back smoothly to a lower brightness temperature which coincided with the visual observation of the entire sample collapsing into the shape forced by the surrounding RF field. For this reason, the stated deviation in precision was reported as twice the calculated standard deviation.

Conclusions

Application of the levitation phenomenon to the measurement of surface brightness shows distinct advantages and monochromatic emissivities for several liquid metals have been determined at their respective melting points with a 450 KHz generator and levitation coil. The possible variation

of emissivity as a function of phase is still subjected to question. Continuing work at various levitation frequencies where the skin depth is much larger is in progress.

Acknowledgments

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