

THE EMISSIVITY OF METALS AND OXIDES

II. MEASUREMENTS WITH THE MICROPYROMETER

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As indicated in a communication describing the micropyrometer,¹ this instrument may be used conveniently for the approximate determination of the monochromatic emissivities of metals, oxides, and other substances in microscopic quantities at high temperatures. This method has the further advantages of simplicity and rapidity of operation and also permits the taking of observations on rare elements, alloys, and compounds which are available only in minute quantities. It is possible, for example, under favorable conditions to measure with an accuracy of about 1 per cent the emissivity of a substance having a mass of 0.01 mg, an area of 0.25 mm², and thickness of 0.005 mm. The method lends itself readily to the determination of a temperature coefficient of emissivity and to the detection of a variation of emissivity with change of state, as at the melting point. The temperature range of the micropyrometer for these purposes is from about 700 to 3000° C.

THE METHOD

In the form here used this is a secondary method, requiring a substance of known emissivity as a comparison standard. For this purpose platinum is taken, and in what follows it is assumed that for solid platinum, at all temperatures, $e = 0.33$ for $\lambda = 0.650\mu$ and $e = 0.38$ for $\lambda = 0.547\mu$. The method is most precise for substances having an emissivity nearly equal to that of the comparison substance.

¹ G. K. Burgess, *A Micropyrometer*, Jour. Wash. Acad., 3, p. 7, 1912; *Bulletin Bureau of Standards*, 9, p. 475, 1912.

For the determination of its emissivity, a speck of the substance, say 0.01 mg, is placed on a platinum strip, or one of iridium or tungsten for substances melting above 1750° C, contained in a suitable atmosphere, as air, hydrogen, or in a vacuum. The strip is heated electrically until the speck melts, when, if observations on the emissivity of the solid are to be taken, the temperature of the strip is immediately lowered below the freezing point to prevent alloying. The solid substance should now have a plane, clean surface, and observations of its emissivity in terms of that of platinum may then be taken. For this purpose the micropyrometer, provided with a suitable monochromatic glass in the eyepiece, and for very high temperatures with a calibrated absorption glass before the objective of the microscope, is brought alternately to the same brightness as the platinum strip and the surface the emissivity of which is sought; the apparent temperatures of the surfaces are then measured in succession. With liquid metals observations have to be taken rapidly and before the effects of alloying have reached the surface.

The micropyrometer is first calibrated for use with a platinum or other strip by the method of known melting points (*loc. cit.*). For convenience in computation the calibration may be expressed graphically in terms of the equivalent or "black-body" temperatures p of platinum for any given wave length.² The pyrometer sighted on the platinum strip then gives p directly from which t the same true temperature of the platinum and substance is obtained graphically; sighting on the substance gives s , its equivalent temperature directly.

The emissivity, e_λ , of the substance is then calculated from Wien's equation:

$$\log_{10} e = \frac{c \log E}{\lambda} \left(\frac{1}{T} - \frac{1}{S} \right)$$

in which $c = 14\,450$, E the Napierian base, λ the wave length, T and S the absolute true and equivalent temperatures of the substance.

² See G. K. Burgess, Note on Graphic Solutions of Wien's Spectral Equation, *Jour. Wash. Acad.*, 1, p. 105, 1911.

Both tungsten and carbon lamps with fine filaments were used in the micropyrometer. Either type of lamp gave satisfactory and reliable results, the greater current sensibility of the carbon lamps about balancing the sharper photometric match of the tungsten when sighting on a metallic surface.

THE OBSERVATIONS

Measurements have been taken, mainly with red and green light of wave lengths 0.650μ and 0.547μ , respectively, of the emissivity of a number of metals and oxides over a considerable temperature range both in the solid and liquid states. The principal results for the metals are shown in Table I, together with those obtained by other observers.

It will be seen that the emissivities determined by the micro-pyrometric method agree for the most part with those obtained by others when working with substances upon which good surfaces may be maintained. For example, comparison of the results here obtained with those of Stubbs and Prideaux on solid and liquid gold, silver, and copper indicates differences of 0° to 5° C in the determination of the equivalent temperatures. The values found with the micropyrometer are for several other substances practically identical with those obtained by other methods; thus, compare in Table I the values for Pd, Ir, Rh, Ni, and Fe.

TABLE 1
Measurements of Emissivity of Elements

Substance	Micropycrometer observations						Other observers			
	Atmosphere	Solid		Temp. °C.	Liquid		At room temperatures	At high temperatures		
		Temp. °C.	Emissivity λ 0.65		Emissivity λ 0.55	Temp. °C.			Emissivity λ 0.65	Emissivity λ 0.55
Copper	H	930	0.096		1100	0.150	0.36	Drude ³	e λ 0.65	Observer
		1025	.105					Hagen and Rubens ⁶	0.112	Solid, Stubbs ⁴
		1080	.117	0.38				Tate ⁶	.148	Liquid, Stubbs ⁴
Silver	H	940	.044	<.35	980	.072	<.35	Tool ⁸	.16	Burgess ⁷
								Drude ³	.105	Bidwell ⁹
								Hagen and Rubens ⁶	.080	Hoiborn and Henning ¹⁰
Gold	H	1000	.145	<.38	1065	.219	<.38	Hagen and Rubens ⁶	.072	Liquid, Stubbs ⁴
								Tate ⁶	.055	Henning ¹¹
								Drude ³	.127	Bidwell ⁹
Palladium	H	1530	.33	.38	1555	.37		Hagen and Rubens ⁶	.130	Hoiborn and Henning ¹⁰
								Tate ⁶	.220	Solid, Stubbs and Pri- deaur ¹³
								Tool ⁸	.125	Liquid, Stubbs and Pri- deaur ¹³
Platinum	H		.33	.38	1800	.38		Wartenberg ¹² 0.35 ($\lambda=0.579$)	.335	deaur ¹³
								Drude ³	.295	Waidner and Burgess, ¹⁴ 975°
									.335	Waidner and Burgess, ¹⁴ 1325°

Molybdenum	H	2000	.43	2500	.40	.51	Coblentz ²⁰	.44	Mendenhall and Forsythe, ²³ 1000°, 2400°
Tungsten	H	1750	.39			.474	Coblentz ²⁰ Littleton, ²⁵ 0.545 ($\lambda=0.589$)	.37 .60 .45 .66	Forsythe, ²⁴ 3000° Mendenhall and Forsythe, ²² 1100°, 2900°
Uranium	H	<M. P.	.55	>M. P.	.34			.478 .69 .51	Pirani, ²⁶ 1910, 3000° Pirani, ²⁷ 1912, 2000° Wartenberg, ²⁸ 1907, 3000° Wartenberg, ¹³ 1910, 3000°

³ Drude, *Wied. Annalen*, **39**, p. 537, 1890.

⁴ Hagen and Reichen, *Annale der Physik*, **8**, p. 16, 1902.

⁵ Tate, *Physical Review* (*2*), **34**, p. 321, 1912.

⁶ Wolf, *Physical Review* (*1*), **31**, p. 1-25, 1910.

⁷ Wartenberg, *Verh. der Deutschen Phys. Gesellschaft*, **12**, pp. 105-127, 1910.

⁸ Coblentz, *Bureau of Standards Scientific Paper No. 152*.

⁹ Bidwell, *Physical Review* (*2*), **1**, pp. 452-483, 1913.

²³ Mendenhall and Forsythe, *Astrophysical Journal*, **37**, pp. 380-390, 1913.

²⁴ Forsythe, *Astrophysical Journal*, **34**, p. 353, 1911.

²⁵ Littleton, *Physical Review*, **85**, pp. 306-311, 1912.

²⁶ Pirani, *Verh. der Deutschen Phys. Gesellschaft*, **12**, pp. 301-348, 1910.

²⁷ Pirani, *Physikalische Zeitschrift*, **13**, pp. 753-754, 1912.

²⁸ Wartenberg, *Berichte der Deutschen, Chemischen Gesellschaft*, **40**, p. 3287, 1907.

²⁹ Foote, *Physical Review*, **34**, p. 96, 1912.

The work with oxides (see Table 2) was done with smooth surfaces, usually with material which had been melted. This gives a surface of different character from that obtained by oxidizing a relatively heavy sheet of metal in air. We should expect the values for emissivity obtained by observing these smooth surfaces to be somewhat lower than the results of other observers using the matte surface, which is usually produced when a metal is oxidized by heating in the air. Most of the published work on emissivity of oxides has been with total radiation, but the results of Burgess and Foote²⁹ on the monochromatic emissivity ($\lambda=0.65\mu$) of nickel oxide differs slightly (2 per cent) in the direction expected, while those of Pirani¹⁷ or Rubens³⁰ on thorium oxide (0.10 and 0.08, respectively) are much lower than here obtained (0.57), a difference we are unable to explain. Our observations were taken both on the oxide placed as such on the comparison strip and that obtained by melting the metal on the strip in hydrogen and oxidizing afterwards by heating in air.

TABLE 2
Measurements of Emissivity of Oxides

Oxide of—	Micropyrometer observations					
	Atmosphere	Solid			Liquid	
		Temp. °C	Emissivity		Temp. °C	Emissivity $\lambda=0.65\mu$
			$\lambda=0.65\mu$	$\lambda=0.55\mu$		
Nickel	Air	1000	0.89	}	1550	0.68
		1200	.83			
		1450	.69			
Cobalt	Air	1320	.77		1550	.63
Iron	Air	1200	.63		1610	.53
Manganese	Air				1600	.47
Titanium	Air	1450	.52	0.51		
Thorium	Air	1350	.57	.69		
Yttrium	Air	1400	.61			
Beryllium	Air	1470	.37			
Columbium	Air	1450	.71			
Vanadium	Air	1160	.69			
Chromium	Air	1430	.60			
Uranium	Air	1650	.30		1700	.31

²⁹ Burgess and Foote, Bureau of Standards Scientific Paper No. 224.

³⁰ Rubens, *Annalen der Physik* (4), 20, p. 598, 1906.

In general, the oxides have higher values of monochromatic emissivity than their metallic components, although the oxides of U, Be, Mn, and Ti appear as exceptions. More difficulty was experienced in obtaining uniform results for oxides than for metals.

For the metals, most of the observations were taken in hydrogen, thus preserving a clean surface. In those cases in which it was possible to vary the atmosphere, as for palladium, platinum, and rhodium, no difference was detected in their emissivities in air, in hydrogen, and in vacuo. Most of the white metals are seen to have emissivities, both in the red and green, lying between 0.30 and 0.45.

PHENOMENA ACCOMPANYING CHANGE OF STATE

Palladium appears to have an unstable radiation behavior after solidifying in the region of its melting point. For example, the higher value 0.38 of the emissivity for $\lambda = 0.65\mu$, characteristic of the liquid surface as compared with 0.33 for the solid, will occasionally persist for some time after freezing and at temperatures well below the freezing point. We are perhaps here in the presence of a radiation phenomenon analogous to surfusion, in that the molecular mechanism of the surface to which the radiation is due may maintain its liquid characteristics after freezing.

It is also of interest to note that the emissivity of platinum for $\lambda = 0.65\mu$ appears to have a well-marked discontinuity at the melting point, passing abruptly from 0.33 in the solid state to 0.38 in the liquid state, an increase in red brightness of some 15 per cent on melting. This phenomenon would tend to destroy the constancy of such a standard as the Violle unit of light, which is based on the luminous radiation from the surface of platinum at its melting point.

This discontinuity of emissivity with change of state is not limited to platinum, but is very marked with red light for gold or 0.145 to 0.219, and similarly for copper and silver, while for most of the white metals, and with green light for practically all the metals examined, this discontinuity is very slight or absent; exceptions appear to be Be, Er, Cb, and U. In the case of gold

and copper, the metals may be seen to change color, from a green to an orange, on melting. With palladium mounted on platinum the abrupt change in red brightness is easily recognized, for the palladium is practically invisible until melting takes place.

TEMPERATURE COEFFICIENT

There have been published numerous observations on the temperature coefficient of monochromatic emissivity of metals, and much of this material is inconclusive or contradictory. These results are collected in Table 1, together with observations by various observers at room temperatures, based on reflection measurements, and may be compared with the micropyrometric observations of Tables 1, 3, 5, and 6.

For both white and colored metals in the solid state it will be noted that, in general, for a given wave length the value of the emissivity of a cold metal is not very appreciably different from that of the very hot metal, the difference between observed emissivities hot and cold usually being not greater than among the values obtained by several observers at high temperatures; so that the uncertainty of the existence of a temperature coefficient of monochromatic emissivity in the visible spectrum for the temperature range 20° C to the melting point is, for metals, of the same order of uncertainty as the agreement among several observers of their observations on emissivity at any given temperature, hot or cold. For example, taking the metal for which the observations are the most numerous, the average value found by nine observers of $e_{.65\mu}$ for platinum at temperatures between 970° and 1750° is 0.316, and of three observers at 20° is 0.315. The agreement, hot and cold, is for nickel about as good, or 0.358 and 0.347, respectively. For the colored metal, gold, we apparently have $e_{.65\mu}$ equals 0.116 cold and 0.127 hot in the solid state, but the emissivity is here changing very sharply with wave length, which effect may possibly account for the difference noted. In the case of iron there appears to be a slight but well-defined negative temperature coefficient of emissivity for red light, since $e_{.65\mu}$ ranges from 0.42 at 20° C to 0.38 at 1050° and 0.36 at the melting point, 1530° C, and beyond. (See Tables 1 and 3.) Nickel oxide (Table 2) shows a negative coefficient, e for red light

decreasing from 0.89 (or 0.91 according to Burgess and Foote (loc. cit.) using large sheets) at 1000° C to 0.68 at the melting point, 1452° C, and beyond.

TABLE 3

Observations on Iron

[$\lambda=0.65 \mu$ (see p. 592 for symbols)]

Strip No.	Atmos- phere	Temperature °C			State	Emissivity			
		p	s	t		Solid	Liquid		
103	H	1388	1400	1538	Liquid		0.366		
		1405	1426	1559	Liquid		.389		
		1401	1412	1554	Liquid		.359		
		1297	1317	1430	Solid	0.399			
		1212	1226	1330	Solid	.382			
141	H	984	993	1067	Solid	.386			
		1383	1397	1532	Liquid		.372		
203	H	1384	1398	1534	Liquid		.367		
		1383	1397	1532	Liquid		.372		
205	H	1390	1405	1540	Liquid		.375		
682	H	1374	1391	1521	Liquid		.382		
		1337	1347	1477	Solid	.362			
		1259	1271	1385	Solid	.372			
		1197	1207	1313	Solid	.368			
		1125	1136	1229	Solid	.377			
		973	982	1055	Solid	.375			
		1060	1070	1154	Solid	.379			
		1125	1137	1229	Solid	.381			
		1193	1206	1309	Solid	.379			
		1265	1277	1393	Solid	.369			
		1337	1348	1478	Solid	.362			
		1383	1393	1533	Liquid		.354		
		683	H	1331	1341	1470	Solid	.362	
				1257	1268	1383	Solid	.368	
1187	1209			1310	Solid	.360			
1059	1069			1153	Solid	.378			
977	986			1060	Solid	.374			
1060	1069			1154	Solid	.375			
1128	1140			1233	Solid	.376			
1195	1208			1311	Solid	.380			
1259	1271			1386	Solid	.370			
1333	1340			1473	Solid	.350			
1379	1390			1528	Solid	.360			
1415	1426			1571	Liquid		.356		
684	H			1373	1385	1521	Liquid		.360
		1305	1319	1440	Solid	.372			
Mean a. d.						.368 ± .009			

TABLE 3—Continued
Mean of Observations on Solid Iron

t	e
1530	0.360
1460	.362
1390	.370
1315	.374
1200	.378
1060	.378

A few observations made on alloy and carbon steels indicate a slight increase in emissivity when carbon, nickel, or manganese are present in relatively considerable quantities. (See Table 4.) The average value of $e_{.65\mu}$ for seven steels is 0.38, as compared with 0.38 to 0.36 for iron. It is hoped to make a more thorough study of the emissivity of steels.

TABLE 4
Observation on Steels

[$\lambda=0.65\mu$ (see p. 592 for symbols)]

Strip No.	Atmosphere	Temperature ° C			State	Emissivity		Analysis		
		p	s	t		Solid	Liquid	C	Ni	Mn
190	H	1385	1399	1535	Liquid		0.368	Per cent 0.08	Per cent	Per cent 3.5
191	H	1377	1397	1525	Liquid		.390			
149	H	1401	1413	1554	Liquid		.362	.15		5.4
158	H	1384	1412	1534	Liquid		.380	.26		13.0
167	H	1400	1403	1552	Liquid		.391	.37		.50
211	H	1355	1368	1499	Liquid		.367	.23	15.48	.93
398	H	1369	1383	1516	Liquid		.370	.31	2.6	1.8
702	H	1373	1384	1521	Liquid		.357	.97	.13	.12
		1305	1314	1440	Solid	0.410				
		1180	1197	1293	Solid	.396				
704	H	1283	1305	1414	Solid	.400				
		1278	1298	1408	Solid	.393				
		1151	1069	1259	Solid	.404				

PRECISION OF THE MEASUREMENTS

The precision obtainable in the measurement of monochromatic emissivities by the micropyrometric method is illustrated in Table 5 by the observations with red light on nickel in the range 1200°

to 1550° C, all of which observations are here recorded, giving for solid nickel $e_{.65\mu} = 0.356 \pm 0.008$ and for the liquid 0.367 ± 0.008 with no certain evidence of temperature coefficient and slight evidence of a discontinuity at the melting point. For a substance such as gold, possessing a very low value of emissivity in the red, and for which also observations are necessarily made at lower temperatures under less sensitive conditions, the precision obtained is shown in Table 6.

TABLE 5
Observations on Nickel
[$\lambda = 0.65 \mu$ (see p. 592 for symbols)]

Strip No.	Atmos- phere	Temperature °C			State	Emissivity	
		p	s	t		Solid	Liquid
94	H	1323	1340	1461	Liquid		0.382
		1305	1309	1439	Solid	0.345	
98	H	1316	1331	1453	Liquid		.375
130	H	1316	1328	1453	Liquid		.366
218	H	1321	1335	1459	Liquid		.371
219	H	1238	1247	1361	Before melting	(* .365)	
		1315	1324	1451	Liquid		.363
		1268	1274	1396	Solid	.350	
283	H	1383	1394	1532	Liquid		.362
335	H	1320	1336	1457	Liquid		.382
438	H	1343	1352	1485	Liquid		.354
		1286	1288	1417	Solid	.358	
		1243	1249	1366	Solid	.356	
		1243	1246	1366	Solid	.344	
		1126	1134	1230	Solid	.367	
		1320	1330	1457	Liquid		.362
439	H	1330	1337	1469	Liquid		.350
		1314	1323	1450	Solid	.360	
		1304	1318	1438	Solid	.377	
		1316	1325	1453	Solid	.356	
442	H	1320	1331	1457	Liquid		.368
		1305	1315	1440	Solid	.358	
		1153	1161	1268	Solid	.340	
		1143	1150	1250	Solid	.358	
		1011	1017	1098	Solid	.361	
		1314	1321	1450	Solid	.354	
		1288	1298	1419	Solid	.368	
697	H	1140	1159	1258	Solid	.336	
Mean a. d.					.356 ± .008	.367 ± .008	

* Not taken for mean.

TABLE 6
Observations on Gold

[$\lambda=0.65 \mu$ (see p. 592 for symbols)]

Strip No.	Atmos- phere	Temperature °C			State	Emissivity	
		p	s	t		Solid	Liquid
104	H	1028	997	1118	Liquid		0.218
		1033	962	1134	Solid	0.136	
		1033	1006	1124	Liquid		.230
440		922	860	997	Before melting	(*.101)	
		935	886	1012	Before melting	(*.154)	
		984	926	1068	Solid	.140	
		995	961	1080	Liquid		.214
		995	940	1080	Solid	.150	
		993	938	1078	Solid	.148	
		993	965	1078	Liquid		.222
		993	938	1078	Solid	.148	
		994	963	1079	Liquid		.215
		993	941	1078	Solid	.150	
		989	926	1074	Solid	.129	
441		998	965	1084	Liquid		.213
		940	872	1018	Before melting	(*.110)	
		984	932	1067	Solid	.157	
Mean a. d.					.145 ± .007	.219 ± .005	

* Not taken for mean.

SUMMARY AND CONCLUSIONS

The micropyrometer has been shown to be an instrument comparable in accuracy and range with much more elaborate experimental installations for the determination of monochromatic emissivity. Starting with the cold substance, measurements of emissivity and of its temperature coefficient, accurate to about 1 per cent, may be taken at high temperatures (900 to 3000° C.) within a few minutes with a mass of less than 0.01 mg. presenting a surface of 0.25 mm².

Measurements of emissivity with red and green light have been made of 23 metals in hydrogen and 12 oxides in air; a summary of most of the results is given in Table 7.

TABLE 7

Emissivities of Metals and Oxides with Micropyrometer

Metals.....	Cu	Ag	Au	Pd	Pt	Ir	Rh	Ni	Co	Fe	Mn	Ti
$e_{\lambda=0.65}$ {solid	0.10	0.04	0.14	0.33	0.33	0.30	0.29	0.36	0.36	0.37	0.59	0.63
liquid15	.07	.22	.37	.3830	.37	.37	.37	.59	.65
$e_{\lambda=0.55}$ {solid38	<.35	<.38	.38	.3829	.4475
liquid36	<.35	<.384675

Metals.....	Zr	Th	Y	Er	Be	Cb	V	Cr	Mo	W	U	
$e_{\lambda=0.65}$ {solid	0.32	0.36	0.35	0.55	0.61	0.49	0.35	0.39	0.43	0.39	0.54
liquid30	.40	.35	.38	.61	.40	.32	.39	.4034
$e_{\lambda=0.55}$ {solid3661	.61	.29	.5377
liquid30	.81

Oxides near F. P. s.....	NiO	Co ₃ O ₄	Fe ₂ O ₄	Mn ₃ O ₄	TiO ₂	ThO ₂	Y ₂ O ₃	BeO	CbO ₂	V ₂ O ₃	Cr ₂ O ₃	U ₃ O ₈
$e_{\lambda=0.65}$ {solid	0.89	0.77	0.63	0.52	0.57	0.61	0.37	0.71	0.69	0.60	0.30
liquid68	.63	.53	0.47	.51	.6931

In the solid state practically all the metals examined appear to have a negligible or a very small temperature coefficient of emissivity for $\lambda = 0.65\mu$ and $\lambda = 0.55\mu$, within the temperature range 20° C. to the melting point. Nickel oxide has a well-defined negative coefficient, at least to the melting point.

There is a discontinuity in emissivity for $\lambda = 0.65\mu$ at the melting point for some but not all of the metals and oxides. This effect is most marked for gold, copper, and silver, and is appreciable for platinum and palladium.

Palladium, in addition, possesses for radiation a property analogous to surfusion, in that the value of emissivity ($\lambda = 0.65\mu$) natural to the liquid state may persist for a time after solidification of the metal.

The Violle unit of light does not appear to define a constant standard.

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