THE OPTICAL PROPERTIES OF MOLTEN METALS.

BY A. K. ASTER.

SYNOPSIS.

Optical Properties of Molten Bi, Pb, Sn, and Wood's Alloy to 500° and of Hg to 345° C.—While there is considerable evidence that the optical properties of metals in the solid state do not vary with temperature, the question has not yet been investigated for molten metals. A vacuum tight furnace enabled a nitrogen atmosphere to be used so that surfaces free from oxidation could be studied. The optical properties were determined by letting plane polarized light of wave-length about 6020 Å.U. fall at an angle of 45° upon the metal surface, and analyzing the reflected light with the help of a Jellet split nichol having a Brace elliptic half-shade mounted just before it. The method of calibration and use of the apparatus is described. The optical properties were found to be independent of the temperature for all the metals tried. The mean values, correct to better than one per cent., are as follows: for Bi, $\nu = 0.493$, $k = 1.32$; for Hg, $\nu = 0.442$, $k = 1.43$; for Pb, $\nu = 0.415$, $k = 1.76$; for Sn, $\nu = 0.398$, $k = 1.46$; for Wood's alloy, $\nu = 0.397$, $k = 1.78$. From a discussion it appears that the constancy of the optical properties is not consistent with Drude's equations.

INTRODUCTION AND PREVIOUS WORK.

THE optical properties of metals as a function of the temperature have been investigated to a certain extent for metals in the solid state. Kundt[1] investigated silver, antimony, copper, platinum, iron and nickel between 20 and 100 degrees C., using a direct method, employing thin metallic prisms. He found a slight variation of the index of refraction with the temperature. Drude[2] investigated gold and platinum up to 200 degrees C., and found only a very slight change in the index of refraction, but did not consider the work conclusive. Sissingh[3] investigated iron but did not find any change with the temperature. Zeeman[4] investigated platinum up to 800 degrees C., but did not find any change in the coefficient of reflection. Pfleuger[5] investigated nickel, gold and iron between 20 and 100 degrees C., by the same method as Kundt, direct observations on thin metallic prisms, and did not find any change with the temperature. Very little work has been done on metals in the molten state. C. V. Kent[6] investigated bismuth, cadmium, tin, and lead and their binary alloys. He did not definitely determine whether the optical properties were constant with the temperature or not and

[1] Kundt, Wied. Ann., 36, 834, 1889.
[2] Drude, Wied. Ann., 39, 538, 1890.
[3] Sissingh, Arch. Nierlandaisses, tome XX.
[4] Zeeman, Comm. of the Phys. Lab. Leyden, 20, 1895.
[5] Pfleuger, Wied. Ann., 58, 493, 1896.
[6] Kent, PHYS. REV., XIV., 6, 495.

states in his paper that some work should be done to determine this point. His calculations are on the basis that the optical properties are constant.

It was the object of this investigation to determine whether or not the optical properties of molten metals are functions of the temperature.

DESCRIPTION AND USE OF APPARATUS.

Various methods have been used for determining the constants of elliptically polarized light. The Babinet-compensator and the Babinet-Soleil modification of it have been used for large ellipticities while a more recent development, the Brace elliptic half-shade, has been used for small ellipticities. The apparatus used in this work is of the latter type. The arrangement used was similar to that used by A. Q. Tool [1] in his work on the optical properties of metals. The entire polarizing and analyzing systems were mounted in the arms of a vertical spectrometer especially constructed for the purpose. The polarizing system consisted of the usual collimator with a nicol prism mounted directly after the collimator lens. The analyzing system consisted of a compensator (mica between optical flats) mounted on a circle movable with respect to a fixed vernier and the analyzing nicol, a Jellet split nicol with an elliptic half-shade mounted just before it, was mounted on a second circle movable with respect to a vernier which was fixed with respect to the first circle. The half-shade was set with its dividing line at right angles to that of the split nicol. The entire analyzing system was mounted in the telescope arm of the spectrometer which was fitted with a short focus ocular. The spectrometer was fitted with a special device connecting the telescope and collimator arms so that when the collimator was set for a given angle of incidence the telescope was automatically set in the proper position for the reflected beam.

The source of light was a spectroscope fitted with a constant deviation prism and illuminated with an arc lamp using specially treated commercial carbons giving a strong band at approximately 6020 Å.U.

The theory of this analyzing system has been given by Tuckerman[2] in an article on elliptic analyzing systems. The procedure is to obtain a match of all four parts of the field and then make the complementary setting. Let R and r be the positions of the compensator and the nicol respectively for a match, and R' and r' for the complementary match and

$$R' - R = c,$$
$$r' - r = n;$$

[1] Tool, PHYS. REV., XXXI., 1, 1.

[2] Tuckerman, Univ. of Neb. Studies, IX., 2, 157.

then if plane polarized light is let fall on the analyzing system, Tuckerman finds that

$$\cos 2\Pi N_1 = \frac{\tan c}{\tan n}, \tag{1}$$

$$\tan 2\eta = \sqrt{\frac{\sin (n - c) \sin (n + c)}{\sin c}}, \tag{2}$$

where 2η is the effective order of the half-shade and $2\Pi N_1$ is the order of the compensator. If the initial light is not plane polarized, he finds that

$$\tan 2\Pi N_1 = \sqrt{\frac{\sin (c - n)}{\sin (c + n)}} (1 - \alpha \tan 2\eta + 1/2\alpha^2 \tan^2 2\eta - \cdots), \tag{3}$$

$$\tan 2\psi = \sqrt{\frac{\sin (c - n) \sin (c + n)}{\sin n}} (1 - 1/2\alpha^2 \tan^2 2\eta - \cdots) \tag{4}$$

where

$$\alpha = \frac{\sin c}{\sqrt{\sin (c - n) \sin (c + n)}} \tag{5}$$

and if $2\gamma = (R' - R) - (R_0' - R_0) - 2\Phi$ and Φ is 45° as is customarily used, then

$$v_\theta = -\frac{\sin \Phi \tan \Phi \cos 2\psi \cos 2\psi}{1 - \cos 2\psi \sin 2\gamma}, \tag{6}$$

$$K_\theta = -\frac{\tan 2\psi}{\cos^2 \gamma}, \tag{7}$$

where R_0' and R_0 are the settings on plane polarized light,

v_θ = index of refraction,
K_θ = coefficient of absorption,
θ = angle of incidence.

By letting plane polarized light fall on the analyzing system, taking the necessary readings and applying equations 1 and 2, it is possible simultaneously to calibrate the compensator and the half-shade. By analyzing plane polarized light (for $\Phi = 45°$) when it is reflected from the metal surface and applying equations 4, 5, 6 and 7 the optical properties for that angle of incidence and wave length of light used, can be obtained.

EXPERIMENTAL WORK.

The nicol prism of the polarizer was first adjusted for an azimuth of 45° by means of an auxiliary nicol. The compensator and elliptic half-shade were next simultaneously calibrated. This was done by setting the analyzer in direct line with the polarizer and making the two settings

for a match. Substitution of the data thus obtained in equations 1 and 2 gives the following results:

$$\cos 2\Pi N_1 = 0, \qquad 2\Pi N_1 = 90°,$$
$$\tan 2\eta = 0.366, \qquad 2\eta = 20.1°.$$

A special vacuum-tight furnace was designed because in order to prevent oxides from forming on the surface of the molten metal it was necessary to have the furnace filled with nitrogen. A reducing atmosphere would probably have been better, but the risk of an explosion with the use of hydrogen was considered too great to warrant using it, so an inert gas was resorted to. Ordinary commercial nitrogen was found satisfactory. The commercial product contains about 5 per cent. of oxygen according to the manufacturer. In order to keep the amount of oxygen a minimum, the nitrogen was kept in the furnace at a pressure just high enough to prevent boiling of the metal. This pressure was from 20 to 30 cms. of mercury. The remaining oxygen was easily removed by skimming the metal a few times after it was molten, thus converting the oxygen to metallic oxide. After a few skimmings, it was possible to keep the surface clean for a considerable time. It should be stated at this point that the furnace was first exhausted before filling with nitrogen. It was also washed several times before the final filling with nitrogen, this being done to reduce the amount of oxygen to a minimum. This entire operation was completed before the furnace was heated to a point where the metal melted. It was necessary to have the furnace at least 25 degrees above the room temperature while exhausting it, in order to drive out most of the residual gas in the magnesia packing, etc.

The windows of the furnace were constructed of optical glass which was tested so as to be sure that it was free from optical strain. It was necessary to limit the observations to one angle of incidence (45°) in order that the entering and emerging light should always be normal to the plane of the windows to prevent introduction of errors. To be able to vary the angle of incidence it would have been necessary to reconstruct the major portion of the furnace housing for each angle. The furnace was mounted on a special anti-vibration mounting in order to prevent the vibration of the building from disturbing the surface of the molten metal while observations were being taken. This special mounting consisted of a box containing sand, on top of which were placed several marble plates separated by rubber stoppers. The furnace was set on top of the marble plates. The temperature of the metal was measured by means of a chromel-alumel thermocouple. The cold juncture was

kept in a Dewar flask filled with distilled water, the temperature of which was measured with a good mercurial thermometer. A Leeds-Northup potentiometer type pyrometer indicator reading directly in millivolts was used as the indicator. The calibration of the couple was taken from data available in the laboratory. See Fig. 1 for a cross-section of the furnace.

A number of metals were investigated, the results of which are listed below. It was found impossible to continue the investigation above about 500 degrees C., as at this point the metal begins to glow a dull cherry red and this light masks the light from the collimator so that on further settings could be made. It was impossible to use filters as the two colors were nearly alike and any filter which would exclude the one beam would so reduce the other that it would be impossible to make accurate settings and in this sort of work it is necessary to have the maximum possible intensity so as to insure sufficient sensitivity of the apparatus. The sensitivity of the system drops off very rapidly with diminishing intensity. It was found impossible to make any determinations just at the melting point because at this point the metal surface is still rough. It was found necessary to raise the temperature at least about ten degrees above the melting point of the metal to get the metal liquid so as to get a smooth surface. How far one has to go above the melting point depends on the metal. It was found impossible to take any data above 345 degrees C. for mercury, because above this point the mercury vapor condensed on the windows of the furnace making it impossible to see through them. Two attempts were made to get data for cadmium but both were failures. In the first attempt, the cadmium combined with the graphite crucible, and it was impossible to get a clean surface. In the second trial an alundum crucible was substituted for the graphite one, but it was still found impossible to get a clean surface. (Ordinary chemically pure metals were used for all tests.)

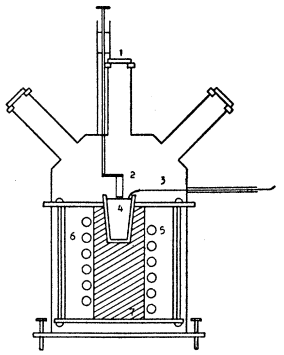

Fig. 1.

1, Glass window. 2, Stirrer. 3, Thermocouple. 4, Crucible and metal. 5, Heater conductor. 6, Magnesia packing. 7, Iron heater core.

RESULTS.

Lead.

Temp.	ν_θ.	K_θ.
335° C.	0.414	1.76
345	0.413	1.74
365	0.415	1.75
385	0.417	1.78
405	0.414	1.77
427	0.416	1.74
440	0.414	1.78
475	0.415	1.77
485	0.416	1.76
Mean	0.415±0.0006	1.76±0.005

Tin.

Temp.	ν_θ	K_θ.
250° C.	0.396	1.46
315	0.398	1.44
335	0.397	1.48
345	0.399	1.45
357	0.400	1.46
375	0.397	1.47
395	0.398	1.44
425	0.396	1.46
450	0.400	1.48
480	0.398	1.44
Mean	0.398±0.0005	1.46±0.0045

Bismuth.

Temp.	ν_θ.	K_θ.
275° C.	0.493	1.31
285	0.492	1.32
295	0.494	1.31
317	0.491	1.30
345	0.495	1.34
375	0.491	1.33
395	0.493	1.32
405	0.492	1.34
425	0.494	1.31
450	0.491	1.33
465	0.493	1.32
485	0.495	1.32
Mean	0.493±0.0005	1.32±0.006

Mercury.

Temp.	ν_θ.	K_θ.
22° C.	0.441	1.42
65	0.442	1.43
125	0.444	1.45
175	0.440	1.41
212	0.441	1.41
265	0.443	1.43
285	0.443	1.42
300	0.440	1.45
325	0.444	1.41
345	0.444	1.43
Mean	0.442±0.0004	1.43±0.0045

Wood's Alloy.

Temp.	ν_θ.	K_θ.
100° C.	0.397	1.80
125	0.400	1.78
150	0.395	1.76
175	0.396	1.77
200	0.398	1.76
220	0.399	1.80
242	0.395	1.78
265	0.397	1.79
285	0.396	1.79
305	0.398	1.78
325	0.395	1.76
345	0.399	1.76
365	0.400	1.80
385	0.397	1.76
407	0.397	1.78
425	0.398	1.77
450	0.395	1.77
465	0.398	1.78
480	0.397	1.76
Mean	0.397±0.00045	1.78±0.0047

DISCUSSION OF RESULTS.

From the results, it is obvious that within the limits of the investigation and the sensitivity of the apparatus used, the optical properties of the metals investigated are constant.

Since the optical properties of Sn, Pb, and Bi are constant and the factors for Wood's Alloy are constant, and Wood's Alloy is made of Sn, Pb, Bi, and Cd, it seems reasonable to conclude that the optical properties of cadmium are constant.

With the view of possibly making a comparison between the factors of the molten and the solid state some observations were made on a highly oxidizable metal (copper). It was found that the age of the surface after polishing as well as the kind of abrasive used in making the mirror greatly affected the results so that no consistent data could be obtained. From this it was concluded that it would be necessary to prepare the mirror in a reducing atmosphere and without the use of an abrasive if accurate results are to be obtained. To prepare a surface under these conditions seems practically impossible. This condition prevented any comparison of the data for the two states. This difficulty applies only to soft, low melting point, highly oxidizable metals and the other metals could not be investigated because their melting points are above 500 degrees C. This point is the upper limit of the work as was previously stated.

PROBABLE ERROR.

The least squares solutions of the experimental results show that the probable error of these quantities is under one half of one per cent. The probable error of the adjustment of the polarizing and analyzing prisms with respect to their circles was well under one-half of one per cent. It seems therefore probable that the final values of these constants are not in error by more than one per cent.

THEORETICAL.

Drude's equations[1] for the optical constants of metals are:

$$\nu^2(1-\kappa^2) = 1 + \sum \frac{\Phi'}{1-\left(\frac{\tau_h}{\tau}\right)^2} - 4\pi \sum \frac{m'N}{r^2+\left(\frac{m'}{\tau}\right)^2} \tag{8}$$

$$2\nu^2\kappa = 4\pi\tau \sum \frac{Nr}{r^2+\left(\frac{m'}{\tau}\right)^2}, \tag{9}$$

where τ_h = natural period of the electrons of class h.

τ = natural period of the incident light.

N = number of electrons per cubic centimeter.

$m' : me$ $\qquad$ m = inert mass of the electron.

e = charge on an electron.

$r = \frac{N}{\sigma}$ $\qquad$ σ = electrical conductivity.

Φ' = proportional to the displacement of the electrons from their positions due to the influence of a constant force. For conducting electrons Φ' is ∞.

[1] Drude, Theory of Optics, translation by Mann, p. 398.

The experimental work shows that ν_θ and K_θ are constant. Indicating all the constant terms in equations (8) and (9) as such, they become:

$$C = 1 + \sum \frac{\Phi'}{1 - \left(\frac{\tau_h}{\tau}\right)^2} - E \sum \frac{F}{\frac{N}{\sigma^2} + \frac{1}{N} G^2} \tag{10}$$

$$H = J \sum \frac{1}{\frac{1}{\sigma} + \frac{\sigma}{N^2} P} \tag{11}$$

where C, E, F, G, H, J and P are constants. If equation (11) is true then:

$$\left| \frac{1}{\sigma} + \frac{\sigma P}{N^2} \right|_{t_1} = \left| \frac{1}{\sigma} + \frac{\sigma P}{N^2} \right|_{t_2}. \tag{12}$$

Since σ and N vary with the temperature, this identity must hold for all corresponding pairs of values of σ and N. To test this identity, data for mercury will be substituted.

For 0° C. $\quad 1/\sigma = 94 \times 10^{-6}$,
350° C. $\quad 1/\sigma = 135.5 \times 10^{-6}$,

N varies inversely as the expansion of the metal.

For 350° C. $\quad$ Let $N = 1$.
0° C. $\quad N = 1.064$.

Substituting in equation (12), neglecting the first term on each side of the equation (this is possible because of their size in comparison with the following terms) and inverting, the result is:

$$106 = 135,$$

which is obviously not true, the difference being about 21.5 per cent. Since this difference is far greater than the experimental error of the work, the validity of equation 11 seems doubtful. As to equation 10 very little can be said as no data is available as to the variation of Φ' and τ_h with the temperature.

In conclusion, I wish to thank Professors Hall and Minor and all others whose kind assistance made this work possible.

PHYSICAL LABORATORY,
UNIVERSITY OF CALIFORNIA,
April, 1922.