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# THE SURFACE TENSION OF MOLTEN METALS

WITH

## A DETERMINATION OF THE CAPILLARY CONSTANT OF COPPER

BY EARL E. LIBMAN



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#### EARL E. LIBMAN

NATIONAL RESEARCH FELLOW IN PHYSICS

#### ENGINEERING EXPERIMENT STATION

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## THE SURFACE TENSION OF MOLTEN METALS WITH A DETERMINATION OF THE CAPILLARY CONSTANT OF COPPER.

#### I. Introduction

1. Historical Sketch.—When a tube of small bore is placed vertically with its lower end submerged in a liquid, the latter rises or drops within the tube and stands at a higher or lower level than the liquid without. This phenomenon is due to the mutual attractions of the particles of the liquid for each other and for those of the tube. It is most marked in the case of very fine bore tubes, bores of hair size called capillaries (Latin "capilla," meaning hair). This and all phenomena due to the same cause are grouped under the head of "capillary action."

The first to note capillary phenomena was Leonardo da Vinci,\* but accurate observations were not made until 1709 when Francis Hawksbee† studied the action of liquids with glass tubes and plates. His work was augmented by Dr. James Jurin, ‡ and Sir Isaac Newton devoted the 31st query in the last edition of his Optics to molecular forces in which he mentions capillarity.

Alexis Claude Clairaut appears to have been the first to attempt a mathematical investigation of the phenomena, but without success. It is to A. von Segner¶ that the idea of "surface tension" is due. Following this idea Gaspard Monge\*\* asserted that supposing the adherence of the particles of the liquid to be sensible only at the surface and in a direction tangent to it, the entire phenomena may be explained by mathematical analysis, and this was done in 1804 by Thomas Young.†† It remained for Laplace, however, to give a mathematical analysis of the subject based on only two assumptions, the constancy of the angle of contact and the existence of attractive forces between the particles of the liquid. This appeared in the "Mécanique Célest," Supplement to Tenth Book, 1806. The assumption of constant angle of contact was shown to be unnecessary by Gauss. II

In 1831 Simeon Denis Poisson published his "Nouvelle Théorie de l'Action Capillarie." He maintained that there is a rapid variation of

<sup>\*</sup>Pogg. Ann. cI, p. 551.
†Phil. Trans. 1711, 1712.
‡Phil. Trans. 1718, 1719.

‡Phil. Trans. 1718, 1719.

\*Théorie de la Figure de la Terre," Paris, 1808.

¶Comment. Soc. Reg., Götting. 1, 1751.

\*\*'Mémoires de l'Acad. des Sciences," 1787.
††"Essay on the Cohesion of Fluids," Phil. Trans. 1805, p. 65.
‡‡"Principia Generalia Theoriae Figurae Fluidorium in Statu Aequilibrii," 1830.

density of the liquid at its surface and gave numerous reasons for this belief. His results are, however, identical with those of Laplace and Gauss and there is as yet no way to distinguish between the two theories.

W. Thomson\* first applied thermodynamics to capillarity. This phase of the subject was further treated by Gibbs† and still more enlarged by Van der Waals.‡

The theory as it stands today is that of Laplace and Gauss with the thermodynamical aspect due to Thomson, Gibbs, and Van der Waals.

2. Previous Determinations of Surface Tension of Molten Metals.— The accurate determination of the surface tensions of molten metals has been limited to those metals whose melting points are so low that they can be handled in glass or transparent quartz. These are bismuth, lead, tin, cadmium, and zinc Concerning all other metals, we know (except for copper considered in this work) hardly more than the general order of magnitude of this important property. The reason for this state of affairs is the great difficulty involved in handling accurate measurements at high temperatures upon materials in opaque containing vessels. All measurements (except on the metals just noted) have been carried out in air which oxidizes the surface and thus contaminates the very portion whose cleanliness is most essential. Attempts made to avoid oxidation by covering the surface with powdered charcoal but substitute one contaminating source for another. It is, therefore, not surprising that the data obtained are conflicting and unreliable. The following tables indicate the nature of the results up to date. Except for the low melting

Table 1
Capillary Constant of Metals Melting at Temperatures above 1000 Deg. C.

 $a^2 = 2t/g\rho$  in cm.<sup>2</sup> t = surface tension in dynes/cm.  $\rho = \text{density}$  g = acceleration due to gravity

		Ob	server	
Metal	Smith 1914	Gradenwitz 1899	Heydweiller 1897	Quinke 1868
Silver	0.1852	0.145		0.1594
Gold	0.1129		0.069	
Copper	0.2885			0.1444
Iron				0.2648

<sup>\*</sup>Proc. Roy. Soc. 9, 1858. †"Equilibrium of Heterogeneous Substances," Connecticut Acad. Trans. 3, 1876. ‡"Thermodynamische Theorie der Kapillaritat unter voraussetzung kontinuerlicher Dieteanderung," Verhandl. Akad. von Wetensch., Amsterdam, 1893.

Table 2
SURFACE TENSION OF METALS MELTING AT TEMPERATURES
BELOW 1000 DEG. C.

	Surface Tension in dynes/cm.					
Metal	300°C	350°C	400°C	450°C	500°C	
Bismuth	376	373	370	367	363	
Lead		442	438	438	431	
Tin	526	522	518	514	510	
Cadmium		628	625	622	618	
Zinc				755	751	

metals noted no attempt has been made to determine the surface tension at more than one temperature, which is usually in the vicinity of the melting point.

Some results of previous work on capillary constant of metals are presented in Table 1.

All previous work on surface tensions of molten metals melting at temperatures below 1000 deg. C. has been rendered obsolete by the careful work of Hogness\* giving the results presented in Table 2.

### 3. Importance of Surface Tension Data for Metals.—

#### (a) Practical

When a substance is molten the only forces acting upon it are gravity and the intermolecular attractions that manifest themselves in the phenomenon of surface tension. It follows that the behavior of the molten materials will be closely related to their surface tensions and that an extension of our knowledge of this property should lead to a greater insight into the peculiarities exhibited by molten metals.

Surface tension is the governing factor in all processes of welding, soldering, and joining. It has recently been shown (A. W. Coffman, doctor's dissertation, 1927, Chemistry Department, University of Illinois) that those fluxes that are most effective in soldering are just those whose presence causes a lowering of the surface tensions of the metals that become molten in the soldering operation.

The mutual solubilities of the molten metals, and the behavior of such solutions upon cooling and before solidification, should likewise be so related to the surface tensions that a knowledge of the latter will allow a prediction of the former.

<sup>\*</sup>Jour. Am. Chem. Soc. 42, No. 12, 1920.

In casting operations where sharp outline is necessary the surface tension of the molten metal is the governing factor. Metals with high surface tension will not flow into sharp corners or crevices and if the latter be sufficiently fine an enormous pressure would be required to force the liquid into them. The previously-held idea that the metal must expand, or at least not shrink, on cooling, in order to get sharp castings, is giving way before the suspicion that those materials whose addition increase detail in casting are just those that cause a lowering in the surface tension of the melt.

It appears, therefore, that in the progress of metallurgy surface tension data are a growing necessity, and the fact that most of its applications are still in a formative state is due more to the lack of such data than to any doubt concerning their importance.

#### (b) Theoretical

In its search into the properties of the universe, science has concerned itself greatly with increasing our knowledge of the characteristics of the few elements that make up the world upon which we live. A fundamental property is surface tension, and it is of great scientific interest that this be added to those properties already known for the elements.

At present the greater part of the scientific world is investigating the structure of the atom and molecule. The property of the cohesion of fluids (and of solids as well) is one intimately connected with atomic and molecular structure and any knowledge gained concerning the phenomenon, surface tension, which is a direct result of those cohesive forces, is a step in the solution of this great problem.

4. Acknowledgments.—This investigation has been a part of the regular work of the Engineering Experiment Station of the University of Illinois, of which Dean M. S. Ketchum is the director, and of the Department of Physics, of which Prof. A. P. Carman is the head.

The work was carried out under a National Research Fellowship. The author wishes to acknowledge the coöperation of Professor Chas. T. Knipp, of the Department of Physics, in the early stages of the work, and the assistance of Mr. John Thews, Assistant in Physics, who worked with him throughout the course of the investigation.

#### II. THEORETICAL ASPECT

5. General Theory.—An exhaustive treatment of the general theory of capillarity would begin with the assumption that each particle of the liquid is attracted by all the other particles. From this assumption the

theory would progress through involved mathematical analysis to the final formulas required. Such a treatment of the subject is to be found in many excellent texts (see particularly Mathieu "Théorie de la Capillarité" and Minchen "Hydrodynamics").

For the present purpose, however, a more direct route will be taken. Beginning with the same assumption it will be shown that a liquid is subjected at every point of its surface to a pressure normal to its surface at that point. Attention will then be drawn to the fact that if there were no cohesive forces and the liquid were, instead, covered on its surface with a stretched elastic skin (like a piece of sheet rubber) the same condition of normal pressure would result. A calculation will next be made of the tension in this elastic skin necessary to cause the existing pressure, and this tension is the force called "surface tension."

Note that in actuality no "skin" exists. Due to the cohesive forces the liquid acts in a peculiar manner. This action is *the same as would occur if*, instead of the cohesive forces from within, there were an elastic skin without. That is, the liquid acts as if it were possessed at its surface of a skin stretched so that it sustains a tension *t*, called "the surface tension."

Every particle of a liquid is attracted by every other particle not only by gravitational forces but also with cohesional forces directly proportional to the masses of the attracting particles and to some unknown function of the distance between them. These cohesional forces are sensible only through a very small distance e, which distance is called the radius of cohesional activity. The fact that liquids, and indeed crystals as well, cohere with forces that cannot be due to gravitation alone is well known. Experiments by Quinke and others have shown that if such forces as the cohesional forces postulated above do exist, they cannot be sensible over distances exceeding  $5\times10^{-5}\,\mathrm{mm}$ . The mutual gravitational forces have been shown to be small in comparison with the cohesional forces, and in what follows they will be neglected.

Let AB, Fig. 1, represent the surface of a fluid and A'B' an imaginary surface parallel to AB and a distance e below it equal to the radius of cohesional activity. Consider a particle of liquid at P. About P draw a sphere of radius e. Of this sphere only the hemisphere abc exists in the liquid so the cohesional forces acting upon P come only from the particles in this hemisphere. From the symmetrical grouping of these particles about P it is obvious that the resultant force is in the direction Pb which is normal to the surface at P.

Consider next the particle Q. The action of the liquid upon the particle at Q is that of the particles within  $a_1, mb_1, nc_1$ , that portion of the sphere with radius e about Q which exists within the liquid. The re-

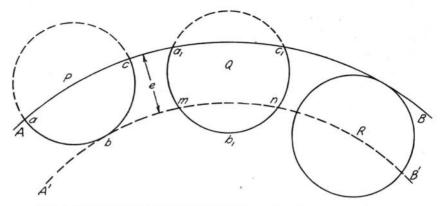


Fig. 1. Surface of a Liquid Showing Spheres of Cohesional Activity

sultant force is obviously in the direction  $Qb_1$  and is, moreover, less than at P for here we have some liquid above Q exerting an upward force. Finally, consider a particle at R. The particle is completely surrounded by liquid in all directions for a distance at least equal to e. The resultant force upon it is, therefore, zero, as it is equally attracted in all directions, and the same is true of any other particle below A'B'.

From the foregoing analysis we see that every particle in the extremely thin layer of thickness e at the surface is being urged inward by a force normal to the surface. If the surface be plane it is evident from its symmetry that this force will be the same over the entire surface. If, however, the surface be curved, the force will vary from point to point and be a function of the curvature of the surface which becomes a constant when the curvature vanishes. Thus, this inwardly directed force distributed over the surfaces causes a pressure within the liquid (in addition to the hydrostatic pressure H) which will be indicated by K + p(curvature), where p (curvature) represents some function of the curvature which vanishes when the curvature becomes zero; that is, when the surface becomes flat. The total pressure is then P = K + H + p. This first term K, the pressure due to cohesion existing within the liquid when its surface is flat, is exceedingly large (of the order of 10 000 atmospheres). Being constant and within the liquid it does not manifest itself with change of shape of the liquid and is not the term which governs the capillary phenomena. It is the third term, p (curvature), which plays the important rôle. This term, depending upon the curvature, changes with a change in shape of the surface and it is to this variation of pressure with surface that the phenomena of capillarity are due.

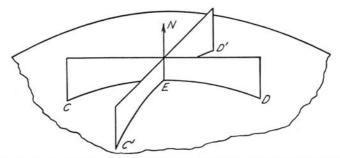


Fig. 2. Sections of a Curved Surface Cut by a Perpendicular Pair of Normal Planes

Now suppose that the liquid possessed no cohesive attractive force but was surrounded with an elastic skin (in tension) at its surface, and also subjected to a constant pressure (as might be accomplished by placing the containing vessel in a room and raising the air pressure to the desired amount). The elastic skin would exert a force upon the surface everywhere normal to it, and this would result in a pressure within the liquid. This pressure would vary with the curvature of the surface and when the surface became flat the pressure would vanish. Hence, if the elastic skin possessed such a tension that the pressure within the liquid due to it were p (curvature), and the constant pressure (exerted by the air as indicated above) were equal to K, then the whole pressure within the liquid would be P = H + K + p (curvature) precisely as before.

Consider now any curved surface (Fig. 2). At any point E of the surface let us erect a normal N. Then through N let us draw two mutually perpendicular planes. These cut the surface in two plane curves CD and C'D'. The curve CD has a certain radius of curvature  $R_1$  at E. The curve C'D' has another radius of curvature  $R_2$  at E. If we rotate the pair of planes about N the curves CD and C'D' will change, and so will their radii of curvature  $R_1$  and  $R_2$ . The sum  $\frac{1}{R_1} + \frac{1}{R_2}$  will, however,

remain a constant, and is therefore a property, not of the curves, but of the surface at the point E. It is called the mean curvature of the surface at the point E.

Now if an elastic skin is stretched over a curved surface in such a way that it possesses throughout a constant tension T, the pressure it exerts upon the surface at any point E is known to be

$$p = T\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{1}$$

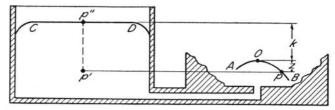


FIG. 3. FREE SURFACE OF A LIQUID CONNECTED WITH A RESERVOIR

and this vanishes when the surface becomes a plane. This then is the function p (curvature) and the tension T is called the "surface tension." The actual pressure P existing within the liquid is P = K + p + H. K is a constant called the "intrinsic pressure"; this constant K cancels out in the consideration of capillary phenomena. p is the pressure within the liquid due to the hypothetical elastic surface skin possessing surface tension T. Hence the total pressure at any point within the liquid is

$$P = K + H + T \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \tag{2}$$

Consider the free surface of a liquid which is subjected only to gravity and the reactions of the walls of its containing vessel. No matter what the form of the surface may be, the container may always be considered joined by a canal to a reservoir sufficiently large so that the liquid in it has a plane surface. Thus let AB, Fig. 3, represent the free surface of a liquid connected by a canal, as shown, with a reservoir in which the liquid has a portion CD of its surface plane. The pressure at p' must be the same as that just within the surface at p and at the same height. The pressure at p' is, by equation (2), K + H (since at p''  $\frac{1}{R_1} + \frac{1}{R_2} = 0$ ), and that at p is  $K + T\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ . Equating these,  $H = T\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ . But  $H = g\rho$  (k + z) where  $\rho$  is the density of the liquid. Hence, writing  $\frac{2T}{g\rho} = a^2$  (the "capillary constant"),

$$z = \frac{a^2}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) - k \tag{3}$$

where k is obviously a constant depending for its value upon the selection of the origin. In this analysis no mention has been made of the fact that any particular arrangement was being considered. O is arbitrarily selected as the origin from which to measure z. Hence equation

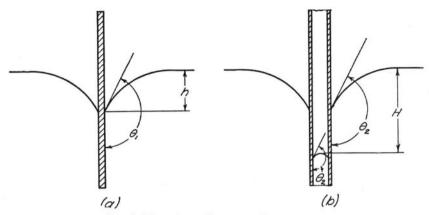


FIG. 4. PLANE AND CAPILLARY DEPRESSIONS

(3) is perfectly general and holds for all liquids subject only to gravity. This is the fundamental equation required for a discussion of the method used in this investigation. Note that  $\frac{1}{R_1} + \frac{1}{R_2}$  is the curvature at the point whose ordinate is z.

6. Theory of Method Employed in this Investigation.—If a vertical plane be dipped into the level surface of a fluid which does not wet the plane, the fluid is depressed at the plane, that is, the line of contact of the fluid with the plane will be lower than the level of the fluid. The magnitude h (Fig. 4) of the depression will depend upon the properties of the liquid and the solid forming the plane, that is, upon the surface tension  $T_1$  and the angle of contact  $\theta_1$ .

$$h = F_1 (T_1, \theta_1) \tag{4}$$

If a capillary tube be placed with its lower end beneath the level surface of a liquid which does not wet the tube, the liquid will stand within the tube at a lower level than the surface without. The depression H (Fig. 4) is again a function of  $\theta_2$  and  $T_2$ , or

$$H = F_2 \left( T_2, \theta_2 \right) \tag{5}$$

Now if the material forming the plane is the same as that composing the tube, and if the liquid is the same in both cases, then  $\theta_1 = \theta_2$ ,  $T_1 = T_2$ , and

$$h = F_1(T, \theta)$$

$$H = F_2(T, \theta)$$
(6)

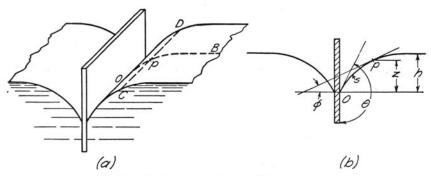


FIG. 5. DETAILS OF PLANE DEPRESSION

two equations connecting the two unknowns T and  $\theta$  which can then be determined when h and H are known.

To determine the form of  $F_1$   $(T,\theta)$ , consider an infinite plane dipped vertically into the plane, horizontal surface of an infinite liquid which does not wet it. The liquid will then be depressed in the neighborhood of the plane and its surface will be cylindrical with generators parallel to the plane. Let p be any point on the surface and make two sections through p, one perpendicular to the plane and the surface and represented by OB, Fig. 5, the other through p perpendicular to the first section and the surface and represented by CD, Fig. 5, which obviously is a generator of the surface and therefore a straight line. The curvature  $\frac{1}{R_2}$  of this last section is zero and so the equation of the surface is, from equation (3),

$$z = \frac{a^2}{2} \frac{1}{R_1} - k. (7)$$

Take the origin at the point of greatest depression at the plane (Fig. 5). Then from the figure it is plain that when z = h,  $\frac{1}{R_1} = 0$ , and substituting in (7) gives h = -k, so that equation (7) may be rewritten

$$(z - h) = \frac{a^2}{2} \frac{1}{R_1}.$$
 (8)

Now

$$\frac{1}{R_1} = \frac{d\phi}{ds} = \frac{d\phi}{dz} \frac{dz}{ds} = \frac{d\phi}{dz} \sin \phi$$

and as z varies from 0 to h,  $\phi$  varies from  $\theta - \frac{\pi}{2}$  to 0.

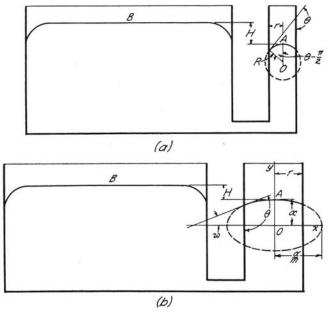


FIG. 6. CAPILLARY SURFACE APPROXIMATED BY SPHERE AND BY ELLIPSOID

Therefore

$$(z-h) = \frac{a^2}{2} \frac{d\phi}{dz} \sin \phi \text{ or } \int_0^h 2 (z-h) dz = a^2 \int_{\theta-\frac{\pi}{2}}^0 \sin \phi d\phi, \text{ whence}$$

$$h^2 = a^2 (1-\sin \theta) \tag{9}$$
and, since  $a^2 = \frac{2T}{g\rho}$ ,
$$F_1(T,\theta) = \sqrt{\frac{2T}{g\rho} (1-\sin \theta)}$$

To determine the function  $F_2$   $(T, \theta)$ , consider a large vessel with a capillary tube attached, and suppose the vessel of sufficient size so that the surface of the liquid it contains has a plane portion. If the tube is sufficiently small the surface in the capillary resembles a sphere and if it be assumed truly spherical there results the arrangement indicated in Fig. 6.

Take the center of the sphere as origin. Equation (3) then is

$$z = \frac{a^2}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) - k.$$

At point B,  $\frac{1}{R_1} + \frac{1}{R_2} = 0$  and z = R + H, so that R + H = -k, and the equation becomes

$$z - (R + H) = \frac{a^2}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \tag{10}$$

the equation of surface. For point A, z = R, and if any pair of mutually perpendicular normal sections through A be taken it is obvious, since the surface is one of revolution, that the radii of curvature will be the same for both sections, that is,

$$\frac{1}{R_1} = \frac{1}{R_2} = -\frac{1}{R}$$

at A. Hence equation (10) becomes for A,  $H = \frac{a^2}{R}$ . From the figure

it is seen that  $r = R \sin \left(\theta - \frac{\pi}{2}\right)$  or  $\frac{1}{R} = -\frac{1}{r} \cos \theta$  and

$$H = -\frac{a^2}{r}\cos\theta \text{ or } a^2 = \frac{Hr}{-\cos\theta} \text{ (approximate)}.$$
 (11)

Equation (11) is approximate, for it is based upon the assumption that the surface in the capillary tube is a sphere: this is true only for the very smallest tubes. If the tube is of the size employed in this work (about 3 mm. radius) then the surface flattens out at A and departs from the spherical form, resembling a prolate ellipsoid of revolution. A more accurate expression for  $a^2$  will next be obtained on the assumption that the surface within the capillary is an ellipsoid, and it will be found that the result is but to add a correction term to (11).\*

Figure 6 represents an axial section through the surface in the tube which, being a surface of revolution, has every axial section the same. Taking the vertical axis of the ellipsoid as  $\alpha$ , and the horizontal axis as  $\frac{\alpha}{m}$ , then the equation of the section is

$$\frac{x^2}{\left(\frac{\alpha}{m}\right)^2} + \frac{y^2}{\alpha^2} = 1 \text{ whence } y = \sqrt{\alpha^2 - m^2 x^2}$$

Also,

$$\tan \omega = \frac{dy}{dx} \bigg|_{x = -r} = \frac{-m^2x}{\sqrt{a^2 - m^2x^2}} \bigg|_{x = -r} = \frac{m^2r}{\sqrt{a^2 - m^2x^2}}$$

<sup>\*</sup>See Desains, Ann. Chem. Phys. (3), 51, 417 1857.

But 
$$\theta = \omega + \frac{\pi}{2}$$
,  $\cot \theta = -\tan \omega$ ,  $\cot \theta = \frac{-m^2r}{\sqrt{\alpha^2 - m^2x^2}}$ . (12)

From (3) we have the equation of the surface as

$$z = \frac{a^2}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) - k$$

At point B,  $z = \alpha + H$  and  $\frac{1}{R_1} + \frac{1}{R_2} = 0$ . Hence  $\alpha + H = -k$  and

$$z - (\alpha + H) = \frac{a^2}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$
 (equation of surface) (13)

At the point A, since the surface is one of revolution,  $\frac{1}{R_1} = \frac{1}{R_2} = \frac{1}{R_A}$ , the curvature of the ellipse at A, while  $z = \alpha$ 

$$\frac{1}{R_A} = \frac{d^2y}{dx^2} \left\{ 1 + \left( \frac{dy}{dx} \right)^2 \right\}^{-\frac{3}{2}} = \frac{d^2y}{dx^2} \bigg|_{x=0}$$
Since  $\frac{dy}{dx} \bigg|_{x=0} = 0, \frac{1}{R_A} = \frac{d^2y}{dx^2} \bigg|_{x=0} = \frac{-m^2}{a}$ 

and substituting in (13)

$$H = \frac{a^2 m^2}{a} \tag{A}$$

Using this in conjunction with (12) gives

$$m^2 = \frac{r^2}{\frac{a^4}{H^2} - r^2 \tan^2 \theta}$$
 (B)

Since  $\frac{m}{\alpha}$  is a function of  $\theta$  as shown in (12) it follows that  $F_2(T,\theta)$  has the form given by (A), namely,  $\left(\frac{2T}{g\rho} \frac{m^2}{\alpha}\right)$ , and the attempt might be made to determine  $\frac{m}{\alpha}$  as a function of  $\theta$  and substitute. Because of the mathematical difficulties involved it is found more expedient to pursue another course. Consider a section of the capillary at O, Fig. 6b, and determine the total force upon it from beneath; then determine the total force upon it from above. Equating the two gives the desired relation involving  $\alpha$  and m which is required in order to complete the analysis under consideration.

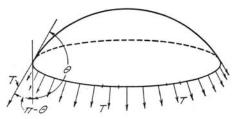


Fig. 7. Surface Tension Forces Acting on Capillary Surface

The pressure on the section at O from beneath is, by equation (2), K+H+p (where  $p=T\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$  is the pressure transmitted to the section by the liquid, and due to the elastic skin at B). Since the surface at B is plane this last term is zero. The hydrostatic pressure is  $g\rho$  (H+a) and so the total pressure from beneath is  $K+g\rho$  (H+a) and the total force is  $\pi r^2 [K+g\rho (H+a)]$ .

The total force exerted on the section at O from above is that due to the intrinsic pressure K, that due to the weight of the liquid above the section at O, and that due to the elastic skin. The total force due to the pressure K is  $\pi r^2 K$ . That due to the weight of the liquid above the section at O is  $g\rho$  (volume of liquid above section at O) =  $g\rho$   $\int_{0}^{r} 2\pi xy dx$ .

$$2\pi g \rho \int_0^r xy dx = 2\pi g \rho \int_0^r x \sqrt{a^2 - m^2 x^2} dx$$
$$= 2\pi g \rho \left[ \frac{-(a^2 - m^2 r^2)^{\frac{3}{2}}}{3m^2} + \frac{a^3}{3m^2} \right].$$

If, then, F represents the force exerted by the elastic skin, the force  $\Gamma = (a^2 - m^2r^2)^{\frac{3}{2}}$ 

from above is 
$$\pi r^2 K + F + 2\pi g \rho \left[ \frac{-(\alpha^2 - m^2 r^2)^{\frac{3}{2}}}{3m^2} + \frac{\alpha^3}{3m^2} \right]$$
.

Equating the forces from above and below on the section at O

$$\pi r^{2} \left[ K + g\rho \left( H + \alpha \right) \right] = \pi r^{2} K + F + 2\pi g\rho \left[ \frac{-\left( \alpha^{2} - m^{2}r^{2} \right)^{\frac{3}{2}}}{3m^{2}} + \frac{\alpha^{3}}{3m^{2}} \right]$$

or

$$\pi r^2 g \rho (H + \alpha) = F + 2\pi g \rho \left[ \frac{-(\alpha^2 - m^2 r^2)^{\frac{3}{2}}}{3m^2} + \frac{\alpha^3}{3m^2} \right] \cdot (14)$$

Note that the intrinsic pressure K has cancelled out, as indeed it does in all capillary phenomena.

F has now to be found. Across every line of unit length in the surface there acts the force T of surface tension in a direction normal to the line and tangent to the surface. Along the line of contact of the

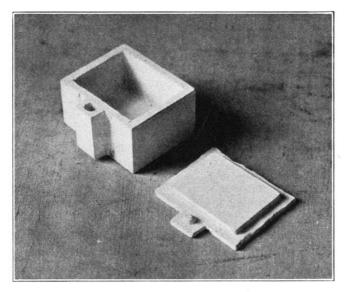


Fig. 8. Special Crucible

liquid surface with the tube there acts, therefore, on every unit length a force T normal to the line of contact and making an angle of  $(\pi - \theta)$  with the vertical, Fig. 7. The vertical component of this force is  $T \cos (\pi - \theta) = -T \cos \theta$  and the total vertical force exerted upon the surface is  $F = -2\pi r T \cos \theta$ . Introducing this in equation (14)

$$a^{2} = \frac{rH}{-\cos\theta} + \frac{\left[r\alpha + \left[\frac{2(\alpha^{2} - m^{2}r^{2})^{\frac{3}{2}}}{3m^{2}r}\right] - \frac{2\alpha^{3}}{3m^{2}r}\right]}{-\cos\theta}$$
 (C)

Note that this is the same as equation (11) with the quantity in brackets as a correction term. Gathering the useful equations (A), (B), and (C) we have

$$\begin{cases} m^{2} = \frac{r^{2}}{\left(\frac{a^{4}}{H^{2}}\right)} - r^{2} \tan^{2} \theta \\ a = \frac{a^{2} m^{2}}{H} \\ a^{2} = \frac{rH}{-\cos \theta} + \frac{\left[ra + \left\{\frac{2\left(\alpha^{2} - m^{2} r^{2}\right)^{\frac{3}{2}}}{3m^{2} r}\right\} - \frac{2\alpha^{3}}{3m^{2} r}\right]}{-\cos \theta} \end{cases}$$
(15)

Equations (9), (11), and (15) are the fundamental equations used to calculate the capillary constants from observed data. They are used as follows: From the values of h and H obtained experimentally we get by means of equations (9) and (11) approximate values for  $a^2$  and  $\theta$ . Substituting these in equations (15) we get the correction term to our approximate value of  $a^2$ . (If desired this corrected value of  $a^2$  can again be used for a more accurate value of the correction term although in the present work the first application was sufficient.) The detailed method of use of these equations on the experimental data is to be found in Tables 10 and 11.

7. Discussion of Errors.—The experimental details will be given later, but before entering into a discussion of errors it is necessary to give in barest outline a sketch of the method sufficient to make intelligible the matter which is to follow. The plane depression h and capillary depression H being arranged within a vacuum furnace, an X-ray photograph is taken through the entire furnace. On the photograph h, H, and r are measured. The vertical plane against which the depression h occurs, and the capillary tube within which the depression H takes place, are both part of a special crucible shown in Fig. 8 and completely described further on.

In the theoretical treatment the case of an infinite liquid into which is dipped an infinite vertical plane has been considered. The mathematical analysis availed itself of this infinite liquid only to insure that the surface was, at some point, sufficiently removed from the influence of the plane to be horizontal. Hence, in the experimental work, it is necessary only to insure that the containers used are sufficiently large to allow the liquid to have a portion of its surface horizontal. If this is done the theoretical formulas that we have deduced are applicable. If this is not done, then an estimation of the error involved is necessary.

In order to be certain that the surface within the container is flat it would be necessary to use a crucible of prohibitive dimensions. It is, therefore, necessary to determine the error involved in the use of apparatus of practical size.

Consider the case of two parallel vertical planes dipped into the liquid, and assume that they are such a distance l apart that the surface between them, at the midpoint, is depressed an amount d below the original level.

From equation (3) for the free surface of the liquid

$$z = \frac{a^2}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) - k.$$

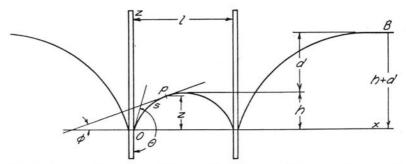


Fig. 9. Surface Depression d Due to Two Parallel Planes at Distance l

At B, Fig. 9, the surface is flat, and  $\frac{1}{R_1} + \frac{1}{R_2}$  vanishes. Also, at B z = h + d and so k = -(h + d). Since the surface is cylindrical,  $\frac{1}{R_2} = 0$  everywhere, and the equation becomes

$$z - (h + d) = \frac{a^2}{2R_1}$$
 (16)

Now

$$\frac{1}{R_1} = \frac{\frac{d^2z}{dx^2}}{\left|1 + \left(\frac{dz}{dx}\right)^2\right|^{\frac{3}{2}}}$$

and so

$$2\left[z - (h+d)\right] = \frac{a^2 \frac{d^2 z}{dx^2}}{\left\{1 + \left(\frac{dz}{dx}\right)^2\right\}^{\frac{3}{2}}}$$

Integrating

$$\[z - (h+d)\]^2 = \frac{C - a^2}{\left\{1 + \left(\frac{dz}{dx}\right)^2\right\}^{\frac{1}{2}}}$$
 (17)

where C is a constant of integration. When z = h,  $\frac{dz}{dx} = 0$  and  $d^2 = C - a^2$ , hence  $C = d^2 + a^2$  and

$$d^{2} + a^{2} - [h + d - z]^{2} = \frac{a^{2}}{\left\{1 + \left(\frac{dz}{dx}\right)^{2}\right\}^{\frac{1}{2}}}$$
(18)

$\sqrt{2} r/a$	$\sqrt{2} d/a$	$\sqrt{2} r/a$	$\sqrt{2} d/a$	$\sqrt{2} r/a$	$\sqrt{2} d/a$
1.75	0.76	3.25	0.19	6.0	0.015
2.00	0.59	3.50	0.15	6.5	0.009
2.25	0.46	4.00	0.09	7.0	0.006
2.50	0.37	4.50	0.054	8.0	0.0023
2.75	0.30	5.00	0.035	9.0	0.0009
3.00	0.24	5.50	0.022	10.0	0.00034

Table 3
Reservoir Corrections

Solving for  $\frac{dz}{dx}$  gives

$$\frac{dz}{dx} = \frac{\sqrt{a^4 - (d^2 + a^2 - [h + d - z]^2)^2}}{d^2 + a^2 - [h + d - z]^2}$$

which may be written

$$\frac{dz}{dx} = \frac{\sqrt{1 - \left(\frac{d^2 + a^2}{a^2} - \frac{[h + d - z]^2}{a^2}\right)^2}}{\frac{d^2 + a^2}{a^2} - \frac{(h + d - z)^2}{a^2}}$$
(19)

If an attempt is made to carry the integration of (19) further, an elliptical integral of some difficulty is arrived at. Before proceeding it will therefore be well to obtain an idea of the order of magnitude of d. The quantity d is, of course, the error in H (Fig. 6) due to the assumption that the surface in the reservoir is plane.

Richards and Carver\* have considered this error for the case of cylindrical reservoirs, and have arrived at certain conclusions. These are in agreement with the independent investigations of Sugden† and of Rayleigh.‡ Table 3, compiled from these data by N. E. Dorsey, Consulting Physicist, U. S. Bureau of Standards, gives reservoir corrections (that is, error due to the assumption that the surface contains a plane portion) for the case of right circular cylindrical reservoirs. In this table d is the depression in the reservoir due to the curvature of the surface (there would be no depression at a point where the surface is flat), r is the radius of the right circular cylindrical reservoir, and  $a^2 = 2T/g\rho$ .

<sup>\*</sup>Jour. Am. Chem. Soc. 43, p. 836, 1921. †J. Chem. Soc. (London) 119, p. 1483, 1921. ‡Proc. Roy. Soc. (A) 92, p. 184, 1916.

For the case of copper  $a^2$  is 0.304 cm.<sup>2</sup>, so that a = 0.551 cm. If we consider a right circular cylinder of radius 1.85 cm. then  $\sqrt{2} r/a = 4.75$ . From Table 3 this corresponds to  $\sqrt{2} d/a = 0.045$  and d = 0.018. That is, the surface of the liquid in a cylindrical tube 1.85 cm. in radius is sufficiently close to the walls to be influenced by them to the extent of a depression of 0.018 cm.

In the present work the reservoirs were rectangular boxes 3.7 cm. imes 4.7 cm. and inasmuch as the walls of these rectangular crucibles are everywhere at a distance from the center greater than 1.85 cm. (except at two points where the distance equals 1.85 cm.) it follows that the influence of these walls will be less than those of a cylindrical crucible, and so the depression d will be less than 0.018. Hence  $d^2 < 0.000324$  and  $1 < \frac{a^2 + d^2}{a^2} < \frac{0.304324}{0.304} < 1.0012$ . Hence without any considerable error,

 $\frac{a^2+d^2}{a^2}=1$ . Equation (19) then gives

$$\frac{dz}{dx} = \frac{\sqrt{2 \frac{(h+d-z)^2}{a^2} - \frac{(h+d-z)^4}{a^4}}}{1 - \frac{(h+d-z)^2}{a^2}}$$
(20)

Put  $\frac{h+d-z}{a}=y$  and  $\frac{x}{a}=w$ , then  $\frac{dz}{dx}=-\frac{dy}{dw}$ , and (20) gives

$$\frac{dy}{dw} = \frac{-y\sqrt{2-y^2}}{1-y^2}$$
 (21)

Now when x = 0, z = 0, w = 0, and  $y = \frac{h+d}{a}$ ; then  $x = \frac{l}{2}$ , z = h,

$$w = \frac{l}{2a}$$
, and  $y = \frac{d}{a}$ . Integrating (21) from  $x = 0$  to  $x = \frac{l}{2}$ ,

$$-\int_{\frac{h+d}{2}}^{\frac{d}{a}} \frac{1-y^2}{y\sqrt{2-y^2}} \, dy = \int_0^{\frac{1}{2a}} \, dw$$

or

$$\frac{l}{2a} = \frac{1}{\sqrt{2}} \log \frac{\sqrt{2} + \sqrt{2 - y^2}}{y} - \sqrt{2 - y^2} \Big|_{\frac{h + d}{a}}^{\frac{d}{a}}$$

$$\frac{l}{2a} = \frac{1}{\sqrt{2}} \log \left( \frac{h+d}{d} \frac{\sqrt{2} + \sqrt{2 - d^2/a^2}}{\sqrt{2} + \sqrt{2 - \left(\frac{h+d}{a}\right)^2}} \right) - \sqrt{2 - \frac{d^2}{a^2}} + \sqrt{2 - \left(\frac{h+d}{a}\right)^2}$$

which may be written in the form

$$l = \sqrt{2}a \log \left[ \frac{a^2}{(h+d) d} \left( \sqrt{2} + \sqrt{2 - \frac{d^2}{a^2}} \right) \left( \sqrt{2} - \sqrt{2 - h \frac{h+2d}{a^2} - \frac{d^2}{a^2}} \right) \right]$$
$$-2a \left( \sqrt{2 - \frac{d^2}{a^2}} - \sqrt{2 - h \frac{h+2d}{a^2} - \frac{d^2}{a^2}} \right)$$

Since it is known that  $d^2 < 0.000324$ ,  $\frac{d^2}{a^2} < 0.0011$ ,  $\frac{d^2}{a^2}$  may be neglected in comparison with 2. Then

$$l = a\sqrt{2}\log\frac{2\sqrt{2}a^2\left(\sqrt{2} - \sqrt{2 - h\frac{h + 2d}{a^2}}\right)}{(h+d)d}$$
$$-2a\left(\sqrt{2} - \sqrt{2 - h\frac{h + 2d}{a^2}}\right). \tag{22}$$

At 1271 deg. C. h = 0.5,  $a^2 = 0.306$ , and for other temperatures the values of h and  $a^2$  are but little changed. Putting these in (22)

$$l = 1.7942 \log_{10} (1.7197) \frac{\sqrt{2} - \sqrt{2 - \frac{1 + 4d}{1.216}}}{(1 + 2d) d} - 1.102 \left(\sqrt{2} - \sqrt{2 - \frac{1 + 4d}{1.216}}\right)$$
(23)

The curve represented by equation (23) is given in Fig. 10.

From Fig. 10 it is seen that two parallel planes 3.7 cm. apart cause a depression of 0.003 cm., while two planes 4.7 cm. apart cause a depression of 0.0008 cm. These figures completely justify the neglect of  $d^2/a^2$  in comparison to unity for  $d^2/a^2 < 0.00003$ . Assuming that the effect of both pairs of planes (forming the sides of the crucible, 3.7 cm.  $\times$  4.7 cm.) will be the sum of the effects of each separately, the depression in the crucible is 0.0038 cm. In making this assumption the effect, if any exists, of the corners is neglected. An examination of the melt in the crucible shows that the depression at the corners differs little from that at the

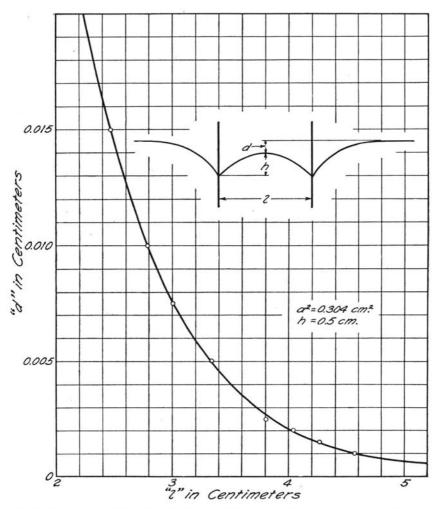


Fig. 10. Variation of Surface Depression d with l for Values of a and h as Given

planes. Moreover, the corners are furthest removed from the center (3 cm.), so that there can be little question concerning the validity of the procedure.

Since the quantity H measured is the difference of the depressions in the reservoir and capillary tube, the error involved in assuming no reservoir depression is 0.0038 cm. (The value of H being very near to 1 cm. this is then an error of 0.38%).

In order to get the error in h caused by the reservoir depression, reference is made to equation (16). In this, from equation (8),  $\frac{1}{R} = \sin \phi \, \frac{d\phi}{dz}$ , giving  $z - (h+d) = \frac{a^2}{2} \sin \phi \, \frac{d\phi}{dz}$ . Now as z goes from 0 to h,  $\phi$  changes from  $\left(\theta - \frac{\pi}{2}\right)$  to 0, and, integrating,

$$\int_0^h 2\left[z - (h+d)\right] dz = a^2 \int_{\theta - \frac{\pi}{2}}^0 \sin \phi \ d\phi, \text{ which gives}$$

$$\left[z - (h+d)\right]^2 = -a^2 \cos \phi \Big|_{\theta - \frac{\pi}{2}}^0 \text{ or}$$

$$h^2 + 2dh = a^2 (1 - \sin \theta). \tag{24}$$

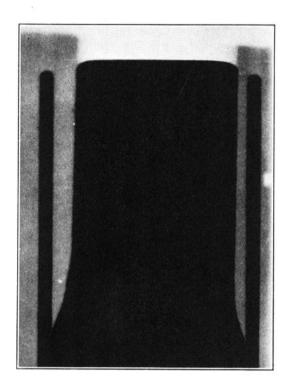
Comparing this with equation (9), it is seen that the error in  $h^2$  due to the reservoir depression d is 2hd which, since 2h = 1, is 0.0038 cm. Now if  $e_h$  is the probable error in  $h^2$ , then the probable error in h is  $\frac{dh}{d(h^2)}e_h = e_h/2h = 0.0038$ . (This corresponds to a percentage error of 0.76 per cent in h.)

Reference to the data of observation (Table 6) shows that the probable errors 0.0038 in H and in h, due to the restricted size of the crucible, both exceed the probable error of measurement, so that these are the accuracies with which these quantities are known. Also, r, which is about 0.3 cm., has a probable error of less than 0.0009 (see Table 6), corresponding to 0.3 per cent.

The method of using the theoretical equations (9), (11), and (15) to calculate  $a^2$  from the experimental data has already been indicated. The first step, that of obtaining an approximate value for  $a^2$ , is to eliminate  $\theta$  between equations (9) and (11). This gives

$$a^2 = \frac{1}{2} \left( \frac{H^2 r^2}{h^2} + h^2 \right)$$
 (25)

If  $e_H$ ,  $e_h$ , and  $e_r$  are the probable errors of H, h, and r, it is well known from the method of least squares that the probable error E in  $a^2$  will be



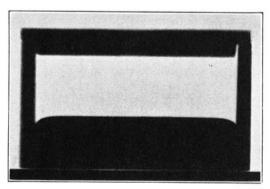


Fig. 11. Reproduction from X-ray Photographs of Plane and Capillary Depressions for Mercury

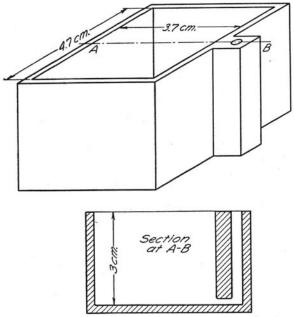


FIG. 12. DIMENSIONS OF SPECIAL CRUCIBLE

$$E = \sqrt{\left(\frac{\partial a^2}{\partial H}\right)^2 e_H^2 + \left(\frac{\partial a^2}{\partial h}\right)^2 e_h^2 + \left(\frac{\partial a^2}{\partial r}\right)^2 e_r^2}$$
 (26)

Using  $e_{H} = 0.0038$ ,  $e_{h} = 0.0038$ ,  $e_{r} = 0.0009$ , H = 1, h = 0.5, r = 0.3,

$$\left(\frac{\partial a^2}{\partial H}\right)^2 = \frac{H^2 r^4}{h^4} = 0.13, \ \left(\frac{\partial a^2}{\partial h}\right)^2 = \left(h - \frac{H^2 r^2}{h^3}\right)^2 = 0.05$$
$$\left(\frac{\partial a^2}{\partial r}\right)^2 = \frac{H^4 r^2}{h^4} = 1.44$$

and E = 0.0017. This is the maximum probable error in the determinations of  $a^2$ .

8. Test with Mercury.—The method was tried with mercury. Figure 11 is typical of the photographs from which the measurements were taken. The results for the surface tension of mercury as obtained from these experiments range from 472 to 480 dynes per cm., which is in good agreement with the data of the literature. Due to the difficulty of obtaining a pure mercury surface there is a wide variation in the data published. The best of the data published give between 470 and 480 dynes per cm.\*

<sup>\*</sup>Private communication from Dr. E. W. Washburn, Editor "Critical Constants."

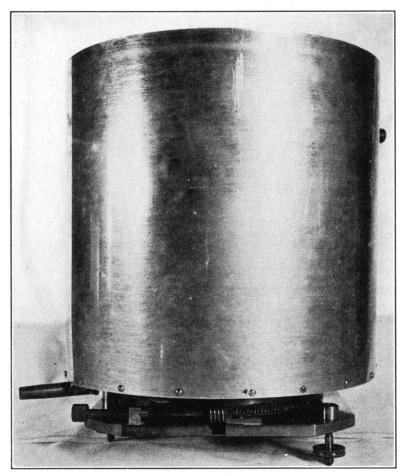


Fig. 13. View of Furnace Water Jacket with Levelling Table and Rotation Mechanism

### III. APPARATUS USED IN INVESTIGATION—THE CRUCIBLES

9. Form of Crucibles Used.—Throughout the theoretical treatment of the method employed in this work, it has been assumed that the vertical plane and the capillary tube are composed of the same material. This can be true only if both vertical plane and capillary tube are subjected to identical treatment. To insure this the crucibles used were of the form shown in Figs. 8 and 12. The depression h occurs at the middle of the vertical long sides and the capillary depression H in the side tube adjoining. Hence measurements of H and h are obtained simultaneously, and since both plane and tube are parts of a single unit, their histories are identical.

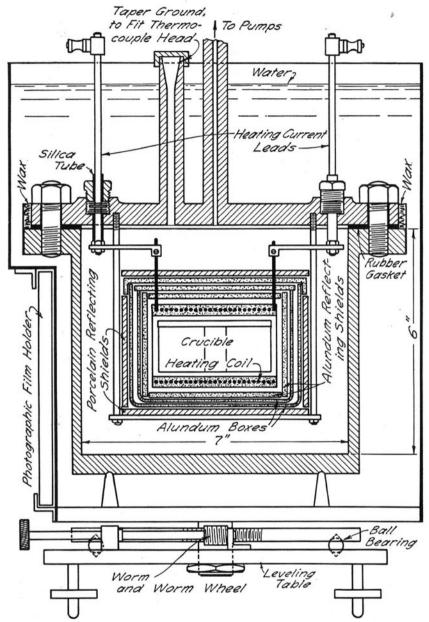


FIG. 14. SECTIONAL DETAILS OF VACUUM FURNACE



FIG. 15. FURNACE HOUSING

The crucibles were made from alundum No. 563 obtained from the Norton Company. The alundum was formed into rectangular blocks and allowed to dry thoroughly. The crucibles were then formed by machining with special tools of hard steel. Each crucible has a cover as shown in Fig. 8.

The crucibles were embedded in pure calcined Al<sub>2</sub>O<sub>3</sub> and burned in saggers in a gas-fired kiln to Seger cone No. 8 (about 1350 deg. C.).

## IV. Apparatus Used in Investigation—The Vacuum Furnace

10. Housing.—The furnace used to melt the metal under investigation is made up of three parts, the housing, the heating element, and the pumping system. The housing consists of a cast aluminum cylinder. The cylinder is provided with a cover through which insulated leads are sealed for conducting a current to the heating coil within. Suspended

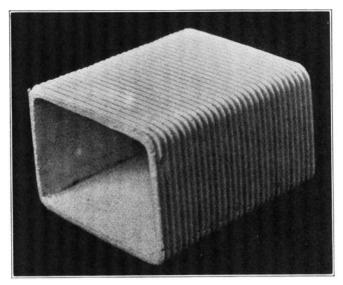


FIG. 16. ALUNDUM FURNACE CORE

from this cover is a hanger upon which the heating element rests. Around the edge of the cover is a well into which a mixture of half beeswax and half rosin is poured. This, together with a rubber gasket and nine bolts, makes a perfect vacuum seal. All the details are shown in the accompanying Figs. 13, 14, and 15.

When first made the aluminum casting allowed air to stream through it so that it was impossible to attain a vacuum. The pores of the cast aluminum were closed up in the following manner: The pot was painted with sodium silicate ("water glass") and heated in a gas oven until the silicate coating frothed into great white blisters. After the pot had cooled these were brushed off, leaving a thin veneer of an aluminosilicious compound. The cylinder was next treated with several coats of bakelite lacquer each being thoroughly baked. Finally the whole was covered with a number of coats of shellac which were likewise baked. The result was entirely satisfactory. The vacuum attained at room temperature was of the order of 10<sup>-6</sup> mm. of mercury, while that at high temperature (1300 deg. C.) was seldom poorer than 10<sup>-3</sup> mm. of mercury.

The housing proper is cooled by water circulating in a water jacket into which the pot is placed. This water jacket is provided with a leveling base. It is, moreover, mounted on ball bearings, and provided with an arrangement to allow rotation about the vertical axis of the cylinder. At the back is a pair of slides for the film holder.

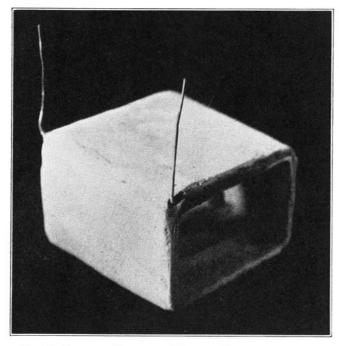


FIG. 17. FURNACE CORE WITH HEATING ELEMENT IN PLACE

- 11. Heating Element and Container.—The furnace proper consists of a heating coil of No. 18 B & S molybdenum wire wound upon an alundum core, covered with a layer of pure MgO, and then a layer of alundum. This is surrounded by alundum plates for the purpose of heat reflection, and the whole fits into a nest of two alundum boxes. The boxes themselves are surrounded by porous porcelain reflecting screens. The arrangement is shown in Fig. 14. The alundum core is shown in Fig. 16, the finished coil-wound core in Fig. 17, and the boxes in Fig. 18.
- 12. Vacuum System.—The pumping system consists of two Cenco Hyvac oil pumps supporting two Knipp mercury vapor pumps in parallel. These lead through a liquid-air trap to the furnace. The pumping system operating upon the furnace is shown in Fig. 19. The vacuum attained at room temperature is  $10^{-6}$  mm. of mercury, and at high temperatures (1300 deg. C.) is seldom poorer than  $10^{-3}$  mm. mercury.

### V. Temperature Measurements

13. Method of Measuring Temperature.—In order that no trace of oxide remain on the copper surface it was thought advisable to treat the



Fig. 18. Alundum Reflecting Boxes

heated material with hydrogen. It was found that this treatment with hydrogen caused the platinum—platinum-rhodium thermocouple used to measure the temperature to crystalize and disintegrate so that another method of making temperature measurement was necessary. This was effected by means of the resistance of the molybdenum furnace winding.

The furnace was provided with a block of alundum in place of the crucible. In this block a hole was drilled well into the center. Into this hole was inserted a platinum—platinum-rhodium thermocouple and the furnace was then heated without using hydrogen. Simultaneous readings of temperature and resistance were made, sufficient time being allowed before each reading to insure equilibrium. In this way the temperature was obtained as a function of the resistance of the coil plus an unknown contact resistance where the heating coil was connected to the leads within, and the supply to the leads without. This unknown resistance is different for each furnace set-up. Plotting the results gives a straight line, as shown in Fig. 20, and to determine the actual position of this line for a given furnace set-up one point upon it must be known. This point is determined for each run by noting the resistance at the moment when the X-ray pictures show that melting is occurring. Here the temper-

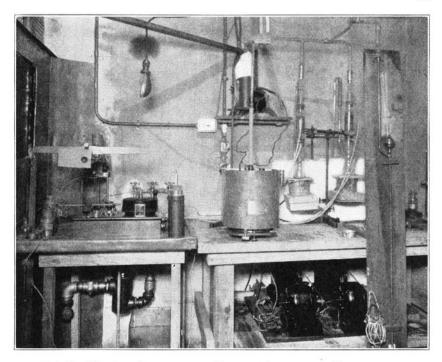


Fig. 19. Furnace Arrangement, Pumping System, and Temperature Measuring Instruments

ature is known, being the melting temperature of the metal, and the resistance is read from the instruments. These data determine a point through which the true curve, parallel to the calibration curve, must pass.

For the calibration the thermocouple used was sealed into a tapered glass tube, which was ground to fit an inverted taper on the cover. The taper on the cover can be seen in Fig. 14.

The resistance of the coil is known from simultaneous readings of a voltmeter and ammeter permanently connected in the circuit. The temperature read in this way is accurate to 5 deg. C. within the range from 500 to 1400 deg. C.

The thermocouple was standardized against U. S. Bureau of Standards metals Copper, Aluminum, Tin, Zinc, and Lead.

The details of the manipulation are given in Chapter VII.

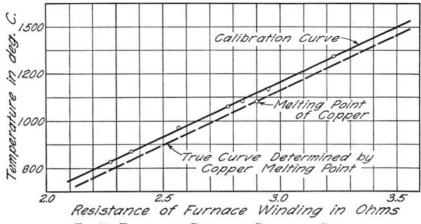


Fig. 20. Temperature-Resistance Calibration Curve

### VI. THE X-RAY EQUIPMENT

14. High Tension Apparatus.—The source of high tension current to supply the X-ray tube was a four kenetron tube rectifying apparatus consisting of a transformer stepping up 110 volts 60 cycles to 100 000 volts 60 cycles, a rectifying ring of four kenetron tubes changing the 100 000 volts alternating current to direct current, and the necessary control and safety devices. The apparatus is shown in Fig. 21, and the connections in Fig. 22.

15. Tube, Stand, and Filament Supply.—The X-ray tube used is a Victor Corporation Universal fine focus tube. It was operated at full 100 000 volts and 5 milliamperes at ten minute intervals. The tube was mounted on a stand, composed of two large porcelain insulators, in such a way that it could be raised and lowered at will, and was provided with a hard rubber frame holding a lead glass bowl. The tube with its standard frame is shown in Fig. 23.

The filament of the tube was supplied with current from storage batteries. These were supported on an insulated stand of a type similar to the tube stand. The current was regulated by a stove-pipe rheostat which was remotely controlled by a long bakelite rod. The batteries and insulating support are shown in Fig. 23.

16. Lead Room.—The furnace, pumping outfit, and X-ray tube were situated in a room entirely sheathed in ¼-inch sheet lead. A sliding lead door closed over the ordinary wooden door, and the apparatus was viewed through a window composed of four sheets of lead glass. The

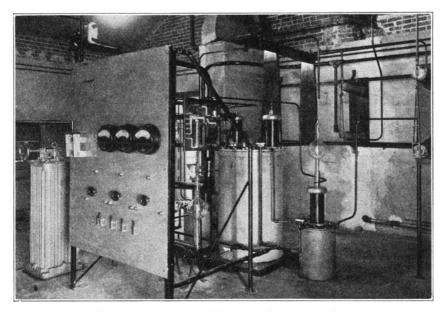


Fig. 21. 100 000-Volt Kenetron Rectifying Set

filament of the tube was controlled by a bakelite rod which slid through a circular hole in the leaden wall. The 100 000-volt supply was conducted into the lead room through two insulating cylinders. The entire lead structure was well grounded.

The films used were Eastman X-ray films. They were enclosed in Victor  $5\times 7$  in. film holders equipped with Patterson Fluorescent screens.

### VII. DETERMINATION OF CAPILLARY CONSTANT OF COPPER

17. Method of Procedure.—What follows is a detailed description of a determination of the surface tension of copper.

The crucible is charged with a block of copper of sufficient size to fill it (when melted) to within 1/8 inch of the cover. The latter is put in place and the covered crucible slipped into the furnace coil. The alundum reflecting shields are arranged in the inner alundum box and the coil with its crucible is placed therein. The inner box is then placed in the outer box, the top shields and covers put on, and the furnace proper is ready for the housing. It will be referred to as "the heater."

The lower porous porcelain reflecting shield is next put into place in the framework that hangs from the housing cover, the heater is placed upon it, and the heating wires are fastened to the leads. The housing is

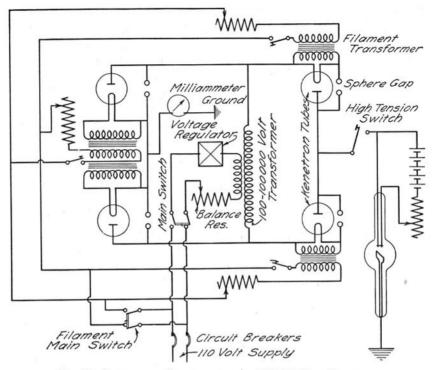


Fig. 22. Diagram of Connections for 100 000-Volt Rectifier

now supplied with its rubber gasket, the cover with its framework supporting the heater is lowered into place, and the nuts turned down on the nine bolts holding the cover.

The furnace housing with its cover is then placed in the water cooling jacket, is connected to the pumping system, and the oil pumps are started. After about an hour a flame is applied to the well around the cover until it is quite warm and a very hot mixture of half beeswax and half rosin is poured into the well. The oil pumps are allowed to act for twelve hours (usually over night), then liquid air is applied to the liquidair trap and the mercury vapor pumps started. Within half an hour the vacuum is in the neighborhood of  $10^{-6}$  mm. mercury.

The heating current is now turned on, and the heating allowed to progress at the rate of about 50 deg. C. per hour until 400 deg. C. has been reached. At about 400 deg. C. the cooling water is turned on. This is to allow the furnace walls to warm up and be "outgassed" before cooling them. At 900 deg. C. hydrogen is allowed to stream slowly into the furnace until the vacuum has entirely disappeared. This is pumped out

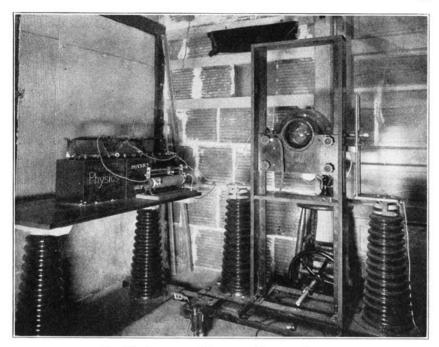


FIG. 23. INSULATED TUBE AND BATTERY STANDS

and the treatment twice repeated. It takes about one-half hour after this to reach a vacuum of about  $10^{-5}$  mm.

The X-ray machine is then started and photographs are taken. The photographs show the orientation of the crucible, and the entire furnace is rotated slightly by means of the rack and pinion until the photographs show that one side of the crucible is parallel to the rays.

The current is now increased slowly and photographs are taken in rapid succession (about six an hour) until they show that melting is occurring. By careful regulation of the current it is possible to keep the solid and liquid copper in equilibrium for over an hour. At this point a reading of the resistance of the furnace coil is taken. This gives the data necessary to locate the calibration curve described on page 34. The solid and liquid copper are shown in equilibrium in Fig. 24.

The current is then raised a given amount, and resistance readings are taken until they remain constant, showing that temperature equilibrium has occurred. Several photographs are taken and the process is continued. As the temperature rises the photographs begin to show that distillation and condensation of copper are occurring. Thus the data give the capillary constants of the interface between liquid copper and its vapor.

18. Development, Intensification, and Measurement of Photographs.—
The pictures are taken with 100 000 volts across the tube and an exposure at 5 milliamperes for 10 minutes. This greatly overloads the tube but nevertheless the pictures are very dim and accurate measurements are difficult. For this reason it is usually found advisable to intensify the films.

The pictures are taken, immediately developed, fixed, examined, and placed in the washing tank. After the run there are from thirty to forty films in the tank. These are intensified in rapid succession, rewashed, and allowed to dry. The measurements are made on the intensified films. Lead intensification is used.\*

The photographs are measured by means of a cathetometer. In order to determine the actual dimensions of the melt from those of the photographs, the furnace is set up with a steel plate of known dimension, in place of the crucible. This is photographed. If l is the length of the plate and p the length of its image on the film, then  $\frac{l}{p}$  is a factor which converts the image dimensions to the true dimensions.

In order further to correct for any change in size of the films due to developing, washing, drying, etc., a steel plate was fastened to the face of the film holder. If L is the length of this plate and P is the length of its image on the film at the time of measuring, then  $\frac{L}{P}$  is a factor which, applied to the dimensions of the photograph, corrects for such shrinkage or expansion. The error due to this cause was found in every case to be less than 0.15 per cent and might well be neglected.

19. Capillary Constant of Copper.—The copper used was chemically pure copper. In the preliminary experiments no elaborate precautions were taken to avoid contamination. About six runs were made before the experimental technique was fully developed. In the course of these runs the same sample of copper was handled and machined several times. Hence it gathered impurities. The data on this copper for the last preliminary run when all experimental difficulties were overcome are given in Table 4 for the purpose of comparison and to indicate the effect of impurities.

For the sample of copper from which the final results were obtained elaborate precautions were taken to avoid any contamination. The copper was melted in a large cylinder cut out of graphite and provided with an inlet at the bottom. Through this hydrogen was bubbled and the

<sup>\*</sup>For details of the method and data concerning the solutions used, see Cassell's Cyclopaedia of Photography, page 330.

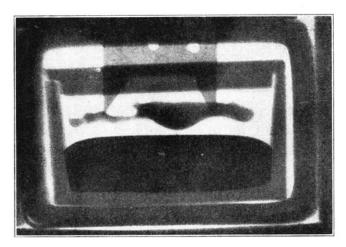


Fig. 24. Solid and Liquid Copper in Equilibrium at the Melting Point

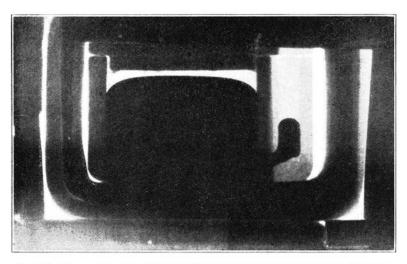


Fig. 25. Reproduction of Typical X-ray Photograph from the Negative of Which Measurements Were Made

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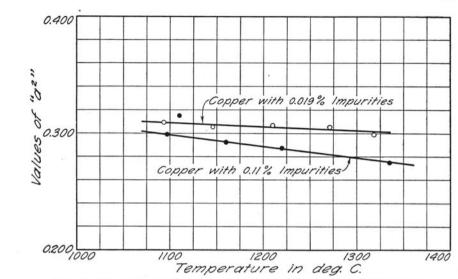


Fig. 26. Variation of Capillary Constant of Copper with Temperature (in cm<sup>2</sup>)

whole allowed to solidify in an atmosphere of hydrogen. This effectively eliminated all oxide, with which copper is known to form a eutectic.

From the large cylinder thus obtained a small block was cut from the very center on a power planer, using a very hard steel tool and no lubricant. An analysis made after the run showed this sample to be very pure.

Table 5 gives the temperature calibration of the molybdenum furnace coil used for this run. It is plotted in Fig. 20.

Table 6 gives the results of the film measurements for the final run with their probable errors. Table 7 gives the measurements on the steel plate for the purpose of obtaining the distortion correction factor discussed on page 40. Table 8 gives the results of a typical set of measurements to obtain correction for film expansion or shrinkage. Table 9 gives the corrected values of the film measurements. Tables 10 and 11 show the method of calculation and also the final data for  $a^2$  of copper. Figure 26 shows the plotted results. Figure 25 is a typical X-ray picture from the negative of which measurements were made.

A glance at Fig. 26 shows the effect of impurities upon the capillary constant. The presence of 0.11 per cent impurities has caused the capillary constant to fall much more rapidly with temperature than does that of the (comparatively) pure material.

Since  $a^2 = \frac{2T}{g\rho}$  where T is the surface tension, it is obvious that the surface tension can be calculated if  $\rho$  is known. Unfortunately, there exists no reliable data for  $\rho$ . The writer hopes soon to supply this deficiency in our knowledge of the metals. In most capillary phenomena, and in any practical case, the governing factor is  $a^2$  which is here given over a range of temperatures from the melting point to about 1400 deg. C.

Table 4

Results of Preliminary Determination of Capillary
Constant of Copper

Copper—Analysis, Impurities,  $Fe_2O_3 + Al_2O_3 = 0.07\%$ ,  $SiO_2 = 0.04\%$ 

H	h	r	π-θ	$a^2  ext{ (cm}^2)$	Temp. deg. C
				(0.301)*	1083
0.906	0.428	0.285	19°23′	0.299	1097
0.956	0.475	0.293?	12°28′	0.315?	1110
0.920	0.485	0.286	6°37′	0.292	1160
0.912	0.437	0.275	15°18′	0.290	(1195)†
0.939	0.518	0.278	0°	0.287	1220
0.907	0.519	0.272	1°23′	0.275	1335

\*Extrapolated.

Table 5
Temperature Calibration of Molybdenum Furnace Coil

Voltage	Amperes	Resistance ohms	Temperature deg. C.
24.9	10.55	2.360	866.
28.1	10.94	2.566	969.
32.5	11.45	2.840	1083.
34.7	11.77	2.950	1135.
41.0	12.70	3.230	1275.
31.4	11.30	2.780	1062.
21.9	9.64	2.274	826.

In actual run copper melted at resistance 2.90.

<sup>&#</sup>x27;This set of readings was taken long after all the others. The others were taken, and then the furnace was cooled to get this reading to fill the gap between 1168° and 1220°. Here the material of the crucible has soaked up copper, and so the data are quite different but the calculated value of a² agrees with the other values.

 $\begin{tabular}{ll} Table 6 \\ Film Measurements for Case of Pure Copper \\ Analysis—Total Impurities 0.019\% \end{tabular}$ 

Film No.	Temp. h deg. C. cm.		Devi- ation from mean	Probable error 0 .6745 $\sqrt{\frac{\sum v^2}{n(n-1)}}$	H cm.	Devi- ation from mean	Probable error $0.6745\sqrt{\frac{\sum_{b^2}}{n(n-1)}}$	2r cm.	Devi- ation from mean	Probable error $0.6745\sqrt{\frac{\Sigma v^*}{n(n-1)}}$
6	1093	0.508 0.505 0.507 0.508 0.506	0.001 0.002 0.000 0.001 0.001	12	1.034 1.037 1.030 1.035 1.032	0.000 0.003 0.004 0.001 0.002		0.589 0.585 0.581 0.578 0.580	0.006 0.002 0.002 0.005 0.003	
	Av.	0.507		0.000398	1.034		0.000827	0.583		0.00134
7	1093	0.493 0.493 0.493 0.493 0.492	0.000 0.000 0.000 0.000 0.000 0.001		1.035 1.032 1.030 1.030 1.034	0.003 0.000 0.002 0.002 0.002		0.585 0.585 0.580 0.580 0.580 0.580	0.003 0.003 0.002 0.002 0.002	
	Av.	0.493		0.000151	1.032		0.000692	0.582		0.000827
8	1093	0.492 0.492 0.492 0.492 0.492	0.000 0.000 0.000 0.000 0.000		1.042 1.042 1.040 1.038 1.041	0.001 0.001 0.001 0.003 0.000		0.572 0.572 0.572 0.574 0.575	0.001 0.001 0.001 0.001 0.002	
	Av.	0.492		0.000000	1.041		0.000523	0.573		0.000428
9	1093	0.503 0.502 0.504 0.502 0.502	0.000 0.001 0.001 0.001 0.001		1.040 1.040 1.042 1.042 1.040	0.001 0.001 0.001 0.001 0.001		0.586 0.583 0.585 0.580 0.582	0.003 0.000 0.002 0.003 0.001	
	Av.	0.503		0.000302	1.041		0.000338	0.583		0.000719
10	1093	0.520 0.520 0.515 0.515 0.515	0.002 0.002 0.003 0.003 0.003		1.053 1.055 1.047 1.043 1.043	0.005 0.007 0.001 0.005 0.005		0.595 0.598 0.598 0.600 0.600	0.003 0.000 0.000 0.002 0.002	
	Av.	0.518		0.000891	1.048		0.00168	0.598		0.000622
11	1093	0.493 0.493 0.502 0.503 0.505	0.006 0.006 0.003 0.004 0.006		1.056 1.053 1.052 1.054 1.055	0.002 0.001 0.002 0.000 0.001		0.588 0.585 0.588 0.592 0.592	0.001 0.004 0.001 0.003 0.003	
	Av.	0.499		0.00174	1.054	11 ((4))	0.000476	0.589		0.00089

Table 6 (Continued)

Film Measurements for Case of Pure Copper
Analysis—Total Impurities 0.019%

 $\frac{\Sigma v^2}{n(n-1)}$  $\frac{\Sigma v^2}{n(n-1)}$ 7 error error  $\Sigma v^2$ Probable error 2 22 n(n v Devi-Devi-Devi-Probable h HProbable 2rFilm Temp. deg. C. ation 6745 ation ation 6745 cm. cm. from No. from em. 6745 from mean mean mean 12 1146 0.548 0.001 1 055 0.001 0.585 0.005 0.548 0.552 0.547 0.545 0.552 $0.003 \\ 0.002$ 1.055  $0.001 \\ 0.001$ 0.585  $0.005 \\ 0.003$ 1.053 0.577  $0.004 \\ 0.003$ 1.055 0.001 0.5760.004 1.052 0.0020.578 0.002 Av. 0.549 0.00094 1.054 0.0004280.580 0.00135 1146  $0.001 \\ 0.003$ 13 0.540 0.001 1.058  $0.572 \\ 0.570$ 0.5420.001 1.058 0.5420.001 1.058 0.578  $0.005 \\ 0.002$ 0.5420.001 0.540 0.001 0.001 0.572Av. 0.5410.0003381.058 0.00000 0.573 0.00095 0.535  $1.055 \\ 1.055$ 14 1146  $\begin{array}{c} 0.001 \\ 0.001 \\ 0.002 \end{array}$  $0.007 \\ 0.001$ 0.5720.535 0.580 0.532 1.055 0.5810.002 0.002 0.581 0.583 0.004 Av. 0.534 0.000675 1.055 0.00000 0.579 0.001296  $\begin{array}{c} 0.585 \\ 0.585 \\ 0.585 \\ 0.587 \\ 0.584 \end{array}$  $\begin{array}{c} 0.000 \\ 0.000 \\ 0.000 \end{array}$ 16 1210 0.553 0.002 1.054 0.008 0.557 0.002 1.050 0.004 0.557 0.002 1.048 0.002 0.002 0.555 0.000 1.043 0.003 0.555 0.000 1.038 0.008 1.048 0.002 1.050 0.004 1.040 0.006 1.043 0.003 1.046 0.000 0.555 Av. 0.0005231.046 0.00105 0.5850.000338  $\begin{array}{c} 0.002 \\ 0.001 \\ 0.001 \\ 0.002 \end{array}$  $\begin{array}{c} 0.002 \\ 0.004 \\ 0.004 \\ 0.001 \end{array}$ 17 1210 0.555 0.002 1.052  $\begin{array}{c} 0.580 \\ 0.578 \end{array}$  $0.555 \\ 0.550$ 0.002 1.055 1.053  $0.586 \\ 0.583$ 0.553 0.000 1.056 0.551 0.002 0.001 1.053 0.001 0.583 Av. 0.5530.0006921.054 0.000501 0.582 0.00093 19 1271 0.524 $0.000 \\ 0.002$ 1.038  $0.004 \\ 0.001$  $0.592 \\ 0.594$  $0.009 \\ 0.011$ 0.524 0.522 0.524 0.5241.035 0.000 1.033 0.001 0.574 0.009 0.577 0.006 1.031 0.003 0.5870.0040.5800.003 0.5850.0020.584 0.001 0.579  $0.004 \\ 0.005$ 0.578 0.524 Av. 0.000384 1.034 0.00101 0.583 0.001404

Table 6 (Concluded)
Film Measurements for Case of Pure Copper
Analysis—Total Impurities 0.019%

Film No.	Temp. deg. C.	h cm.	Devi- ation from mean	Probable error $0.6745\sqrt{\frac{\Sigma v^2}{n(n-1)}}$	$_{ m cm.}^{H}$	Devi- ation from mean	Probable error $0.6745\sqrt{\frac{\sum v^2}{n(n-1)}}$	2r cm.	Devi- ation from mean	Probable error $0.6745\sqrt{\frac{\Sigma v^2}{n(n-1)}}$
20	1271	0.522 0.528 0.528 0.525 0.525	0.003 0.003 0.003 0.000 0.000		1.048 1.048 1.048 1.050 1.044	0.000 0.000 0.000 0.002 0.004		0.581 0.578 0.585 0.583 0.591	0.002 0.005 0.002 0.000 0.008	
	Av.	0.525		0.00084	1.048		0.000675	0.583		0.00148
21	1318	0.508 0.506 0.513 0.512 0.512	0.002 0.004 0.003 0.002 0.002		1.002 0.997 0.995 1.000 1.003 1.000	0.002 0.003 0.005 0.000 0.003 0.000		0.593 0.596 0.593 0.590 0.590	0.001 0.004 0.001 0.002 0.002	
	Av.	0.510		0.000915	1.000		0.000847	0.592		0.000768
22	1318	0.495 0.498 0.495 0.495 0.493	0.000 0.003 0.000 0.000 0.000		0.998 1.000 0.997 0.997 1.000	0.000 0.002 0.001 0.001 0.002		0.595 0.592 0.597 0.593 0.586 0.578 0.588 0.585 0.585 0.585	0.006 0.003 0.008 0.004 0.003 0.011 0.001 0.004 0.004	
	Av.	0.495		0.000542	0.998		0.000476	0.589		0.00121
23	1318	0.498 0.502 0.502 0.498	0.002 0.002 0.002 0.002		0.995 0.998 0.997 0.997 1.000	0.002 0.001 0.000 0.000 0.003		0.584 0.581 0.588 0.588 0.586 0.589 0.596 0.580 0.578	0.001 0.004 0.003 0.002 0.001 0.004 0.011 0.005 0.007	
	Av.	0.500		0.000775	0.997		0.000563	0.585		0.00116

Table 7

Distortion Correction on Film Measurements for Case of Pure Copper

Film No.	Length of Steel Plate	Deviation from Mean	Probable Error $0.6745\sqrt{\Sigma v^2/n} \ (n-1)$	Length of Steel Plate Image
	3.625 3.628 3.628 3.626	0.002 0.001 0.001 0.001		
	Mean 3.627		0.0005	
1		0.003 0.0 0.0 0.0 0.002		3.803 3.800 3.800 3.798
	Av.		0.0007	3.800
2		0.001 0.002 0.0 0.001		3.802 3.805 3.803 3.802
	Av.		0.0005	3.803
	Mean		0.0004	3.802 ± 0.0001

Correction factor =  $\frac{l}{p} = \frac{3.627}{3.802} = 0.9540 \pm 0.0002$ 

Table 8
Shrinkage Correction on Film Measurements for Case of Pure Copper

$\begin{array}{c} L \\ \text{Length of} \\ \text{Steel Plate} \end{array}$	Deviation from Mean	Probable Error $0.6745\sqrt{\Sigma v^2/n(n-1)}$	P Length of Image of Steel Plate
2.870	0.001		2.875
2.870	0.001		2.875
2.870	0.001		2.875
2.873	0.002	( 8)	2.875
2.870	0.001		
Iean 2.871		0.0002	2.875

Correction factor  $\frac{L}{P}\,=\,\frac{2\,.\,871}{2\,.\,875}\,=0\,.\,9986\,\pm\,0\,.0002$ 

Table 9
Film Measurements Corrected for Distortion and Shrinkage for Case of Pure Copper Analysis—Total Impurities 0.019%

Film No.	$_{ m cm.}^{h}$	H cm.	$\frac{2r}{\mathrm{cm}}$ .		
6*	0.484	0.986	0.556		
7	0.470	0.985	0.555		
8	0.469	0.993	0.547		
9	0.480	0.993	0.556		
10	0.494	1.000	0.571		
11	0.476	1.006	0.562 0.553 0.547 0.552		
12	0.524	1.006	0.553		
13	0.516	1.009	0.547		
14	0.509	1.007	0.552		
15		(Blurred)			
16	0.530	0.998	0.558		
17	0.528	1.006	0.555		
18	ii+	(Over intensified)			
19	0.500	0.986	0.556		
20	0.501	1.000	0.556		
21	0.487	0.954	0.565		
22	0.472	0.952	0.562		
23	0.477	0.951	0.558		

<sup>\*</sup>First 5 photographs taken before melting and used for orientation of furnace.

0.157 0.218 0.211 0.185 0.158 0.0222 0.0222 0.0072 0.000 0.001 0.001 0.104 0.126 0.126

sin θ -cos θ

-tan 0=

Table 10
Calculation of Approximate Capillary Constant for Pure Co

		$-\cos\theta = Hr/a^2$	0.989 0.978 0.978 0.982 0.982 0.996 0.996 0.996 0.998 0.998 0.998 0.998 0.998 0.998
RE COPPER		$\sin \theta = 1 - h^2/a^2$	0.155 0.218 0.218 0.182 0.156 0.217 0.018 0.00 0.00 0.00 0.001 0.103 0.123 0.125
T FOR PU		h2 a2	0.845 0.787 0.787 0.784 0.844 0.982 0.988 1.00 1.00 0.897 0.897 0.848
r Constan	$\frac{H^2 r^2}{h^3} + h^2 \bigg)$	Approx- imate a <sup>2</sup>	0.277 0.281 0.281 0.281 0.280 0.280 0.279 0.278 0.278 0.278 0.278 0.278 0.278
Calculation of Approximate Capillary Constant for Pure Copper	2 1	$\left(\frac{Hr}{\hbar}\right)^2 + \hbar^2$	0.554 0.554 0.554 0.554 0.554 0.554 0.552 0.553
XIMATI	Approximate a <sup>2</sup> =	h2	0.234 0.221 0.220 0.220 0.227 0.227 0.259 0.259 0.250 0.251 0.223
P APPRO	A	$\left(\frac{Hr}{h}\right)^{2}$	0.320 0.334 0.334 0.333 0.333 0.284 0.288 0.288 0.298 0.298 0.275 0.300 0.300 0.303
TION OF		Hr	0.566 0.556 0.575 0.575 0.575 0.533 0.535 0.524 0.555 0.555 0.555 0.555 0.555
ALCULA		h cm.	0.484 0.470 0.470 0.469 0.480 0.476 0.524 0.530 0.530 0.500 0.500 0.500 0.487 0.472
Ö		Hr	0.274 0.274 0.271 0.271 0.275 0.285 0.278 0.278 0.278 0.278 0.282 0.278
		cm.	0.278 0.278 0.273 0.273 0.273 0.273 0.273 0.278 0.278 0.278
		H cm.	0.986 0.985 0.993 0.993 0.993 1.006 0.998 0.998 0.954 0.955

Film No.

This	s intent	ionally l	

Table 11

Calculation of Corrected\* Capillary Constant for Pure Copper (in cm²)

Analysis—Total Impurities 0.019%

Film No.	Approximate a2	H em.	r cm.	a4	H2	a4/H2	r2	$-\tan \theta$	tan²θ	$r^2 \tan^2 \theta$	Α†	$m^2=r^2/A$	$m^2a^2$	$\alpha = \frac{m^2 a^2}{H}$	ar	m²r	B†	C†	C/m²r	$\frac{2}{3} \cdot \frac{C}{m^2r}$	D†	a <sup>3</sup>	$\frac{a^3}{m^2r}$	$\frac{2}{3} \cdot \frac{a^3}{m^2r}$	Εţ	-cos θ	$\frac{E}{-\cos\theta}$ Correction	Corrected a2		Mean for each Temperature
6	0.277	0.986	0.278	0.0767	0.972	0.0789	0.0773	0.157	0.0247	0.00191	0.0770	1.004	0.278	0.282	0.0784	0.279	0.0438	0.840	3.01	2.01	0.0786	0.0224	0.0803	0.0536	0.0250	0.989	0.0253	0.302	1093	0.308 ± 0.0017
7	0.281	0.985	0.278	0.0790	0.970	0.0814	0.0773	0.218	0.0475	0.00367	0.0777	0.995	0.280	0.284	0.0790	0.277	0.0604	2.20	8.02	5.35	0.0795	0.0229	0.0827	0.0552	0.0243	0.975	0.0249	0.306	**	
8	0.277	0.993	0.273	0.0767	0.986	0.0778	0.0745	0.211	0.0445	0.00332	0.0745	1.000	0.277	0.279	0.0762	0.273	0.0576	1.91	7.00	4.67	0.0767	0.0217	0.0795	0.0530	0.0237	0.978	0.0242	0.301	**	
9	0.281	0.993	0.278	0.0790	0.986	0.0801	0.0773	0.185	0.0342	0.00264	0.0775	0.997	0.280	0.282	0.0784	0.277	0.0512	1.34	4.84	3.23	0.0787	0.0224	0.0809	0.0540	0.0247	0.982	0.0252	0.306		
10	0.289	1.000	0.285	0.0835	1.000	0.0835	0.0812	0.158	0.0250	0.00203	0.0815	0.996	0.288	0.288	0.0821	0.284	0.0449	0.905	3.19	2.13	0.0823	0.0239	0.0842	0.0562	0.0261	0.986	0.0265	0.316	11	
11	0.280	1.006	0.281	0.0841	1.012	0.0831	0.0790	0.222	0.0493	0.00390	0.0792	0.997	0.289	0.287	0.0806	0.280	0.0622	2.41	8.61	5.74	0.0812	0.0236	0.0843	0.0562	0.0250	0.976	0.0256	0.316	314	
12	0.280	1.006	0.277	0.0784	1.012	0.0775	0.0767	0.018	0.00324	0.000249	0.0773	0.992	0.278	0.276	0.0765	0.275	0.00495	0.00121	0.0044	0.00294	0.0765	0.0210	0.0764	0.0510	0.0255	0.997	0.0256	0.306	1146	$0.304 \pm 0.0017$
13	0.276	1.009	0.273	0.0762	1.018	0.0749	0.0745	0.036	0.00130	0.0000969	0.0748	0.996	0.275	0.272	0.0743	0.272	0.00979	0.00938	0.0345	0.0230	0.0743	0.0201	0.0739	0.0493	0.0250	0.989	0.0253	0.301		
14	0.279	1.007	0.276	0.0778	1.014	0.0767	0.0762	0.072	0.00518	0.000395	0.0763	0.999	0.279	0.277	0.0765	0.276	0.0199	0.0788	0.286	0.191	0.0765	0.0213	0.0772	0.0515	0.0250	0.996	0.0251	0.304		
16	0.278	0.998	0.279	0.0773	0.996	0.0776	0.0778	0.000	0.0000	0.000000	0.0776	1.003	0.279	0.280	0.0781	0.278	0.0000	0.000	0.000	0.000	0.0781	0.0220	0.0791	0.0528	0.0253	1.000	0.0253	0.303	1210	$0.305 \pm 0.0017$
17	0.280	1.006	0.278	0.0784	1.012	0.0775	0.0773	0.000	0.0000	0.000000	0.0775	0.997	0.279	0.277	0.0770	0.277	0.0000	0.000	0.000	0.000	0.0770	0.0213	0.0769	0.0513	0.0257	1.00	0.0257	0.306		
19	0.275	0.986	0.278	0.0756	0.972	0.0778	0.0773	0.091	0.00828	0.000640	0.0772	1.001	0.275	0.279	0.0776	0.278	0.0253	0.162	0.583	0.389	0.0776	0.0217	0.0781	0.0521	0.0255	0.996	0.0256	0.301	1271	0.304 ± 0.0017
20	0.280	1.000	0.278	0.0784	1.000	0.0784	0.0773	0.104	0.0108	0.000835	0.0776	0.995	0.279	0.279	0.0776	0.277	0.0288	0.239	0.863	0.576	0.0777	0.0217	0.0783	0.0522	0.0255	0.993	0.0257	0.306	**	
21	0.271	0.954	0.282	0.0734	0.910	0.0815	0.0795	0.126	0.0159	0.00126	0.0802	0.991	0.269	0.282	0.0795	0.280	0.0353	0.440	1.57	1.05	0.0796	0.0224	0.0800	0.0534	0.0262	0.993	0.0264	0.297	1318	0.297±0.0017
22	0.273	0.952	0.281	0.0745	0.906	0.0822	0.0790	0.186	0.0346	0.00273	0.0795	0.994	0.271	0.285	0.0801	0.279	0.0519	1.40	5.02	3.35	0.0804	0.0232	0.0832	0.0555	0.0249	0.982	0.0254	0.298	**	
23	0.269	0.951	0.279	0.0724	0.904	0.0801	0.0778	0.154	0.0237	0.00184	0.0783	0.994	0.267	0.281	0.0784	0.277	0.0427	0.779	2.81	1.87	0.0786	0.0222	0.0801	0.0534	0.0252	0.985	0.0256	0.295	14	

\*Correction to 
$$a^2 = \frac{\left\{ra + \left[2\left(a^2 - m^2r^2\right)^{\frac{3}{2}}/3m^2r\right] - \left[2a^2/3m^2r\right]\right\}}{-\cos\theta}$$
  $m^2 = \frac{r^2}{(a^4/H^2 - r^2\tan^2\theta)}$   $a = \frac{m^{3/2}}{H}$ 

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