

4. The relationship existing between adsorption taking place during precipitation, and that taking place on a solid precipitate of definite surface area has been discussed.

BOULDER, COLORADO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]  
**THE SURFACE TENSIONS AND DENSITIES OF LIQUID MERCURY, CADMIUM, ZINC, LEAD, TIN AND BISMUTH.**

BY THORFIN R. HOGNESS.<sup>1</sup>

Received May 6, 1921.

The purpose of this investigation was to secure data for the examination of metallic solutions from the standpoint of the theory of solubility which has been outlined by Hildebrand and extensively applied by him and his co-workers<sup>2</sup> to non-metallic solutions. Although surface tension has proved to be a criterion of great value with non-metallic solutions, the evident inaccuracy of much of the data heretofore published upon the surface tensions of liquid metals has made the work herein described prerequisite to the accomplishment of the above purpose.

The method selected for our purpose is one originated by Cantor<sup>3</sup> and extensively applied by Jaeger<sup>4</sup> to non-metallic liquids. The method as it is generally employed consists in determining the pressure necessary to force a bubble of inert gas from the end of a sharp edged platinum capillary immersed in the liquid. On account of the impossibility of using a metallic capillary with liquid metals the process has been reversed in the present work so as to measure the pressure necessary to force a tiny drop from the tip of a quartz capillary directed upwards. The theory of this method is as follows.

The free surface energy of a sphere of liquid of surface  $s$  and surface tension  $\gamma$  is  $\gamma s$ . If the drop is increased infinitesimally in size by introducing more liquid, say, through a fine capillary, the work done against the surface tension is  $\gamma ds$ . This is equal to the pressure exerted by the tension upon the interior of the drop multiplied by the increase in volume  $dv$ , so that  $\gamma ds$  equals  $p dv$ . Since  $s = 4\pi r^2$  and  $v = \frac{4}{3}\pi r^3$ , we have  $\gamma = pr/2$ .

If we have a small capillary of radius  $a$  and apply pressure to force out a drop of the liquid, the radius of curvature of the drop will gradually

<sup>1</sup> Thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Hildebrand, *THIS JOURNAL*, **38**, 1452 (1916); **39**, 2297 (1917); **41**, 1067 (1919); **43**, 500 (1921). Hildebrand and Jenks, *ibid.*, **42**, 2180 (1920). Hildebrand and Buehrer, *ibid.*, **42**, 2213 (1920).

<sup>3</sup> Cantor, *Wied. Ann.*, **47**, 399 (1892).

<sup>4</sup> Jaeger, *Z. anorg. Chem.*, **101**, 1 (1917).

diminish as the pressure increases until it reaches a minimum value where  $r$  equals  $a$ . At this point the corresponding pressure will be a maximum, and it is this maximum pressure that is measured. The force of gravity causes a slight distortion of the drop necessitating a correction for the larger capillaries. This distortion is accounted for in the formula derived by Cantor, and corrected by Feustel,<sup>5</sup> where  $d$  is the density of the liquid.

$$\gamma = \frac{pa}{2} \left( 1 - \frac{2}{3} \frac{da}{p} - \frac{d^2 a^2}{p^2} \right)$$

This method has marked advantages over most others applicable to the metals in that it provides for a fresh and uncontaminated surface; it avoids the introduction of contact angle, which is necessary in the capillary depression method; it depends only upon primary standards; and it is free from theoretical uncertainties such as are involved in the drop-weight method.

#### Description of Apparatus.

The apparatus finally adopted is shown in Fig. 1. The whole apparatus was built of Pyrex glass, with the exception of A which is a quartz capillary. The capillary was

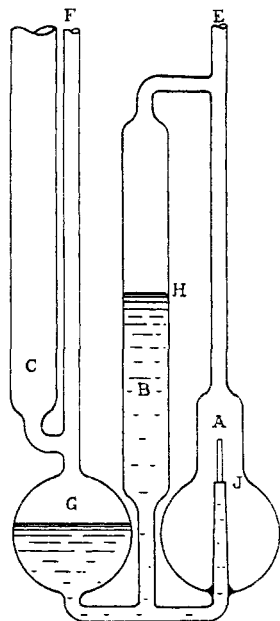


Fig. 1.

sealed to the tube J by means of a cement consisting of zinc oxide and sodium silicate. B is a tube about 1 cm. in diameter into which a head of molten metal was raised. G is a reservoir for the metal and C, a tube for introducing a cast rod of the solid metal. E and F were sealed to different parts of a rather elaborate system providing for the independent and accurate control of the pressure of the hydrogen. It is necessary that the capillary be circular, have a sharp edge and that the edge be perpendicular to the axis. These conditions were obtained by selection from many hundreds of short sections cut from finely drawn tubes. Sharp edges and ends perpendicular to the axes of the capillaries were obtained by scratching the capillaries with a razor blade and breaking. The ends were ascertained to be perpendicular by examination under a microscope. The diameters of the capillaries were measured with a calibrated comparator. The capillaries were not exactly circular in cross section, but the ellipticity was, in all cases, very small. The mean radii and the respective percentage differences between the major and minor axes were as follows: 0.02127, 0.94%; 0.02574, 0.58%; 0.01814, 0.55%; 0.02125, 0.65%.

Expansion of the quartz with the temperature was a negligible factor. The apparatus was heated by means

of an air-bath which had long narrow mica windows on two opposite sides for observation. The bath, kept constant within 2° or 3°, was stirred by a large fan in the bottom, and the temperature was measured by means of a thermocouple. Great

<sup>5</sup> Robt. Feustel, *Ann. phys.*, [4] 16, 61 (1905).

accuracy of temperature control is unnecessary, since the simultaneous decrease in surface tension and density means that the head of liquid metal necessary to force a drop out of the capillary varies but slowly with temperature.

### Experimental Procedure.

Before each determination it was necessary to heat the apparatus at  $500^{\circ}$  for a few hours while being evacuated to remove the adsorbed water vapor. At first this adsorbed water gave considerable trouble, especially at temperatures over  $450^{\circ}$ , but this was finally overcome by the preliminary heating.

When the apparatus had again cooled, a cast rod of the metal was introduced into the tube C which was again sealed. After repeatedly evacuating and washing out the whole line with hydrogen, the apparatus was again heated until the metal in C melted and ran into the reservoir G. Pressure was gradually applied at F, raising the metal into the column B. The change in level of the surface H was followed with a cathetometer, and its height was noted at the instant when drops of metal began to flow out of the top of A. The difference in head between the tip of the capillary and the surface H, multiplied by the density of the metal, gives the maximum pressure necessary to force a drop out of the tip. Shaking of the building caused a premature breaking of the drop so it was necessary to work during the quieter hours of the day.

In some of the determinations there was a slight capillary depression of the metal in the tube B. The magnitude of this depression was determined at the same time as the densities by a method described below. All determinations, with the exception of one with mercury, were made in an atmosphere of hydrogen at pressures somewhat greater than the vapor pressures of the metals.

### Density Determinations.

To calculate the surface tension it was necessary to know the densities of the metals at different temperatures. The densities were determined by measuring the difference in height of the metal in the two arms of a U-tube caused by a measured pressure difference.

The apparatus was designed to fit the furnace used in the surface tension work and is shown in Fig. 2.

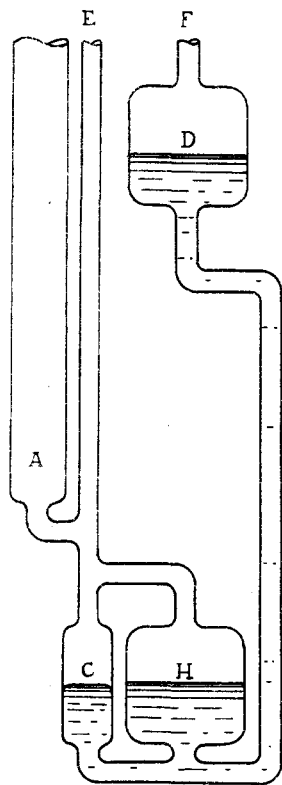


Fig. 2.

D and H are tubes 3.5 cm. in diameter, large enough to have a negligible capillary depression; A, a long tube for inserting a rod of the metal, and C is a tube of the same diameter as B of Fig. 1. The tube C was inserted to determine the correction for capillary depression to be added to the observed heights in the surface tension determinations. E and F were sealed to the line constructed for controlling and measuring the pressure. The difference in pressure in E and F was measured by means of a manometer filled with sulfuric acid, the density of which was accurately determined. The difference in level of the metal in D and H was measured with a cathetometer.

**Purification of Materials.**—Mercury was purified by washing and distilling *c. p.* mercury three times in accordance with methods recommended by Hulett.<sup>6</sup>

Bismuth was prepared by fusing twice reprecipitated bismuth oxychloride with pure potassium cyanide.

Electrolytic purification was used with the other metals, using anodes of as pure metal as was obtainable. The lead, tin and cadmium were pure commercial samples, the zinc from the Bertha mine of the New Jersey Zinc Company. The electrolytes were respectively lead perchlorate, stannic chloride, cadmium sulfate and zinc sulfate.

### Observations and Results.

**Densities.**—The following expressions represent the result of the density determinations. At least four temperatures were used with each substance. The maximum difference between the observed values and those calculated from the equations was 0.1%.

Zinc	$d = 6.59 - 0.00097(t - 419)$
Lead	$d = 10.71 - 0.00139(t - 327)$
Cadmium	$d = 8.02 - 0.00110(t - 320)$
Bismuth	$d = 10.07 - 0.00125(t - 269)$
Tin	$d = 7.01 - 0.00074(t - 232)$

**Surface Tensions.**—The data and the values of surface tensions calculated from the observations are given in Table I.

TABLE I.  
Observed Values of Surface Tension.

	<i>t</i> ° C.	Press. H <sub>2</sub> mm.	No. of Obser- vations.	Radius of capillary cm.	Aver. corrected height.	Density.	Surface tension, Dynes per cm.	
Mercury	20	2.5	6	0.02127	3.30	13.54	465	
	20	< 0.001	5	0.02127	3.30	13.54	465	
	20	470	8	0.02127	3.30	13.54	465	
		(air)						
	22	2	6	0.01814	3.83	13.54	461	
	22	370	4	0.01814	3.83	13.54	461	
	110	5	5	0.01814	3.77	13.33	447	
	112	5	6	0.02127	3.28	13.33	454	
	155	7	11	0.01814	3.75	13.22	441	
	195	25	7	0.01814	3.73	13.13	434	
	200	30	4	0.02127	3.20	13.12	436	
	251	82	6	0.01814	3.64	12.99	421	
	300	440	4	0.02127	3.03	12.87	405	
	303	300	9	0.01814	3.57	12.87	408	
	354	760	4	0.01814	3.47	12.76	394	
Bismuth	320	3	4	0.02574	2.98	10.00	375	
	365	3	6		2.97	9.95	371	
	426	20	3		2.97	9.88	367	
	472	20	5		2.96	9.82	365	
	Cadmium	339	100	7	0.02125	6.04	8.00	606
366		145	7		6.16	7.97	616	
378		100	7		6.18	7.96	617	

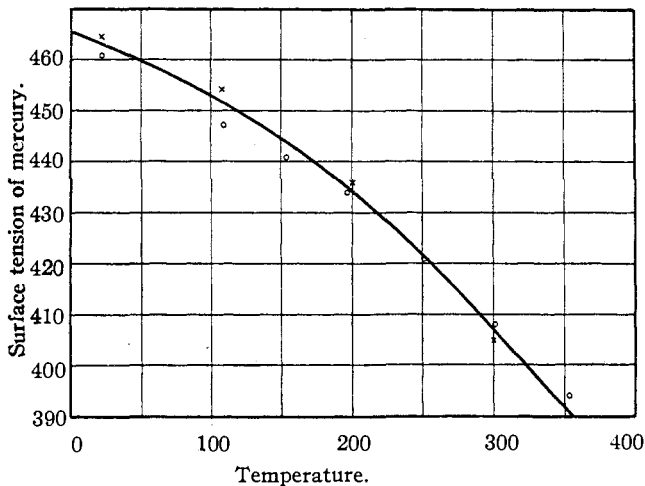
<sup>6</sup> G. A. Hulett, *Phys. Rev.*, **33**, 307 (1911).

TABLE I.—(Continued).

	$t$ ° C.	Press. H <sub>2</sub> mm.	No. of Observations.	Radius of capillary cm.	Aver. corrected height.	Density.	Surface tension. Dynes per cm.
	421	100	3		6.26	7.92	622
	448	145	8		6.28	7.88	621
	508	100	3		6.29	7.82	619
	544	145	7		6.29	7.78	616
Lead	366	6	7	0.02574	3.30	10.65	442
	444	6	9		3.27	10.55	433
	522	6	5		3.27	10.44	429
Tin	302		5	0.01814	8.58	6.99	530
	319		6		8.46	6.95	519
	396		6		8.52	6.89	520
Zinc	477		5	0.02125	11.07	6.53	753
	543		9	0.02125	11.09	6.47	747

The maximum deviation from the averages here given was about 1% and in nearly all instances was very much less. The values for the surface tension of cadmium diminish with temperature below 421°, *i. e.*, the surface tension appears to go through a maximum. These values for cadmium were checked to within 1% by an independent determination using a different capillary but the duplicate set of values is not recorded in the table.

The values in Table I were plotted and the smooth curves drawn through the points are represented by the following equations. Only in the case of mercury does the range of temperature justify more than a linear equation. Fig. 3 gives the plot for mercury.



x-Values obtained with capillary of radius 0.02127 cm.

o-Values obtained with capillary of radius 0.01814 cm.

Fig. 3.

Mercury	$r = 467 - 0.043(t + 39) - 0.000386(t + 39)^2$
Bismuth	$r = 378 - 0.063(t - 269)$
Cadmium	$r = 630 - 0.065(t - 320)$
Lead	$r = 444 - 0.077(t - 327)$
Tin	$r = 531 - 0.080(t - 232)$
Zinc	$r = 758 - 0.090(t - 419)$

The first constant in the right hand member of each of the above equations represents the extrapolated values of the surface tension at the melting point. The equation for cadmium is determined only from the values at 421° and above.

Table II gives values of surface tension calculated at a series of temperatures from the smooth curves.

TABLE II.

Temp. ° C.	Surface Tensions.				
	300	350	400	450	500
Bismuth.....	376	373	370	367	363
Lead.....	...	442	438	438	431
Tin.....	526	522	518	514	510
Cadmium.....	...	628	625	622	618
		(614 obs.)			
Zinc.....	...	...	...	755	751

Table III gives similar smoothed out values for mercury.

TABLE III.

## Surface Tension of Mercury.

Temp. ° C.....	0	20	50	100	150	200	250	300	350
Surface tension.....	465	463	460	453	445	435	422	408	393

## Discussion.

A comparison of the results obtained for the surface tensions in the present research with those obtained by previous observers is given in the following table.

TABLE IV.

## Comparison with Values by Other Observers.

	Temp. ° C.	Hogness.	Quincke. <sup>7</sup>	Siedentopf. <sup>8</sup>	Smith. <sup>9</sup>	Grundmach. <sup>10</sup>
		Cantor drop- pressure method.	Modified drop-weight method.	Dimensions of large drop.	Capillary depression method.	Ripple method
Bismuth.....	269	378	465	429	346	...
Lead.....	327	444	537	509	425	482
Tin.....	232	531	681	612	480	352
Cadmium.....	320	630	815	830	...	...
Zinc.....	419	758	967(air)	...	707	...
			1103(CO <sub>2</sub> )			

<sup>7</sup> B. Quincke, *Pogg. Ann.*, 135, 642 (1868); 138, 141 (1869).

<sup>8</sup> Siedentopf, *Wied. Ann.*, 61, 235 (1897).

<sup>9</sup> S. W. Smith, *J. Inst. Metals*, 12, 168 (1914).

<sup>10</sup> Grundmach, *Ann. Phys.*, 3, 660 (1900).

Quincke used a modification of the drop-weight method which consisted in the melting of metal from a wire of known diameter. With mercury and tin, the usual drop weight was employed. The values given in the table have been corrected by the use of the formula of Lohnstein.<sup>11</sup> The correction is of doubtful accuracy, the experimental procedure was crude, and the metal surfaces undoubtedly contaminated by oxide so that the figures can hardly claim great weight.

The values by Siedentopf were calculated from the dimensions of a drop resting upon a flat surface in an atmosphere of carbon dioxide which would undoubtedly produce contamination of the surface with oxide, as is indicated by the high values.

Smith used the capillary depression method with a hole drilled in a piece of carbon. He made no correction for the angle of contact, which is certainly greater than zero, so that his low results are not surprising.

Grundmach measured the wave length of ripples upon the flat metallic surface, a method difficult to use with accuracy. He worked in an atmosphere of air which undoubtedly vitiates his figures for tin.

The surface tension of mercury has been determined by almost all of the known methods, and the values vary from 340 to 575 dynes per centimeter. The different determinations have been made *in vacuo* and in various gases. Quincke<sup>12</sup> has given a summary of all the earlier work with mercury.

More recently, Cenac,<sup>13</sup> using the drop-weight method, with two different correction terms, Lohnstein's and Rayleigh's, has given the following values for mercury:

	0° C. (air).	(Vacuum).	100° (vac.).	180° (vac.).
Lohnstein.....	437	460	437	419
Rayleigh.....	445	467	443	425

The values *in vacuo* at 0°, agree well with ours, but at higher temperatures the values fall off somewhat more rapidly. Cantor using the method employed in this research obtained 459 dynes at 20° in air, and using the inverse procedure of blowing a bubble of air from a capillary immersed in the mercury obtained 466 dynes at 20° in air. Richards and Boyer,<sup>14</sup> by measuring the dimensions of a drop, found 441 dynes in air, a value considerably lower than ours. Harkins and Ewing,<sup>15</sup> using the drop weight method, give 476 dynes *in vacuo*, and Harkins and Grafton<sup>16</sup> 465 dynes in air.

<sup>11</sup> Lohnstein, *Ann. phys.*, **20**, 237 (1906).

<sup>12</sup> Quincke, *Ann. phys.*, **61**, 267 (1897).

<sup>13</sup> Cenac, *Ann. chim. phys.*, **28**, 298 (1913).

<sup>14</sup> T. W. Richards and S. Boyer, *THIS JOURNAL*, **43**, 274 (1921).

<sup>15</sup> Harkins and Ewing, *ibid.*, **42**, 2539 (1920).

<sup>16</sup> Harkins and Grafton, *ibid.*, **42**, 2534 (1920).

Since some observers claim lower results in air than *in vacuo*, it might be questioned whether the hydrogen present in the apparatus may not have somewhat altered the values. This point was tested by varying the pressure of hydrogen from 300 mm. down to a vacuum giving the green fluorescence of the glass with the electric discharge. The hydrogen was also replaced by an atmosphere of dry air. No detectable difference in the surface tension was found. In view of the large overvoltage of hydrogen on mercury, it would hardly be expected that it could be appreciably adsorbed. It was found, however, that, for some unknown reason, the first readings of these determinations gave low values. These values gradually increased as the determination proceeded and finally reached a limit for which the readings were very constant and concordant. It was also found that, unless all water vapor was removed from the apparatus and mercury by previous heating, results 3 or 4% too low, were obtained.

It should be pointed out that the method here employed avoids the large and somewhat uncertain correction for the diameter of the capillary necessitated by the drop-weight method. The correction factor in the drop-weight method, the  $f(r/a)$  developed by Lohnstein<sup>11</sup> and the  $f(r/V^{1/2})$  used by Harkins<sup>17</sup> is often as small as 0.6 and does not approach the limiting value of unity, while in the Cantor method, the correction term deviates only very slightly from this limiting value. In the present research for all the capillaries used, the correction factor

$$\left( 1 - \frac{2}{3} \frac{da}{p} - \frac{d^2 a^2}{p^2} \right)$$

was greater than 0.99.

#### Summary.

The densities of liquid zinc, cadmium, tin, lead and bismuth have been determined at various temperatures.

The surface tension of mercury, cadmium, zinc, lead, tin and bismuth have been determined by the Cantor method of drop pressure.

It has been shown that there is no appreciable difference in the surface tensions of mercury in dry air, hydrogen and *in vacuo*.

In conclusion the writer wishes to express his sincere appreciation to Professor J. H. Hildebrand, under whose direction the present work was carried on.

BERKELEY, CALIF.

<sup>17</sup> W. D. Harkins and F. E. Brown, THIS JOURNAL, **41**, 499 (1919).