Summary

The crystal structure of tetragonal HgI_2 has been determined, (a) using spectral photographic data alone, and (b) using data from Laue photographs, together with spectra from the (100), (110) and (001) planes. The unit (Fig. 1) has the dimensions $a_0 = 4.34$ Å. and $c_0 = 12.34$ Å. and contains Hg atoms at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and I atoms at $(0,\frac{1}{2},u)$, $(\frac{1}{2},0,\bar{u})$, $(\frac{1}{2},0,\frac{1}{2} - u)$ and $(0,\frac{1}{2},u + \frac{1}{2})$, with $u = .140 \pm .003$. The valence electrons are probably in pairs at tetrahedron corners around both Hg and I atoms, each Hg being bonded to four I atoms and each I to two Hg atoms. The structure may be said to consist of "layer molecules." The interatomic distance (Hg-I) within each layer is 2.77 Å. The shortest distance (I-I) between atoms in different layers is 4.10 Å.

The unit of Hg_2I_2 is a tetragonal prism having the dimensions $a_0 =$ 4.92 Å. and $c_0 = 11.64$ Å. Hg atoms are at $(0,0,u)$, $(0,0,\bar{u})$, $(\frac{1}{2},\frac{1}{2},u + \frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2} - u)$; I atoms at $(0,0,v)$, $(0,0,\bar{v})$, $(\frac{1}{2},\frac{1}{2},v + \frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2} - v)$; u and v being approximately .117 and .353, respectively. The structure (Fig. 3) is thus built up of IHgHgI molecules, within which the Hg-Hg and Hg-I distances are approximately 2.72 Å. and 2.75 Å., respectively.

These results are in good agreement with those obtained by others.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

HYDROGEN GAS THERMOMETER COMPARED WITH THE OXYGEN AND HYDROGEN VAPOR-PRESSURE THERMOMETERS BY MEANS OF A COPPER-CONSTANTAN THERMOCOUPLE

BY W. F. GIAUQUE, H. L. JOHNSTON AND K. K. KELLEY[1]

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In connection with establishing a temperature scale for this Laboratory, a preceding paper[2] gives the results of comparison of copper-constantan thermocouples with the hydrogen gas thermometer from 15 to 283°K.

The present article presents results obtained by comparison of standard thermocouple W of Giauque, Buffington and Schulze (designated hereafter G., B. and S.) with the oxygen and hydrogen vapor-pressure thermometers.

The temperatures obtained from the oxygen vapor pressures as given by Cath[3] are in very satisfactory agreement with those obtained from the thermocouple of G., B. and S. On the other hand, the results obtained by means of the hydrogen vapor-pressure measurements have fortunately

[1] National Research Fellow in Chemistry, University of California.

[2] Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

[3] Cath, *Comm. Phys. Lab. Univ. Leiden*, 152d, **1918**.

led to the prompt discovery of serious error in the hydrogen-gas thermometer results below 25°K. Our results indicate that considerable adsorption of the hydrogen gas must have taken place within the thermometer bulb, particularly at temperatures below the boiling point of hydrogen. This was not to be expected, since it had not been noted in the previous experience of others. The thermometer corrections for gas imperfection were taken from the work of Cath and Onnes[4] in which duplicate bulbs containing hydrogen and helium, respectively, were kept in the same bath and differential pressures recorded. Corrections based on this method would include small adsorption effects. An important difference in the work of G., B. and S. was the use of a Pyrex glass thermometer bulb, whereas Cath and Onnes used one made from Jena glass.

The preparation of the Pyrex glass bulb used by G., B. and S. is perhaps worthy of comment. The bulb was blown and capillary tubing attached by means of a small opening which was left in the bottom until the bulb had been cleaned. Cleaning was accomplished by boiling in distilled water for some time, for one-half hour at least. The bulb was then dried by means of a stream of clean air and the bottom sealed off. We can remember no unusual surface condition resulting from the glass blowing but the apparatus has not been dismantled to confirm this.

There undoubtedly was a small amount of adsorbed water on the walls during the measurements, since the bulb was not heated during the pumping by the mercury diffusion pump. This adsorbed water could contribute no appreciable pressure, but is worth noting from the point of view of its possible effect on the character of the surface. At least until further work is carried out, the use of a Pyrex glass hydrogen thermometer below 25°K. must be regarded with suspicion. The most desirable change would be the use of helium gas.

Apparatus

The apparatus was that used by W. F. Giauque and R. Wiebe in an investigation to be published soon. Since the hydrogen thermometer described in the preceding paper was modeled after the above apparatus, the essential details and operation were practically identical, except that the thermometer bulb and the heavy cylinder which immediately surrounds it are replaced by a gold container connected with the exterior of the apparatus by means of a small glass tube with a platinum seal. The thermocouple was placed in the same manner as described in the preceding paper.

The pressure measurements were made in the same way, except that a manometer with tubes 1.6 cm. in diameter was used. All pressures are expressed in terms of international cms. of Hg. The gravitational

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[4] Cath and Onnes, *Comm. Phys. Lab. Univ. Leiden*, 156a, **1922**.

acceleration used was 979.973 cm./sec.^{2} as given by Sternwarte[5] for this location.

Preparation of Oxygen

Electrolytic oxygen was prepared from a potassium hydroxide solution. It was freed from diffused hydrogen by passage over copper oxide maintained at 400°. The gas was then passed over amalgamated copper and solid potassium hydroxide. It was liquefied by means of liquid air and then fractionated, the middle third being used.

Oxygen Vapor-Pressure Results

The results of the oxygen vapor-pressure measurements are given in Table I, where they are compared with the temperatures given by the equation of Cath.[3]

$$\log_{10} P_{(\text{atmos.})} = \frac{-419.31}{T} + 5.2365 - 0.00648T \qquad (1)$$

TABLE I

OXYGEN VAPOR-PRESSURE COMPARISON

P International cm. of Hg	T Equation (1)	T Thermocouple W
6.046	71.40	71.40
14.359	76.76	76.77
29.634	81.99	82.02
54.278	87.01	87.04
75.715	90.10	90.10

The agreement is better than we had expected and may indicate that the small deviations in the hydrogen gas thermometer comparison were due to the thermometer rather than to the thermocouple.

Preparation of Hydrogen

Electrolytic hydrogen was prepared in the manner described in the preceding paper, although in this case the purity is probably not important since impurities reasonably possible should not affect the vapor pressure appreciably.

Hydrogen Vapor-Pressure Results

The results of the measurements on hydrogen are given in Table II. The readings of Thermocouple W are expressed in terms of Thermocouple Number 17 of G., B. and S. to facilitate comparison. The temperatures given in Col. 3 are calculated from the formula

$$\log_{10} P_{(\text{atmos.})} = -\frac{44.368}{T} + 1.6523 + 0.03240T - 0.0004189T^2 + 0.00000484T^3 \qquad (2)$$

given by Martinez and Onnes.[6]

The thermocouple readings in the first two measurements given in Table II indicate too high a temperature, since a good vacuum had not

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[5] Landolt, Börnstein and Roth, "Physikalisch-chemische Tabellen," Berlin, **1923**.

[6] Martinez and Onnes, *Comm. Phys. Lab. Univ. Leiden*, 156b, **1922**.

TABLE II

HYDROGEN VAPOR-PRESSURE COMPARISON

P International cm. of Hg	Thermocouple Microvolts	T Equation (2)	T Table III	T Calculated from data of G., B. and S.
2.687	6654.53	12.93[a]	13.00	...
5.371	6650.52	13.92	13.96	(13.23)
31.090	6632.47	17.68	17.68	17.21
67.197	6619.60	19.95	19.96	19.66
74.822	6617.48	20.31	20.31	20.07
30.592	6632.80	17.64	17.62	17.14
30.984	6632.60	17.67	17.66	17.18
5.370	6650.71	13.92	13.91	(13.19)
5.368	6650.67	13.92	13.92	(13.20)

[a] From equation (3).

been obtained when the readings were taken, and heat leak apparently influenced the thermocouple. The average value of the triple-point pressure, 5.370 cm., gives 13.92°K. as the temperature of the triple point. We have accepted this value in preference to the value of 13.95 given by Onnes and Gulik[7] since there seems to have been some uncertainty as to the triple-point pressure (see Onnes and Keesom).[8] However, our value for the triple-point pressure is in near agreement with that of Onnes and Braak,[9] namely, 5.382 cm.

At 2.687 cm. pressure the hydrogen was solid and equation (2) could not be used. To find the temperature at this point the calorimetric data of Simon and Lange[10] were used with the triple-point pressure and the temperature to obtain the equation

$$\log_{10} P_{(\text{cm.})} = \frac{-39.2}{T} + 2.70 \log T + 0.4584 \qquad (3)$$

The procedure for obtaining equation (3) was to evaluate the two constants of Berthelot's equation of state by combining equation (2) with the thermodynamic equation $dP/dT = \Delta H/T\Delta V$ and the heat of vaporization data of Simon and Lange. With an equation of state thus established, combined with the calorimetric heat of sublimation and the assumption that infinitely dilute hydrogen gas would have the heat capacity of an ideal monatomic gas, equation (3) was readily obtained.

When the above thermocouple readings are compared with the data of G., B. and S. it is found that the temperatures given (Col. 5, Table II) are too low, which would be explained by adsorption in the gas thermometer. The character of the deviation makes the assumption of adsorption seem probable. Our values near the hydrogen boiling point

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[7] Onnes and Gulik, *Comm. Phys. Lab. Univ. Leiden*, 184, **1926.**

[8] Onnes and Keesom, *ibid.*, 137d, **1913.**

[9] Onnes and Braak, *ibid.*, 95e, **1906.**

[10] Simon and Lange, *Z. Physik*, **15**, 312 (1923).

are rapidly approaching those of G., B. and S., indicating agreement a little above 25°K., while below the boiling point the effect rapidly increases, as would be expected. The agreement at 25°K. and in the range covered by the oxygen vapor pressures leads us to believe that the intermediate data of G., B. and S. are satisfactory.

The values given in Col. 4 are obtained by comparison with Table III,

TABLE III

TEMPERATURE CONVERSION TABLE

T °K.	ϵ	Diff.	$d\epsilon/dt$	Diff.
10	(6665.29)		(3.15)	
		(3.30)		(0.30)
11	(6661.99)		(3.45)	
		(3.59)		(.29)
12	(6658.40)		(3.74)	
		(3.89)		(.29)
13	6654.51		4.03	
		4.17		.29
14	6650.34		4.32	
		4.47		.29
15	6645.86		4.61	
		4.75		.28
16	6641.11		4.89	
		5.03		.28
17	6636.08		5.17	
		5.31		.27
18	6630.77		5.44	
		5.57		.27
19	6625.20		5.71	
		5.85		.27
20	6619.35		5.98	
		6.11		.26
21	6613.24		6.24	
		6.37		.26
22	6606.87		6.50	
		6.62		.25
23	6600.25		6.75	
		6.88		.25
24	6593.37		7.00	
		7.12		.25
25	6586.25		7.25	
		7.38		.25
26	6578.87		7.50	
		7.62		.25
27	6571.25		7.75	
		7.87		.24
28	6563.38		7.99	
		8.12		.25
29	6555.26		8.24	
		8.36		.24
30	6546.9		8.48	

which was constructed from the vapor-pressure data, and should be used to extend the table of G., B. and S. below 30°K.

It may be noted that no work based on the temperature scale of G., B. and S. has yet been published, so that the adsorption error encountered will result in no corrections to the literature.

Summary

One of the standard copper-constantan thermocouples described by Giauque, Buffington and Schulze in the preceding paper has been compared with the oxygen and hydrogen vapor-pressure thermometers.

Complete agreement, within the limits of accuracy, has been found with the Leiden scale at the temperatures of liquid oxygen.

The hydrogen vapor-pressure measurements have shown that the scale of G., B. and S. is in error below 25°K., apparently due to adsorption of hydrogen in the gas thermometer.

A table showing the behavior of a typical copper-constantan thermocouple below 30°K. has been given to extend that of G., B. and S.

The triple-point pressure of hydrogen was found to be 5.370 international cm. of Hg. This value, when combined with the vapor-pressure results of Martinez and Onnes, gives a triple-point temperature of 13.92°K.

An equation for the vapor pressure of solid hydrogen is included.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 141]

ACTIVITY COEFFICIENTS OF ELECTROLYTES. I
A BI-BIVALENT SALT AND THE ION ATTRACTION THEORY

BY ULRIC B. BRAY[1]

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Introduction

The ion attraction theory developed first by Milner,[2] and more recently by Debye and Hückel,[3,4] has offered an apparently satisfactory explanation, at any rate at small concentrations, of the known behavior of strong electrolytes. The mathematical development of the theory shows why, and predicts how, the activity of an ion is related to the ionic strength. The equation for the activity coefficient γ of an ion with charge v as the ionic strength approaches zero is

$$\text{Log}\ \gamma = -Av^2\sqrt{\tfrac{1}{2}\Sigma\, mv^2} \qquad (1)$$

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[1] National Research Council Fellow in Chemistry.

[2] Milner, *Phil. Mag.*, **23**, 551 (1912); *ibid.*, **25**, 742 (1913).

[3] (a) Debye and Hückel, *Phys. Z.*, **24**, 185 (1923); (b) Debye, *ibid.*, **24**, 334 (1923).

[4] For a clear and critical presentation of this theory see A. A. Noyes, THIS JOURNAL, **46**, 1080 (1924).