DETERMINATION OF FIXED POINTS IN THE LOW TEMPERATURE WITH A HYDROGEN THERMOMETER.

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I. Gas Thermometer. The sensitivity of the constant pressure gas thermometer is expressed by

$$S = dV/dT = 273\ V_0/T^2\ ,$$

and that of the constant volume gas thermometer by

$$S = dP/dT = P_0/273\ ,$$

where V_0 is the volume of the bulb of constant pressure gas thermometer at 0°C., and P_0 the pressure of gas in constant volume gas thermometer also at 0°C. From these expressions we see that the sensitivity of the former becomes larger with the lowering of temperatures, and the volume V_0 must, in consequence, be sufficiently large. On the other hand, if we neglect for a time the error due to the dead space, the sensitivity of the latter would be almost independent of the temperature and the volume of the bulb. The management of the former is very complicated, while the independency of sensitivity from V_0 for the latter may be very convenient, as the dimensions of vessels are limited in the studies at lower temperatures. From these standpoints the authors preferred a thermometer of constant volume to that of constant pressure and constructed one of the former by taking the references of many investigators(1) into consideration.

The thermometer is shown in Fig. 1. Bulb A and the capillary where hydrogen gas is to be filled is made of Jena 16^{III}, and the other parts are of hard glass. B is a bulb for reserving capacity, and C the portion where the level of mercury may be adjusted by means of a platinum wire sealed at its upper part. A, B, and C are connected to the capillary tubes. E_1, E_2, and E_3 are the reservoirs of mercury, the levels of which can be adjusted by changing the pressure. The temperature of the part B is kept at 0°C., and the columns C and D are surrounded by water jackets, the inner pressure of the apparatus being observed with a cathetometer.

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(1) Henning, *Ann. Phys.*, **40** (1913), 635; **43** (1914), 282. Heuse and Henning, *Z. Phys.*, **23** (1924), 105; **5** (1921), 285. Heuse and Otto, *Ann. Phys.*, **9** (1931), 486. Onnes, *Comm. Phys. Lab. Leiden*, No. 97 (1906), No. 99 (1907), No. 100 (1907).

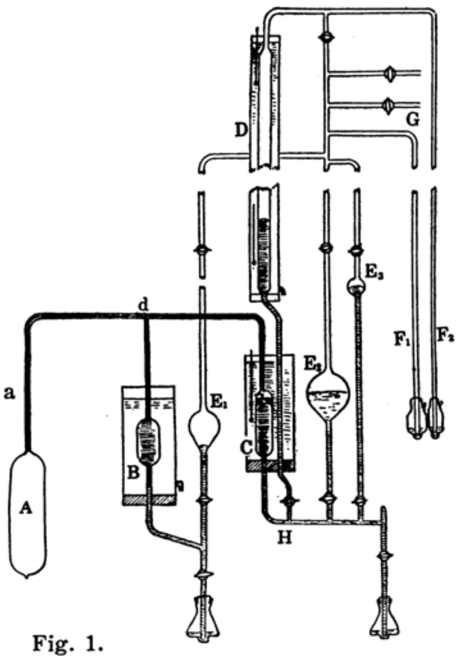

Fig. 1.

Filling of hydrogen. Hydrogen prepared through electrolysis of water is purified by palladium catalyser and also by active charcoal cooled in the liquid nitrogen. The gas is then led into bulbs A, B, and C through the tubes G, D, and H, and the process of filling and evacuating is repeated. After the fifth filling the mercury column cuts off the passage between C and D, and the pressure of hydrogen is adjusted so that it will indicate 90 mm. of mercury when A and B is kept at 0°C.

II. Determination of Temperature. For the convenience of referring in the description, the parts of the thermometer containing gas are indicated by A, B, C, a, and d, the temperatures of which being all different from one another. In Fig. 1 the part A is at a temperature of t° which is to be determined, B is at 0°C., C at the temperature of water which is nearly at room temperature t_r, and a at the mean temperature between t° and t_r. The effect due to the variation of the temperature of the room has been found to be very small, as the apparatus has been set in a special room tripply walled all around admitting no direct rays of the sun.

The volume of each part of the thermometer at 0°C. and under zero atmosphere has been calculated as follows: $V_A = 353.073_4$, $V_B = 19.479_2$, $V_C = 0.258_0$, $V_a = 0.041_3$, and $V_d = 0.344_1$ c.c.

In the determination of temperature the corrections due to the thermal expansion of the glass bulb and the variation of the inner pressure of hydrogen must be applied. The following are the thermal expansion coefficients⁽²⁾ and the compressibility of the glass Jena 16^{III} applied for the correction.

Cubical expansion coefficient	Range of temperatures
1.992×10^{-5}	13°∼−103°C.
$1.53\ \times10^{-5}$	−103°∼−183°C.
0.495×10^{-5}	−183°∼−253°C.

Compressibility: $\mu = 2.94\times10^{-6}$

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(2) Van Agt and K. Onnes, *Comm. Phys. Lab. Leiden*, No. 176 a (1925).

To give an example for calculating the correction, let us suppose that the pressure of the gas is p meter of mercury, and then the volume of the part A at t° (where $t > -103^\circ$C.) may be expressed by

$$V'_{\mathrm{A}} = V_{\mathrm{A}}\,(1+1.992\times10^{-5}\times t+2.94\times10^{-6}\times p).$$

By expressing the pressure of the thermometer when the bulb is at 0°C. or t° by p_0 or p_t, and the pressure coefficient of hydrogen between 0°C. and 100°C. by β, we have the following relation between p_0 and p_t:

$$p_0\left\{V_{\mathrm{A}}+V_{\mathrm{B}}+\frac{V_{\mathrm{a}}}{1+\beta t_{\mathrm{a}}}+\frac{V_{\mathrm{d}}+V'_{\mathrm{c}}}{1+\beta t_{\mathrm{r}}}\right\} = p_t\left\{\frac{V'_{\mathrm{A}}}{1+\beta t}+V_{\mathrm{B}}+\frac{V_{\mathrm{a}}}{1+\beta t'_{\mathrm{a}}}+\frac{V_{\mathrm{d}}+V'_{\mathrm{c}}}{1+\beta t_{\mathrm{r}}}\right\} \quad (1).$$

The second term on the both sides of the above equation will vanish in case B is filled with mercury. The third and fourth terms on the both sides are corrections due to the dead spaces and may be expressed by $\dfrac{V_{\mathrm{s}}}{1+\beta t_{\mathrm{s}}}$ and $\dfrac{V'_{\mathrm{s}}}{1+\beta t'_{\mathrm{s}}}$.

Then we have

$$p_0\left\{V_{\mathrm{A}}+\frac{V_{\mathrm{s}}}{1+\beta t_{\mathrm{s}}}\right\} = p_t\left\{\frac{V'_{\mathrm{A}}}{1+\beta t}+\frac{V'_{\mathrm{s}}}{1+\beta t'_{\mathrm{s}}}\right\} \quad (2).$$

The temperature will thus be determined from the equation

$$t = \frac{1}{\beta}\left[\frac{p_t V'_{\mathrm{A}}}{p_0\left\{V_{\mathrm{A}}+\dfrac{V_{\mathrm{s}}}{1+\beta t_{\mathrm{s}}}\right\}-p_t\dfrac{V'_{\mathrm{s}}}{1+\beta t'_{\mathrm{s}}}}-1\right] \quad (3).$$

In the case of the present experiment the following values of p_0 and β have been adopted: $p_0 = 922.15$ mm. of mercury, $\beta = 0.0036621$(3).

III. Accuracy of Temperature. The accuracy of the standard thermometer for low temperatures is very important, because many problems have to be discussed in the temperature of absolute scale. In the following the authors attempt to discuss on the errors generally encountered in the temperature determination with the constant volume gas thermometer, taking the effect of dead spaces into consideration.

Now, if we neglect the effect of dead spaces, we have

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(3) Heuse and Otto, *loc. cit.*

$$t = \frac{p-p_0}{\beta p_0} \tag{4},$$

then

$$dt = \frac{1}{\beta}\left\{\frac{dp}{p_0} - \frac{1+\beta t}{p_0}\,dp_0 - t\,d\beta\right\}$$

and so

$$\frac{\partial t}{\partial p_0} = -\frac{1+\beta t}{\beta p_0} = -\frac{273+t}{p_0} \tag{5},$$

$$\frac{\partial t}{\partial \beta} = -\frac{t}{\beta} = -273t \tag{6},$$

$$\frac{\partial t}{\partial p} = \frac{1}{\beta p_0} = \frac{273}{p_0} \tag{7}.$$

If we consider the dead space, however, we get from equation (2) the following relation :

$$p_t\left\{\frac{V'_A}{V_A} + \frac{V'_s}{V_A}\,\frac{1+\beta t}{1+\beta t'_s}\right\} = p_0\left\{1+\frac{V_s}{V_A}\,\frac{1}{1+\beta t_s}\right\}(1+\beta t)\ .$$

The coefficient $(1+\beta t)$ on the right side of the above equation is the characteristic quantity assigned to each thermometer, the value of which can be determined when A (Fig. 1) is at 0°C. If we equate this term with p'_0 and express the left side by p', we get the relation which is very analogous to equation (4).

Thus

$$p' = p_0(1+\beta t) \qquad \text{or} \qquad t = \frac{p'-p'_0}{\beta p'_0} \tag{8}$$

where

$$p'_0 = p_0\left\{1+\frac{V_s}{V_A}\,\frac{1}{1+\beta t_s}\right\} \tag{9}$$

and

$$p' = p_t\left\{1+\alpha t+\mu p+\frac{V'_s}{V_A}\,\frac{1+\beta t}{1+\beta t'_s}\right\} \tag{10}.$$

Then the maximum error of temperature will be

$$\varDelta t = \frac{273+t}{p'_0} \times \varDelta p'_0 + 273t \times \varDelta\beta + \frac{273}{p'_0} \times \varDelta p' \tag{11}.$$

The amounts of $\Delta p'_0$ and $\Delta p'$ are determined by the maximum errors of p_0, p_t, V_s/V_A, and t_s in the actual measurements, calculated by the equations (9) and (10). In order to calculate the maximum errors at 0°C. and −200°C. the above method is applied to the thermometer constructed by the authors. In the present case $V_s/V_A = 0.00182$, $\Delta p_0 = 0.05$ mm. Hg, and $\Delta t_s = 0.02°$.

(a) Errors due to p'_0: $\Delta t_{p'_0} = \dfrac{273+t}{p'_0}\Delta p'_0$, $p_0 = 922.15$, $p'_0 = 923.9$, and $\Delta p'_0 = 0.0584$.

Accordingly, $\Delta t_{p'_0} = 0.0173$ at 0°C., and $\Delta t_{p'_0} = 0.0046$ at −200°C.

(b) Errors due to β: $\Delta t_\beta = 273 \times \Delta\beta$.

If we estimate as $\beta = 0.0000001$ ($\beta = 0.0036621$), then $t_\beta = 0$ at 0°C., and $t_\beta = 0.0055°$ at −200°C.

(c) Errors due to p': $\Delta t_{p'} = \dfrac{273}{p'_0}\Delta p'$.

The largest term of corrections for gas pressure is due to the variation of temperature of the mercury column. If we let h be the difference of the height of mercury columns observed with the cathetometer, α' the expansion coefficient of mercury and t_r the temperature of mercury, we then have from the equation (10)

$$p' = h(1-\alpha' t_r)\left\{1+\alpha t+\mu p+\frac{V_s}{V_A}\frac{1+\beta t}{1+\beta t_s}\right\} .$$

As $\Delta h = 0.05$ mm. Hg, and $\Delta t_r = 0.02°$,

$$\Delta p' = \Delta p'_h + \Delta p_{t_r} + \Delta p_{t_s V_s} ,$$

$$\Delta p' = 0.0500+0.00336+0.00914 = 0.0625 \quad \text{at } 0°\text{C.},$$

and $$\Delta p' = 0.0500+0.0001 \ +0.00007 = 0.05017 \text{ at } -200°\text{C.}$$

Accordingly, $\Delta t_{p'} = 0.0185°$ at 0°C., and $\Delta t_{p'} = 0.0148°$ at −200°C.

Summarizing the above results, we get the following total maximum errors of the temperature: $\Delta t = 0.0358°$ at 0°C., $\Delta t = 0.0249°$ at −200°C.

From the above calculation it is clear that in the range 0° and −200°C. the amount of error decreases from 0.0358° to 0.0249° with the lowering of temperature.

IV. Comparison with the Thermodynamical Scale. The difference between the scale of the constant volume gas thermometer t_v and the thermodynamical scale of temperature t can be expressed by

$$t_v - t = p_0\left\{2.73(t_v - 100)k_0 - 3.73t_v k_{100} + (273 + t_v)k_t\right\}$$

where k_0, k_{100}, and k_t mean the inclination of the isothermal curve of the gas in question at 0°C., 100°C., and t°C. respectively. The difference is found to be proportional to the initial pressure p_0. In the present case it is as follows:

t	$t - t_v$	t	$t - t_v$
$-225°$	0.055	$-100°$	0.014
$-200°$	0.043	$-\ 75°$	0.009
$-175°$	0.034	$-\ 50°$	0.005
$-150°$	0.026	$-\ 25°$	0.003
$-120°$	0.019	$0°$	0.000

V. Determination of Fixed Points. In order to check the accuracy of the thermometer constructed, determinations of the boiling points of nitrogen and oxygen, and that of the sublimation point of carbon dioxide have been made.

(a) *Boiling point of nitrogen.* The apparatus used for the determination of the boiling point of nitrogen is shown in Fig. 2. A Dewar vessel C contains fresh liquid nitrogen, A is the bulb of the gas thermometer, B and D together act as a vapour pressure thermometer, and E and F are the portions of the apparatus where liquid nitrogen is purified through evaporation followed by condensation.

Nitrogen to be filled in B is generated by the addition of an aqueous solution of sodium nitrite dropwise to a mixture of warm saturated aqueous solution of ammonium sulphate and potassium chromate. The gas thus generated is passed through a red heated copper gauze and then purified through the process of repeated evaporation and condensation in E and F, respectively. The gas is finally condensed in B, the temperature of the bath being determined with the gas thermometer, and the vapour pressure of nitrogen in B is observed with the vavour pressure thermometer.

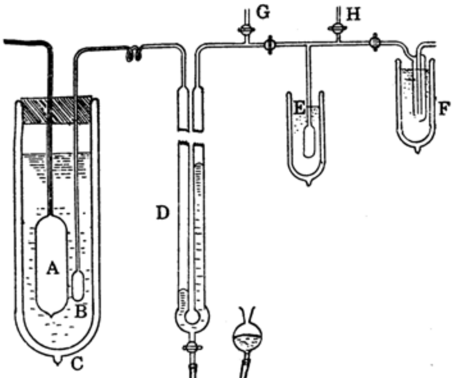

Fig. 2.

Using the temperature coefficient of the vapour of nitrogen ($\varDelta p/\varDelta t$), the values of which have been obtained from the vapour pressure thermometer scale, the normal boiling point is determined as follows:

Vapour pressure	Temperature	$\varDelta p/\varDelta t$	Boiling point
870.90	−194.68°C.	94.9	−195.85°C.
857.45	−194.76	94.4	−195.81
815.10	−195.24	93.1	−195.83
			mean −195.83$_3$ ± 0.03

The mean value corresponds to −195.79°C. on the thermodynamical scale of temperature. According to Henning⁽⁴⁾ or Onnes,⁽⁵⁾ the fixed point is −195.81° ± 0.02° or −195.78°, being very close to that obtained in the present experiment.

(b) *Boiling point of oxygen.* Oxygen generated through the electrolysis of the aqueous solution of potassium hydroxide is freed from hydrogen with heated platinum asbestos. The gas is then condensed in a trap cooled in liquid air, and the vapour of oxygen together with any trace of hydrogen present is pumped out. The oxygen of extra purity thus prepared is introduced into B, and the normal boiling point is determined as in case (a). The following are the results obtained:

Vapour pressure	Temperature	$\varDelta p/\varDelta t$	Boiling point
727.60	−183.44°C.	79.1	−183.03°C.
739.45	−183.28	,,	−183.02
764.00	−182.95	,,	−183.00
			mean −183.01$_7$ ± 0.03

By calculating the mean value to the thermodynamical scale, it corresponds to −182.98°C. Henning and Heuse⁽⁴⁾ give the boiling point −183.00°C. ± 0.02°, Onnes⁽⁵⁾ −182.95°C., and Heuse and Otto⁽⁶⁾ −182.962°C.

(c) *Sublimation point of carbon dioxide.* Carbon dioxide is prepared by the addition of dilute sulphuric acid to the milky aqueous mixture of sodium bicarbonate, and it is condensed in a trap cooled by a mixture of solid carbon dioxide and ether. In the bath C a mixture of solid carbon dioxide and ether is placed and well stirred. In the determination of the sublimation

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(4) Henning and Stock, *Z. Phys.*, **4** (1921), 226; Henning and Heuse, *loc. cit.*

(5) "Onnes-Festschrift," II (1923).

(6) Heuse and Otto, *loc. cit.*

point, the temperature coefficient of vapour tension $\Delta p/\Delta t = 62.7$ mm. Hg is applied. The observed values are as follows :

Vapour pressure	Temperature	$\Delta p/\Delta t$	Sublimation point
762.35	−78.48°C.	62.7	−78.52°C.
758.85	−78.52	,,	−78.50
768.10	−78.41	,,	−78.53
			mean $-78.51_7 \pm 0.009$

The mean value will correspond to −78.51°C. on the thermodynamical scale. Keys and Young(7) give −78.53°C., and Heuse and Otto(8) −78.48°C.

VI. Calibration of Thermocouples. The calibration of copper-constantan thermocouple is made with the hydrogen thermometer in a cryostat as shown in Fig. 3. Dewar vessel A contains another Dewar vessel B containing pentane and a copper cylinder wound with heating coil H and the space between the two vessels is filled with liquid nitrogen. Gas thermometer G and the thermocouples J and J′ are immersed in the liquid in vessel B. This vessel has a side tube through which hydrogen gas can be either introduced or evacuated to high vacuum. The cooling of vessel B is effected by the cold source of liquid nitrogen through the thermal conduction of hydrogen kept in the space between the double walls of vessel B. The control of the temperature is made possible by evacuating hydrogen and warming the liquid in the vessel gently with coil H. Small particles of aluminium also fill the space between the vessels A and B, and hence a good constancy of temperature has been able to be obtained by the aid of the thermal conductivity of aluminium even in the range of lower temperatures where liquid pentane is frozen. The constancy during the calibration has been ±0.02°.

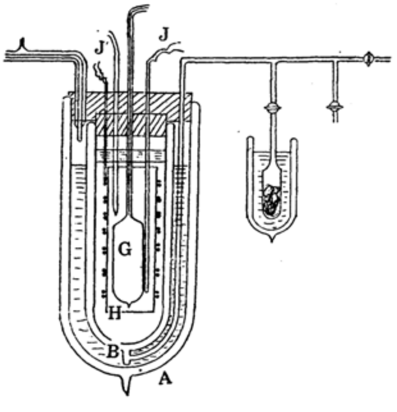

Fig. 3.

The following is the results of calibration :

Couples of Cu–Ni-Cu alloy (Ni 51.86, Cu 47.66, Mn 0.09, Fe 0.38%).

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(7) *J. Math. Phys.*, **1** (1922), 241.

(8) *Loc. cit.*

Temperature	e. m. f. (m.v.)	Temperature	e. m. f. (m.v.)
−40.13°C.	1.507	−114.50°C.	3.882
−55.48	2.060	−123.75	4.118
−67.15	2.441	−135.55	4.402
−78.32	2.828	−155.41	4.877
−85.51	3.036	−172.36	5.221
−94.65	3.318	−183.50	5.456
−107.83	3.699	−194.70	5.650

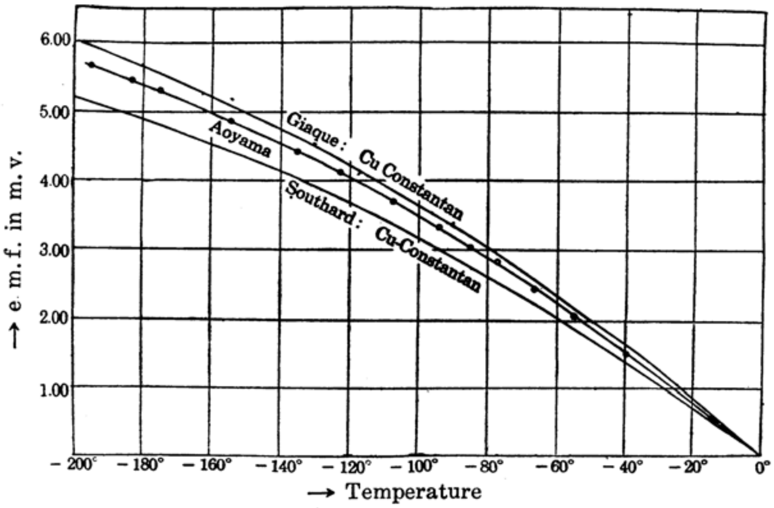

Fig. 4.

The curve in Fig. 4 shows the results given in the above table together with those of other investigators for a comparison. It may be seen that the electromotive force of the couples Cu and Ni-Cu alloy of the present authors is very close to that of copper-constantan thermocouples calibrated independently by Giaque(9) and Southard.(10)

Summary.

A hydrogen gas thermometer for the standard of the low temperature measurement was constructed wholly of glass. The accuracy of temperature obtained, ±0.036° at 0°C. and ±0.025° at −200°C., was discussed, the

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(9) Giaque, Buffington, and Schulze, *J. Am. Chem. Soc.*, **49** (1927), 2343.

(10) Southard and Andrews, *J. Franklin Inst.*, **207** (1929), 323.

volume of thermometer bulb, the dead spaces, and the temperature of the room being taken into consideration. The determination of the boiling points of liquid nitrogen and liquid oxygen and that of the sublimation point of solid carbon dioxide were made with this thermometer. The calibration of copper-constantan thermocouples was also made against the thermometer at various low temperatures.

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