sium ion.   This discrepancy is not so surprising since we should hardly expect the deformation of the water to be the only cause of the contraction or expansion.

Thus, we find that the increase in activity coefficients of the halide ions in a concentrated solution of a given strength parallels the effect of the ions on the dissociation of water and also approximately the effect on the contraction or expansion of the water molecule.   These facts lead us to the conclusion that the specific action of the ions in deforming the water molecules plays a very important role in determining the free energy and activity coefficient of an ion.

Summary

1.   The activity coefficients at 25° of potassium bromide, sodium bromide, potassium iodide, and sodium iodide at high concentrations as determined from the electromotive forces of suitable cells are presented.

2.   A comparison of the activity coefficients of the alkali halides in aqueous solutions with the effects they produce on the electrolytic dissociation of water, and also with the contraction effects produced by the solution of these electrolytes in water, leads to the conclusion that the specific deformability of the water molecules brought about by the electrical fields of the different ions is an important factor in determining the differences in free energies of the ions in concentrated solutions.

PHILADELPHIA, PENNSYLVANIA

THE CALIBRATION OF RESISTANCE THERMOMETERS AT THE OXYGEN BOILING POINT AND THE CARBON DIOXIDE SUBLIMATION POINT[1]

BY A. G. LOOMIS AND J. E. WALTERS

Introduction

It has now been well established that the temperature scale to $-193°$ may be accurately defined in terms of platinum-resistance thermometers, and that pure platinum as a thermometric resistance wire is entirely reproducible when used under strain-free conditions at low temperatures.[2] To express the temperature in terms of the resistance of platinum wire we may employ the equation of Hennig and Heuse,[2] $R = r/r_0 = 1 + at$

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[1] Published with the approval of the Director, U. S. Bureau of Mines.

[2] Henning, *Ann. Physik*, [4] **40**, 635 (1913). Also *Z. Instrumentenk.*, **44**, 349 (1924).   Henning and Heuse, *Z. Physik*, **23**, 95 (1924).   Also Heuse, *ibid.*, **37**, 157 (1926).   Van Dusen, THIS JOURNAL, **47**, 326 (1925).   Loomis and Walters, *ibid.*, **47**, 2851 (1925).

$+ bt^2 + ct^4$, where a, b and c are constants, r is the resistance of the thermometer at a given temperature t, and r_0 the resistance at the ice point; or the Van Dusen equation, $t = 1/\alpha(r/r_0-1) + \delta(t/100-1)t/100 + \beta(t/100-1)t^3/100^3$, where t is the temperature, α is the temperature coefficient of the platinum, δ is the familiar constant of the Callendar equation and β is an additional constant. The Henning and Heuse equation applies to pure platinum with specifications[3] $\alpha > 0.00386$ and $\delta < 1.51$, and for such platinum the constant c may be placed equal to -5.08065×10^{-12}, or to -5×10^{-12} for convenience,[4] the difference being absorbed in the other constants without significant change in the value given by the equation. It remains that the constants a and b be evaluated and for this purpose the resistance of the thermometer must be determined at two fixed points, such as the normal boiling point of oxygen and the normal sublimation point of carbon dioxide. However, if both α and δ are known—and they should both be determined in order to test the thermometer for purity of wire and absence of strain[5]—Henning and Heuse suggest that we calculate the resistance at the fixed point of freezing mercury ($-38.87°$) by means of the Callendar equation (this equation is valid to $-40°$) and then only the oxygen point need be determined to evaluate the remaining constant.

In the Van Dusen equation we also need only the oxygen point to evaluate β, as α and δ are found in the familiar manner from the ice point, the normal steam point, and the normal boiling point of naphthalene or of sulfur.

However, as both of these methods involve a long interpolation between the oxygen point and the region in which the Callendar equation is valid, it is desirable that an intermediate point be experimentally determined as a check on the calculated resistance at that point;[6] the normal sublimation point of carbon dioxide is an excellent one for this purpose.

It is the purpose of this paper to present the experimental methods which we have found most convenient and accurate and which we have used for several years in the Cryogenic Laboratory.

The Normal Boiling Point of Oxygen

Henning and Heuse[2] give the following equation representing the vapor pressure of oxygen as a function of T, valid between $-183°$ and $-205°$, where $T = t + 273.20°$: $\log P_{mm.} = -(379.95/T)/-0.0096219T + 1.75 \log T + 4.53939$, on the thermodynamic scale; the determination is made with a constant-volume helium thermometer and subsequently

[3] Similar specifications to apply to the Van Dusen equation have not been published.

[4] Report from the Reichsanstalt, Z. Instrumentenk., 44, 517 (1924).

[5] Sligh, Bur. Standards Sci. Papers, 407 (1921).

[6] Loomis and Walters, THIS JOURNAL, 47, 2851 (1925).

corrected to the thermodynamic scale of temperature. The normal boiling point of oxygen is taken as —183.00° ± 0.02°. The gas is prepared by heating potassium permanganate and purified in the usual manner.

Cath,[7] who also used a constant-volume helium thermometer, represents his observation by means of the equation, $\log P = -419.31/T + 5.2365 - 0.00648T$, where P is in international atmospheres. According to the equation the normal boiling point of oxygen is $T = 90.13°K$. and $\theta = -182.96°C$.

Onnes and Braak[8] obtained the value —182.93°C. and $T = 90.11°K$. using $T_{0°C.} = 273.09°K$. and 0.0036628 as the pressure coefficient of hydrogen at 1100 mm. freezing-point pressure.[9]

Henning[10] obtained —182.97°C. with a hydrogen constant-volume gas thermometer.

The temperature measurements of von Siemens[11] have been reduced to those of Onnes and his collaborators by Holst[12] and agree very closely with the observations of Cath except for the lowest points at 68.57°K. and 62.37°K.

The latest Leiden[13] value is —182.95°.

Keyes, Townshend and Young[14] obtain —182.94° with constant-volume hydrogen and nitrogen thermometers. This value is based on the relation from the Keyes equation of state that $(\partial P/\partial t)_v = 0$, which means that a gas thermometer of constant volume containing one of these gases would have no correction to the thermodynamic scale; experimental evidence is furnished by these investigators to support this assumption.

The equations expressing t as a function of P most convenient for calculation are given in the International Critical Tables.[15] We have accepted

TABLE I
THE NORMAL BOILING POINT OF OXYGEN

Author	Year	Normal boiling point of oxygen on the thermodynamic scale, °C.
Henning and Heuse[2]	1924	—183.00 ± 0.02
Keyes, Townshend and Young[14]	1922	—182.94
Crommelin[13]	1922	—182.95
Cath[7]	1918	—182.96
Henning[10]	1914	—182.97
Onnes and Braak[8]	1908	—182.93

[7] Cath, Leiden Comm., 152d (1918).

[8] Onnes and Braak, ibid., 107 (1908).

[9] Ref. 7, p. 48, Note 1.

[10] Henning, Ann. Physik, 43, 282 (1914).

[11] von Siemens, ibid., [4] 42, 871 (1913).

[12] Holst, Leiden Comm., 148 (1915).

[13] Leiden Comm. Supplement, 45, p. 4 (1922).

[14] Keyes, Townshend and Young, J. Math. Physics, Massachusetts Inst. Techn., 1, 243 (1922).

[15] "International Critical Tables," 1926, vol. I, p. 53.

—183.00 ± 0.02° as the most probable value of the normal boiling point of oxygen on the thermodynamic scale.

The results of the various observers are summarized in Table I.

Determination of the Resistance of the Thermometer at the Normal Boiling Point of Oxygen

Oxygen is prepared by heating pure potassium permanganate in the Pyrex container a (see Fig. 1). Before any gas is evolved, however, the entire
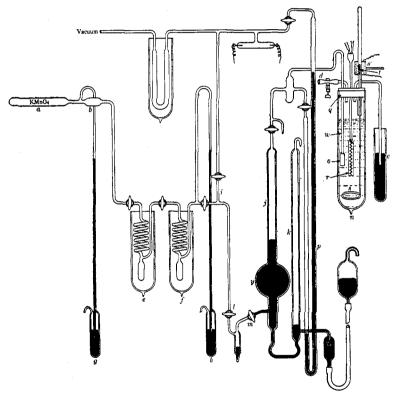

Fig. 1.—Oxygen thermometer.

generating and purifying system is completely evacuated by means of a mercury-diffusion pump and washed out several times by generating some oxygen gas. The gas is filtered through the glass wool b, and may be freed of possible traces of carbon dioxide by passing over moist potassium hydroxide (a small auxiliary bulb of water, completely out-gassed, may be used to moisten the potassium hydroxide), and dried with phosphorus pentoxide before condensing into e by means of liquid air. However, it is much more convenient to condense the gas in e as soon as it is generated and then fractionate it by condensing all but the last portion into f; since the

vapor pressures of carbon dioxide and ice are negligible at such a low temperature none of these impurities pass over into f. It is important that the safety trap g be placed between a and b, for the latter may become plugged. The liquid oxygen condensed in f is vigorously boiled during shaking by opening the cocks to the pump, in order to remove traces of dissolved nitrogen. It is then fractionated, the first portion being used to wash out the vapor-pressure apparatus. The middle portion is condensed in the thimble o, which may be made of glass or of copper.[16] The cryostat bath in the Dewar vessel n may be of liquid air that has lost most of its nitrogen and hence is mostly liquid oxygen. In order to produce temperatures on both sides of the normal boiling point the pressure on the bath is controlled by the mercury head in c, allowing most of the oxygen vapor to escape through d. Stirring, which should be vigorous and continuous, is obtained magnetically, either by hand or by a suitable mechanism. Pressures are read by means of a cathetometer on the open manometer j-k or the closed manometer p, one arm of which is evacuated completely with a mercury diffusion pump. The sample of oxygen should always be tested for purity by removing some of it by expanding into y (about 200 cc. capacity) and checking the constancy of vapor pressure at a given temperature. In case newly-made liquid air is used for the cryostat bath it is essential that the thimble o should be of copper, because the temperature of the bath rises fairly rapidly and we have found that an error of 0.03° to 0.04° is made under these conditions, due to lag alone if the container is of glass, and if the thermometer is of the lag-free type.

It is strongly recommended, however, that the cryostat liquid be made from commercial oxygen, and in this case we may dispense with the stopper at q and the mercury regulator c in case the barometric pressure is sufficient to give a temperature slightly above the normal boiling point. For slightly lower temperatures small quantities of fresh liquid air may be added to the bath.

We have found it most convenient to measure pressures at temperatures just above and just below the normal boiling point, a second observer reading the resistance of the thermometer at the same moment. The resistance is plotted as a function of the pressure[17] and as the range is small

[16] The capacity of the copper thimble is from 1 to 2 cc., wall thickness 0.25 mm. and with several copper vanes soldered in.

[17] The pressures as read on the cathetometer are reduced to 0°C. and 45° lat. by means of the equation: $P_0 = P_t [1 \pm \sigma + \beta (t_a - t_b)] [g/G] [1 - \alpha t_h]$, where P_0 is the corrected pressure, P_t the observed pressure, σ the scale error of the cathetometer, β the temperature coefficient of the cathetometer, t_a the temperature and t_b the calibration temperature of the cathetometer, g the acceleration of gravity at the place of measurement, G the standard acceleration of gravity, α the mean coefficient of expansion of mercury between 0° and t_h [$\alpha = 0.000180555 + 0.0_71244t + 0.0_{10}254t^2$ (Callendar and Moss, *Phil. Trans.*, **211A, 1** (1911)], t_h the mean temperature of the mercury column.

we may pass the best straight line through the points, deriving the values of the constants a and b of the equation $r = a + bP$ by means of least squares or other suitable methods. We may then calculate the value of r at $P = 760$ mm. and hence know the resistance of the thermometer at the definitely known normal boiling point of oxygen.

The Normal Sublimation Point of Carbon Dioxide

Henning and Heuse[2] give $t = -78.51° \pm 0.01°$ as the normal sublimation point of carbon dioxide, modified to the thermodynamic scale from the value of $-78.51_6°$, obtained on the scale of a hydrogen thermometer of constant volume at $p_0 = 740$ mm. of mercury.

The following equation[10] is given expressing T as a function of the vapor pressure P of carbon dioxide:

$$T = 194.584/[1 - 0.14428 \log P/(760)]$$

Keyes, Townshend and Young[14] obtain the value $t = -78.53°$ on the hydrogen scale.

Determination of the Resistance of the Thermometer at the Normal Sublimation Point of Carbon Dioxide

Carbon dioxide is prepared by heating sodium bicarbonate or by dropping a dilute solution of sulfuric acid on the salt. In the latter case the gas is washed by bubbling through a solution of sodium bicarbonate, dried over calcium chloride and phosphorus pentoxide and condensed in the bulb e by means of liquid air. The snow is now pumped free of air by means of a mercury-diffusion pump and after closing the cock to the pump the snow is distilled into f and again pumped free of air; it is necessary to repeat this process four to five times to completely free the snow of air.

It is the usual practice in determining the carbon dioxide point to use as a cryostat bath a mixture of commercial carbon dioxide snow and ether or alcohol. However, it is difficult to obtain efficient stirring with such a bath and hence have the thermometer and the thimble at the same temperature. In repeated experiments with a carbon dioxide-ether bath under varying conditions we were unable to obtain satisfactory results; many points showed large error, and we have replaced the carbon dioxide bath with the cryostat as described by Walters and Loomis,[18] using ethyl bromide[19] as the bath. With this cryostat it is possible to control the temperature within $\pm 0.01°$ for long periods and within a few thousandths of a degree during a period of measurement. With this arrangement it is most convenient to replace the glass stem of the thimble o with a long steel tube of bore about 1 mm. The pure carbon dioxide is now easily condensed from f to o by means of liquid air and then dipped into the

[18] Walters and Loomis, THIS JOURNAL, **47**, 2302 (1925).

[19] Kanolt, *Bur. Standards Sci. Papers*, **520** (1926).

cryostat in proper position near the thermometer. By this method the experimental points lie beautifully on a straight line and an accurate determination may be made. As in the case of the oxygen point, observations are made in the immediate vicinity of the normal sublimation point, and the final resistance at this point is calculated in the same manner.

Discussion of Errors

The value of the oxygen point is known within $\pm 0.02°$ and the carbon dioxide point to $\pm 0.01°$.

By differentiating the equations expressing P as a function of T it is found that $(dP/dT)_{1\ atm.} = 0.8$ mm. of mercury per $0.01°$ change for oxygen and 0.6 mm. per $0.01°$ for carbon dioxide, and as the temperature scale is not known to better than $\pm 0.01°$ at low temperatures it is sufficient to measure the pressure within these limits.

It has already been pointed out that freshly-made liquid air should not be used as the bath for the oxygen vapor-pressure measurements because the lag effect (assuming that the resistance thermometer is practically lag-free) causes an error of $0.03°$ to $0.04°$ unless a copper thimble with copper vanes is used, and even then the temperature of the bath is changing so rapidly that considerable uncertainty exists. Also, for the carbon dioxide point large errors result when the bath is made of commercial carbon dioxide and ether because of ineffective stirring, while the error when using the cryostat of Walters and Loomis is negligible.

On the basis of 25 observations for either the oxygen or the carbon dioxide point, typical determinations showed the probable error of a single observation to be $\pm 0.01°$ and the probable error of the mean $\pm 0.001°$.

Check runs should be made with freshly prepared samples of oxygen or carbon dioxide, and each value weighted by least square methods for the final value.

Summary

The need for the accurate calibration of resistance thermometers at the normal boiling point of oxygen and the normal sublimation point of carbon dioxide is discussed.

It is concluded that the most probable value of the oxygen point is —183.00 $\pm$ 0.02°, and of the carbon dioxide point —78.51 $\pm$ 0.01°, both on the thermodynamic scale.

Various precautions for the accurate determination of these points are described, including the preparation of pure oxygen and carbon dioxide, the use of suitable cryostats, and means of avoiding lag in the vaporizing substance.

The magnitude of probable errors is discussed.

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