the data within the experimental limits of error. This equation obtained is, $p_{\text{atm.}} = \frac{2.92855\,T}{v-\delta} - \frac{1623.63}{(v+0.2954)^2}$ where $\log \delta = 0.18683 - \frac{0.3113}{v}$.

2. The weight of a liter of nitrogen at N.T.P. was calculated from the equation of state to be 1.2509 g. as compared with the generally accepted value of 1.2507 g.

3. The compressibility coefficient at 0° was calculated and found to be 0.00061 as compared with 0.00056 from Holborn and Otto's equation and the work of Rayleigh, and 0.00043 and 0.00044 from Chappuis and Maverick, respectively.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 154]

THE MELTING POINT OF ICE ON THE ABSOLUTE TEMPERATURE SCALE

BY LEIGHTON B. SMITH AND ROBERT S. TAYLOR

Received June 25, 1923

Chappuis,[1] Day and Clement,[2] Holborn and Henning[3] and Eumorfopoulos[4] have made measurements on the expansion coefficients from 0° to 100° both for the constant volume and the constant pressure thermometers. Keyes[5] calculated ϵ, the expansion coefficient for a perfect gas, using the data of the above-mentioned workers and the equation of state which he based on Amagat's data for atmospheric nitrogen. Since then Henning,[6] and Henning and Heuse[7] have done some work on expansion coefficients for nitrogen and some other gases. It is, therefore, thought worth while to review the above data using the new equation of state of nitrogen[8] and also the method of obtaining ϵ using the equation of state, since this has never been given in detail before.

Instead of using a constant-pressure thermometer, a constant-π thermometer will be considered where π is defined by the equation $\pi\omega = RT$. From the Keyes equation of state $\omega = v - \delta$ or, for low pressures $\omega = v - \beta$ and $\pi = p + A/(v+l)^2$, which reduces at low pressures to the form, $\pi = p + (A/v^2)$.

---

[1] Chappuis, *Trav. mem. bur. intern.*, **6**, 59 (1888) and **13**, 66 (1903).

[2] Day and Clement, *Am. J. Sci.*, **26**, 405 (1908).

[3] Holborn and Henning, *Ann. Physik*, **35**, 761 (1911).

[4] Eumorfopoulos, *Proc. Roy. Soc. London*, **90A**, 189–203 (1914).

[5] Keyes, THIS JOURNAL, **42**, 54 (1920).

[6] Henning, *Z. Physik*, **5**, 264 (1921).

[7] Henning and Heuse, *ibid.*, **5**, 285 (1921).

[8] Smith and Taylor, THIS JOURNAL, **45**, 2115 (1923).

Then ϵ, the coefficient of expansion for a perfect gas, is given by the equation,

$$\epsilon = \left(\frac{\omega_t - \omega_0}{\omega_0\, t_{(ab)}}\right)_\pi \tag{1}$$

where $t_{(ab)} = T - T_0$ or, in other words, is centigrade thermodynamic temperature. The above equation is, therefore, identical with the following,

$$\epsilon = \frac{v_t{}^\pi - v_0}{(v_0 - \beta)\; t_{(ab)}} \tag{2}$$

where v_0 is the volume measured at 0° and v_t^π is the volume at $t°$ when π has the same value as at 0°.

$\epsilon_{p_0}^t$ is defined by the following equation,

$$\epsilon_{p_0}{}^t = \frac{v_t{}^p - v_0}{v_0 t_c} \tag{3}$$

where v_t^p is measured on the constant-pressure thermometer. The constant-π thermometer has never been investigated experimentally hence v_t^π must be eliminated from Equation 2. By adding and subtracting v_t^p from the numerator of Equation 2 the following is obtained.

$$\epsilon = \frac{(v_t{}^{p_0} - v_0) + (v_t{}^\pi - v_t{}^p)}{(v_0 - \beta)\; t_{(ab)}} \tag{4}$$

Dividing numerator and denominator by $v_0 t_c$, Equation 4 becomes

$$\epsilon = \left[\frac{\dfrac{v_t{}^{p_0} - v_0}{v_0 t_c} + \dfrac{v_t{}^\pi - v_t{}^{p_0}}{v_0 t_c}}{\left(1 - \dfrac{\beta}{v_0}\right)\dfrac{t_{ab}}{t_c}}\right]_\pi \tag{5}$$

Substituting from Equation 5

$$\epsilon = \left[\frac{\epsilon_p + \dfrac{v_t{}^\pi - v_t{}^{p_0}}{v_0 t_c}}{\left(1 - \dfrac{\beta}{v_0}\right)\dfrac{t_{ab}}{t_c}}\right]_\pi \tag{6}$$

Since p_t^π is very close to p_0, Boyle's law may be assumed to hold without, in this instance, introducing too great an error, or $v_t^\pi p_t^\pi = v_t^{p_0} p_0$.

Hence $v_t^\pi = v_t^{p_0}\dfrac{p_0}{p_t^\pi}$. Using this relation, Equation 6 becomes

$$\epsilon = \frac{\epsilon_p + \dfrac{v_t{}^{p_0}}{v_0 t_c}\left[\dfrac{p_0}{p_t{}^\pi} - 1\right]}{\left[1 - \dfrac{\beta}{v_0}\right]\dfrac{t_{ab}}{t_c}} \tag{7}$$

Since $\dfrac{v_t^{p_0}}{v_0} = \left(1 + \epsilon_{p\,0^\circ}^{\,t^0}\right)$ and since the pressures are involved only in the correction term, Equation 7 may be written

$$\epsilon = \frac{\epsilon_p + \dfrac{1 + \epsilon_p{}^t}{t_c}\left[\dfrac{p_0 - p_t{}^\pi}{p_t{}^\pi \equiv p_0}\right]}{\left[1 - \dfrac{\beta}{v_0}\dfrac{t_{ab}}{t_c}\right]} \tag{8}$$

Furthermore, $\pi_t = \pi_0$; therefore $p_t + \frac{A}{(v_t)^2} = p_0 + \frac{A}{(v_0)^2}$ or $p_t - p_0 = \frac{A}{v_0^2} - \frac{A}{v_t^2}$. But $v_t = v_0(1 + \epsilon_p t_c)$; therefore $p_t - p_0 = \frac{A}{v_0^2}\left[1 - \frac{1}{(1+\epsilon_p t_c)^2}\right]$.

Therefore,[9] $\frac{p_0 - p_t}{p_0} = -\frac{A}{p_0 v_0^2}\left[\frac{(1+\epsilon_p t_c)^2 - 1}{(1+\epsilon_p t_c)^2}\right] = -\frac{A\epsilon_p t_c}{p_0 v_0^2}\left[\frac{2+\epsilon_p t_c}{(1+\epsilon_p t_c)^2}\right]$.

Equation 8 now becomes,

$$\epsilon\left(1 - \frac{\beta}{v_0}\right)\frac{t_{ab}}{t_c} = \epsilon_p - \frac{A\epsilon_p}{p_0 v_0^2}\left[\frac{2+\epsilon_p t_c}{1+\epsilon_p t_c}\right] \qquad (9)$$

Since $t_c = 100 - t_{ab}$ and since $p_0 v_0 = RT_0$, Equation 9 becomes

$$\epsilon = \epsilon_p + \frac{\beta\epsilon}{v_0} - \frac{A\epsilon_p}{R^2T_0^2}\left[\frac{2+\epsilon_p t_c}{1+\epsilon_p t_c}\right]p_0 \qquad (10)$$

or since in the correction term it suffices to say that $\epsilon_p = \epsilon = 1/T_0$,

$$\epsilon_p = \epsilon + \left[\frac{A}{R^2T_0^3}\left(\frac{2+\epsilon_p t_c}{1+\epsilon_p t_c}\right) - \frac{\beta}{RT_0^2}\right]p_0 \qquad (11)$$

It is now seen that with the aid of certain approximations which, however, are permissible since they involve only the correction factor, the limitation of the constant-π thermometer has been removed and the resulting formula is general.

In the case of the constant-volume coefficient the same procedure is employed but the derivation is very much simplified, as will be seen. For the constant-ω thermometer

$$\epsilon = \left[\frac{\pi_t - \pi_0}{\pi_0 t_{ab}}\right]_\omega = \left[\frac{p_t - p_0}{\left(p_0 + \frac{A}{v_0^2}\right)t}\right]_\omega,$$

since constant ω is identical with constant volume and A/v^2 is independent of the temperature. By definition,

$$\epsilon_v = \frac{p_t - p_0}{p_0 t}. \quad \text{Hence,} \quad \epsilon_v = \epsilon + \frac{A\epsilon}{v_0^2 p_0}, \quad \text{or} \quad \epsilon_v = \epsilon + \frac{A}{R^2T_0^3}p_0. \qquad (12)$$

From the equation of state of nitrogen, Equation 12 becomes $\epsilon_v = \epsilon + 0.00000029\ p_0$ (atm.). Since $1/\epsilon = T_0$, the absolute temperature of melting ice can be calculated from measured expansion coefficients.

In Table I are given the measured values of ϵ_p, and calculated values of T_0. In Table II are the measured values of ϵ_v and calculated values of T_0.

It is seen from these tables that in no way can the above data be averaged to give a value of 273.20 as the ice point on the absolute centigrade scale as obtained by Henning and Heuse. The data of Henning and Heuse on nitrogen vary from an ice point of 273.130 to one of 273.231.

---

[9] In Keyes' paper, THIS JOURNAL, **43,** 1461 (1921), there is a typographical error in this equation, the square term in the denominator of the expression in brackets being omitted.

An average of their data alone, however, gives 273.175°. A consideration of the other data leads one to believe that even this is too high by several hundredths of a degree. Keyes,[5] after a review of the data on coefficients

TABLE I

ABSOLUTE ICE-POINT TEMPERATURES COMPUTED FROM MEASURED CONSTANT PRESSURE EXPANSION COEFFICIENTS

p (atm.)	Therm. material	$\epsilon_p \times 10^3$ (obs).	ϵ(calc.)	T_0(calc.)
1.318	Pt Ir	3.67315[a]	3.66121	273.134
1.825	Pt Ir	3.67775[a]	3.66123	273.132
0.520	Quartz	3.66561[b]	3.66090	273.157
0.546	Quartz	3.66587[b]	3.66093	273.155
1.042	Quartz	3.67005[b]	3.66061	273.179
1.032	Quartz	3.67019[b]	3.66085	273.161
0.996	Quartz	3.66991[b]	3.66089	273.158
0.289	59^{III} glass	3.6630[c]	3.66038	273.196
0.671	59^{III} glass	3.6679[c]	3.66082	273.163
1.460	59^{III} glass	3.6742[c]	3.66098	273.151

Mean of above values gives for T_0, 273.159.

[a] Ref. 1. [b] Ref. 4. [c] Ref. 7.

TABLE II

ABSOLUTE ICE-POINT TEMPERATURES COMPUTED FROM MEASURED CONSTANT VOLUME EXPANSION COEFFICIENTS

p (atm.)	Therm. material	$\epsilon_v \times 10^3$	Observer	ϵ(calc.)	T_0(calc.)
1.044	verre dur	3.6718	Chappuis (1902)	3.66210	273.067
0.698	verre dur	3.6685	Chappuis (1902)	3.66202	273.073
1.310	Pt Ir	3.6747	Chappuis (1887)	3.66253	273.035
1.318	Pt Ir	3.6744	Chappuis (1907)	3.66215	273.064
0.742	Quartz	3.6699	Chappuis (1914)	3.66301	273.000
0.727	Quartz	3.66943	Chappuis (1914)	3.66267	273.025
0.740	Quartz	3.66959	Chappuis (1914)	3.66272	273.021
0.413	Pt	3.665	Day and Clement	3.66116	273.137
0.724	Pt	3.668	Day and Clement	3.66128	273.129
0.979	Pt	3.670	Day and Clement	3.66091	273.156
1.2961	Pt	3.673	Day and Clement	3.66095	273.153
0.8305	59^{III} glass	3.6706	Holborn and Henning	3.66288	273.009
0.8175	59^{III} glass	3.6699	Holborn and Henning	3.66231	273.052
0.8166	Quartz	3.66843	Holborn and Henning	3.66085	273.161
0.2895	59^{III} glass	3.6626	Henning and Heuse	3.65991	273.231
0.6710	59^{III} glass	3.6675	Henning and Heuse	3.66126	273.130
1.4605	59^{III} glass	3.6752	Henning and Heuse	3.66062	273.178
0.800	Quartz	3.6687	Keyes, Townshend, Young	3.66127	273.129

Mean of the above gives T_0 = 273.097; omitting Chappuis' values, T_0 = 273.134; average of all nitrogen data gives T_0 = 273.119.

of expansion for all gases for which data are available, reached the conclusion that T_0 = 273.14. Buckingham decided on 273.13. From the above data it is evident that 273.12° is about as good a value as can be obtained from the nitrogen coefficients alone. A paper will soon be forthcoming from this Laboratory dealing with the data on other gases, but for the present it appears that 273.13° is about as good a value for T_0 as can be decided upon.

In conclusion it is desired to thank Dr. Keyes for his valuable suggestions and assistance.

Summary

The value of T_0, the absolute temperature of melting ice, from the nitrogen volume and pressure expansion coefficients gives a mean value of 273.12°. The mean value obtained by using the data of other gases including the Joule-Thomson coefficient is 273.13° ± .01°.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 29]

THE CRYSTAL STRUCTURE OF POTASSIUM HYDROGEN FLUORIDE

BY RICHARD M. BOZORTH

Received June 25, 1923

Introduction

Crystals of potassium hydrogen fluoride, KHF_2, were prepared by the spontaneous evaporation at room temperature of an aqueous solution of potassium fluoride and hydrofluoric acid. They are known[1] to belong to the tetragonal system and to have an axial ratio $a:c = 1:0.601$.

The X-ray data were obtained (1) from photographs of line spectra from the principal planes, using rhodium as the target, and (2) from two Laue photographs taken with the beam approximately perpendicular to the (001) planes. The methods of analysis and treatment are the same as those previously employed.[2]

The Unit of Structure

The data from the spectral photographs are given in Table I; d is the interplanar distance expressed in Ångstrom units and n the order of reflection. The wave length of the rhodium $K\alpha_1$ line was taken to be 0.6121 Å., and that of the unresolved $K\alpha$ line to be 0.614 Å.

Combining the values of d/n with the density of the crystals, determined by a suspension method to be 2.37, it was found that the data are consistent with a unit containing 1 molecule of KHF_2. Examination of the Laue photographs, however, showed that many values of $n\lambda$ calculated for this unit by means of the well-known Bragg equation were smaller

---

[1] P. Groth, "Chemische Krystallographie," Engelman, Leipzig, **1906**, vol. 1, p. 312.

[2] Bozorth, THIS JOURNAL, **44**, 317 (1922); **44**, 2232 (1922). See also Wyckoff, *Am. J. Sci.*, [5] **1**, 127 (1921) and Dickinson, THIS JOURNAL, **44**, 276 (1922).