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THE JOULE-THOMSON EFFECT FOR AIR.

BY FREDERICK G. KEYES.

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There has recently been completed by L. G. Hoxton¹ a very painstaking experimental investigation of the Joule-Thomson effect in the case of air. In this investigation the effect was measured at several pressures and temperatures, use being made of the experimental values obtained to compute the position of the ice point on the absolute-temperature scale, as well as the constant-pressure air-thermometer-scale corrections to reduce gas-scale readings to the absolute scale. From the temperature coefficient of the Joule-Thomson effect the pressure coefficient of the specific heat for air was computed and compared with the experimental value found by Holborn and Jacobs.²

For the absolute temperature of the ice point 273.36 was obtained, while the constant-pressure air-thermometer corrections were in agreement with the mean of the corrections arrived at by Rose-Innes, Callendar, Berthelot, and Buckingham for the nitrogen thermometer. The pressure coefficient of the constant-pressure specific heat for air computed from the temperature coefficient of the Joule-Thomson effect is moreover in good agreement with the first pressure coefficient of Holborn and Jacobs' empirical equation based on their experimental values.

The attention given to possible sources of error and in fact to all details of the experimental procedure by Hoxton is such as to make the work a most important contribution to the experimental study of the Joule-Thomson coefficient. The values obtained, nevertheless, are higher than those obtained by previous workers as noted by Hoxton, and, in consequence, lead to a higher value of the ice point (273.36) than that arrived at by other methods. Hoxton indeed calls attention to the fact that in general the use of the Joule-Thomson effect in computing this constant has, in the calculations of everyone, led to a high value. Thus Buckingham³ found for the absolute ice-point temperature, making use of the respective Joule-Thomson effects, for air 273.273, for nitrogen 273.286, for carbon dioxide 273.267, while in the case of hydrogen 273.049 was obtained. Berthelot,⁴ however, making use of a method of computation based on his equation of state concluded that 273.09 was the correct ice-point temperature, and recently there were presented the results of some calculations by means

¹ Hoxton, *Phys. Rev.*, **13**, 438 (1919).

² Holborn and Jacobs, *Z. Ver. deut. Ing.*, **58**, 1429 (1914).

³ Buckingham, *Bur. Standards, Bull.* **3**, 237 (1907).

⁴ Berthelot, *Trav. Nem Bur. Int.*, **13**, (1907).

of my⁵ equation of state, applied to nitrogen, hydrogen and helium in the case of both the constant-pressure and constant-volume gas thermometers, which lead to a value somewhat higher (273.14) than Berthelot gives.

In the procedure wherein use is made of the Joule-Thomson coefficients as well as in the equation of state method of arriving at the ice-point temperature, the experimentally determined constant-pressure and constant-volume coefficients of volume and pressure increase between the melting and boiling points of water must be employed. Evidently, if these coefficients were in error, the error would be carried through into the values obtained for the ice-point temperature, and, indeed, high accuracy is demanded since to obtain an accuracy of 0.1° in the ice-point temperature requires that the coefficients should be known to about 1 part in 27000. On the other hand, for this degree of correctness, in the case of air, it is sufficient to have approximately 1% accuracy in the Joule-Thomson coefficient which is involved in the correction term applied to the expansion coefficient.

Apropos of the extreme accuracy with which the expansion coefficient must be known, it is of interest to call attention to the importance in precise measurements of the adsorptive effect of the container walls. The discrepancies in the coefficients of expansion as measured by the same and by different observers may well be assigned to surface adsorptive effects on the inner surface of the thermometer bulb; not perhaps in general to adsorption of the gas on the envelope surface directly but to adsorption or absorption by the water layer which always attaches tenaciously to surfaces.⁶ For example, Eumorphopoulos,⁷ employing a quartz thermometer bulb with the Callendar compensating type of instrument, after cleaning the bulb with nitric acid and mixed chromic and sulfuric acids, washing repeatedly with distilled water, drying and heating to 500° under exhaustion, found that pure nitrogen dried by phosphoric acid admitted and re-exhausted several times, gave the coefficient of volume increase per degree per cc. 3.671×10^{-3} at 760 mm. Heating and loading as before reduced the value to 3.6701×10^{-3} . It would appear then that the difficulty of extracting adsorbed material from the walls is great even in quartz, and in fact, the gas expansion values of other observers, notably those coefficients measured in glass thermometer bulbs, are invariably high,⁸ as compared to values obtained in metal bulbs.

⁵ Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917). This equation is: $p = RT/(v - \delta) - A/(v - l)^2$, where $\ln \delta = \ln \beta - \alpha/v$.

⁶ See also for example, concerning the weight of a liter of ammonia: "Thermodynamic Properties of Ammonia," Keyes and Brownlee, p. 216, Wiley and Sons, 1916.

⁷ Eumorphopoulos, *Proc. Roy. Soc.*, **90A**, 189 (1914).

⁸ Holborn and Henning, *Ann. Physik.*, **35**, 766 (1911). They obtained for nitrogen in 59^{III} glass 3.6703×10^{-3} at 620 mm., but in quartz 3.6684×10^{-3} .

The purpose of the present paper is to give the results of some calculations of the Joule-Thomson coefficients based on the use of my equation of state.⁵ The equation of nitrogen for example, has been shown to give the Amagat pressures to about 1000 atmospheres with great exactness over a range of 200°. In the case of air, as will be shown below, the pressures given by Amagat are also in good agreement as well as are the pressures given by other observers at temperatures as low as -130°, although in the latter case not high pressures for reasons which can be more appropriately discussed in another paper. It is conceivable, however, that an equation of state might serve to calculate pressures over a comparatively limited temperature range to a very satisfactory degree and still be defective in form, and in consequence lead to erroneous values for the derived quantities, such as, for example, $\left(\frac{\partial v}{\partial T}\right)_p$ and $\left(\frac{\partial p}{\partial T}\right)_v$ which are involved in calculating the Joule-Thomson coefficients.

The form of function has, however, been tested by comparing the term (corresponding to van der Waals' b) and ϕ the cohesive pressure term separately at high pressures over a temperature range extending 100° on each side of the fixed points (0° and 100°) under discussion in the present paper. The functional forms for δ and ϕ in the equation have been shown to be exact, and at low pressures should give accordingly the derived quantities with great precision.

To give a survey of the degree of exactness with which the equation of state for air accords with the measurements, there are presented in Tables I, II and III the data of Amagat⁹ upon which the constants of the equation are based, those of Witkowski¹⁰ and finally, the recent pressure volume and temperature observations for air by Holborn and Schultz.¹¹

The agreement of the calculated and observed pressures is not perhaps as good as in the case of nitrogen because the oxygen of the air in Amagat's work might have reacted to some extent with the mercury used to confine it at higher temperatures and pressures. Each observer's data are, however, well represented, and the equation is, therefore, concluded to be exact from -130 to 200° over a wide pressure range.¹²

⁹ Amagat, *Ann. chim. phys.*, **29**, 52 (1893).

¹⁰ Witkowski, *Bull. Acad. Cracovie*, **1891**, 181; or *Phil. Mag.*, **41**, 288 (1896).

¹¹ Holborn and Schultz, *Ann. Physik.*, **47**, 1089 (1915).

¹² It has been suggested that any equation of state containing four constants should represent the data. The habit of regarding an equation as simply one containing a number of arbitrary constants which will represent the data with better accuracy as the number of constants is increased is certainly common enough, but not particularly adequate. In the case of an equation of state, there is a relation between three variables, and the *form* of the function becomes of more importance than the mere number of constants.

There are examples enough in the literature of equations having many constants

TABLE I.
EQUATION OF STATE FOR AIR.
Observations of Amagat.

V.	Pressures in atmospheres of 760 mm., volumes in cc. per g.			
	0°.	99.4°.	200.4°.	
7.525	100.0	146.0	193.0	Observed pressure Amagat
	99.71	146.08	193.19	Calculated Eq. of state.
5.073	150.0	227.0	303.0	Obs.
	149.71	226.14	303.8	Calc.
3.906	200.0	310.0	420.0	Obs.
	200.29	309.85	421.15	Calc.
3.245	250.0	395.0	538.0	Obs.
	250.50	394.28	540.37	Calc.
2.829	300.0	479.0	655.0	Obs.
	298.81	476.25	656.55	Calc.
2.550	350.0	564.0	770.0	Obs.
	349.51	560.77	775.42	Calc.
2.348	400.0	646.0	881.0	Obs.
	403.07	646.05	892.93	Calc.
2.194	450.0	728.0	993.0	Obs.
	443.50	717.23	995.23	Calc.

$$p = \frac{2.833}{v - \delta} T - \frac{A}{(v - l)^2}, \text{ where } \log_{10} \delta = 0.20113 - \frac{0.296}{v} A = 1605.3; l = -0.088.$$

Having shown that the pressures for air are given by the equation over a wide range of pressure, volume and temperature, the Joule-Thomson coefficients calculated from the equation are valuable as a standard of reference from which to discuss the experimental values. Moreover, by means of a comparison of calculated and experimental values, some light will be thrown upon the magnitude of the possible errors affecting the expansion coefficients and the Joule-Thomson numbers, thus assisting in extending the accuracy with which these important constants can be measured.

A peculiarity of the particular equation¹³ of state for air, so far above its critical temperature, is that the pressure at constant volume is a linear and still failing to represent the pressure, volume and temperature data as accurately as desirable. In a recent article (THIS JOURNAL, 41, 591 (1919)), I have gone into this matter at some length to make clear the importance of the form of function, and in the article referred to special measurements were made to test the functional form, and further data are being obtained with improved apparatus.

¹³ In a previous paper (THIS JOURNAL, 41, 589 (1919)), it has been shown that the equation in the simple form is particular in that it applies to a system whose molecules remain of invariable species in a given phase. That is to say, there is assumed to be no association, which at so many degrees above the critical point is true enough for the so-called permanent gases. It is only for a one-type molecular assemblage that the linear increase of pressure with temperatures at constant volume is conceivable. Indeed, for such a system, any other manner of pressure increase appears illogical unless we are

TABLE II.
Observations of Witkowski.
Pressures in atmospheres, volumes in cc. per g.

V.	0°.	V.	100°.	V.	—35°.	V.	—130°.
773.37	0.99985 Calc.	1057.2	0.99996 Calc.	674.09	0.9996 Calc.	404.4	0.9965 Calc.
	1.0000 Obs.		1.00000 Obs.		1.0000 Obs.		1.0000 Obs.
76.959	9.9920 Calc.	105.78	10.001 Calc.	12.815	50.012 Calc.	10.147	31.478 Calc.
	10.000 Obs.		10.000 Obs.		50.000 Obs.		30.000 Obs.
7.487	100.202 Calc.	10.789	100.13 Calc.	6.9245	90.353 Calc.		
	100.00 Obs.		100.00 Obs.		90.000 Obs.		
5.7849	130.403 Calc.	9.064	120.11 Calc.	5.1598	120.634 Calc.		
	130.000 Obs.		120.00 Obs.		120.000 Obs.		

At -103.5° and at $V = 21.871$, the calculated pressure is 20.304, for an observed pressure of 20.000.

TABLE III.
Observations of Holborn and Schultz.
Pressures in atmospheres of 760 mm., volumes in cc. per g.

V.	0°.	V.	50°.	V.	100°.	V.	150°.	V.	200°.
30.271	25.208 Calc.	36.069	25.305 Calc.	53.982	19.619 Calc.	56.161	21.451 Calc.	55.357	24.398 Calc.
	25.230 Obs.		25.339 Obs.		19.633 Obs.		21.464 Obs.		24.405 Obs.
30.349	25.138 Calc.	36.128	25.263 Calc.	54.084	19.582 Calc.	56.105	21.472 Calc.	55.315	24.416 Calc.
	25.165 Obs.		25.289 Obs.		19.599 Obs.		21.499 Obs.		24.422 Obs.
15.276	49.447 Calc.	18.269	49.925 Calc.	54.242	19.525 Calc.	24.286	50.008 Calc.	27.188	50.120 Calc.
	49.528 Obs.		49.943 Obs.		19.545 Obs.		50.009 Obs.		50.175 Obs.
15.318	49.319 Calc.	18.309	49.831 Calc.	21.466	49.592 Calc.	24.261	50.061 Calc.	27.259	49.988 Calc.
	49.390 Obs.		49.952 Obs.		49.710 Obs.		50.140 Obs.		50.023 Obs.
10.234	73.387 Calc.	12.444	73.486 Calc.	21.465	49.594 Calc.	16.700	73.302 Calc.	18.724	73.407 Calc.
	73.509 Obs.		73.659 Obs.		49.691 Obs.		73.425 Obs.		73.502 Obs.
10.235	73.380 Calc.	12.452	73.428 Calc.	14.589	73.408 Calc.	16.642	73.562 Calc.	18.696	73.442 Calc.
	73.493 Obs.		73.636 Obs.		73.611 Obs.		73.695 Obs.		73.599 Obs.
7.6570	97.970 Calc.	9.4679	96.960 Calc.	14.581	73.458 Calc.	12.658	97.610 Calc.	14.083	98.645 Calc.
	98.091 Obs.		97.310 Obs.		73.650 Obs.		97.800 Obs.		98.730 Obs.
7.6630	97.899 Calc.	9.4685	97.022 Calc.	11.043	97.768 Calc.	12.654	97.634 Calc.	14.081	98.645 Calc.
	98.010 Obs.		97.313 Obs.		98.044 Obs.		97.823 Obs.		98.740 Obs.
	25.208 Calc.			11.017	97.989 Calc.				
	25.208 Obs.				98.281 Obs.				

function of the temperature. In the region of the critical temperature and of small volumes (10 cc. per g.), this is no longer true. The linear increase of pressure with temperature at constant volume requires as a thermodynamic consequence that the constant-volume specific heat shall be independent of the volume. The constant-pressure specific heat C_p will, therefore, follow from the thermodynamic equation $C_p =$

$C_v + T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_v$ on applying the equation to compute the expres-

sion for the second term of the right-hand member. There is obtained from

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{v - \delta} \quad \text{and} \quad \left(\frac{\partial v}{\partial T} \right)_p = \frac{v - \delta}{T} \times \frac{1}{1 - \frac{\alpha \delta}{v^2} - \frac{2A}{RT} \frac{(v - \delta)^2}{(v - l)^3}}$$

and the air constants, the following equation,

$$C_p = C_v + \frac{R}{1 - \frac{\alpha \delta}{v^2} - \frac{2A}{RT} \frac{(v - \delta)^2}{(v - l)^3}} = \left[0.241 + 2.5 \times 10^{-4} p \right]_{58^\circ} \text{approximately.}$$

Holborn and Jacobs¹⁴ find 2.86×10^{-4} for the pressure coefficient in their equation $C_p = 0.2413 + 2.86 \times 10^{-4} p + 5.0 \times 10^{-8} p^2 - 1.0 \times 10^{-9} p^3$. At 200 atmospheres the calculated specific heat is 0.291 as compared with Holborn and Jacobs' 0.2925 from the equation representing their measurements.

The thermodynamic equation of the Joule-Thomson effect is $\frac{dT}{dp} =$

$$\mu = - \frac{T \left(\frac{\partial v}{\partial T} \right)_p - v}{C_p} \quad \text{and the equation of state gives then}$$

$$\mu = \frac{\frac{2A}{RT} \frac{(v - \delta)^2}{(v - l)^3} v - \delta \left(1 - \frac{\alpha}{v} \right)}{C_v \left(1 - \frac{\alpha \delta}{v^2} - \frac{2A}{RT} \frac{(v - \delta)^2}{(v - l)^3} \right) + R}$$

willing to accept that temperature can influence the residual electro-magnetic fields which are the assumed cause of the mutual attraction between the molecules composing the fluid, and such a temperature effect has not been established so far as known.

¹⁴ The coefficients to the higher powers have been omitted since the first pressure coefficient of Holborn and Jacobs' empirical equation is the most accurate. In the equation given, the p coefficient is taken as $R \times \frac{2A}{R^2 T^2}$ being the first approximation of

$$\frac{R}{1 - \frac{\alpha \delta}{v^2} - \frac{2A}{RT} \frac{(v - \delta)^2}{(v - l)^3}} \text{ it being assumed that the specific heat at one atmosphere is } C_p + R = 0.238.$$

The equation given is complete, but for the low pressures that are here to be considered, it suffices to make the following reductions. For $\frac{(v - \delta)^2 v}{(v - l)^3}$, may be written $\left(1 - \frac{2\beta}{RT} p\right)$; for $\delta \left(1 - \frac{\alpha}{v}\right)$, $\beta \left(1 - \frac{2\alpha\beta}{RT} p\right)$; and for $\frac{(v - \delta)^2}{(v - l)^3}$, $\frac{p}{RT}$.

There results then the equation

$$\mu_p = \mu_0 + \left[\mu_0 \frac{C_v}{C_{p_0}} \frac{2A}{R^2 T^2} - \frac{4A\beta}{C_{p_0} R^2 T^2} + \frac{2\alpha\beta}{C_{p_0} RT} \right] p.$$

where μ_0 represents the quantity $\left(\frac{2A}{RT} - \beta\right)/C_{p_0}$, the Joule-Thomson effect at infinitely low pressure, and $C_{p_0} = C_v + R$, the constant-pressure specific heat at infinitely low pressures. It will be observed that the pressure coefficient can be positive or negative depending upon the temperature, although it is to be observed that the coefficient of p is the tangent to the μ, p curve at the μ axis only.

TABLE IV.

Experimental and Computed Joule-Thomson Coefficients for Air.

<i>t.</i>	Calculated.		J. and T. Buckingham.		Noell.		Hoxton.	
	1 atm.	1 to 6 atm.	Corr. states.	1 to 3 atm.	1.3 atm.	3.4 atm.	4.9 atm.	
0°	0.2615	0.275	0.284	0.277	0.303	0.284	0.272	
50°	0.1957	0.197	0.205	0.185	0.226	0.211	0.205	
100°	0.1477	0.147	0.161	0.125	0.170	0.160	0.154	

The temperature coefficient may be positive or negative depending on the temperature. The effect itself (μ) is zero at low pressures when $T = \frac{2A}{R\beta}$, but the temperature of inversion diminishes as the pressure increases at high pressures.

Substituting the numerical values of the constants given under Table I, there results the following equation, $\mu_0 = \frac{115.8}{T} - 0.1625$ where $C_{p_0} = 0.238$ is assumed constant. The pressure coefficient is at 0°; -4.7×10^{-4} and at -100 ; $+9.2 \times 10^{-4}$ for low pressures. The mean pressure coefficient 0 to 200 atmospheres is 7.1×10^{-4} at zero degrees.

Table IV gives a survey of the experimental values together with those computed by the equation. It is perceived that the values of the effect obtained by Hoxton at the higher pressures are not far from those obtained by Joule and Thomson. The Joule and Thomson numbers were obtained by expanding from about 6 atmospheres down to 1 atmosphere, and, therefore, represent the integrated effect over the pressure drop.

The differences in the various values are, however, so great and the pressure effect so small (-4.7×10^{-5} per atmosphere calculated for low pressures) that for the accuracy attained it is futile to take into account whether the pressure amounted to one or several atmospheres. It is to be noted, however, that Hoxton has observed a large pressure effect experimentally amounting to 5.6×10^{-3} or the order of ten times the calculated value (4.7×10^{-4}). Vogel's¹⁵ pressure coefficient (8.6×10^{-4}) is lower than Hoxton's, but somewhat larger than that calculated, while Dalton¹⁶ working in Onnes' laboratory finds 6.0×10^{-4} . Bradley and Hale,¹⁷ however, made a series of measurements at temperatures from 0 to -110° expanding through pressure differences of 68, 102, 136, 170 and 204 atmospheres to one atmosphere, thereby obtaining the integral Joule-Thomson effect.

Bradley and Hale measured the fall in temperature attending the throttling of air from 68, 75, 101, 150 and 204 atmospheres to one atmosphere when the gas on the high pressure side of the plug was maintained at a series of different temperatures. By plotting the pressures with the attendant temperature drops, a series of curves was described, one for each initial temperature. The tangent at any point on the curves is the value of dt/dp the Joule-Thomson coefficient. From the curves of Bradley and Hale's data the values at the pressures of 50, 100, 150 and 200 atmospheres were read. Each of these constant-pressure series of values was then plotted with the reciprocal of the corresponding absolute temperature, which permitted the value of μ at the ice point to be read corresponding to each constant pressure. These ice-point temperature values are: $\mu = 0.2330$ at 50 atmospheres, $\mu = 0.1915$ at 100 atmospheres, $\mu = 0.1615$ at 150 atmospheres, and $\mu = 0.1166$ at 200 atmospheres. The values are related to the pressure with sufficient exactness for the present purpose by the equation $\mu = 0.268 - 7.3 \times 10^{-4}p$. This equation gives for μ at 50 atmospheres 0.232, at 100 atmospheres 0.194, at 150 atmospheres 0.158, at 200 atmospheres 0.121. At 0° , therefore, Bradley and Hale's work indicates that the pressure coefficient of the Joule-Thomson effect is -7.3×10^{-4} . The complete equation for the effect at zero degrees derived from the equation of state gives at 200 atmospheres 0.1196 while the one atmosphere value is 0.261. The average coefficient is therefore 7.1×10^{-4} which agrees very well with the Bradley and Hale value.¹⁷ At low pressures the pressure coefficient is the order of 5×10^{-4} , so that the numerical value of the coefficient increases slowly with pressure. It appears, therefore, that the pressure coefficient as found by Hoxton is the order of 8-fold too large.

¹⁵ E. Vogel, Landolt-Börnstein, "Tabellen," p. 786, 4th edition.

¹⁶ Dalton, *Comm. Phys. Lab. Leiden*, 1909, 109a and 109c.

¹⁷ Bradley and Hale, *Phys. Rev.*, 29, 258 (1909).

The Expansion Coefficients of a Gas.

The computation of the expression giving the constant-pressure expansion coefficient may be readily obtained from the equation of state. For the large volumes which are here in question, it suffices to assume $\delta = \beta$ and to neglect l in the cohesive pressure term $\phi = \frac{A}{(v-l)^2}$. The equation assumes the form, therefore, $p = \frac{R}{v-\beta} T - \frac{A}{v^2}$ for low pressure analogous in form to the van der Waals equation. Setting $p + \frac{A}{v^2} = \pi$ and $(v - \beta) = \omega$ the equation of an actual gas at not too small volumes becomes $\pi\omega = RT$ identical in form with the perfect gas equation. If π can be kept constant, therefore, the absolute centigrade temperatures will be given by the expression

$$t_a = \left[\frac{\omega_t - \omega_o}{\omega \epsilon} \right]_{\pi} \quad (1)$$

where ϵ is the expansion coefficient of a perfect gas. The quantity ω_o will always be invariable in magnitude in a given apparatus filling, but ω_t must be always taken with π or $(p_1 + \phi_1)$ constant. Since, however, the volume is increasing with temperature rise, ϕ will diminish progressively, and since $(p_o + \phi_o)$ must always equal $(p_1 + \phi_1)$, where the zero subscripts refer to the ice-point values of the quantities designated and the numeral to the value of the quantities at any temperature, it is clear that $p_1 > p_o$ and $p_1 - p_o = \phi_o - \phi_1 = A \left(\frac{1}{v_o^2} - \frac{1}{v_1^2} \right)$ will therefore always remain a positive quantity. If further ω' is taken to represent the value of $(v_1 - \beta)$ at the constant initial pressure p_o according to the usual constant pressure thermometer procedure, ω_1 will be given by multiplying ω'_1 by the ratio $\frac{p_o}{p_1}$. Substituting then in Equation 1 there results,

$$\frac{\omega'_1 \frac{p_o}{p_1} - \omega_o}{\omega_o t_a} = \epsilon = \frac{\frac{v_1 - v_o}{v_o t} - \left(\frac{v'_1}{v_o t} - \frac{\beta}{v_o t} \right) \left(1 - \frac{p_o}{p_1} \right)}{\left(1 - \frac{\beta}{v_o} \right) \frac{t_a}{t}} \quad (2)$$

At 100° $t_a = t$ and $\frac{v'_1 - v_o}{v_o t} = \epsilon_p$, the expansion coefficient of the gas under measurement. The value of $\left(1 - \frac{p_o}{p_1} \right)$ may be obtained in terms of the constants of the equation, for since $p_1 - p_o = \phi_o - \phi_1$; $\left(1 - \frac{p_o}{p_1} \right)$ may be taken

equivalent to $\frac{A}{p_o} \left(\frac{1}{v_o^2} - \frac{1}{v_1^2} \right)$ or $\frac{A \epsilon_p t}{R^2 T_o^2} \left(\frac{2 + \epsilon_p t}{1 + \epsilon_p t} \right) p_o$ assuming $p v = RT$ for v_o

and v_1 . The equation for ϵ_p may now be reduced to the following equation

$$\epsilon_p = \epsilon + \left[\epsilon_p \frac{A(2 + \epsilon t)}{R^2 T_o^2 (1 + \epsilon t)} - \frac{\beta}{RT_o^2} \right] p_o - \left[\frac{A \beta \epsilon_p (2 + \epsilon t)}{R^3 T_o^3 (1 + \epsilon t)^2} \right] p_o^2. \quad (3)$$

Using 1 mm. of mercury as the unit of pressure, substitution of the numerical values of the constants for air gives the following equation for the mean constant-pressure expansion coefficient between 0° and 100° assuming ϵ as the reciprocal of 273.135,

$$\epsilon_p = 0.00366119 + 12.45 \times 10^{-9} p_o - 4.43 \times 10^{-14} p_o^2. \quad (4)$$

It is to be observed that the constant-pressure coefficient is a function of the temperature interval within which the expansion is measured since the coefficients of p_o and p_o^2 in Equation 3 are a temperature function.

The formula for the constant volume coefficient is more simply obtained. Proceeding as before

$$\left[\frac{\pi_1 - \pi_o}{\pi_o t} \right] \omega = \epsilon = \frac{p_1 - p_o}{(p_o + \phi_o) t}$$

Constant ω is identical with constant volume and therefore $\phi_1 = \phi_o$ at all temperatures is constant. $\frac{p_1 - p_o}{p_o t}$ is defined as ϵ_v the constant volume coefficient of the actual gas and consequently

$$\epsilon_v = \epsilon + \epsilon \frac{\phi_o}{p_o} = \epsilon + \frac{A}{R^2 T_o^3} p_o. \quad (5)$$

The numerical values of the constants for air give the following equation where the pressure unit is mm.,

$$\epsilon_v = 0.00366119 + 12.93 \times 10^{-9} p_o. \quad (6)$$

It is to be noted that the pressure coefficient is independent of the temperature.

TABLE V.

THE VALUES OF THE EXPANSION COEFFICIENTS OF AIR CALCULATED IN THE ABOVE MANNER TOGETHER WITH THOSE MEASURED BY REGNAULT AND CHAPPUIS.

p_o .		$\epsilon_p \times 10^3$.		p_o .		$\epsilon_v \times 10^3$.	
Mm.	Found.	Calc.		Mm.	Found.	Calc.	
760	3.67060 (R)	3.67063		760	3.66500 (R)	3.67100	
1000	3.67282 (C)	3.67360		1002	3.67440 (C)	3.67412	
2525	3.69440 (R)	3.69230		2000	3.69030 (R)	3.68700	
2620	3.69640 (R)	3.69380					

R = Regnault

C = Chappuis

The Absolute Ice-Point Temperature.

The thermodynamic equation for the Joule-Thomson effect may be written as follows,

$$\mu c_p = T^2 \frac{\partial \frac{v}{T}}{\partial T}. \quad (7)$$

Integration of this equation leads to the equation of the constant pressure gas thermometer

$$\frac{v}{T} - \frac{v_0}{T_0} = c_p \int_{T_0}^T \frac{\mu}{T^2} dT = J_0^{100}. \quad (8)$$

The expansion coefficient ϵ_p is defined through the equation $v_{100} = v_0 (1 + \epsilon_p 100)$ and for the fixed points 0° and 100° , Equation 8 may be rearranged to give T_0 , the absolute temperature of the ice point.

$$T_0 = \frac{1}{\epsilon_p - \frac{T_{100}}{v_0 100} J_0^{100}}.$$

The integration of the Joule-Thomson effect member may be made by using the value of μ formed from the equation of state and is as follows.

$$c_p \int_0^{100} \frac{\mu}{T^2} dT = \frac{2A}{R} \int_0^{100} \frac{dT}{T^3} - \beta \int_0^{100} \frac{dT}{T^2} = 1.963 \times 10^{-3}.$$

The ice-point temperature becomes then where the pressure is in mm.,

$$T_0 = \frac{1}{\epsilon_p - 12.46 \times 10^{-9} p_0}.$$

Using the values of the expansion coefficients at constant pressure given in Table V gives the values of T_0 appearing in Table VI.

TABLE VI.

p_0 . mm.	$\epsilon_p \times 10^8$.	ϵ_p .	$\frac{1}{\epsilon_p}$.	T_0 .	μ values used.
760	3.67060	Regnault	272.435	273.139	Calc.
1000	3.67282	Chappuis	272.270	273.197	Calc.
1000	3.67282	Chappuis	272.270	273.36	Hoxton
1000	3.67360	Calc.	272.212	273.305	Hoxton
2525	3.69440	Regnault	270.681	273.021	Calc.
1000	3.67282	Chappuis	272.270	273.273	{ Joule and Thomson
1000	3.67360	Calc.	272.212	273.215	{ Buckingham
760	3.67063	Calc.	272.431	273.135	Calc.

It is evident that Regnault's value at 760 mm. and Chappuis' at 1000 mm. for the expansion coefficient are different when reduced to the same

pressure, by about 1 part in 4500, but also that the value of T_0 from Regnault's coefficient (760 mm.) is more nearly in accord with the probable values of T_0 , which latter is certainly not lower than 273.1 nor greater than 273.15. The 2525 mm. observation of Regnault is not sufficiently exact (1 part in 1700) for the present purpose for at such a pressure the distortion of the thermometer bulb by pressure becomes a serious factor.

The values of T_0 derived from the measured values of ϵ_p and ϵ_v for nitrogen, hydrogen and helium have been given in a previous paper¹⁸ and in the method of calculation employed, use was made of the pressure coefficients alone derived from the equation of state for the respective gases. In this method of computing T_0 in no case does T_0 come out greater than 273.153 while the most trustworthy expansion coefficients (ϵ_v) measured by Day and Clement, ranging in initial pressure from 314 mm. to 985 mm. give 273.133, 273.128, 273.147 and 273.139 or a mean value of 273.137. The expansion coefficients of the gases referred to lead to values of T_0 which indicate therefore that Chappuis' ϵ_p value of air at 1000 mm. is too small. The hydrogen ϵ_v and ϵ_p values of Chappuis, indeed, give by the same method of calculation $T_0 = 273.147$, and 273.115, respectively.

The conclusion appears inevitable, therefore, that the ice-point temperature as calculated from the Chappuis 1000 mm. value is too large because the latter value is too small by about one part in 4700 and the experimental values of μ correlated as a function of the temperature to correct the ϵ_p value are too large. The last horizontal entry in Table VI shows that the μ equation derived from the equation of state gives with the calculated value of ϵ_p an ice-point temperature (273.135) in accord with values of this constant obtained by other methods from the data on several gases.

If this value ($T_0 = 273.135$) is accepted there is thus no escape from the conclusion that Chappuis' 1000 mm. ϵ_p value for air is in error and at all events inconsistent with T_0 deduced from his values obtained for other gases.

There is, however, still another method which may be used to obtain T_0 which is independent of any equation of state. This consists simply of plotting the values of ϵ_p and ϵ_v with the corresponding pressures and finding where the most representative line cuts the ϵ axis. Such a plot is given in Fig. 1 wherein there have been drawn the lines for ϵ_p and ϵ_v derived from the respective equations of state as a function of the pressure for the several gases; and the dimensions of the original chart are such that 1 mm. indicates 1 part in 90,000 for ϵ . The most numerous and usable data are those for nitrogen; the series of Chappuis' ϵ_v values are higher than those of Day and Clement, but, nevertheless, the representative line for Chappuis' data cuts the ϵ axis at about 3.66132×10^{-3} giving

¹⁸ THIS JOURNAL, 42, 54 (1920).

$T_0 = 273.126$. The Day and Clement values are clearly represented by the line resulting from the equation of state, and accordingly T_0 would be about 273.14. The constant-pressure values for nitrogen due to Eumorphopoulos obtained with the use of a quartz-bulb thermometer lead by extrapolation to $T_0 = 273.147$. The mean of all three values is close to 273.135. It will be noted in addition that the pressure coefficients

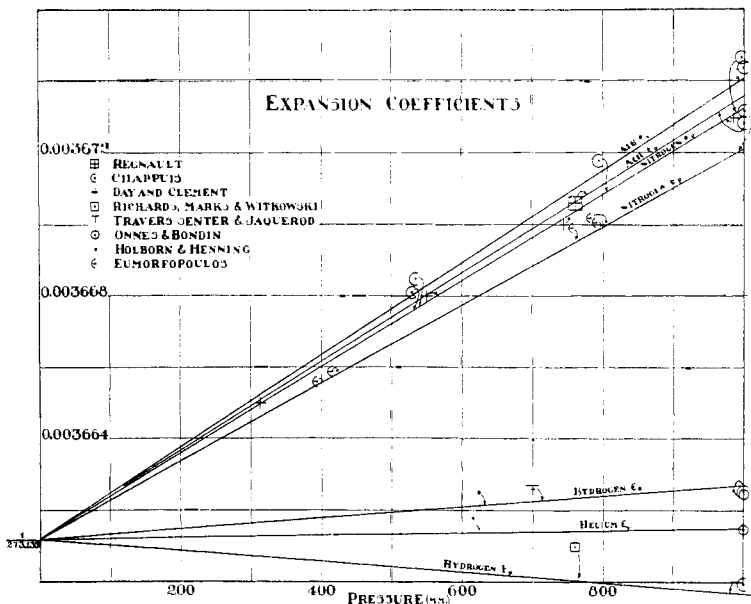


Fig. 1.

for ϵ_p and ϵ_v in the case of hydrogen are nearly equal numerically, but of opposite sign. The mean value of the two coefficients should be close to $\frac{1}{T_0}$ and, in fact, amounts to 3.366123×10^{-3} whose reciprocal is 273.128.

Helium⁸ is so nearly an ideal gas that almost any equation of state which approximately represents the isotherms should suffice. The equation which I have obtained based on the work of the Onnes laboratory leads to $T_0 = 273.113$. The mean of the graphically extrapolated ϵ_v and ϵ_p values then of Chappuis' ϵ_v , nitrogen values, Eumorphopoulos' ϵ_p , nitrogen values, Day and Clement's ϵ_v , nitrogen values is 273.137. Including the single helium ϵ_v value of Holborn and Henning, the mean T_0 amounts to 273.131.

It appears clear that T_0 must be taken as very nearly 273.13 and the probability is that it does not exceed 273.14 in value, while Berthelot's value, 273.09, is judged therefore to be too low. With T_0 assured, the conclusion is inevitable that all the measured Joule-Thomson numbers

are too large. A study of the original Joule-Thomson papers and all of the later communications offers no certain clue as to the probable reason for obtaining too large numbers, but if heat leaks or radiation effects of all kinds as well as "velocity cooling" disturbances may be assumed disposed of, there remain only two conceivable methods of changing the temperature of an isolated quantity of gas, in the sense that the internal energy change shall be equal to the energy element either $p dv$ or $d(pv)$. In the former case, the temperature change produced per atmosphere at one atmosphere is about 70° , whereas in the latter it does not much exceed 0.25° .

The fine pores of the plug offer a resistance to the passage of the gas such as to maintain the pressure difference and it issues from the low-pressure face of the plug in fine streams of high velocity which presumably persist momentarily. There could be, therefore, local differences in density which result in further expansion against the gas on the low pressure side. It is in this region that a lower temperature results and only at a considerable distance from the plug would density and temperature differences be inappreciable. Unfortunately there is great difficulty in avoiding other sources of error such as heat conductance or radiation at a distance from the plug. It was noticed that the pressure coefficient observed by Hoxton is larger and this is the trend the measurements would take since the temperature change for the fine stream-persistence

suggested above is given by the equation $\frac{dt}{dp} = \frac{T \left(\frac{\partial v}{\partial T} \right)_p}{C_p} \equiv \frac{RT}{p} \cdot \frac{1}{C_p}$ when $pv = RT$.

That is to say the effect of finite density differences expressed as a temperature change of this kind would be less at higher pressures. Thus there would result an apparent pressure coefficient much too large; furthermore, Joule-Thomson measurements made with high pressure differences would be more reliable than those with small pressure differences as is evident in the work of Bradley and Hale.

It is difficult to infer much from the work of Joule and Thomson on other gases than air, since in no case were the gases sufficiently pure to warrant great confidence in the numbers obtained. It is true in the case of nitrogen, oxygen, hydrogen and carbon dioxide, the attempt was made to correct for the impurities, but the relation between the Joule-Thomson effect in a given mixture and the Joule-Thomson effects in the constituents was then, as now, entirely unknown.

An examination of all the Joule-Thomson data available shows that the effect as related to temperature can be adequately represented within the limits of experimental error as a linear function of the inverse abso-

lute temperature as indicated in Fig. 2. This is clearly brought out by comparing the data plotted to different powers of the reciprocal absolute temperature. If the temperature function is linear in the reciprocal absolute temperature, there are no corrections required for the constant volume temperature scale,¹⁹ supporting the form of the equation of state which adequately represents the pressures observed over such a wide range of both pressure and temperature. In any event, a very accurate means of establishing the linearity of the pressure increase with temperature at constant volume does lie in obtaining accurate measurements of the Joule-Thomson coefficients at various temperatures and low pressures (1 to 5 atmospheres) although the experimental difficulties are considerable.

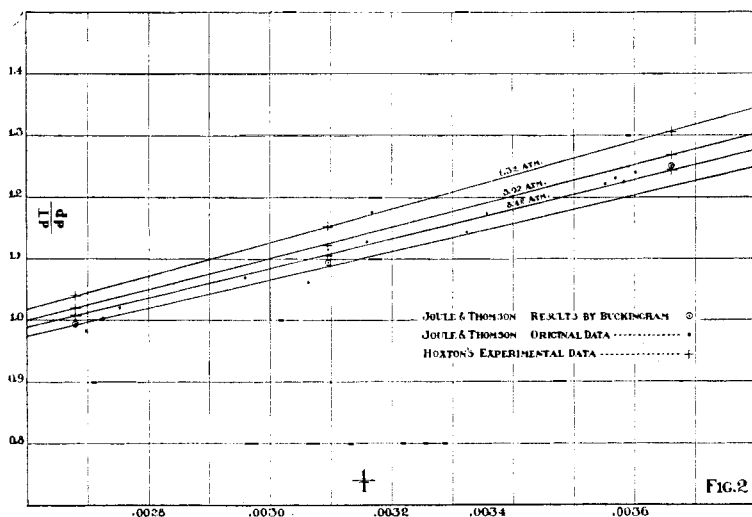


Fig. 2.

There is, however, one other method of attack bearing on the temperature function of the Joule-Thomson coefficient which consists of measuring the constant-volume specific heat at increasing pressures. Joly's data for air appear to indicate an increase of C_v with pressure, but an examination of his data for this gas leaves one entirely unconvinced regarding the dependence of the constant-volume specific heat on pressure. It becomes, in fact, a conviction that C_v is indeed constant from the data given when correction is made for the change in heat capacity of the copper sphere used due to the tension in the copper caused by the pressure of air within, for the compensating sphere on the opposite scale pan was exhausted. An attempt to make this correction follows.

¹⁹ The calculated corrections for the constant-pressure scale from the equation of state for air follow easily from Equation 2 and accord well with the nitrogen scale corrections although several thousandths of a degree smaller than those calculated by Hoxton.

The Joly Constant-Volume Specific-Heat Values for Air.

Joly presents seven measurements in the case of air at pressures varying from about 7 atmospheres to about 27 atmospheres. The copper spheres weighed 92.4 gr. and had a capacity of 159.8 cc. at 15°. There was, therefore, in each sphere 10.36 cc. of copper and the internal and external radii were respectively 3.3660 and 3.4373 cm. with a wall thickness of 0.0713 cm. Considering a patch on the surface of the sphere, it is perceived to be stretched under the internal pressure in two dimensions while the stresses along the radius will be neglected. Considering the thickness moreover as insignificant in comparison with the radius the tension on the copper section of a great circle due to the pressure of one atmosphere on a great area will be 24 atmospheres per cc. of copper. Consider then that each cubic centimeter of the copper has applied to its 4 faces intersected by a plane a uniform pull outward of 24 atmospheres for each atmosphere of gaseous pressure within the actual copper sphere. Assume further that a uniform pull of $\frac{2}{3} \times 24 = 16$ atmospheres uniform tension on each face of the cubic centimeter will represent with sufficient approximation the actual state of tension in the copper sphere.

The change of specific heat with pressure is given by the equation,

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 v}{\partial T^2}\right)_p.$$

This equation is to be applied to the case of a tension in the material and $\left(\frac{\partial^2 v}{\partial T^2}\right)_p$ assumed constant. Designating the specific heat of copper at zero tension as C_{p_0} there is obtained for the difference of the specific heats at any tension p ,

$$C_p - C_{p_0} = \left(\frac{\partial^2 v}{\partial T^2}\right)_p p.$$

Since the compensating sphere was exhausted it is unnecessary to subtract 1 from p to take account of the fact that the surrounding pressure was that of the atmosphere.

From Henning's recent work on the expansion of copper from -191° to 500° the following equation was formulated giving the true expansion at every temperature T ,

$$\frac{1}{v_0} \frac{\partial v}{\partial T} = 31.94 \times 10^{-6} + 6.347 \times 10^{-8} T - 3.7 \times 10^{-11} T^2, \text{ and}$$

$$\frac{1}{v_0} \frac{\partial^2 v}{\partial T^2} = 6.35 \times 10^{-8} - 7.4 \times 10^{-11} T.$$

The numerical equation for the difference of the specific heats becomes for the 10.36 cc. of copper composing the sphere in calories per degree per atmosphere tension

$$C_p - C_{p0} = 5.07 \times 10^{-5} p$$

Joly's equation of the specific heat of air at constant volume is given as $C_v = 0.17151 + 0.02788 \times \text{density}$. The same equation in which the pressure is the variable instead of the density is $C_v = 0.17151 + 3.3 \times 10^{-5} p$. The coefficient of the increase of the specific heat of the copper sphere used to contain the gas is as has been shown to be 5.07×10^{-5} a number which is of the order of magnitude of Joly's coefficient 3.3×10^{-5} .

The actual experimental values are given in the order of pressure increase in the first column of Table VII. The third column gives the

TABLE VII.

The Joly Constant-Volume Specific Heat of Air.

C_v Air measured.	Pressure Atm.	Tension Sp. Heat corr.	C_v Air corrected.	Deviation from mean.
0.17202	6.81	0.00035	0.17169	+0.00048
0.17111	9.56	0.00049	0.17062	-0.00059
0.17193	13.56	0.00069	0.17124	+0.00003
0.17192	14.53	0.00074	0.17118	-0.00003
0.17252	14.58	0.00074	0.17178	+0.00057
0.17223	23.35	0.00119	0.17104	-0.00017
0.17225	26.62	0.00135	0.17090	-0.00031

Mean value 0.17121

correction corresponding to the pressure given in the second column as calculated by means of the specific-heat difference equation above for the copper sphere, while the fourth column contains the final specific-heat values whose mean is 0.1712. The last column contains the deviations from the mean value 0.1712. It is evident that the constant-volume specific heat of air is independent of pressure over the range of about 27 atmospheres at least.

The equation for the change of the constant-volume specific heat with volume is

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_v.$$

The left hand member is zero as shown by the measurements of Joly and hence $\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0$ or $\left(\frac{\partial p}{\partial T}\right)_v = \text{const.}$ which when integrated again gives $[p]_v = \text{const.} \times T + \text{another constant.}$ The pressure is therefore a linear function of the temperature and at low pressures the Joule-Thomson effect must vary with respect to temperature linearly with the

inverse of the absolute temperature. This is also, as stated above, the conclusion from the data on the volume, pressure and temperature of air as given by my equation. The experimental data, in fact, of the Joule-Thomson effect at not too high pressures are represented by an equation of the form $\mu = \frac{a}{T} - b$ as is indicated by Fig. 2.

The Joly data indicating independence of pressure of the constant-volume specific heat indicate also of course that the constant-volume air thermometer reads directly on the absolute scale and requires no correction. While explicit experimental confirmation is not as complete in the case of nitrogen, upon which our temperature scale rests, the same statement applies.¹⁸

Summary.

1. The Joule-Thomson coefficients of air have been calculated from my equation of state for air based on the measurements of pressure, volume and temperature by Amagat, and have been compared with the coefficients as measured by Joule and Thomson, Noell and Hoxton. The measurements of Joule and Thomson accord well with the calculations except at zero degrees, while the recent careful measurements of Hoxton exceed the calculated values between 0 and 100° by about 15%.

2. The value of the ice-point absolute temperature (273.36) deduced from the Chappuis 1000 mm. constant-pressure expansion coefficient for air corrected by means of the Hoxton Joule-Thomson coefficients is too large, due to the fact that the Chappuis expansion coefficient is too small and the Joule-Thomson values too large. The calculated expansion coefficient and the Hoxton Joule-Thomson coefficients lead to $T_0 = 273.197$. The value $T_0 = 273.135$ is on the other hand shown to be substantially correct in that this value is the mean value obtained by graphically extrapolating the measured constant volume and constant-pressure expansion coefficients of air, nitrogen, hydrogen and helium measured at various ice-point pressures. The value 273.135 is also the mean of T_0 as deduced from the same data by means of the equations of state for the respective gases.

3. The pressure coefficient at zero of the Joule-Thomson coefficient as obtained by Hoxton is shown to be much larger than that obtained by other observers. The pressure coefficient given by Vogel and Noell (8.8×10^{-4}) is twice that calculated from the equation (4.5×10^{-4}) for low pressures, but agrees approximately with that calculated for high pressures, by means of the equation of state. The Bradley and Hale average pressure coefficient to 200 atmospheres at 0° is shown to be 7.3×10^{-4} while the average value over this range computed by the equation of state

is 7.1×10^{-4} . The Joule-Thomson coefficient itself at 1 atmosphere as given by Vogel and Noell is 0.277° and from Bradley's work 0.268° . The equation gives 0.261° .

4. An explanation of the discrepancies in the observed Joule-Thomson numbers is suggested which assumes that at the low-pressure surface of the plug a temperature drop is superposed on the Joule-Thomson temperature change due to the momentary persistence of the fine gas streams issuing from the pores of the plug and their subsequent expansion. It is shown that this effect would produce a large apparent pressure coefficient since the specific effect of the velocity-persistence-effect is shown to vary inversely as the pressure. The value of the measured Joule-Thomson effect at 0° and one atmosphere pressure is given as 0.303 by Hoxton, while that deduced from the high-pressure measurements of Bradley and Hale is 0.268 , as compared with 0.261 calculated by the equation of state.

5. The Joly constant-volume specific heats of air are considered, and it is shown that a correction is required to compensate for the increased specific heat of the copper sphere used by Joly to contain the air. The corrected Joly values are shown to be independent of pressure, which fact confirms the validity of the form of the air equation of state employed. As a further consequence, it is pointed out that at low pressures the Joule-Thomson effect must vary inversely with the absolute temperature. Another important consequence is that the constant-volume air-thermometer scale reads directly on the absolute scale and therefore requires no correction.

CAMBRIDGE, 39, MASS.

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COMPOUND FORMATION AND SOLUBILITY IN SYSTEMS OF THE TYPE, FORMIC ACID:METAL FORMATE.

BY JAMES KENDALL AND HOWARD ADLER.

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The experimental work presented in the following pages has been carried out with the object of determining how far the conclusions arrived at in a similar study of systems of the type sulfuric acid: metal sulfate¹ may be considered as generally valid for systems HX : RX. In order to make the test as rigorous as possible, a careful selection of an acid diverse in all properties from sulfuric acid was necessary. Formic acid was finally chosen as a typical weak monobasic organic acid, contrasting strikingly with sulfuric acid, a typical strong dibasic inorganic acid. It

¹ Kendall and Landon, *THIS JOURNAL*, **42**, 2131 (1920); Kendall and Davidson, *ibid.*, **43**, 979 (1921).