AUGUST 1, 1929 PHYSICAL REVIEW VOLUME 34

THE JOULE-THOMSON EFFECT AND HEAT CAPACITY AT CONSTANT PRESSURE FOR AIR.

By Oscar C. Bridgeman[1]
Research Laboratory of Physical Chemistry
Massachusetts Institute of Technology*

(Received June 10, 1929)

Abstract

The constants for air in the equation of state of Beattie and Bridgeman are evaluated from the p-v-T data of Holborn and Schultze, and this numerical equation is used to compute μC_p at various temperatures and densities. From the C_p data at one atmosphere of the Reichsanstalt for air, corresponding values of C_p at the same temperatures and densities are calculated by means of the equation of state. The values of μ obtained from these two sets of calculations are plotted along isotherms against the corresponding pressures and the values at even pressures and various temperatures are in good agreement with the experimental data of Roebuck. The computed C_p data are compared with those of Roebuck and of Holborn and Jakob and are in good agreement with the values obtained by these experimenters. The Joule-Thomson inversion curve obtained from the equation of state is in good agreement with the experimental values given by Roebuck.

All the thermodynamic properties of a substance may be evaluated over a given range of variables, if pressure-volume-temperature data are available and if any thermal property is known as a function of temperature over the range concerned. The evaluation in general can be effected most conveniently by means of an equation of state which represents the pressure-volume-temperature data. For accuracy, it is necessary that the equation of state reproduce all the pressure and volume trends with temperature as well as the actual pressures. If an equation satisfying these requirements is available, it is possible to calculate all the thermodynamic properties of a substance with an accuracy comparable to that obtained by direct experimentation, and hence such values serve a useful purpose in cases where data have not been obtained directly or where the field has only been partially covered.

Recently J. A. Beattie and the author[2] have formulated an equation of state which reproduces the data on 10 gases to 0.1–0.2 percent, and which gives derivatives of considerable accuracy. This equation is of the form

$$p=\frac{RT(1-\epsilon)}{v^2}[v+B]-\frac{A}{v^2} \tag{1}$$

where $B=B_0(1-b/v)$; $A=A_0(1-a/v)$ and $\epsilon=c/vT^3$. The existence of good p–v–T data and C_p data at one atmosphere for air has made it possible to

---

* Contribution No. 204.

[1] National Research Fellow in Chemistry.

[2] Beattie and Bridgeman, J. Am. Chem. Soc. **49**, 1665 (1927); ibid, **50**, 3133 (1928); ibid, **50**, 3151 (1928); Proc. Am. Acad. Arts. Sci. **63**, 229 (1928).

compute the Joule-Thomson coefficients and C_p at various temperatures and pressures, and thereby test the equation of state by comparing the computed values with those determined experimentally.

The most recent, accurate p–v–T data on air have been published by Holborn and Schultze[3] who covered the range from 0° to 200°C up to pressures of approximately 100 atmospheres. The constants in the equation of state (1) were evaluated from these data using the method previously outlined.[2] The constants are as follows:[4]

$$R=0.08206 \qquad c=\ 0.12\times 10^6$$

$$B_0=0.04070 \qquad b=-0.02174$$

$$A_0=1.0763 \qquad a=\ 0.01697$$

$$T=t+273.13$$

in units of liters per mole, atmospheres and absolute Centigrade degrees. A comparison of the observed and calculated values, expressed in the original units, is given in Table I. The agreement is very good, the average deviation in pv over the whole field being 0.0002 or 0.014 percent.

TABLE I. *Comparison of observed pv products with values computed from the equation of state. Pressures in meters of mercury; temperatures in °C; pv products in Reichsanstalt units referred to pv = 1.0000 at 0°C and 1 meter of mercury.*

Pressure		Values of pv				
		200°	150°	100°	50°	0°
10	obs.	1.7406	1.5555	1.3695	1.1825	0.9934
	o-c	−0.0002	0.0001	0.0001	0.0001	−0.0001
20	obs.	1.7484	1.5612	1.3726	1.1818	0.9870
	o-c	0.0000	0.0002	0.0002	0.0002	−0.0001
30	obs.	1.7565	1.5674	1.3762	1.1818	1.9817
	o-c	0.0000	0.0002	0.0002	0.0002	0.0000
40	obs.	1.7650	1.5740	1.3805	1.1826	0.9774
	o-c	0.0000	0.0002	0.0003	0.0001	0.0000
50	obs.	1.7739	1.5811	1.3854	1.1841	0.9742
	o-c	0.0001	0.0001	0.0003	−0.0001	0.0001
60	obs.	1.7831	1.5887	1.3909	1.1864	0.9720
	o-c	0.0000	0.0001	0.0003	−0.0003	0.0002
70	obs.	1.7927	1.5967	1.3970	1.1804	0.9709
	o-c	0.0001	0.0001	0.0004	−0.0006	0.0003
80	obs.	1.8027	1.6052	1.4037	1.1932	0.9708
	o-c	0.0002	0.0001	0.0005	−0.0007	0.0004

Total average deviation = 0.0002

---

[3] Holborn and Schultze, Ann. d. Physik **47,** 1089 (1915); see also Holborn and Otto, Zeits. f. Physik **10,** 367 (1922); ibid, **23,** 77 (1924); ibid, **33,** 1 (1925).

[4] These constants are somewhat different from the values obtained by correlating all the p-v-T data on air in the literature (see ref. 2). The present data were employed since they are the most recent and are the only set of values which cover the temperature range used by Roebuck in his Joule-Thomson work.

For the evaluation of μC_p in terms of the equation of state, it is convenient to write equation (1) in the form

$$p=\psi T-\phi-\Gamma/T^2 \tag{2}$$

where

$$\psi=\frac{R}{v^2}[v+B]\ ;\ \phi=\frac{A}{v^2}\quad\text{and}\quad\Gamma=\frac{\psi_c}{v}$$

and hence all three are functions of volume only. Differentiating (2) with respect to temperature at constant pressure, there results

$$\left(\frac{\partial v}{\partial T}\right)_p=\frac{\psi+2\Gamma/T^3}{\psi'T-\phi'-\Gamma'/T^2}$$

where ψ', ϕ', and Γ' are the first derivatives with respect to volume. The usual expression for the Joule-Thomson effect then becomes

$$\mu C_p=T\left(\frac{\partial v}{\partial T}\right)_p-v=\frac{\psi T+2\Gamma/T^2}{\psi'T-\phi'-\Gamma'/T^2}-v. \tag{3}$$

By substitution of the respective volume functions and rearrangement, equation (3) reduces at zero pressure to the following

$$\mu C_{p_0}=\frac{2A_0}{RT}-B_0+\frac{4c}{T^3}\cdot \tag{4}$$

In equations (2) and (3), v and T are the independent variables and hence values of μC_p were calculated for a number of constant densities at various temperatures from 0° to 280°C. These densities were evenly spaced (every mole per liter) and the number used on each isotherm was such as to correspond to a pressure range from 0 to about 250 atmospheres. The values at zero pressure were obtained from equation (4). The use of p and T as the variables would be very laborious since along any isobar there would be a different value of the volume functions in equation (3) at each temperature.

To obtain the values of μ from μC_p, it is necessary to have the corresponding values for C_p. The heat capacity of air at a pressure of one atmosphere has been measured at the Reichsanstalt[5] over a considerable range of temperature and can be represented by the following formula:

$$C_p=0.2405+0.000019t.$$

The computation of C_p directly at higher pressures fom the one atmosphere values requires the use of the second derivative of volume with respect to temperature at constant pressure and the integration of a complicated function of v and T at constant temperature from 1 to p atmospheres. This function is too involved for convenient manipulation and so ΔC_v and C_p-C_v

---

[5] Scheel and Heuse, Ann. d. Physik **37,** 79 (1912); ibid, **40,** 492 (1913); Heuse, Ann. d. Physik **59,** 86 (1919); Holborn and Austin, Wissensch. Abh. **4,** 131 (1905); Holborn and Henning, Ann. d. Physik **18,** 739 (1905); ibid, **23,** 810 (1907).

were used, both of which are comparatively simple functions of v and T. As given by the equation of state, these relations are

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v = -\frac{6\Gamma}{T^3}$$

$$\Delta C_v = C_v - C_{v0} = -\frac{6}{T^3}\int_\infty^v \Gamma dv$$

$$= \frac{6Rc}{v^2T^3}\left[v + \frac{1}{2}B_0 - \frac{1}{3}\frac{bB_0}{v}\right] \tag{5}$$

$$C_p - C_v = T\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_v = -\frac{T(\psi + 2\Gamma/T^3)^2}{\psi'T - \phi' - \Gamma'/T^2}$$

$$= (\mu C_p + v)(\psi + 2\Gamma/T^3) \tag{6}$$

$$C_p = C_{v0} + \Delta C_v + [C_p - C_v]. \tag{7}$$

The C_p values of the Reichsanstalt at one atmosphere were changed to C_v values at zero pressure using equations (5) and (6) and these can be accurately represented by the following relation over the temperature range from 0° to 300° in 15° calories per gram.

$$C_{v_0} = 0.1714 + 2.3 \times 10^{-5}t - 1.0 \times 10^{-8}t^2 \quad (0° - 300°\text{C}).$$

A series of values of ΔC_v and $C_p - C_v$ were computed by (5) and (6) corresponding to the densities and temperatures used for μC_p and were added to

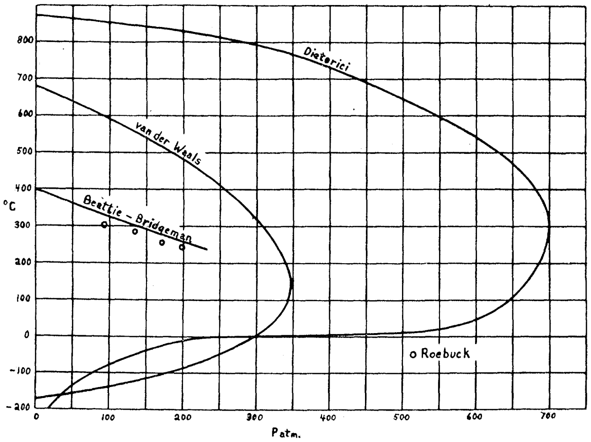

Fig. 1.

the C_{v0} values to give C_p according to relation (7). These C_p data were then divided into the corresponding values of μC_p thereby giving μ in terms of density and temperature as the variables.

The transformation of variables from density ($1/v$) to pressure was effected by plotting μ along isotherms against the pressures corresponding to these even densities, which were calculated by means of the equation of state. From this plot, the values of μ were read off at even pressures. A comparison of these calculated values with those obtained experimentally by Roebuck[6] is given in Table II, the pressures and temperatures being those used in his paper. The agreement is satisfactory with the exception of the 0° isotherm, and the part of the 25° isotherm at higher pressures. Examination of the original data of Roebuck indicates that his values of μ are considerably more uncertain in this portion of the field. On the other isotherms, the agreement is essentially the same at high as at low pressures, notwithstanding that the constants of the equation of state were deduced from data extending only to 100 atm. and the pressure range of Table II is a little more than twice that amount.

TABLE II. *Comparison of computed values of μ with the experimental values of Roebuck.*
$\mu \times 10^3$ (°C/atm.)

Press. (atm.)		0°	25°	50°	75°	100°	150°	200°	250°	280°
1	obs.	266	227	189	158	133	93	63	40	30
	calc.	274	227	189	159	134	95	66	43	32
	o-c	−8	0	0	−1	−1	−2	−3	−3	−2
20	obs.	249	212	178	149	124	86	56	35	25
	calc.	259	213	177	148	124	87	59	38	28
	o-c	−10	−1	1	1	0	−1	−3	−3	−3
60	obs.	214	182	153	128	106	71	45	25	16
	calc.	225	185	152	126	105	71	47	28	19
	o-c	−11	−3	−1	2	1	0	−2	−3	−3
100	obs.	178	152	128	107	89	59	35	16	8
	calc.	190	156	128	106	87	58	36	19	11
	o-c	−12	−4	0	1	2	1	−1	−3	−3
140	obs.	145	124	105	88	72	47	26	9	1
	calc.	157	129	106	87	71	46	26	11	4
	o-c	−12	−5	−1	1	1	1	0	−2	−3
180	obs.	113	97	83	70	58	37	19	3	−5
	calc.	129	106	87	71	57	35	18	4	−2
	o-c	−16	−9	−4	−1	1	2	1	−1	−3
220	obs.	81	72	63	54	45	29	13	−2	−11
	calc.	106	88	71	58	46	26	11	−2	−8
	o-c	−25	−16	−8	−4	−1	3	2	0	−3

In Table III (a) the calculated values of μ at 1 atm. and at 0°, 50° and 100° are compared with those given by Roebuck,[6] Joule and Thomson,[7] Noell[8] and Hoxton,[9] while in Table III (b) a comparison is made with data

---

[6] Roebuck, Proc. Am. Acad. Arts Sci. **60,** 537 (1925).

[7] Joule and Thomson, Scientific Papers (Joule), **11,** p. 16. Collected Papers (Thomson), **1,** p. 333.

[8] Noell, Selbstverlag d. Verein. Deut. Ing., No. 184, Julius Springer, Berlin, 1916.

[9] Hoxton, Phys. Rev. (2), **13,** 438 (1919).

computed from the measurements of Bradley and Hale[10] by Keyes.[11] The agreement between the results of Bradley and Hale and those calculated at 0° by the author adds confirmation to the opinion that the data of Roebuck are in error at this temperature.[12]

TABLE III (a). *Comparison of observed and computed values of μ at 1 atmsophere pressure.*

Temp.	Joule-Thomson	Noell	Hoxton	Roebuck	Computed
0°C	0.275	0.278	0.303	0.266	0.274
50°	0.204	0.185	0.226	0.189	0.189
100°	0.147	0.125	0.170	0.133	0.134

TABLE III (b). *Comparison of observed and computed values of μ at 0°C.*

Pressure	Bradley & Hale	Computed
50 atm.	0.233	0.234
100	0.192	0.190
150	0.152	0.149
200	0.117	0.117

Porter[13] has pointed out that the Joule-Thomson inversion curve, conditioned by $\mu = 0$, is a very sensitive test of an equation of state. Points on this curve have been computed by means of the equation of state (1) and the agreement with the experimental inversion points obtained by Roebuck is shown in the figure, where for comparison curves calculated by means of the equations of van der Waals and Dieterici are also included. These latter curves were taken from Roebuck's paper. Considering the accuracy with which Joule-Thomson or p–v–T measurements must be made in order to obtain accurate inversion points either experimentally or by computation, the agreement of the Beattie-Bridgeman curve with the data of Roebuck is satisfactory.

The computed values of C_p based on the one atmosphere data of the Reichsanstalt and the equation of state were transformed from units of liter-atmospheres per mole into 15° calories per gram (one 15° calorie per gram equals 1.1960 liter-atmospheres per mole, where the molecular weight of air is taken as 28.960).[14] These values were plotted against the corresponding pressures in a similar manner to that employed for μ. Values were read off at even pressures and are compared with the data of Roebuck in Table IV. The agreement is good, being about 1 percent over practically the entire field, the main deviations occurring at low temperatures and high pressures similarly to those found for μ. Since the data of Roebuck are obtained from his measurements of the Joule-Thomson coefficients, this is to be expected.

---

[10] Bradley and Hale, Phys. Rev. (1), **29,** 258 (1909).

[11] Keyes, J. Am. Chem. Soc. **43,** 1452 (1921).

[12] At 150 atm. the value of 0.1515 is used instead of 0.1615 as given by Keyes, since the former lies on a smooth curve through the other points, and apparently is the correct value.

[13] Porter, Phil. Mag. (VI) **11,** 554 (1906).

[14] Beattie and Bridgeman, J. Am. Chem. Soc. **50,** 3151 (1928).

TABLE IV. *Comparison of computed values of C_p with the experimental values of Roebuck. C_p in 15° calories per gram.*

Press. (atm.)		0°	25°	50°	75°	100°	150°	200°	250°	280°
20	obs.	0.249	0.249	0.248	0.248	0.247	0.247	0.246	0.247	0.247
	calc.	0.250	0.249	0.248	0.247	0.247	0.246	0.247	0.247	0.247
	o-c	−0.001	0.000	0.000	0.001	0.000	0.001	−0.001	0.000	0.000
60	obs.	0.266	0.263	0.260	0.258	0.256	0.253	0.251	0.250	0.249
	calc.	0.274	0.266	0.260	0.257	0.255	0.252	0.251	0.250	0.250
	o-c	−0.008	−0.003	0.000	0.001	0.001	0.001	0.000	0.000	−0.001
100	obs.	0.280	0.276	0.272	0.268	0.265	0.260	0.257	0.254	0.252
	calc.	0.298	0.283	0.273	0.267	0.263	0.258	0.255	0.254	0.253
	o-c	−0.018	−0.007	−0.001	0.001	0.002	0.002	0.002	0.000	−0.001
140	obs.		0.287	0.282	0.277	0.273	0.266	0.261	0.257	0.254
	calc.		0.299	0.285	0.276	0.270	0.263	0.259	0.257	0.256
	o-c		−0.012	−0.003	0.001	0.003	0.003	0.002	0.000	−0.002
180	obs.		0.296	0.290	0.284	0.279	0.271	0.264	0.260	0.257
	calc.		0.314	0.296	0.285	0.277	0.268	0.262	0.259	0.258
	o-c		−0.018	−0.006	−0.001	0.002	0.003	0.002	0.001	−0.001
220	obs.		0.302	0.296	0.289	0.284	0.275	0.268	0.262	0.259
	calc.		0.327	0.306	0.292	0.283	0.272	0.265	0.262	0.260
	o-c		−0.025	−0.010	−0.003	0.001	0.003	0.003	0.000	−0.001

In Table V a comparison is made with the data of a number of investigators[15] at 59° and various pressures. The data of Holborn and Jakob[16] are expressed as the mean heat capacity between 20° and 100°C which is taken by Partington and Schilling as equivalent to 59°. The data of Roebuck are calculated from those at 60° as given in his paper. Very good agreement is obtained with the values of Holborn and Jakob and of Roebuck.

TABLE V. *Comparison of observed and computed values of C_p at 59°C.*

Press kg/cm²	Holborn & Jakob	Joule & Thomson	Vogel	Noell	Roebuck	Computed
25	0.2490	0.2481	0.2480	0.2493	0.2493	0.2485
50	0.2554	0.2557	0.2543	0.2568	0.2563	0.2557
100	0.2690	0.2721	0.2664	0.2701	0.2699	0.2697
150	0.2821	0.2919	0.2770	0.2812	0.2813	0.2827
200	0.2925	0.3150	0.2853	0.2893	0.2901	0.2942

---

[15] The data of Joule and Thomson, Vogel and Noell are taken from Partington and Schilling, The Specific Heat of Gases, Van Nostrand, New York, 1924, p. 161.

[16] Holborn and Jakob, Forschungsarbeiten d. Verein. Deut. Ing., 187 and 188, 1916. Holborn, Scheel and Henning, Wärmetabellen der Physikalisch-Technischen Reichsanstalt. Friedr. Vieweg & Sohn, Braunschweig, 1919.