Thermodynamic Properties of Helium at High Pressure

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It is shown in the preceding papers[1] that for helium, neon and hydrogen the equation of state

$$vp = R\psi + ap\,(a_0\psi_0 e^{\kappa} - \psi e^{\nu})\,(1 - e^{\eta})$$

is valid. v denotes here the volume (m^3), p the pressure (kg./sq. cm.) and ψ the absolute temperature (°A.). The above equation for helium fairly covers the experimentally investigated region from 800 to 2°A. and from 0 to 15,000 atm. In the present paper, especially, the region of high pressure ($p \geqq 100$ atm.) is investigated, and it is shown that the quantitative definition of the thermodynamic properties in all the regions of state can be made without any variation of the old[2] constants. The equation is based on the so-called "conditions of reality" or on the "theorem of preliminary selection"[3] which points out that not all the mathematical arbitrary functions accompanying the solution of any differential equation can be used to define the structure of equation of state but only those which fulfil the above-mentioned conditions of reality. There are eventually $v \geqq 0$, $\psi \geqq 0$, the "Planck–Hausen's criterion" $(\partial v/\partial p)_t \leqq 0$, etc.[4] Contrary to the molecular-kinetic point of view attacking the knowledge of the individual properties of isolated *particle* (atom, electron, etc.) the thermodynamic theory of equation of state deals with the *matter in bulk* regardless of internal structure of the body. The first theoretical explanation of this method is given by Lord Kelvin using the porous-plug experiment for vp-representation of actual gases. The further attempts in this direction are given by Rudolph Plank, Max Jakob, Eichelberg and others to obtain the equation of state for oxygen and steam.

A very important opportunity for the convenient resolution of the problem of the thermodynamic equation of state has been given by the recent measurements of the compressibility of fluids and solid bodies accomplished in Cambridge (U. S. A.), Charlottenburg (Germany) and Leiden (Netherlands), so that this problem for helium now can be investigated successfully.

Computation of the Exponents κ and ν

At high pressure ($p \geqq 100$ atm.) we have $e^{\eta} \cong 0$. Therefore the preceding equation for the considered region can be rewritten in the simpler form

$$vp = R\psi + ap\,(a_1 e^{\kappa} - \psi e^{\nu}) \qquad (1)$$

where for helium $a_1 = 11\psi_0$, $a = 0.0_51085$, $R = 211.82$ and $\psi_0 = 273.22°$.[5]

The product vp ("volume-work") cannot be negative, for $\psi \geqq 0$. Hence from (I) at $\psi = \infty$ it follows that

$$R - ape^{\nu} \geqq 0 \qquad (2)$$

The minimum of the difference $R - ape^{\nu}$ is defined by the condition

$$1 + p\left(\frac{\partial\nu}{\partial p}\right)_{\psi} = 0 \qquad (3)$$

where the exponent ν is to the first approximation proportional to p^x, *i. e.*

$$\nu = \nu_0 p^x \qquad (4)$$

From the relations (2), (3) and (4) we have

$$\nu_0 \leqq -\frac{1}{xe}\,(a/R)^x \qquad (5)$$

where $e \cong 2.7183$ and for helium $x = {}^1/_4$.[6] Hence $\nu_0 \leqq -0.01245$, and we shall set

$$\nu_0 = -0.0125 \qquad (6)$$

Now the values of the exponent $(\kappa)_{\text{exptl.}}$ for some temperature and pressure can be computed from (I), *i. e.*

$$(\kappa)_{\text{exptl.}} = \lg \frac{\dfrac{(vp)_{\text{exptl.}} - R\psi}{p(v_0p_0)_{1\,\text{atm.}}} + 0.0_{10}1875\,\psi e^{\nu}}{0.0_75631} \qquad (7)$$

where $(v_0p_0)_{1\,\text{atm.}} = 57{,}904$ kgm./kg. is the "Amagat unit" for helium in the meter–kilogram–second system and the $(vp)_{\text{exptl.}}$ values are defined by Wiebe, Gaddy and Heins'[7] and also Bridgman's[8] experimental data. Figures 1 and 2 represent a synthesis of several experimental data

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(1) W. Jacyna, *Z. Physik*, **103**, 61, 67 (1936); **105**, 267 (1937); see also *Phys. Rev.*, **51**, 677 (1937), etc.

(2) See, for instance, W. Jacyna, *Z. Physik*, **95**, 246 (1935), etc.

(3) W. Jacyna, *Bull. Acad. Pol. Sci. Lettres*, **A**, Oct.–Nov., 375 (1934); also *Z. Physik*, **25**, 133 (1924). See also *ibid.*, **101**, 77 (1936).

(4) Starting with these conditions Lévy's problem [see *Compt. rend.*, **87**, 449, 554, 649 and 826 (1878)] on the universality of the generalized form $p = \psi\varphi(v) + \zeta(v)$ of van der Waals' equation is resolved [W. Jacyna, *Z. Physik*, **100**, 205 (1936)].

(5) See W. Jacyna, *Acta Phys. Pol.*, **2**, 419 (1934); **4**, 243 (1935); also *Z. Physik*, **95**, 252 (1935), and **97**, 107 (1935), etc.

(6) W. Jacyna, *ibid.*, **103**, 61 (1936).

(7) R. Wiebe, V. L. Gaddy and Conrad Heins, THIS JOURNAL, **53**, 1721 (1931).

(8) P. W. Bridgman, *Proc. Am. Acad. Sci.*, **59**, 173 (1924); **70**, 1, 285 (1935); **71**, 387 (1936); **72**, 46 (1937); *J. of Geol.*, **44**, 653 (1936); *J. Chem. Phys.*, **3**, 597 (1935); *Phys. Rev.*, **48**, 825, 893 (1935); *J. Applied Phys.* (U. S. S. R.), **8**, 328 (1937); *Proc. Nat. Acad. Sci.*, **23**, 202 (1937), etc.

for the 65° isotherm of helium on the ground of equations (7) and (1), respectively.

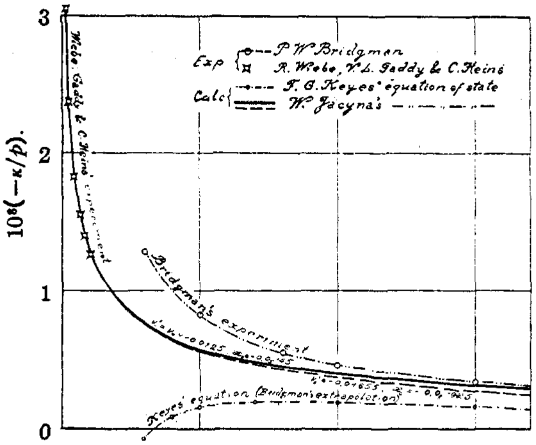

Fig. 1.—Graphical representation of the synthesis of several experimental data for helium at 65° (pressure in kg./sq. cm.).

In order to make the above-mentioned synthesis of the several data at high pressure, *i. e.*, to join the results of the measurement due to Wiebe, Gaddy and Heins ($p \leqq 1000$ atm.)—which I consider here as being correct—with Bridgman's measurement and calculation ($3000 \leqq p \leqq 15{,}000$ atm.), I take the two following fundamental series of computations: (1) calculation of the thermodynamic properties under the assumption that Bridgman's experimental data for $p < 10{,}000$ atm. are exact and (2) analogous calculation under the assumption that Bridgman's experimental data in the years 1924 for helium are subjected to some systematic error, namely, in the lower range of the pressure values. The computations show that in the latter case the Planck–Hausen's criterion[4] and also the conditions $C_p \geqq 0$ and $C_v \geqq 0$ are satisfied in all the region of pressure to 30,000 atm., while in the first case the specific heat at constant volume already has become negative at 8500 atm. Thus the first assumption appears to be unwarranted; the computations show also that the exponent κ is almost independent of temperature over the whole range of Wiebe, Gaddy and Heins' experiments, so that it can be put down as

$$\kappa = \kappa_0 p^{1-x}\, e^{\nu_0^1 p^x} \tag{8}$$

where $\kappa_0 = -0.000001920$, $\nu_0^1 = -0.01655$ and $x = {}^1/_4$. Practically without appreciable systematic deviation from the experimental data one can write

and

$$\left.\begin{aligned} \nu_0^1 = \nu_0 &= -0.0125 \\ \kappa_0 &= -0.00000145 \end{aligned}\right\} \tag{9}$$

The selection of values (9) has been made in order to approach more nearly Bridgman's experimental data at pressure $p \geqq 10{,}000$ atm. and to simplify the use of the formulas. The results of calculation for some isotherms are given in Table I

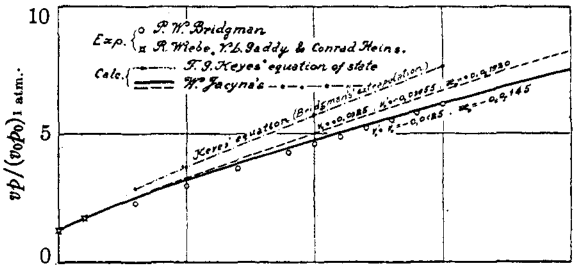

Fig. 2.—$(vp)_{65°}$—Data for helium in Amagat units; pressure in kg./sq. cm.

In many cases the true *value of volume, v*, is necessary. From the equation of state (I) it follows that this value is composed additionally from the *ideal gas* volume

$$v_{\text{id.}} = R\psi/p \tag{10}$$

and from the "volume-deviation" (total)

$$\Delta v = v - v_{\text{id.}} = a(11\psi_0 e^{\kappa} - \psi e^{\nu}) \tag{11}$$

Hence, the volume can be represented by the sum

$$v = v_{\text{id.}} + \Delta v$$

All these values diminish with the increase of pressure at constant temperature, but the isobaric variations are positive for volume and negative for volume-deviation Δv at all values of pressure. It is, however, remarkable that the volume-deviation at 100 atm. and 0° which is equal to nearly 5% of "ideal gas volume," $v_{\text{id.}}$ becomes at 15,000 atm. and the same temperature 85% of the corresponding value of volume v and 500% of the corresponding ideal gas volume, $v_{\text{id.}}$ (see Table II).

This fact gives an explanation of the final form of the equation without the ideal gas volume $R\psi/p$ for the condensed state.

Gay-Lussac's Coefficient and Specific Heat C_p and C_v and their Relations.—The simple relation can be found for the true Gay-Lussac coefficient

$$\alpha = \frac{1}{v_0}\left(\frac{\partial v}{\partial t}\right)_p$$

where, in accordance with (I)

$$\left(\frac{\partial v}{\partial t}\right)_p = \frac{R}{p} - ae^{\nu}$$

TABLE I

"VOLUME-WORK" vp OF HELIUM IN AMAGAT UNITS

Calculated from equation (1) (calcd.) in comparison to the experimental data (exptl.) of Wiebe, Gaddy and Heins (from 103.3 to 1033.3 kg./sq. cm.) and of Bridgman (from 3000 to 15,000 kg./sq. cm.). The vp data in parentheses ( ) are doubtful; *Bridgman's extrapolation of Keyes' equation.

p, kg./sq. cm.		t, °C.						
		−70	−35	0	50	65	100	200
103.3	Calc.	0.797	0.925	1.052	1.2345	1.289	1.417	1.781
	Calcd. − exptl.	05	0	0	0	....	05	05
206.7	Calcd.	0.849	0.976	1.1035	1.2855	1.340	1.467	1.830
	Calcd. − exptl.	0	0	0	0	....	1	(2)
620.0	Calcd.	1.048	1.174	1.300	1.479	1.5335	1.658	2.018
	Calcd. − exptl.	0	0	0	1	....	15	(3)
1033.3	Calcd.	1.234	1.358	1.4835	1.661	1.7155	1.840	2.193
	Calcd. − exptl.	...	0	0	1	....	(4)	(4)

p, kg./sq. cm.		3000	5000	7000	10000	15000	30000
Calc.		2.49	3.20	3.86	4.77	6.16	9.79
t = 65°	exptl.	2.31	2.99	3.66	4.60	6.11	......
		(2.88)*	(3.72)*	.....	(5.73)*	(7.61)*	......

and

$$v_0 = \frac{R\psi_0}{p} + a\psi_0\,(11e^\kappa - e^\nu)$$

depends in the temperature range from −70 to 200° on the pressure only; hence

$$\alpha = \alpha_m = \frac{1}{\psi_0}\left\{1 - \frac{11ape^\kappa}{R + ap(11e^\kappa - e^\nu)}\right\}$$

where $\alpha_m = (v-v_0)/v_0t$ denotes the mean value of the Gay-Lussac coefficient, and t the temperature measured from 0°.

Therefore the Gay-Lussac coefficient for helium diminishes uniformly at room temperature with the increase of pressure, but at sufficiently low temperature and pressure $p < 50$ kg./sq. cm. an increase of α and α_m can be seen.[9]

TABLE II

COMPARISON OF THE VALUES OF SPECIFIC VOLUME v AND OF "VOLUME-DEVIATION" Δv IN CC./KG. COMPUTED FROM EQUATIONS (1) AND (11)

p, kg./sq. cm.		t, °C.			
		−70	0	100	200
103.3	$10^4\,v$	446	587.5	794	998
	$10^4\,\Delta v$	30.1	29.6	28.9	28.1
1033.3	$10^4\,v$	69.1	82.9	103	123
	$10^4\,\Delta v$	27.5	27.15	26.6	26.05
30,000	$10^4\,v$	18.25	18.6	19.1	19.6
	$10^4\,\Delta v$	16.8	16.6	16.45	16.25

The above discussion concerning the Gay-Lussac coefficient shows that at high pressure in the region of temperature considered the specific heat at constant pressure, C_p, depends on the temperature alone. Hence, C_p at high pressure is equal to $C_p(t)$ at the lower limit of the considered interval of pressure. I have calculated in the preceding paper[10] for helium at 100 kg./sq. cm.

$$C(t) = C_{p=\infty} = 1.251 - 0.1194\left(3 - 5\frac{\psi_0}{\psi}\right)\left(\frac{\psi}{100}\right)^{-4}$$

Hence, generally, at high pressure it can be put

$$C_p = 1.251 - 0.1194\left(3 - 5\frac{\psi_0}{\psi}\right)\left(\frac{\psi}{100}\right)^{-4} \qquad (12)$$

The specific heat at constant volume, C_v, on the contrary, varies with the pressure on the isothermal line most appreciably. The values of $C_p - C_v$, C_v and $C_p/C_v = K$ calculated with the equation

$$C_p - C_v = AR\left(1 - \frac{ap}{R}e^\nu\right)^2 \Big/ \left\{1 - \frac{ap}{R}e^\nu \left[11\frac{\psi_0}{\psi}\kappa_0 e^\kappa\,(1 - x + x\nu)p^{1-x} - x\nu\right]\right\} \qquad (13)$$

where, as passim, $A = 1/427$, $\psi_0 = 273.22$ and for helium $R = 211.82$—are assembled in Table III. The difference of the two specific heats at high pressure increases with the increase of temperature at p = const. but uniformly diminishes with increasing pressure at t = const. This shows that the specific heat at constant volume, C_v, increases with the increase of pressure and at high pressure, as follows from Table III, is nearly equal to the specific heat, C_p, so that the ratio $C_p/C_v = K$ approaches unity at the lower temperature limit.

Joule–Kelvin and Joule–Gay-Lussac Effects.—Both effects for the pressures $p \leqq 100$ kg./sq. cm. are discussed in the preceding papers[11] in con-

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(9) W. Jacyna, *Z. Physik*, **96**, 692 (1935).

(10) W. Jacyna, *ibid.*, **92**, 661 (1934), where the formula (21) must be expressed as $C(t) = 1.2510 + 0.1194\,\rho\left(\frac{\psi}{100}\right)^{-4}$ where $\rho = -\left(3 - 5\frac{\psi_0}{\psi}\right)$.

(11) W. Jacyna, refs. 9 and 10.

TABLE III

SPECIFIC HEAT AT CONSTANT VOLUME (C_v) AND RATIO $C_v/C_v = K$, AND THE DIFFERENCE $C_p - C_v$ COMPUTED BY THE HELP OF EQUATIONS (12) AND (13)

p, kg./sq. cm.		t, °C. −70	0	200
103.3	c_v	0.786	0.764	0.760
	$c_p - c_v$	.491	.491	.491
	K	1.625	1.64	1.65
1033.3	c_v	0.828	0.800	0.789
	$c_p - c_v$	.4495	.455	.462
	K	1.54	1.57	1.585
15,000	c_v	1.138	1.091	1.040
	$c_p - c_v$	0.139	0.164	0.211
	K	1.12	1.15	1.20
30,000	c_v	1.206	1.168	1.127
	$c_p - c_v$	0.071	0.0875	0.124
	K	1.06	1.075	1.11

nection with the investigations of Roebuck and Osterberg.[12] The recent consideration[13] on the thermodynamic theory of these effects shows that for helium above 50 kg./sq. cm. at any temperature the Joule-Kelvin effect μ_j must be negative; the negative values of Joule effect μ_u can be observed, however, at the temperature $\psi >$ 200°A. But in the region of state considered *both* effects are negative. This conclusion is confirmed by the new calculation (Table IV) accomplished with the help of the equations

$$\mu_j = -\frac{11Aa\psi_0}{C_p}e^{\kappa} \tag{14}$$

and

$$\mu_u = \left\{\mu_j c_p + A\left(\frac{\partial(vp)}{\partial p}\right)_t\right\} \Big/ \left\{c_p - A\left(\frac{\partial(vp)}{\partial t}\right)_p\right\} \tag{15}$$

where $\mu_j = (\delta t/\delta p)_j$, $\mu_u = (\delta t/\delta p)_u$; u denotes the internal energy and j is the enthalpy.

The *absolute* values of the Joule-Kelvin effect $|\mu_j|$ decrease uniformly with the increase of pressure but these values of the Joule–Gay-Lussac effect $|\mu_u|$ attain a maximum approximately at 7000 kg./sq. cm. (Table IV). A small increase of both effects with the increase of temperature at high pressure can almost be disregarded. But from the other extrapolations it results that the dependence of some thermodynamic properties upon temperature at high pressure generally cannot be neglected. Perhaps the variability in some cases (coefficient of expansion, Joule-Kelvin effect, etc., see for instance the formulas 13, 14 and 15) is joined to the variability of the negative volume-deviation with the temperature. Nevertheless it seems to me that the exact estimation of this doubtful effect is not yet possible in the present state of experimental knowledge, and that the above thermodynamic synthesis gives, therefore, a result which has not been, so far as I know, attained with such a great quantitative adequacy, as is given here.

TABLE IV

JOULE-KELVIN EFFECT (μ_j) AND JOULE–GAY-LUSSAC EFFECT (μ_u) FOR HELIUM AT HIGH PRESSURES COMPUTED FROM EQUATIONS (14) AND (15) IN °C./(KG./SQ. CM.)

p, kg./sq. cm.		t, °C. −70	0	200
103.3	$-10^3\mu_j$	58	59	59
	$-10^3\mu_u$	6	7.5	12
1033.3	$-10^3\mu_j$	52.5	53.5	53.5
	$-10^3\mu_u$	9	10.5	13
15,000	$-10^3\mu_j$	36.5	37	37.5
	$-10^3\mu_u$	11.5	12	13.5
30,000	$-10^3\mu_j$	31.5	32	32.5
	$-10^3\mu_u$	10	10.5	11

Summary

Starting with the thermodynamic *equation of state* for helium—which covers the whole range of experimental data of Holborn and Otto, Kamerlingh Onnes and Boks, Keesom and Kraak, Bridgman, Wiebe, Gaddy and Heins, and others from 2 to 800°A. and from 15,000 kg./sq. cm. to zero—are given (1) the tabular and graphical comparison and *synthesis* of several experimental *vp*-data at high pressure, (2) the thermodynamic properties of helium: the "*volume-work*" vp, the *specific volume* v and *volume-deviation* Δv, *coefficient of expansion* α, *specific heat* C_v, C_p, $C_p - C_v$ and the ratio $C_p/C_v = k$, *Joule effect* μ_u and *Joule-Thomson effect* μ_j, which all are computed in the region from −70 to 200°C. and from 103.3 to 30,000 kg./sq. cm. and respectively tabulated.

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[12] J. R. Roebuck and H. Osterberg, *Phys. Rev.*, **43**, 60 (1933); *ibid.*, **45**, 332 (1934).

[13] W. Jacyna, *loc. cit.*; also *Z. Physik*, **96**, 119 (1935).