A SEMIEMPIRICAL EQUATION OF STATE FOR DENSE HELIUM

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Using eight isotherms in the range 83-323°K at pressures less than 700 bar a semiempirical equation of state for dense helium is constructed, permitting extrapolation into the high-pressure region.

In recent years a number of studies [1, 2] have calculated the thermophysical properties of helium in the temperature range from 2 to 3000°K at moderately high pressures. A virial equation of state or an equation of state based on elementary functions was utilized [3, 4].

It has recently been shown [5-7] that the equation of state of a dense gas at sufficiently high temperatures can be formulated as the equation of state of an assemblage of hard spheres with a diameter dependent on temperature with the force of interatomic attraction considered only in the second virial coefficient:

$$Z=\frac{P}{\rho RT}=\left(\frac{P}{\rho RT}\right)_0+4y\left(\frac{B}{b}-1\right). \qquad (1)$$

Here $(P/\rho RT)_0$ is the equation of state of a set of hard spheres of diameter a; $b = {}^2/_3\pi N a^3$; $y = \rho b/4$.

To calculate the compressibility of the system of solid spheres an equation derived in [6] was used:

$$\left(\frac{P}{\rho RT}\right)_0=\frac{\exp\left(-\frac{5}{3}\,y^3\right)}{(1-y)^4}. \qquad (2)$$

To determine $a(T)$, it is necessary to know the intermolecular potential [5, 6, 8] or utilize PVT data [9]. In the latter case the diameter $a(T)$ is determined directly from Eq. (1) for a series of isotherms. Then interpolated solid sphere diameter values serve to extrapolate the available compressibility data to the high-pressure region.

The experimental data used were the precision values of compressibility and second virial coefficient from the studies of Canfield et al. [10-12], encompassing a temperature range from 83 to 323°K (the isotherm T = 158.15°K of [12] was eliminated from consideration because of the internal disagreement in measurements performed thereon). The solid sphere diameter determined in this manner is shown in Table 1. The table also shows the uncertainty in determination produced by errors in determination of B and Z (the latter assumed to be independent).

Compressibility factor values extrapolated with Eq. (1) together with absolute uncertainties are presented in Table 2. The extrapolated values agree well with the data of [13],which measured helium compressibility at pressures up to 1000 atm; discrepancies at the 273 and 323°K isotherms do not exceed 0.1%.

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TABLE 1. Effective Solid-Sphere Diameter at Base Temperatures

T, °K	83,15	103,15	113,15	143,15	183,15	223,15	273,15	323,15
$a\cdot 10^{10}$ m	2,4073	2,3689	2,3533	2,3103	2,2634	2,2320	2,2000	2,1690
$\Delta a\cdot 10^{10}$ m	0,0021	0,0026	0,0020	0,0017	0,0027	0,0034	0,0054	0,0069
$a_{\mathrm{cl}}\cdot 10^{10}$ m	2,0690	2,0651	2,0632	2,0524	2,0354	2,0255	2,0133	1,9973

TABLE 2. Extrapolated Compressibility Factor Values for Base Temperatures

T, °K	83,15		103,15		113,15		143,15	
P, bar	Z	$\Delta Z\cdot 10^4$	Z	$\Delta Z\cdot 10^4$	Z	$\Delta Z\cdot 10^4$	Z	$\Delta Z\cdot 10^4$
500	1,8502	37	1,6834	32	1,6227	21	1,4907	13
1000	2,6136	77	2,2979	68	2,1829	46	1,9321	29
1500	3,3108	117	2,8607	106	2,6967	71	2,3382	47
2000	3,9661	158	3,3896	144	3,1796	98	2,7203	64
2500	4,5920	200	3,8943	184	3,6404	125	3,0847	83
3000	5,1958	243	4,3807	225	4,0842	152	3,4355	101
4000	6,3545	330	5,3126	308	4,9341	210	4,1064	140
5000	7,4653	421	6,2042	394	5,7466	269	4,7465	180

T, °K	183,15		223,15		273,15		323,15	
P, bar	Z	$\Delta Z\cdot 10^4$	Z	$\Delta Z\cdot 10^4$	Z	$\Delta Z\cdot 10^4$	Z	$\Delta Z\cdot 10^4$
500	1,3812	13	1,3100	10	1,2496	11	1,2082	10
1000	1,7241	30	1,5907	25	1,4777	27	1,3993	25
1500	2,0408	49	1,8512	42	1,6904	46	1,5783	44
2000	2,3392	69	2,0971	60	1,8918	67	1,7481	65
2500	2,6238	90	2,3319	79	2,0844	89	1,9107	87
3000	2,8977	112	2,5579	99	2,2699	113	2,0674	110
4000	3,4209	156	2,9896	140	2,6245	162	2,3671	160
5000	3,9195	203	3,4007	184	2,9620	214	2,6524	212

TABLE 3. Values of Coefficients c_i, d_i, g_i

i	c_i	d_i	$g_i\cdot 10^6$
0	1,9201	1,9977	5,4403
1	0,32780	0,68081	10,811
2	—0,23902	—0,40589	—6,0968
3	0,057655	0,10224	1,4490
4	—	—	—0,12698

We write the diameter a(T) as the sum of classical and quantum components [14]:

$$a(T)=a_{\mathrm{cl}}(T)+\frac{h}{4(\pi mkT)^{1/2}}\,. \tag{3}$$

Such a representation is arbitrary to a certain degree, since Eq. (1) does not include quantum corrections [8]. However, it is useful, since a_{cl} depends significantly less on temperature than a (Table 1), and its extrapolation is more reliable. a(T) and a_{cl}(T) are representable within the limits of the accuracy of their determination by

$$a_{\mathrm{cl}}(T)=\sum_{i=0}^{3}c_i\left(\frac{100}{T}\right)^i,\quad a(T)=\sum_{i=0}^{3}d_i\left(\frac{100}{T}\right)^i, \tag{4}$$

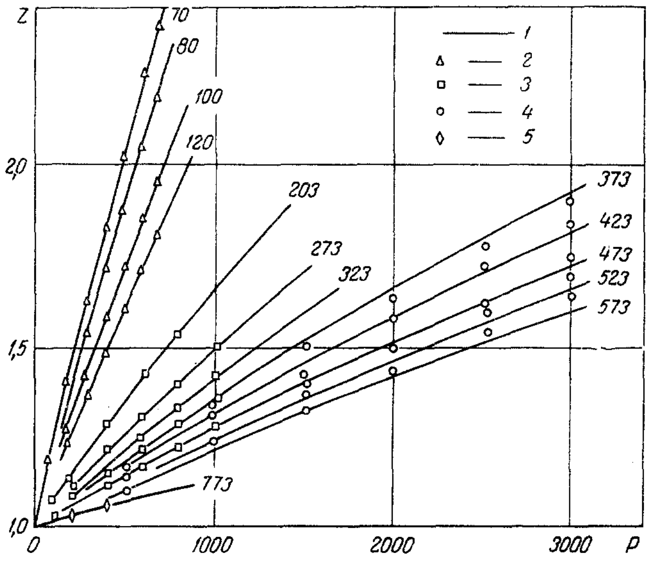

Fig. 1. Compressibility factor of helium versus pressure: 1) calculation by Eq. (1); experiment: 2) data of [15]; 3) [13]; 4) [16]; 5) [17]. P, bar.

TABLE 4. Maximum and Mean Deviation of Calculated Compressibility Factor from Experimental Data

Source	[15]	[13]	[16]	[17]	Net	Net excluding [16]
No. of points	28	29	30	12	99	69
$\delta Z_{\max}$, %	0,52	0,27	3,92	0,35	3,92	0,52
δZ_{mean} %	0,25	0,10	1,26	0,18	0,50	0,18

where the coefficients c_i and d_i are presented in Table 3. The possibility of extrapolation of Eq. (1) to high pressures has been demonstrated previously [5].

The error in computing the compressibility factor is produced by inaccuracies in the determination of $\alpha(T)$ and B(T) and neglect of quantum corrections in Eq. (1).

Equation (1) with solid sphere diameters from Eqs. (3) and (4) was used to calculate the helium compressibility factor and make comparisons with experimental data at both low [15] and high [13, 16, 17] temperatures.

For the second virial coefficient (m^3/mole) in the range 70-350°K, the following approximation of data from [10-12] was used:

$$B(T)=\sum_{i=0}^{4} g_i\left(\frac{T}{100}\right)^i. \tag{5}$$

Coefficients g_i are presented in Table 3. At higher temperatures the Petersen formula [2] valid to 1800°K was used:

$$B(T)=3{,}697\cdot 10^{-5}\cdot T^{-0{,}2}. \tag{6}$$

Figure 1 presents a comparison of calculated and experimental data on the helium compressibility factor, while Table 4 shows maximum and mean divergence between the values ($\delta Z = |Z_{\text{exp}} - Z_{\text{calc}}|/Z_{\text{exp}}$).

There is good agreement between the calculated values and all the experimental studies except [16], which is due to inaccuracies in the PVT measurements of the latter. In particular, the compressibility factors calculated therein differ from those obtained by Wiebe et al. [13], which in turn agree well with later data at low pressures [18, 19], within 1.5% at individual points.

In 1973, Tsiklis, Maslennikova, and Gluvka measured helium compressibility in the temperature range 293-423°K at pressures to 7000 bar [20]. Discrepancies between their measured values and the calculated ones do not exceed 2.8% (at $T = 423°K$, $P = 3500$ bar), which indicates the high accuracy of the equation of state employed.

NOTATION

Z is the compressibility factor; T is the absolute temperature, °K; ρ is the molar density, mole/m^3; B and b are the second virial coefficients of real gas and gas of solid spheres, m^3/mole; a is the solid-sphere diameter, m; m is the molecular mass, kg; R is the universal gas constant; N is Avogadro's number; k is Boltzmann's constant; h is Planck's constant.

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