A METHOD TO EXTRAPOLATE THE p, v, T RELATIONSHIPS FOR COMPRESSED GASES AT ELEVATED TEMPERATURES

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UDC 536.763

A new extrapolation is proposed, based on the behavior of the (z – 1) v isotherms in a ρ, T diagram. We have derived refined tables for the compressibility factor of argon and krypton by this method for pressures up to 200-700 bar at temperatures as high as 650-800°C.

As we know, for the overwhelming majority of industrially important gases the p, v, T relationship has been studied experimentally only to temperatures of the order of 150-300°C. Exact measurements at higher temperatures are rare and usually encompass a range of low densities. This situation necessitates resorting to generalized tables for diagrams for the compressibility factor to determine the thermal properties of compressed gases at high temperatures [1-3], and these tables and diagrams have been compiled with the use of the modified principle of appropriate states. For many problems the accuracy of such determinations is inadequate, which led to the appearance of other calculation methods [4, 5].

The calculation technique in [4] differs from that in [5], but in both cases relative calculation methods with respect to some other substance are employed (a hypothetical substance in [4] or to one that actually exists in [5]), preferably with a similar thermodynamic surface. At the same time, for this base substance, according to [5], we must have at our disposal exact experimental data for the entire range of temperatures and densities, which is by no means always possible.

The extrapolation method proposed in this article is not relative and unlike [4, 5] does not involve the principle of appropriate states. This approach to the problem of extrapolating the p, v, T relationship for compressed gases at elevated temperatures is more correct fundamentally and made it possible to raise the calculational accuracy.

By studying various cross sections of the thermodynamic surface of compressed gases, the authors found that the (z – 1) v = const isotherms in the ρ, T diagram are slightly distorted and form a grid of regularly displaced lines, which change the sign of their curvature on passing through the value (z – 1) v = 0. From the virial equation of state

$$z = 1 + B_1(T)\rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots \tag{1}$$

it follows that

$$(z - 1)v = B_1(T) + B_2(T)\rho + B_3(T)\rho^2 + \cdots, \tag{2}$$

i.e., when $\rho = 0$ we must necessarily have $(z - 1)v \equiv B_1(T)$. The $(z - 1)v = 0$ isotherm is an exact straight line and with extrapolation to $\rho = 0$ yields a Boyle temperature value T_B at which $B_1(T_B) = 0$.

It is now clear that the specified isotherm $(z - 1)v = a$, constructed from experimental data at low temperatures, can be extended to higher temperatures, all the way to T_a when $\rho = 0$, where $a = B_1(T)$. The higher values of the complex (z – 1) v in this case correspond to higher temperatures T_a. It is therefore possible to move comparatively far beyond the limits of the experimentally investigated range of temperatures and to calculate the p, v, T relationship of the compressed gas being examined here for the case of elevated temperatures and pressures (Fig. 1). The accuracy of the calculation, as demonstrated by a verification with CO_2, Ar, Kr, Xe, air, and other gases, is commensurate in a specific region with the accuracy of contemporary experimental data at elevated temperatures.

Power Engineering Institute, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 16, No. 2, pp. 320-325, February, 1969. Original article submitted April 12, 1968.

TABLE 1

ρ, g/cm^3	Values of (z−1)v, cm^3/g, of argon at t, °C												
	200	250	300	350	400	450	500	550	600	650	700	750	800
0,05	0,1665	0,2448	0,3068	0,3583	0,4010	0,4355	0,4670	0,4917	0,5130	0,5343	0,5510	0,5665	0,5790
0,10	0,1925	0,2705	0,3312	0,3822	0,4240	0,4577	0,4880	0,5127	0,5340	0,5540	0,5710	0,5845	0,5980
0,15	0,2203	0,2977	0,3575	0,4077	0,4487	0,4817	0,5110	0,5350	0,5570	0,5750	0,5915	0,6030	
0,20	0,2497	0,3263	0,3860	0,4347	0,4745	0,5070	0,5350	0,5595	0,5810	0,5980			
0,25	0,2813	0,3565	0,4160	0,4630	0,5017	0,5340	0,5620	0,5850					
0,30	0,3150	0,3887	0,4470	0,4930	0,5310	0,5630							
0,35	0,3505	0,4235	0,4805	0,5250	0,5622								
0,40	0,3890	0,4610	0,5162	0,5595									
0,45	0,4300	0,5000	0,5545										
0,50	0,4737	0,5420											
0,55	0,5200												
0,60	0,5700												
p_{max}, barn	335	330	312	356	339	328	326	328	279	303	238	255	176

TABLE 2

ρ, g/cm^3	Values of (z − 1)v, cm^3/g, of argon at t, °C									
	200	250	300	350	400	450	500	550	600	650
0,10	−0,1040	−0,0337	0,0240	0,0685	0,1060	0,1375	0,1655	0,1890	0,2090	0,2270
0,20	−0,0813	−0,0105	0,0445	0,0870	0,1243	0,1560	0,1835	0,2057	0,2250	0,2435
0,30	−0,0585	+0,0120	0,0650	0,1070	0,1440	0,1760	0,2018	0,2240	0,2440	
0,40	−0,0344	0,0345	0,0860	0,1280	0,1652	0,1960	0,2220	0,2435		
0,50	−0,0090	0,0577	0,1075	0,1513	0,1880	0,2173	0,2445			
0,60	+0,0172	0,0825	0,1320	0,1763	0,2115	0,2400				
0,70	0,0445	0,1083	0,1590	0,2018	0,2373					
0,80	0,0740	0,1370	0,1885	0,2280						
0,90	0,1060	0,1690	0,2213							
1,00	0,1410	0,2040								
1,10	0,1793	0,2430								
1,20	0,2200									
p_{max}, barn	712	723	614	585	545	492	430	358	279	192

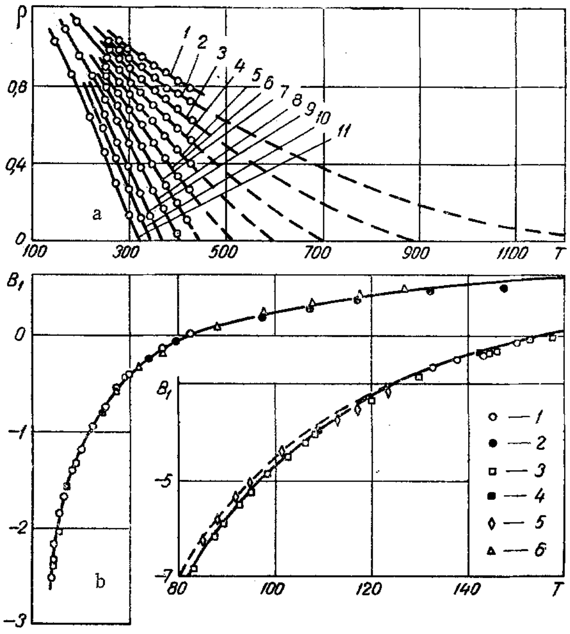

Fig. 1

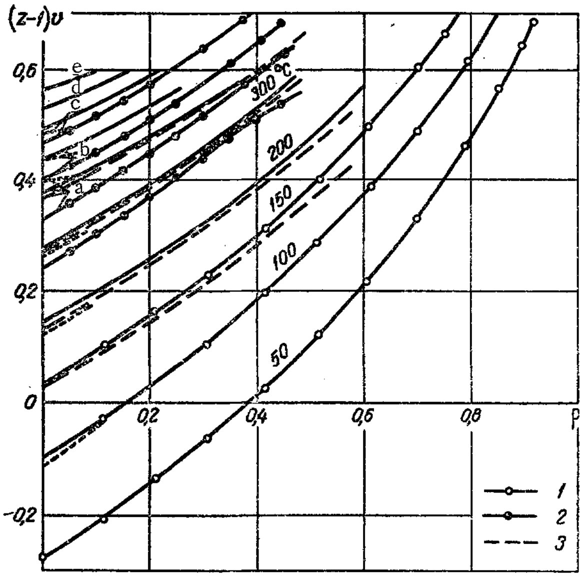

Fig. 2

Fig. 1. The $(z - 1)v$ = const isotherms for argon in the ρ, T diagram for $(z - 1)v$ in cm^3/g, ρ in g/cm^3, and T in °K (the solid lines are taken from the experimental data [7, 8], and the dashed lines denote the extrapolation segments) (a); the second virial coefficient of argon as a function of temperature for B_1 in cm^3/g and T in °K (b): a) 1 – $(z - 1)v = 0.7$; 2 – 0.6; 3 – 0.5; 4 – 0.4; 5 – 0.3; 6 – 0.2; 7 – 0.1; 8 – 0; 9 – (–0.1); 10 – (–0.2); 11 – (–0.3); b) 1 – from [7, 8]; 2 – [15]; 3 – [19]; 4 – [18]; 5 – [17]; 6 – [16] (1-6 are experimental data); the solid line denotes the 18:6 potential; the dashed line denotes a 16:6 potential.

Fig. 2. Argon isotherms in the $(z - 1)v$, ρ diagram for $(z - 1)v$ in cm^3/g and ρ in g/cm^3: 1) [7, 8]; 2) [15]; 3) [16]: 1-3) are experimental data; the solid lines denote the data from Table 1, and the dash-dot lines indicate the data from Eq. (4) of [14]; a) 400°C; b) 500°; c) 600°; d) 700°; e) 800°.

To achieve the proposed extrapolation method we must have at our disposal experimental data on the compressibility of the gas under consideration for a certain range of temperatures, all the way up to the high densities, and we must even know the function $B_1(T)$ at elevated temperatures.

We have chosen argon and krypton as the subjects of our investigation in this article.

Argon. Our point of reference begins with the experimental data [7, 8] which encompass the temperature interval $t = -140 \div +150$°C to $\omega_{\max} = 2.1$-2.5. The experimental data of [15] for $t = 300$-950°C to $\rho_{\max} = 0.45$-0.23 g/cm^3 and from [16] for $t = 0$-600°C and pressures up to 80 atm are kept as control data.

To determine $B_1(T)$ with $t > 150$°C we employed a model potential of the form

$$\varphi(r) = \alpha\varepsilon\left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^6\right], \tag{3}$$

where

$$\alpha = \frac{n}{n-6}\left(\frac{n}{6}\right)^{6/n-6}.$$

The basis for the selection of the n:6 potential was based on the fact that the widely used Lennard–Jones 12:6 potential is not suitable for inert gases [10-12], while the two-parameter n:6 potential is a convenient alternative to the more complex potentials in describing both virial and transport properties [12]. The method of finding the characteristic parameters of the n:6 potential is the same as in [12], with the only difference that T_B is determined by the extrapolation of the $(z - 1)v = 0$ isotherm to $\rho = 0$.

According to the experimental data of [7, 8] for argon we have found $T_B = 407°K$,† and $B_0 = -(B_1)_{T_0=0.7\,T_B} = 0.466\ cm^3/g$, we have determined the characteristic parameters for several n:6 potentials (when n = 12-20), and with the aid of the tables [12, 13] we have calculated $B_1(T)$. It turned out that the best results are given by the 18:6 potential for which $\varepsilon/k = 159.1°K$ and $b_0 = 1.1148\ cm^3/g$ (see Fig. 1b). The extrapolation of the experimental data from [7, 8] was therefore accomplished with the values of B_1 calculated for this potential.

The probable error in the data recommended in Table 1 is of the order of 0.1-0.2% (with respect to z). If we tolerate a greater error, the extrapolation zone can be substantially broadened.

The compressibility isotherms which we derived are compared (Fig. 2) with the experimental data of [7, 15, 16] as well as with those calculated according to the virial equation

$$z = 1 + B'(T^*)\rho^* + C'(T^*)\rho^{*2} + D'(T^*)\rho^{*3}, \tag{4}$$

whose coefficients have been found in [14] from the experimental data for N_2, CH_4, Ar, Xe, etc. For Ar, Eq. (4) is recommended in [14] for $t \le 443°C$ and $\rho \le 0.7\ g/cm^3$.

The data of Table 1 are in good agreement with the experimental data of [16] and the divergence at t = 200-600°C does not exceed 0.07%. The divergence from [14] is greater than 0.2% only when $\rho > 0.4\ g/cm^3$ and $t < 200°C$, and it is a result of the deviation of Eq. (4) from the original experimental data of [7] near the upper limit of applicability for the equation. The Lecocq data [15] are systematically lower, and the divergence increases with increasing density and temperature, varying from 0.2-0.4% at 300°C to 0.6-0.7% at 650-800°C, which is substantially in excess of the possible calculation error. The deviation of the data from [15] – great in magnitude and systematic – from the analytically extrapolated isochors [7, 8] has also been found by the authors of [20]. However, no significance has been imparted to this deviation and for the compilation of the tables we prepared two equations of state which are joined at t = 150-300°C: one according to the data of [7, 8]; and the other according to the data of [15] (see [20], pp. 167-172).

Krypton. Our reference data are the experimental values from [9], which encompass the temperature range from 0-150°C to $\omega_{max} = 2.6$. From these data $T_B = 566.2°K$ and $B_0 = 0.269\ cm^3/g$, while the corresponding values of the characteristic parameter, e.g., for the 18:6 potential, are $\varepsilon/k = 221.3°K$ and $b_0 = 0.6435\ cm^3/g$. Comparison of the values of $B_1(T)$ calculated for n:6 (when n = 12-20) and the experimental values from [9, 17-19, 21-22] demonstrated that it is also the 18:6 potential that yields the best results.

Table 2 shows that portion of the data derived by extrapolation of the $(z-1)v$ isotherms, plotted from the measurements of [9], to the selected values of B_1 for t = 200-650°C. Just as in the case of argon, the extrapolation zone in this case can be broadened, if we permit an error in excess of 0.2-0.3%.

The agreement between the data of Table 2 and the experimental data from [21] for t = 150-600°C atm is excellent and the divergence does not exceed 0.05-0.1%. The experimental data derived by Beattie and his coauthors [22] at t = 150-300°C and $\rho \le 0.8\ g/cm^3$ are lower than our figures by 0.1-0.3%. Although this divergence may be acknowledged as normal, we note that when t = 0-150°C the data of [22] are systematically lower than those of [9], and in terms of magnitude this divergence reaches 0.3-0.6% at densities of the order of 1.0-1.2 g/cm^3. This divergence is explained by the fact that the gas specimen studied in [22] contains impurities of xenon and, moreover, of particular importance in the experiments of [22] might have been the correction factor associated with the presence of mercury vapor in the test material, a factor which had not been taken into consideration by the authors of the cited reference. According to [14], Eq. (4) for krypton also deviates noticeably from both the experimental data of [9] when $t \le 150°C$ and our data for t = 150-300°C, but as the temperature rises, the divergence diminishes. Thus, for example, with $\rho = 0.80\ g/cm^3$ the divergence amounts, respectively, to 0.8, 0.5, and 0.2% for the isotherms at 150°, 200°, and 300°C.

In conclusion, we note that the proposed method of graphical procedure provides for a more reliable judgement as to the correlation between the various groups of measurements, including those at the boundary of the subject domain of states. Here it also turns out to be possible markedly to reduce the scope of the experimental information with regard to the thermal properties of a compressed gas in a region of elevated temperatures and pressures, where measurements of this type are difficult.

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†The value of T_B differs from those values found in [11, 14] and [16] by 1° and 5°, respectively.

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