THE EQUATIONS OF STATE AND THE THERMODYNAMIC PROPERTIES OF INERT GASES IN THE INTERVAL FROM THE NORMAL BOILING POINT TO 1300°K AT PRESSURES BELOW 1000 BAR

I. KRYPTON

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Statistical processing on a computer of the most reliable p, v, and T data provided the basis for the plotting and discussion of the equation of state for gaseous krypton with T = 120-1300°K and p = 1-1000 bar.

Much experimental data has been accumulated on the thermodynamic properties of inert gases (He, Ne, Ar, Kr, Xe) for a comparatively wide range of temperatures and pressures. However, as demonstrated by a survey of the handbook literature (see, for example, [1-3], etc.), the earlier derived equations of state, as a rule, encompass only a portion of the experimentally investigated range of state or they are in need of refinement, and the recommended tables are neither complete nor standardized. This circumstance led the authors, once again, to generalize the experimental data on thermodynamic properties for the class of materials under discussion, to derive experimentally valid equations of state by means of a uniform procedure, and to calculate the required tabular material by means of these equations. In performing this work, the authors tried, in addition to all else, to ensure that the analytical apparatus is convenient for computer utilization.

Within the framework of the formulated problem, it is recognized as expedient [4] to seek the equation of state in the form of a virial expansion in powers of density

$$z = \frac{p}{\rho RT} = 1 + \sum_{i=1}^{r} B_i(T)\rho^i, \tag{1}$$

in which the virial coefficient (or the temperature functions) are approximated by empirical polynomials of the form

$$B_i(T) = \sum_{j=0} \frac{b_{ij}}{\tau^j}, \tag{2}$$

where $\tau = T/T_{cr}$. The initial equation of state is thus brought to the form

$$z = 1 + \sum_{i=1}^{r} \sum_{j=0}^{s_i} \frac{b_{ij}}{\tau^j} \rho^i. \tag{3}$$

The authors developed three methods of determining the coefficients $\{b_{ij}\}$ for Eq. (3) by means of a high-speed computer, and these methods were covered in detail in [4-6]. Here we employ a direct method of derivation for the interpolation equation of state [4]. According to this method, the coefficients $\{b_{ij}\}$ of Eq. (3) are found on the basis of a statistical treatment of the experimental thermodynamic data with respect to

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TABLE 1. Listing of Experimental Investigations of the Thermodynamic Properties of Krypton above the Normal Boiling Point

Year	Authors	Measured quantities	Interval T, °K	Interval p, atm	Source
In the one-phase region					
1901	Ramsay and Travers	p, v, T	284—510	до 100	[8]
1952	Beattie et al.	p, v, T	273—573	21—415	[9]
1954	Whalley and Schneider	p, v, T	273—873	10—80	[10]
1962	Fender and Halsey	B_1	105—140	$p<1$	[11]
1962	Thomas and Steenwinkel	B_1	110—270	$p<1$	[12]
1966	Trappeniers et al.	p, v, T	273—423	18—3032	[13]
1967	Wir et al.	B_1	110—224	$P<1$	[14]
At the liquid–vapor equilibrium line					
1937	Meihuizen and Crommelin	$p_н$	116—209,4	—	[15]
1937	Mathias Crommelin and Meihuizen	ρ', ρ''	126—208	—	[16]
1952	Michels etal.	$p_н$	116—209	—	[17]
1956	Freeman and Halsey	$p_н$	116—121	—	[18]
1961	Beaumont et al.	$p_н$	83—119	—	[19]
1967	Blagoi et al.	a'	117—202	—	[20]

two variables (ρ and τ). The sought set of coefficients $\{b_{ij}\}$ corresponds to the best description of the thermodynamic surface $F(z, \rho, T) = 0$ in the sense of mean square deviation of z. The required thermodynamic quantities were also calculated on a digital computer, with a program which realizes an algorithm [7].

Below we give the results found from krypton.

Original Experimental Data. It follows from Table 1 that the thermal properties of compressed krypton in the one-phase region were studied at $T \geq 273$°K. Only the second virial coefficient $B_1(T)$ was measured at the low temperatures. The comparative analysis of the experimental data given in Table 1 demonstrated that the values of $B_1(T)$ derived in [9-14] agree satisfactorily with each other, but the p, v, and T data of [9] deviate systematically from the measurements of the Amsterdam laboratory [13] at elevated pressures, and the differences reach 0.5-0.6% in a number of cases. This difference is not surprising, since the gas specimen – the research work with this specimen is described in [9] – contains impurities of xenon (0.9%). In addition, no correction factor to allow for the presence of mercury vapors in the substance being investigated [21] was introduced in [9] for the measured values of p_{opt}.

Initially, in deriving the equation of state for gaseous Kr, as the initial p, v, and T data we used the measurements of [13] and [10] for the case in which $t > 0$°C, while for the case in which $t < 0$°C the averaged values for $B_1(T)$ were taken from [11, 12, 14]. It was found, however, that the data from [10] did not provide for sufficiently reliable extrapolation of the equation of state to high temperatures and pressures. A similar situation arises for certain other inert gases. A special investigation was therefore undertaken to develop an efficient means of extrapolating the "low-temperature" experimental p, v, and T data to high temperatures. The results of this investigation are described in [22] and they reduce to the following. It was established that the $(z - 1)v = \text{const}$ isolines in the $\rho - T$ diagram are slightly distorted and form a grid of regularly spaced lines, changing the sign of curvature on passing through $(z - 1)v = 0$. In accordance with the equation of state (1), since $[(z - 1)v]_{\rho=0} \equiv B_1$, the isoline $(z - 1)v = a$ plotted from the "low-temperature" experimental data, can be extended in the $\rho - T$ diagram to the higher temperatures, all the way to T_a for $\rho = 0$, where $a = B_1$, and we can calculate the p, v, and T functions of the gas being investigated (with the required accuracy) in a specific zone of elevated temperatures and pressures.

For Kr, as "low-temperature" data we used the [22] experimental data of the Amsterdam laboratory [13], and the required values of B_1 were found with the aid of the 18 : 6 potential whose characteristic parameters are $\varepsilon/k = 221.3$°K and $b_0 = 0.6435$ cm^3/g.

Figure 1 shows the region of state in which the probable error in the p, v, and T data for krypton, as calculated in [22] by the above-considered method, is in the order of 0.2-0.3%. We used these theoretical data, together with the measurements from [13] and [14], to construct the equation of state for gaseous Kr.

The temperature dependence of the pressure for the staturated Kr vapor is given by the empirical equation

$$p_s = \sum_{j=0}^{7} A_{s_j} \tau^j, \qquad (4)$$

TABLE 2

i	Values of b_{ij} for j equal to				
	0	1	-	3	4
1	0,4915444	—1,092102	0,717090	0,170102	—0,1136513
2	—0,1362322	0,370673	—1,065307	1,445104	—0,36832437
3	—0,1335165	0,3733153	0,0568949	—0,086791	0
4	0,3264436	—0,7569125	0,0810234	0	0
5	—0,2169021	0,6682404	0,3141063	0	0
6	0,046289	—0,1500961	0,1017273	0	0

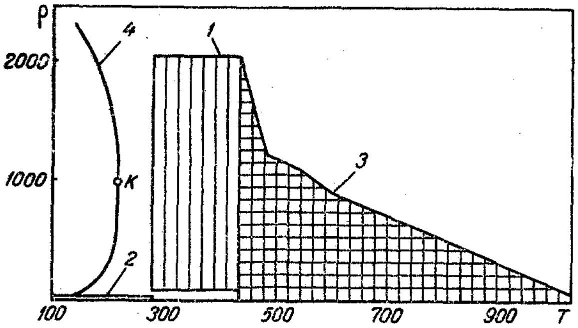

Fig. 1

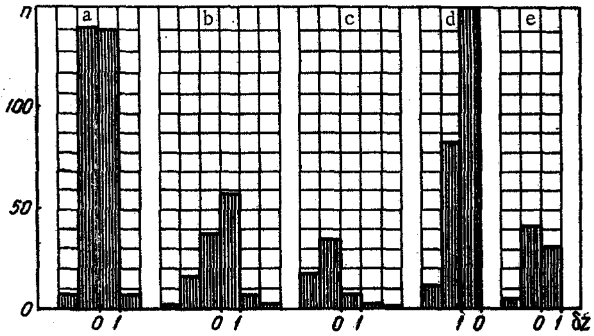

Fig. 2

Fig. 1. Zone of specified initial values for the compressibility of krypton in the plane of independent variables for the equation of state (ρ in kg/m^3 and T in °K): 1) [13]; 2) [14]; 3) [22]; 4) saturation curve.

Fig. 2. Histograms of deviations for various data groups: a) [13]; b) [14]; c) [22] (used in the construction of the equation of state); d) [9]; e) [10] (not used in the contruction of the equation of state); the scale for the segment [0, 1]: a) 0.025%; b and c) 0.05; d) 0.2; e) 0.1.

whose coefficients have been found from the experimental data of the Amsterdam laboratory [17] and are equal to

$$\begin{array}{ll} A_{s_0} = -40{,}25808, & A_{s_4} = -115{,}5962, \\ A_{s_1} = 258{,}0686, & A_{s_5} = 17{,}72264, \\ A_{s_2} = -584{,}9822, & A_{s_6} = -24{,}42784, \\ A_{s_3} = 516{,}3658, & A_{s_7} = 28{,}10447. \end{array}$$

The deviation of p_s^{opt} [17] from the values calculated in accordance with (4) is usually smaller than 0.06% and amounts to 0.12% at only a single point. In our case, Eq. (4) is an auxiliary equation in the procedure for the calculation [7] of the thermodynamic quantities on the liquid–vapor equilibrium line from T_{nbp} to T_{cr}, but it may stand alone, since it reflects the value of p_s better than the logarithmic equations of [15-17].

From Eq. (4) the parameters of the nodal point on the liquid–vapor equilibrium line are the following: the critical point T_{cr} = 209.40°K, p_{cr} = 54.997 bar; the triple point T_0 = 115.78°K, p_0 = 0.7357 bar; the normal boiling point T_{nbp} = 119.73°K.

The equation of state for gaseous Kr has the form

$$z = 1 + \sum_{i=1}^{6} \sum_{j=0}^{s_i} \frac{b_{ij}}{\tau^j} \rho^i, \tag{5}$$

where τ = T/209.4; ρ is expressed in units of g/cm^3; the matrix of the coefficients

$$\|s_i\| = (s_1, s_2, s_3, s_4, s_5, s_6) = (4, 4, 3, 2, 2, 2).$$

The equation of state (5) reproduces the original p, v, and T data with a mean-square error of 0.013% (with respect to z). The quality of approximation for the separate measurement groups is illustrated by the histograms shown in Fig. 2, where n = n(δz) shows the deviations of the theoretical values of z from the

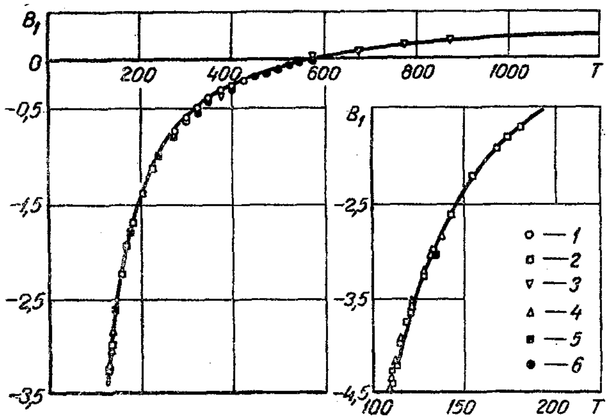

Fig. 3

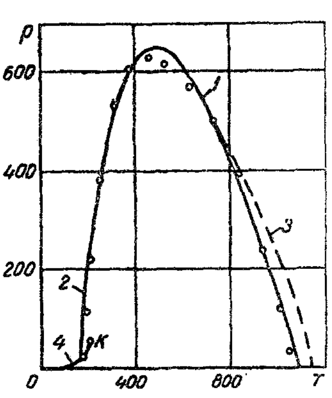

Fig. 4

Fig. 3. Second virial coefficient for krypton (cm^3/g): 1) [13]; 2) [14]; 3) [10]; 4) [11]; 5) [12]; 6) [9]; 1-6) experimental data; solid line) calculation according to Eq. (5).

Fig. 4. Curve for the inversion of krypton in the p–T diagram (in bar and °K): 1) according to the equation of state (5); 2) according to a generalized equation [23]; 3) according to the equation of state constructed with consideration of the data [10]; 4) saturation curve.

experimental values. Here n is the number of experimental points whose deviations from the theoretical points falls within the interval $\delta z\%$.

As we can see from Fig. 2, the law governing the distribution of deviations with respect to the original data is one that is nearly normal, while in terms of magnitude the deviations are everywhere smaller than the probable inaccuracy in the original data.

The values of $B_1(T)$ calculated from the equation of state are in satisfactory agreement with the experimentally found values (Fig. 3).

Control calculations with (4) and (5) demonstrated that the calculated values for the density ρ'' of the saturated vapor are in rather good agreement with the measurements of the Leiden laboratory [16]. This indicates that the equation of state (5) can be used for the calculation of the thermodynamic quantities of gaseous Kr, not only in the one-phase region, but also on the upper boundary curve.

Among the advantages of Eq. (5) we also have the fact that, unlike the initial equation constructed from the experimental data of [10] and [13], it exhibits a "normal shape" for the right-hand branch of the inversion curve (Fig. 4).

Tables of Thermodynamic Quantities. Using the equation of state (5) that has been derived here, the authors calculated and tabulated the following thermodynamic quantities: ρ', z, h, s, c_p, c_v, a, $\delta_T = -(\partial h/\partial p)_T$, $\mu = (\partial T/\partial p)_h$, $p_t = T(\partial p/\partial T)_\rho$.

The thermodynamic quantities for gaseous Kr, to the best of our knowledge, has been tabulated only for the interval between 0 and 150°C for equal values of the density d_A [13].

Comparison showed that for all temperatures from 0 to 150°C in the density interval $d_A = 600$ the entropy and enthalpy values which we have calculated are in good agreement with those that are tabulated [13] and the divergence does not exceed $8 \cdot 10^{-4}$ kJ/kg · deg and 0.4 kJ/kg, respectively. The differences in the magnitudes of the isobaric heat capacity c_p and the speed of sound are insignificant and, as a rule, less than 0.5%. The parameters (z, ρ) found from the tabular [13] values of μ on the curve for the inversion of Kr virtually coincide with the values calculated from the equation of state (5).

In conclusion, we note that the equation of state derived in this paper is recommended for the calculation of the thermodynamic quantities of gaseous Kr in the range of pressures from 1 to 1000 bar, but only at temperatures above 270°K. For temperatures as low as 120°K we can use Eq. (5) with sufficient assurance, but only at densities $\rho \leq 0.3\text{-}0.4$ g/cm^3, including the saturation curve. At greater densities and with T = 250-120°K, as well as in the near-critical region the required calculation accuracy cannot presently be assured because of the absence of experimental data.

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