

A METHOD OF CALCULATING THE THERMODYNAMIC PROPERTIES OF GASES AT PRESSURES UP TO 12 KILOBARS AND AT A TEMPERATURE ABOVE 700°K

A. A. Antanovich, G. Ya. Savel'ev, and M. A. Plotnikov

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An analysis is presented of the contemporary methods of calculating the thermodynamic properties of real gases at pressures up to 12 kbar. We propose a semiempirical method of calculating the parameters of real gases in the range of temperatures from 700 to 1200° K. The method is illustrated with calculations for nitrogen.

A large number of experimental and theoretical articles have been devoted to the study of thermodynamic properties of real gases. In the majority of cases, the diagrams and tables of thermodynamic functions and parameters of state have been derived with the aid of graphical and graphoanalytical methods of processing experimental thermal and caloric data. At the present time, the most exact and most detailed data regarding the thermodynamic properties of real gases pertain to the range from the saturation line to pressures of 1000 bar and a temperature of 1300° K [1].

A number of authors have published the results of systematic experimental investigations into the thermodynamic properties of real gases at pressures from 10 to 12 kbar and at comparatively low temperatures. Among these publications is the Din monograph [2] which covers the range of pressures below 10 kbar and temperatures of up to 400°K, as well as the latest study of Tsiklis [3] for pressures below 12 kbar and temperatures below 700°K

Investigations at higher temperatures within the indicated range of pressures have not yet been undertaken because of the well-known difficulties involved in the design of appropriate equipment. However, engineering applications require approximate data, at the very least, with respect to the thermodynamic properties of industrially important gases for pressures of up to 10-15 kbar and for temperatures all the way to 3000° K.

In this connection, we need to refine the theoretical methods of determining the thermodynamic properties of gases within the indicated range of parameters.

The most general form of the equation of state for gases of moderate density is the virial form of the equation, which represents an expansion of the compressibility factor $Z = Pv/RT$ into a series in powers of the density

$$\frac{Pv}{RT} = 1 + B(T)\rho + C(T)\rho^2 + D(T)\rho^3 + \dots \quad (1)$$

However, Eq. (1) cannot be used to determine the thermodynamic properties of gases at high density. The region of applicability for Eq. (1) is restricted by the condition of smallness for the volume of the gas molecule relative to the volume occupied by a single

molecule within the gas — used in the Bogolyubov theory in expanding the distribution functions for a real gas into the corresponding series in powers of the small parameter.

The most complete function expressing the potential energy of interaction between two molecules is the Lennard-Jones potential

$$\varphi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (2)$$

The parameters ε and σ in (2) are, respectively, expressed in units of energy and length and characterize the chemical individuality of the gas.

From the practical standpoint, the calculation of the virial coefficients in Eq. (1), with the use of potential (2), is quite complex, and the literature, until recently, only gave the results of the Hirschfelder [4] calculations of the values for the second virial coefficient $B(T)$ in the interval of the reduced temperatures $kT/\varepsilon = 0.3-400$, as well as of the third virial coefficient $C(T)$ in the interval $kT/\varepsilon = 0.7-400$.

The calculational data of Barker [5] on the values of the fourth coefficient $D(T)$, as well as of the fifth virial coefficient $E(T)$ have recently been published for the interval $kT/\varepsilon = 0.625-20$, and these calculations also involved the use of the intermolecular interaction potential (2). Moreover, the values of the third and fourth virial coefficients for the broader range $kT/\varepsilon = 0.3-400$ have now been calculated by Savel'ev, also with the use of potential (2). The results of these calculations are in good agreement with the Hirschfelder and Barker data (see Table 1).

Another form of the equation of state for real gases, also recently published, is the Rowlinson equation [6]. This equation has been derived by summing the virial series (1) which is possible on introduction of several simplifying assumptions which, however, are valid when

$$T \geq 12 \frac{\varepsilon}{k}. \quad (3)$$

The Rowlinson equation has the form

$$\frac{Pv}{RT} = \frac{1 + \xi + \xi^2}{(1 - \xi)^3}, \quad (4)$$

where the quantity ξ , when we use the intermolecular interaction potential (2), is expressed as

$$\xi = \left(\frac{V\sqrt{2}b_0}{4v} \right) \left(\frac{\varepsilon}{kT} \right)^{1/4} \left[1 + \frac{1}{12} F \left(\frac{\varepsilon}{kT} \right) \right]^3. \quad (5)$$

The numerical values of the function $F(\varepsilon/kT)$, in (5), are given in reference [6] over a wide range of values of the argument

Table 1

Values of the Third and Fourth Virial Coefficients for the Lennard-Jones Potential

$$T^* = kT/\epsilon, \quad C^* = C(T)/b_0^2, \quad b_0 = 2\pi N\sigma^3, \quad D^* = D(T)/b_0^3$$

T*	C*		D*	
	Savel'ev	Hirschfelder	Savel'ev	Barker
0.30	-2235.24	—	-828895	—
0.35	-584.308	—	-89390.0	—
0.40	-203.366	—	-15928.1	—
0.45	-84.7816	—	-3927.03	—
0.50	-39.7798	—	-1207.50	—
0.55	-20.1722	—	-433.780	—
0.60	-10.7306	—	-174.240	—
0.625	—	—	—	-121.08
0.65	-5.83398	—	-75.8241	—
0.70	-3.14876	-3.37664	-34.8728	—
0.75	-1.61325	-1.79197	-16.5832	-18.840
0.80	-0.70782	-0.84953	-7.96679	-9.3880
0.85	-0.16259	-0.27657	-3.74751	—
0.875	—	—	—	-3.2430
0.90	+0.06959	+0.07650	-1.62910	—
0.95	0.37229	0.29509	-0.55418	-0.9440
1.00	0.49460	0.42966	-0.12828	-0.02769
1.05	0.56619	0.51080	+0.25034	+0.0691
1.10	0.60543	0.55762	0.36712	0.2379
1.15	0.62392	0.58223	0.40717	0.3126
1.20	0.62911	0.59240	0.40788	0.3359
1.25	0.62584	0.59326	0.38948	0.3324
1.30	0.61729	0.58815	0.36296	0.3157
1.40	0.59211	0.56831	0.30619	0.2695
1.50	0.56325	0.54339	0.25748	0.2250
1.60	0.53491	0.51803	0.22034	0.1894
1.70	0.50881	0.49425	0.19355	0.1630
1.80	0.48551	0.47277	0.17490	0.1442
1.90	0.46502	0.45376	0.16232	0.1313
2.00	0.44716	0.43710	0.15416	0.1228
2.10	0.43165	0.42260	0.14916	0.1175
2.20	0.41819	0.40999	0.14639	0.1145
2.30	0.40652	0.39900	0.14517	0.1131
2.40	0.39637	0.38943	0.14503	0.1128
2.50	0.38753	0.38108	0.14560	0.1131
2.60	0.37981	0.37378	0.14665	—
2.70	0.37301	0.36737	0.14799	—
2.80	0.36711	0.36173	0.14949	—
2.90	0.36187	0.35675	0.15106	—
3.00	0.35723	0.35234	0.15263	0.1198
3.50	0.34054	0.33638	0.15947	—
4.00	0.33039	0.32662	0.16371	0.1311
4.50	0.32354	0.32000	0.16556	—
5.00	0.31841	0.31508	0.16572	0.1341
6.00	0.31067	0.30771	0.16243	—
7.00	0.30409	0.30166	0.15760	—
8.00	0.29819	0.29618	0.15078	—
9.00	0.29262	0.29103	0.14446	—
10.0	0.28732	0.28610	0.13836	0.1156
20.0	0.24608	0.24643	0.09724	0.0832
30.0	0.21962	0.21954	0.07732	—
40.0	0.20076	0.20012	0.06524	—
50.0	0.18618	0.18529	0.05673	—
60.0	0.17437	0.17347	0.05026	—
70.0	0.16454	0.16376	0.04514	—
80.0	0.15620	0.15560	0.04097	—
90.0	0.14901	0.14860	0.03752	—
100	0.14275	0.14251	0.03460	—
200	0.10628	0.10679	0.01948	—
300	0.08915	0.08943	0.01352	—
400	0.07872	0.07862	0.01039	—

Moreover, it is indicated in [6] that the calculational results involving the use of Eq. (4) are in good agreement with the computer data (the Monte Carlo method) for the pressures of dense gases, with the measurements of gas compressibility at high reduced temperatures, as well as with the results of a number of measurements for the density of argon compressed by shock waves at pressures of up to 200 kbar.

Thus, in the range of pressures under consideration, at temperatures of $T \leq 700^\circ \text{K}$, we have experimental data on the thermodynamic properties of the gases, while in the temperature interval

governed by condition (3) there exists a more-or-less reliable theoretical method for the determination of these properties. Among the indicated temperature intervals there is a certain region for which we presently have absolutely no methods by means of which to determine the thermodynamic parameters of the gases. In this region we can use only the empirical and semiempirical methods of interpolation. (For nitrogen, for example, condition (3) corresponds to 1200°K).

The calculation results for the compressibility factor, the specific volume, and the entropy and enthalpy of the nitrogen in the region under consideration, obtained from Eq. (1) with four and five virial coefficients, are in good agreement with the calculation data derived from Eq. (4) for temperatures of $T \geq 1200^\circ \text{K}$. The values of the parameters $\epsilon/k = 91.5^\circ \text{K}$ and $\sigma = 3.681 \text{\AA}$ of the intermolecular interaction potential (2) were used in Eq. (1) here. However, these results are not in agreement with the corresponding experimental data of reference [3] when $T \leq 700^\circ \text{K}$. Here the divergence of the values for the indicated parameters amounts to 10–15%.

It should be noted that the numerical values of the parameters ϵ and σ of the intermolecular interaction—experimentally determined by various authors with the use of various physical research methods—differ to a considerable extent from one another (see table 2).

Results from numerous calculations of the thermodynamic properties of nitrogen, involving the use of various values for the quantities ϵ and σ within the limits of the extreme values shown in Table 2 show that a change in the magnitude of σ has a substantial effect on the results of the calculation at temperatures around 700°K and has virtually no effect at temperatures of $T \geq 1200^\circ \text{K}$.

This circumstance is explained by the fact that with a reduction in the density the effective dimensions of the molecules are reduced and the real gas—in terms of its properties—approaches an ideal gas, while the magnitude of the compressibility factor Pv/RT tends to unity at the limit.

The conclusions and considerations just presented indicated the possibility of setting up a semiempirical method of calculating the thermodynamic properties of gases in the temperature interval from 700 to 1200°K at pressures below 12 kbar.

Table 2

Parameters of the Lennard-Jones Intermolecular Interaction Potential for Nitrogen

Derived from viscosity measurement results		Derived from the second virial coefficient	
$\epsilon/k, ^\circ \text{K}$	$\sigma, \text{\AA}$	$\epsilon/k, ^\circ \text{K}$	$\sigma, \text{\AA}$
91.5	3.681	95.05	3.698
79.8	3.749	95.9	3.71

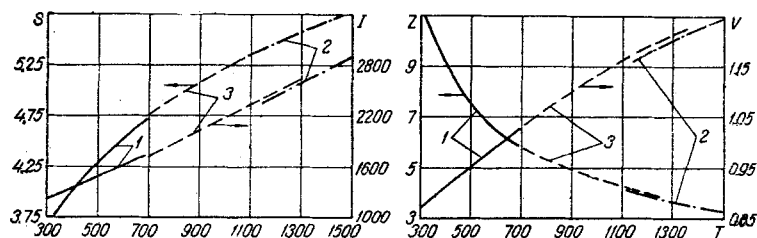


Fig. 1. Entropy (J/g·deg) and enthalpy (J/g) (a) compressibility factor and specific volume (cm³/g) (b), versus temperature for nitrogen at a pressure of 12 kbar: 1) experimental data from [3]; 2) calculation according to Eq. (4); 3) calculation according to Eq. (1) with five virial coefficients at $\sigma = 3.639 \text{ \AA}$.

Such a method can be achieved if the effective molecule diameter is replaced in calculations involving the use of Eq. (1) with four or five virial coefficients by some fictitious value of the quantity σ^* determined from the condition of coincidence between the calculation of the thermodynamic properties of nitrogen in the temperature interval $T = 700\text{--}1200^\circ \text{K}$ at a pressure of 12 kbar.

The calculations were carried out according to Eq. (1) with five virial coefficients. For the parameter ϵ we used the generally accepted quantity $\epsilon/k = 9.15^\circ \text{K}$, while the value for σ was found from the condition of coincidence between the calculated compressibility factor $Z = Pv/RT$ and its experimental value at $T = 700^\circ \text{K}$ (see figure). The found value for σ^* was equal to 3.639 \AA . The remaining thermodynamic quantities were calculated for this value of σ^* , i. e., the specific volume, the entropy, and the enthalpy.

As we can see from the figure, the semiempirical method of calculating the thermodynamic properties of gases at high pressures yields results in good agreement with both experimental data for the region of low temperatures and with the calculational results from the Rowlinson equation for the region of high temperatures. The maximum divergence of the indicated parameters in this case does not exceed 1.4%.

NOTATION

P is the pressure; ν is the specific volume; R is the gas constant; T is the temperature; $B(T)$, $C(T)$, and $D(T)$ are virial coefficients; ρ is the density; ϵ and σ are the potential parameters of intermolecular interaction; k is the Boltzmann constant; b_0 is the second virial coefficient for gas consisting of solid spheres whose diameter is σ ; N is the Avogadro number.

REFERENCES

1. A. A. Vasserman, Ya. Z. Kazavchinskii, and V. A. Rabinovich, *Thermophysical Properties of Air and Its Components* [in Russian], Nauka, 1966.
2. F. Din, *Thermodynamic Function of Gases*, 3 London, Butterworths, 1961.
3. D. S. Tsiklis, *ZhFKh*, 41, no. 9, 1967.
4. J. Hirschfelder, C. Curtis, and R. Bird, *The Molecular Theory of Gases and Liquids* [Russian translation], IL, 1961.
5. Barker, Leonard, and Pompe, *J. Chem. Phys.* 44 no. 11, 1966.
6. J. S. Rowlinson, *Molecular Physics*, 7, no. 4, 1963/64

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