

Analytical Approximation of the Thermal and Caloric Equations of State for Real Gases over a Wide Density and Temperature Range

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Abstract—The thermal and caloric equations of state of the main components of gas mixtures normally used in calculations of gas dynamic processes, including combustion and detonation, as well as in problems of internal ballistics, are presented in an analytical form. The formulas obtained for the equations of state contain a relatively small number of parameters and provide an average error of approximation of less than 1% at temperatures from 500 to 2000–2500 K and densities up to the critical.

Keywords: oxygen, nitrogen, water vapor, carbon monoxide, carbon dioxide, hydrogen, thermal and caloric equations of state of a real gas.

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INTRODUCTION

The main gases in the processes and products of combustion and explosion are typically oxygen, nitrogen, water vapor, carbon monoxide, carbon dioxide, and hydrogen. To calculate the characteristics of gasdynamic processes, including combustion and detonation, as well as to solve problems of internal ballistics, it is necessary to know the thermal and caloric equations of state (EOS) of these components. In reference literature, the data on the EOS for these substances are presented mostly in the form of extensive tables. Such tables are of high accuracy, from tenths of a percent to ~1%, but they are inconvenient for computer simulations of gasdynamic processes. The same refers to the analytic approximations of tabulated values (available, for example, for water, nitrogen, and oxygen), each of which contains about 100 coefficients. To speed up time-consuming calculations, in which the EOS should be handled at each step of the space–time computational grid, optimal versions of the EOS are required, which would possess such difficult-to-combine qualities as a fairly high accuracy and a small number of parameters in the approximation formulas. The known EOS of van der Waals type (the van der Waals equation itself, Peng–Robinson equation, etc.) contain a small number of parameters, but they are not accurate enough.

The aim of this work is to derive optimal or nearly optimal, in this sense, thermal and caloric EOS represented by approximation (mathematical) formulas with an accuracy sufficient for gasdynamic applications.

The range of temperatures and gas densities of major interest in gasdynamic problems with combustion can be approximately limited to the conditions $T \leq 3000$ K (4000 K) and $\rho \leq \rho_c$, where ρ_c is the critical density. Higher densities, up to ρ_L , where ρ_L is density of the liquid phase under normal conditions may be of interest in such problems in the liquid–vapor two-phase region (at $T > 273$ K, it refers only to water and carbon dioxide. For the equation of state of the water–vapor system and other systems, see [1] and [2], respectively).

THERMAL EQUATION OF STATE

The thermal equation of state we derived for individual substances contains two components, the “cold” one $P_c(\rho)$, depending only on the density, and the thermal one, proportional to the temperature:

$$P(\rho, T) = P_c(\rho) + \rho RTf(\rho)/\mu, \quad (1)$$

where μ is the molecular mass. This form of equation of state was theoretically substantiated for solids [3] and an ideal gas ($P_c(\rho) = 0$, $f(\rho) = 1$). With respect to liquids and dense gases, Eq. (1) is an approximation, the accuracy of which can be verified by describing available reference data. Equations of state in the form of (1) for water and the detonation products of RDX were obtained in [4, 5].

We determined the functions $P_c(\rho)$ and $f(\rho)$ for each of the six individual components (water vapor, carbon dioxide, carbon monoxide, molecular nitrogen, oxygen, and hydrogen). This was done as follows.

Table 1. Coefficients of the equation of state for gaseous O₂, N₂, H₂O, CO, CO₂, and H₂

	a , MPa · cm ⁶ /g ²	b , MPa · cm ⁹ /g ³	c , MPa · cm ¹² /g ⁴	d , MPa · cm ¹⁵ /g ⁵
O ₂	−95.9962	200.7163	−290.0367	241.0805
N ₂	88.0920	−39.5838	361.2203	323.3721
H ₂ O	−1407.4860	3413.7110	−4595.0910	3019.6670
CO	−21.9137	171.3012	−38.4940	494.3099
CO ₂	−84.9107	143.7330	−125.0645	149.7969
H ₂	2549.7890	71843.9900	379716.0000	5990028.4000

	A , cm ³ /g	B , cm ⁶ /g ²	C , cm ¹⁸ /g ⁶	T_1 , K	μ , g/mol
O ₂	1.21	1.17	0.92	200	31.9988
N ₂	1.64	1.50	1.74	400	28.0134
H ₂ O	3.74	−2.52	10.90	673	18.0153
CO	1.88	1.68	4.38	300	28.0104
CO ₂	1.41	0.71	5.05	453	44.0095
H ₂	11.78	−6.67	81762.40	160	2.0160

Using detailed data on the EOS available in handbooks and monographs in the form of two-dimensional tables for the dependence of the pressure on the temperature and density, we first compiled two one-dimensional tables for the dependence of pressure on the density at two temperatures, $P(\rho, T_1)$ and $P(\rho, T_2)$ isotherms, where T_1 and T_2 are randomly selected temperatures within the reference data range, differing by several hundred kelvins. The choice is limited by the requirement that the lower temperature (T_1) be higher than the critical temperature of the component.

Then, the tabulated data for these two isotherms were approximated by the polynomials

$$\begin{aligned} P(\rho, T_1) &= \rho RT_1/\mu + a_{21}\rho^2 + \dots + a_{51}\rho^5, \\ P(\rho, T_2) &= \rho RT_2/\mu + a_{22}\rho^2 + \dots + a_{52}\rho^5. \end{aligned} \quad (2)$$

Further, according to (1), a system of two equations was written:

$$\begin{aligned} P(\rho, T_1) &= P_c(\rho) + \rho RT_1 f(\rho)/\mu, \\ P(\rho, T_2) &= P_c(\rho) + \rho RT_2 f(\rho)/\mu, \end{aligned} \quad (3)$$

in which only the functions $P_c(\rho)$ and $f(\rho)$ are unknown. Solving system (3) with respect to these unknowns, we find

$$\rho Rf(\rho)/\mu = [P(\rho, T_2) - P(\rho, T_1)]/(T_2 - T_1), \quad (4)$$

$$P_c(\rho) = P(\rho, T_1) - \rho RT_1 f(\rho)/\mu. \quad (5)$$

Note that, for a strictly linear dependence of the pressure on the temperature, the functions $f(\rho)$ and $P_c(\rho)$ would be independent of the arbitrarily chosen temperatures T_1 and T_2 . In fact, they do depend, a fac-

tor that affects the distribution of pressure approximation accuracy on the ρ – T plane.

In accordance with the representation of the isotherms $P(\rho, T_1)$ and $P(\rho, T_2)$ by polynomials (2), the functions given by (4) and (5) are also polynomials. The explicit dependence of the function $P_c(\rho)$ has the form

$$\begin{aligned} P_c(\rho) &= a\rho^2 + b\rho^3 + c\rho^4 + d\rho^5 \\ &\quad - \rho RT_1(f(\rho) - 1)/\mu. \end{aligned} \quad (6)$$

The function $f(\rho)$ in (4) was additionally approximated in the form of a fraction,

$$f(\rho) = (1 + A\rho + B\rho^2 + C\rho^6)/(1 + C\rho^6/6.7) \quad (7)$$

with the same exponent in the leading term of the power series in the numerator and denominator. In low-density limit, at $\rho \rightarrow 0$, approximation (1), (6), (7) transforms, as expected, into the equation of state of an ideal gas. In this limit, $f(\rho) = 1$ and $P_c = 0$. With increasing density, the function $f(\rho)$ increases monotonically and levels off on a plateau $f(\rho)_{\max}$ at large ρ values, in accordance with the theoretical concepts of the thermal pressure of solids [2] and of the Grüneisen coefficient (Γ):

$$\Gamma = P_T V/E_T, \quad (8)$$

where $P_T = R\rho T f(\rho)_{\max}/\mu$ is the thermal pressure, V and E_T are the volume and thermal energy of one mole, equal to $3RT$ (according to the Dulong–Petit law for the heat capacity of solids). At the plateau, the value of the function $f(\rho)$ satisfying (7) is 6.7. The value 6.7 in formula (7) is adjustable. However, as an approximate parameter, it is consistent with the theory.

Table 2. Oxygen (O₂): comparison with tabulated data [8]

ρ , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [8]	$ \Delta P /P$, %	ρ , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [8]	$ \Delta P /P$, %
Isotherm $T = 300$ K				Isotherm $T = 700$ K			
5.251	3.946	4	1.34	3.241	5.971	6	0.49
7.952	5.896	6	1.74	4.295	7.952	8	0.60
10.69	7.843	8	1.96	5.337	9.933	10	0.67
13.452	9.796	10	2.04	7.883	14.880	15	0.80
20.351	14.725	15	1.83	10.349	19.839	20	0.80
27.027	19.717	20	1.42	19.427	39.885	40	0.29
48.387	39.388	40	1.53	27.310	60.185	60	0.31
61.734	57.930	60	3.45	34.133	80.469	80	0.59
74.352	74.352	80	7.06	Isotherm $T = 800$ K			
77.566	94.552	100	5.45	2.836	5.978	6	0.36
Isotherm $T = 400$ K				3.758	7.962	8	0.47
3.846	3.963	4	0.94	4.670	9.947	10	0.53
5.762	5.926	6	1.24	6.901	14.906	15	0.63
7.668	7.883	8	1.46	9.066	19.874	20	0.63
9.561	9.841	10	1.59	17.085	39.917	40	0.21
14.211	14.747	15	1.68	24.157	60.237	60	0.40
18.706	19.695	20	1.52	30.386	80.643	80	0.80
34.457	39.683	40	0.79	35.891	100.959	100	0.96
46.458	59.229	60	1.28	Isotherm $T = 900$ K			
55.616	78.172	80	2.28	2.522	5.983	6	0.28
62.850	96.779	100	3.22	3.343	7.971	8	0.36
Isotherm $T = 500$ K				4.155	9.959	10	0.41
4.560	5.947	6	0.88	6.143	14.926	15	0.50
6.051	7.916	8	1.05	8.075	19.899	20	0.51
7.525	9.882	10	1.18	15.272	39.943	40	0.14
11.132	14.804	15	1.31	21.692	60.263	60	0.44
14.615	19.747	20	1.27	27.421	80.729	80	0.91
27.156	39.787	40	0.53	32.546	101.184	100	1.18
37.422	59.818	60	0.30	Isotherm $T = 1000$ K			
45.775	79.449	80	0.69	2.271	5.986	6	0.23
52.689	98.692	100	1.31	3.011	7.976	8	0.29
Isotherm $T = 600$ K				3.743	9.966	10	0.34
3.786	5.962	6	0.63	5.538	14.939	15	0.40
5.018	7.937	8	0.79	7.285	19.918	20	0.41
6.236	9.912	10	0.88	13.821	39.961	40	0.10
9.212	14.847	15	1.02	19.705	60.271	60	0.45
12.090	19.797	20	1.01	25.008	80.759	80	0.95
22.592	39.845	40	0.39	29.800	101.299	100	1.30
31.508	60.071	60	0.12				
39.038	80.121	80	0.15				
45.457	99.868	100	0.13				

Table 2. (Contd.)

ρ , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [8]	$ \Delta P /P$, %	ρ , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [8]	$ \Delta P /P$, %
Isotherm $T = 1100$ K				Isotherm $T = 1300$ K			
2.066	5.989	6	0.19	10.792	40.000	40	0.00
2.740	7.981	8	0.23	15.512	60.260	60	0.43
3.407	9.973	10	0.27	19.855	80.731	80	0.91
5.044	14.951	15	0.32	23.859	101.338	100	1.34
6.639	19.933	20	0.34	Isotherm $T = 1500$ K			
12.632	39.978	40	0.06	1.519	5.995	6	0.09
18.066	60.273	60	0.45	2.017	7.993	8	0.08
23.003	80.762	80	0.95	2.510	9.989	10	0.11
27.501	101.348	100	1.35	3.724	14.978	15	0.15
Isotherm $T = 1300$ K				4.913	19.972	20	0.14
1.751	5.994	6	0.10	9.431	40.017	40	0.04
2.323	7.988	8	0.15	13.609	60.247	60	0.41
2.890	9.983	10	0.17	17.488	80.680	80	0.85
4.283	14.967	15	0.22	21.097	101.271	100	1.27
5.645	19.957	20	0.21				

At high densities, the thermodynamic properties of substances are determined mainly by the intermolecular repulsion forces. The potential of these forces as a function of the intermolecular distance r can be approximated by a homogeneous function of r proportional to r^{-n} , with an exponent n of ~ 10 [6, p.143]. For example, for the Lennard-Jones potential (12–6 potential), $n = 12$. For the power potential,

$$\Gamma = (n + 2)/6. \quad (9)$$

This can be demonstrated using the virial theorem [3] or the Slater–Landau–Stanyukovich formula [7, p. 500]. From (8), (9) and the above dependence of the thermal energy on the temperature, it follows that

$$f(\rho)_{\max} = 3\Gamma = (n + 2)/2. \quad (10)$$

As noted above, expression (7) implies that $f(\rho)_{\max} = 6.7$. Then, according to (10), $n = 11.4$. Thus, the obtained value of n lies within the limits typical of the exponents of the repulsive power potentials for intermolecular interactions.

We obtained the coefficients A , B , C , a , b , c , and d entering into (6) and (7) for all six substances specified above. The values of these coefficients are given in Table 1. The accuracy of the equation of state for each of the gases is illustrated in Tables 2–7.

Figures 1–6 display the dependences of the pressure on the density for different isotherms, as well as the error of approximation of reference data for the same isotherms, for oxygen (Fig. 1), nitrogen (Fig. 2), water vapor (Fig. 3), carbon monoxide (Fig. 4), carbon dioxide (Fig. 5), and hydrogen (Fig. 6). The symbols represent the corresponding reference data, whereas the curves show the results of calculations by thermal OES (1).

These tables and figures show that, at pressures $P \leq 20$ MPa and temperatures ($500 \leq T \leq T_{\max}$) K (T_{\max} is the maximum temperature covered by the reference data for each substance), equation of state (1), (6), (7) with the coefficients given in Table 1 closely describes the reference data for oxygen, nitrogen, hydrogen,

Table 3. Nitrogen (N₂): comparison with tabulated data [9]

ρ , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [9]	$ \Delta P /P$, %	ρ , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [9]	$ \Delta P /P$, %
Isotherm $T = 300$ K				Isotherm $T = 400$ K			
4.5088	4.089	4	2.21	15.4164	20.483	20	2.42
6.7567	6.178	6	2.97	31.8777	50.309	50	0.62
8.9826	8.281	8	3.51	47.8171	99.551	100	0.45
11.1736	10.386	10	3.86	64.3575	200.011	200	0.01
21.2592	20.780	20	3.90	74.0395	300.622	300	0.21
41.1789	51.619	50	3.24	80.9598	400.507	400	0.13
57.0778	105.31	100	5.31	86.4085	499.96	500	0.01
72.2880	212.804	200	6.40	90.9473	599.403	600	0.10
81.0836	317.161	300	5.72	94.8663	699.136	700	0.12
87.4297	419.629	400	4.91	98.3334	799.329	800	0.08
92.4834	521.473	500	4.29	101.4537	900.040	900	0.01
96.7278	623.304	600	3.88	104.2975	1001.263	1000	0.13
100.4067	725.267	700	3.61	Isotherm $T = 500$ K			
103.6600	827.242	800	3.41	2.6507	4.030	4	0.75
106.5763	928.983	900	3.22	3.9412	6.062	6	1.04
109.2163	1030.209	1000	3.02	5.2075	8.102	8	1.28
Isotherm $T = 350$ K				6.4489	10.147	10	1.47
3.8233	4.062	4	1.55	12.2738	20.375	20	1.87
5.7040	6.125	6	2.09	26.1660	50.376	50	0.75
7.5563	8.199	8	2.49	41.1657	98.88	100	1.12
9.3742	10.277	10	2.77	58.0454	196.216	200	1.89
17.8045	20.588	20	2.94	68.2341	294.644	300	1.79
35.9066	50.576	50	1.15	75.5527	393.343	400	1.66
52.0457	101.293	100	1.29	81.3001	492.041	500	1.59
68.0825	204.681	200	2.34	86.0647	590.788	600	1.54
77.3752	306.915	300	2.31	90.1590	689.715	700	1.47
84.0316	407.816	400	1.95	93.7670	788.946	800	1.38
89.2964	508.158	500	1.63	97.0054	888.567	900	1.27
93.7001	608.532	600	1.42	99.9527	988.632	1000	1.14
97.5130	709.245	700	1.32	Isotherm $T = 600$ K			
100.8903	810.387	800	1.30	2.2077	4.022	4	0.56
103.9292	911.918	900	1.32	3.2825	6.047	6	0.79
106.6949	1013.719	1000	1.37	4.3377	8.079	8	0.98
Isotherm $T = 400$ K				5.3733	10.115	10	1.15
3.3269	4.046	4	1.16	10.2614	20.323	20	1.62
4.9536	6.094	6	1.57	22.3039	50.567	50	1.13
6.5514	8.152	8	1.90	36.2062	99.413	100	0.59
8.1180	10.214	10	2.14				

Table 3. (Contd.)

ρ_s , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [9]	$ \Delta P /P$, %	ρ_s , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [9]	$ \Delta P /P$, %
Isotherm $T = 600$ K				Isotherm $T = 800$ K			
52.9022	195.903	200	2.05	3.2648	8.059	8	0.73
63.3261	293.229	300	2.26	4.0489	10.087	10	0.87
70.8951	391.319	400	2.17	7.7851	20.278	20	1.39
76.8567	489.839	500	2.03	17.3618	50.853	50	1.71
81.7958	588.630	600	1.89	29.3219	100.827	100	0.83
86.0309	687.654	700	1.76	45.0443	198.394	200	0.80
89.7532	786.919	800	1.64	55.4605	295.572	300	1.48
93.0856	886.451	900	1.51	63.2195	393.450	400	1.64
96.1115	986.276	1000	1.37	69.4056	492.140	500	1.57
Isotherm $T = 700$ K				74.5585	591.521	600	1.41
1.8935	4.018	4	0.46	78.9839	691.446	700	1.22
2.8164	6.039	6	0.65	82.8711	791.791	800	1.03
3.7235	8.066	8	0.83	86.3450	892.458	900	0.84
4.6151	10.098	10	0.98	89.492	993.375	1000	0.66
8.8444	20.295	20	1.48	Isotherm $T = 900$ K			
19.5009	50.730	50	1.46	1.4756	4.014	4	0.36
32.3742	100.148	100	0.15	2.1973	6.031	6	0.52
48.6364	196.926	200	1.54	2.9083	8.054	8	0.67
59.1145	293.921	300	2.03	3.6088	10.081	10	0.81
66.8202	391.765	400	2.06	6.9598	20.267	20	1.34
72.9233	490.316	500	1.94	15.6683	50.943	50	1.89
77.9897	589.378	600	1.77	26.8288	101.398	100	1.40
82.3344	688.821	700	1.60	41.9785	199.934	200	0.03
86.1494	788.564	800	1.43	52.2609	297.611	300	0.80
89.5600	888.564	900	1.27	60.0141	395.739	400	1.07
92.6519	988.791	1000	1.12	66.2380	494.656	500	1.07
Isotherm $T = 800$ K				71.4434	594.358	600	0.94
1.6584	4.016	4	0.40	75.9242	694.738	700	0.75
2.4680	6.034	6	0.57	79.8647	795.665	800	0.54

Table 3. (Contd.)

ρ_s , g/cm ³ · 100	<i>P</i> , MPa; calculated by formulas (1), (6), (7)	<i>P</i> , MPa; tabulated data [9]	$ \Delta P /P$, %	ρ_s , g/cm ³ · 100	<i>P</i> , MPa; calculated by formulas (1), (6), (7)	<i>P</i> , MPa; tabulated data [9]	$ \Delta P /P$, %
Isotherm <i>T</i> = 900 K				Isotherm <i>T</i> = 1200 K			
83.3878	897.019	900	0.33	44.6737	303.789	300	1.26
86.5791	998.695	1000	0.13	52.2106	403.432	400	0.86
Isotherm <i>T</i> = 1000 K				58.3775	503.463	500	0.69
1.3294	4.013	4	0.33	63.6003	604.184	600	0.70
1.9805	6.029	6	0.49	68.1342	705.692	700	0.81
2.6228	8.050	8	0.63	72.1440	807.971	800	1.00
3.2563	10.076	10	0.76	75.7424	910.952	900	1.22
6.2969	20.259	20	1.30	79.0094	1014.536	1000	1.45
14.2898	51.009	50	2.02	Isotherm <i>T</i> = 1400 K			
24.7500	101.863	100	1.86	0.9527	4.011	4	0.28
39.3305	201.39	200	0.70	1.4216	6.024	6	0.41
49.4361	299.746	300	0.08	1.8857	8.043	8	0.53
57.1422	398.283	400	0.43	2.3450	10.065	10	0.65
63.3701	497.507	500	0.50	Isotherm <i>T</i> = 1600 K			
68.6008	597.534	600	0.41	0.8346	4.010	4	0.26
73.1156	698.320	700	0.24	1.2461	6.023	6	0.38
77.0927	799.764	800	0.03	1.6539	8.040	8	0.50
80.6519	901.744	900	0.19	2.0579	10.062	10	0.62
83.8775	1004.143	1000	0.41	Isotherm <i>T</i> = 1800 K			
Isotherm <i>T</i> = 1200 K				0.7426	4.010	4	0.25
1.1098	4.012	4	0.30	1.1093	6.022	6	0.36
1.6549	6.026	6	0.44	1.4730	8.038	8	0.48
2.1935	8.046	8	0.57	1.8337	10.059	10	0.59
2.7258	10.070	10	0.70	Isotherm <i>T</i> = 2000 K			
5.2949	20.247	20	1.23	0.6689	4.009	4	0.24
12.1731	51.090	50	2.18	0.9996	6.021	6	0.35
21.4707	102.537	100	2.54	1.3278	8.036	8	0.46
34.9817	203.872	200	1.94	1.6537	10.056	10	0.56

Table 4. Water vapor (H₂O): comparison with tabulated data [10]

$\rho, \text{g/cm}^3 \cdot 100$	$P, \text{MPa};$ calculated by formulas (1), (6), (7)	$P, \text{MPa};$ tabulated data [10]	$ \Delta P /P, \%$	$\rho, \text{g/cm}^3 \cdot 100$	$P, \text{MPa};$ calculated by formulas (1), (6), (7)	$P, \text{MPa};$ tabulated data [10]	$ \Delta P /P, \%$
Isotherm $T = 533.15 \text{ K}$				Isotherm $T = 623.15 \text{ K}$			
1.933	4.165	4	4.12	5.811	12.299	12	2.49
2.245	4.733	4.5	5.17	7.559	14.562	14	4.01
Isotherm $T = 553.15 \text{ K}$				8.711	15.764	15	5.10
1.803	4.098	4	2.45	Isotherm $T = 673.15 \text{ K}$			
2.367	5.185	5	3.69	1.363	3.980	4	0.49
3.015	6.323	6	5.38	2.111	5.961	6	0.65
Isotherm $T = 573.15 \text{ K}$				2.915	7.941	8	0.74
1.699	4.056	4	1.39	3.786	9.922	10	0.78
2.207	5.104	5	2.09	4.744	11.913	12	0.73
2.765	6.179	6	2.98	5.807	13.914	14	0.62
3.360	7.233	7	3.33	7.008	15.929	16	0.44
4.124	8.456	8	5.70	8.396	17.969	18	0.17
Isotherm $T = 593.15 \text{ K}$				10.048	20.034	20	0.17
1.613	4.028	4	0.69	35.638	29.682	30	1.06
2.079	5.053	5	1.06	52.329	40.209	40	0.52
2.580	6.092	6	1.54	57.737	50.282	50	0.56
3.126	7.150	7	2.14	61.162	59.925	60	0.13
3.729	8.232	8	2.90	63.735	69.370	70	0.90
4.409	9.350	9	3.88	65.876	78.970	80	1.29
5.198	10.514	10	5.14	68.493	93.233	90	3.59
Isotherm $T = 623.15 \text{ K}$				69.252	97.954	100	2.05
1.505	4.001	4	0.03	Isotherm $T = 773.15 \text{ K}$			
1.925	5.008	5	0.15	1.158	3.970	4	0.74
2.368	6.017	6	0.29	1.766	5.935	6	1.09
2.838	7.035	7	0.50	2.397	7.887	8	1.41
3.339	8.061	8	0.76	3.052	9.829	10	1.71
4.460	10.147	10	1.47	3.733	11.762	12	1.99

Table 4. (Contd.)

ρ , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [10]	$ \Delta P /P$, %	ρ , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [10]	$ \Delta P /P$, %
Isotherm $T = 773.15$ K				Isotherm $T = 873.15$ K			
4.442	13.687	14	2.24	16.383	48.532	50	2.94
5.184	15.607	16	2.46	20.704	58.832	60	1.95
5.959	17.522	18	2.66	25.176	69.508	70	0.70
6.770	19.430	20	2.85	29.577	80.359	80	0.45
11.522	29.006	30	3.31	33.715	91.135	90	1.26
17.809	38.915	40	2.71	37.467	101.613	100	1.61
25.70	49.462	50	1.08	Isotherm $T = 1073.15$ K			
33.875	60.465	60	0.78	1.225	5.967	6	0.56
40.617	71.073	70	1.53	1.640	7.942	8	0.73
45.704	81.012	80	1.26	2.058	9.912	10	0.88
49.652	90.604	90	0.67	2.478	11.877	12	1.02
52.798	99.920	100	0.08	2.902	13.838	14	1.16
Isotherm $T = 873.15$ K				3.329	15.796	16	1.27
1.012	3.974	4	0.66	3.759	17.754	18	1.37
1.534	5.941	6	0.98	4.191	19.702	20	1.49
2.066	7.898	8	1.27	6.402	29.464	30	1.79
2.609	9.845	10	1.55	8.673	39.234	40	1.92
3.164	11.782	12	1.82	11.011	49.142	50	1.72
3.730	13.710	14	2.07	13.392	59.194	60	1.34
4.308	15.630	16	2.31	15.803	69.421	70	0.83
4.900	17.543	18	2.54	18.222	79.816	80	0.23
5.507	19.456	20	2.70	20.636	90.385	90	0.43
8.741	28.974	30	3.42	23.015	101.042	100	1.04
12.369	38.614	40	3.47				

Table 5. Carbon monoxide (CO): comparison with tabulated data [13]

$\rho,$ $\text{g/cm}^3 \cdot 100$	$P,$ MPa; calculated by formulas (1), (6), (7)	$P,$ MPa; tabulated data [13]	$ \Delta P /P,$ %	$\rho,$ $\text{g/cm}^3 \cdot 100$	$P,$ MPa; calculated by formulas (1), (6), (7)	$P,$ MPa; tabulated data [13]	$ \Delta P /P,$ %
Isotherm $T = 280$ K				Isotherm $T = 350$ K			
4.88162	3.997	4	0.07	3.83437	4.003	4	0.08
7.33811	5.984	6	0.26	5.71981	5.999	6	0.02
9.78989	7.972	8	0.35	7.57698	7.991	8	0.11
12.2266	9.967	10	0.33	9.40315	9.986	10	0.14
14.6321	11.974	12	0.22	11.1954	11.984	12	0.13
16.9858	13.991	14	0.06	12.9501	13.988	14	0.09
19.2656	16.016	16	0.10	14.6631	15.997	16	0.02
21.4521	18.043	18	0.24	16.3302	18.010	18	0.06
23.5315	20.066	20	0.33	17.9472	20.025	20	0.13
38.8283	40.192	40	0.48	31.1247	39.929	40	0.18
48.0106	60.597	60	0.99	40.1158	59.523	60	0.80
54.2925	80.945	80	1.18	46.6846	79.113	80	1.11
59.0300	101.098	100	1.10	51.7743	98.660	100	1.34
Isotherm $T = 300$ K				Isotherm $T = 400$ K			
4.5234	3.999	4	0.03	3.33584	4.007	4	0.17
6.77798	5.988	6	0.20	4.96591	6.007	6	0.11
9.01593	7.976	8	0.29	6.56639	8.005	8	0.06
11.2302	9.969	10	0.31	8.13615	10.004	10	0.04
13.4111	11.971	12	0.25	9.67429	12.005	12	0.04
15.5468	13.981	14	0.14	11.1798	14.009	14	0.07
17.6238	15.998	16	0.01	12.6515	16.018	16	0.11
19.6293	18.018	18	0.10	14.0879	18.030	18	0.17
21.5532	20.037	20	0.18	15.4877	20.046	20	0.23
36.2436	39.979	40	0.05	27.3445	40.075	40	0.19
45.4648	60.012	60	0.02	35.9166	59.649	60	0.58
51.8932	80.058	80	0.07	42.4158	79.096	80	1.13
56.7702	99.982	100	0.02	47.5696	98.496	100	1.50

Table 5. (Contd.)

ρ , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [13]	$ \Delta P /P$, %	ρ , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [13]	$ \Delta P /P$, %
Isotherm $T = 500$ K				Isotherm $T = 800$ K			
2.65589	4.010	4	0.25	1.65864	4.011	4	0.28
3.94840	6.017	6	0.28	2.46769	6.023	6	0.38
5.21542	8.023	8	0.29	3.26304	8.037	8	0.46
6.45690	10.030	10	0.30	4.04490	10.054	10	0.54
7.67294	12.038	12	0.32	4.81348	12.073	12	0.61
8.86384	14.049	14	0.35	5.56908	14.095	14	0.68
10.0298	16.063	16	0.39	6.31203	16.119	16	0.74
11.1709	18.079	18	0.44	7.04263	18.146	18	0.81
12.2874	20.099	20	0.49	7.76123	20.176	20	0.88
22.1224	40.332	40	0.83	14.3458	40.614	40	1.53
29.8009	60.267	60	0.44	19.9875	61.196	60	1.99
35.9151	79.886	80	0.14	24.8607	81.741	80	2.18
40.9485	99.379	100	0.62	29.1147	102.156	100	2.16
Isotherm $T = 600$ K				Isotherm $T = 900$ K			
2.21047	4.011	4	0.28	1.47534	4.011	4	0.27
3.28604	6.021	6	0.35	2.19599	6.022	6	0.37
4.34102	8.032	8	0.40	2.90524	8.037	8	0.46
5.37553	10.044	10	0.44	3.60326	10.054	10	0.54
6.38984	12.058	12	0.48	4.29024	12.074	12	0.62
7.38441	14.074	14	0.53	4.96644	14.097	14	0.69
8.35959	16.093	16	0.58	5.63211	16.123	16	0.77
9.31581	18.114	18	0.63	6.28749	18.151	18	0.84
10.2534	20.138	20	0.69	6.93285	20.182	20	0.91
18.6714	40.483	40	1.21	12.8867	40.637	40	1.59
25.5491	60.747	60	1.25	18.0605	61.284	60	2.14
31.2203	80.734	80	0.92	22.5959	81.978	80	2.47
36.0045	100.525	100	0.53	26.6068	102.615	100	2.62
Isotherm $T = 700$ K				Isotherm $T = 1000$ K			
1.89468	4.012	4	0.29	1.32873	4.010	4	0.26
2.81757	6.022	6	0.37	1.97868	6.022	6	0.36
3.72379	8.036	8	0.44	2.61897	8.036	8	0.45
4.61348	10.051	10	0.51	3.2498	10.054	10	0.54
5.48699	12.068	12	0.57	3.87132	12.074	12	0.62
6.34461	14.088	14	0.63	4.48374	14.097	14	0.69
7.18674	16.110	16	0.69	5.08722	16.123	16	0.77
8.01378	18.135	18	0.75	5.68202	18.152	18	0.84
8.82605	20.162	20	0.81	6.26834	20.183	20	0.92
16.2057	40.567	40	1.42	11.7080	40.646	40	1.61
22.4083	61.034	60	1.72	16.4870	61.327	60	2.21
27.6613	81.348	80	1.69	20.7243	82.114	80	2.64
32.1751	101.471	100	1.47	24.5113	102.908	100	2.91

Table 6. Carbon dioxide (CO₂): comparison with tabulated data (up to 1273.15 K inclusive [12]; for 1500 K [14])

ρ , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [12]	$ \Delta P /P$, %	ρ , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [12]	$ \Delta P /P$, %
Isotherm $T = 373.15$ K				38.94	29.878	30	0.41
1.4529	1.002	1	0.22	49.75	39.822	40	0.45
2.979	2.009	2	0.46	58.14	49.813	50	0.37
4.586	3.022	3	0.73	64.68	59.810	60	0.32
6.281	4.040	4	1.00	Isotherm $T = 523.15$ K			
8.074	5.065	5	1.30	2.047	1.997	2	0.17
9.975	6.097	6	1.61	3.087	2.992	3	0.26
14.147	8.183	8	2.29	4.137	3.986	4	0.35
18.88	10.297	10	2.97	5.198	4.979	5	0.42
48.16	21.007	20	5.03	6.269	5.972	6	0.47
66.29	31.172	30	3.91	8.438	7.954	8	0.57
Isotherm $T = 423.15$ K				10.639	9.936	10	0.64
1.2696	1.0003	1	0.03	12.865	11.916	12	0.70
2.578	2.002	2	0.08	15.110	13.897	14	0.74
3.925	3.003	3	0.09	17.370	15.882	16	0.74
5.314	4.006	4	0.15	19.620	17.857	18	0.79
6.745	5.010	5	0.20	21.870	19.840	20	0.80
8.200	6.003	6	0.05	32.66	29.705	30	0.98
11.303	8.034	8	0.42	42.17	39.546	40	1.13
14.562	10.057	10	0.57	50.11	49.391	50	1.22
32.70	20.219	20	1.09	56.60	59.206	60	1.32
49.23	30.364	30	1.21	Isotherm $T = 573.15$ K			
60.76	40.420	40	1.05	5.642	5.968	6	0.53
68.75	50.286	50	0.57	7.559	7.948	8	0.65
Isotherm $T = 473.15$ K				9.489	9.926	10	0.74
1.1291	0.999	1	0.06	11.426	11.901	12	0.82
2.279	1.998	2	0.12	13.367	13.877	14	0.88
3.450	2.995	3	0.16	15.309	15.854	16	0.91
4.642	3.992	4	0.20	17.240	17.827	18	0.96
5.854	4.988	5	0.24	19.160	19.800	20	1.00
7.086	5.984	6	0.27	28.43	29.656	30	1.15
9.610	7.976	8	0.30	36.83	39.483	40	1.29
12.207	9.969	10	0.31	44.13	49.256	50	1.49
14.869	11.964	12	0.30	50.34	58.970	60	1.72
17.580	13.958	14	0.30	Isotherm $T = 673.15$ K			
20.330	15.954	16	0.29	4.728	5.972	6	0.47
23.100	17.952	18	0.27	6.304	7.954	8	0.57
25.87	19.951	20	0.24	8.438	7.954	8	0.57

Table 6. (Contd.)

ρ , g/cm ³ · 100	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [12]	$ \Delta P /P$, %	ρ , g/cm ³ · 1000	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [12]	$ \Delta P /P$, %
Isotherm $T = 673.15$ K				Isotherm $T = 1073.15$ K			
7.876	9.933	10	0.67	6.700	14.010	14	0.07
9.442	11.91	12	0.75	7.620	16.012	16	0.07
11.001	13.887	14	0.81	8.532	18.017	18	0.10
12.550	15.863	16	0.86	9.433	20.021	20	0.10
14.088	17.838	18	0.90	13.79	30.042	30	0.14
15.613	19.815	20	0.93	17.91	40.092	40	0.23
22.98	23.779	30	1.02	21.78	50.113	50	0.23
29.79	39.535	40	1.16	25.43	60.149	60	0.25
35.98	49.358	50	1.28	Isotherm $T = 1273.15$ K			
41.49	59.082	60	1.53	3.270	8.017	8	0.21
Isotherm $T = 773.15$ K				4.069	10.025	10	0.25
4.085	5.980	6	0.34	4.861	12.036	12	0.30
5.434	7.967	8	0.41	5.644	14.045	14	0.32
6.774	9.952	10	0.48	6.421	16.060	16	0.38
8.105	11.935	12	0.54	7.189	18.073	18	0.40
9.426	13.919	14	0.58	7.950	20.089	20	0.44
10.735	15.901	16	0.62	11.63	30.159	30	0.53
12.033	17.884	18	0.64	15.13	40.275	40	0.69
13.317	19.866	20	0.67	18.44	50.377	50	0.75
19.52	29.778	30	0.74	21.58	60.488	60	0.81
25.31	39.678	40	0.81	Isotherm $T = 1500$ K			
30.66	49.560	50	0.88	0.2498	0.7096	0.7	1.4
35.56	59.401	60	1.00	0.3567	1.014	1	1.4
Isotherm $T = 1073.15$ K				1.416	4.069	4	1.7
3.881	8.002	8	0.01	2.459	7.116	7	1.9
4.830	10.005	10	0.05	3.487	10.23	10	2.3

Table 7. Hydrogen (H₂): comparison with tabulated data (up to 400 K inclusive [12]; from 600 K and higher [14])

ρ , g/cm ³ · 1000	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [12, 14]	$ \Delta P /P$, %	ρ , g/cm ³ · 1000	P , MPa; calculated by formulas (1), (6), (7)	P , MPa; tabulated data [12, 14]	$ \Delta P /P$, %
Isotherm $T = 280$ K				Isotherm $T = 350$ K			
3.3814	4.0033	4	0.1	12.506	20.04	20	0.2
5.0112	6.0061	6	0.1	22.723	39.80	40	0.5
6.6012	8.0085	8	0.1	31.222	59.12	60	1.5
8.1520	10.010	10	0.1	38.422	77.97	80	2.5
11.859	14.996	15	0.0	44.631	96.40	100	3.6
15.343	19.963	20	0.2	Isotherm $T = 400$ K			
27.328	39.518	40	1.2	2.3793	4.006	4	0.2
36.876	58.53	60	2.5	3.5356	6.013	6	0.2
44.701	77.081	80	3.7	4.6699	8.021	8	0.3
51.311	95.365	100	4.6	5.7848	10.03	10	0.3
Isotherm $T = 300$ K				8.4813	15.06	15	0.4
3.1589	4.004	4	0.1	11.059	20.08	20	0.4
4.6840	6.008	6	0.1	20.302	39.98	40	0.05
6.1746	8.013	8	0.2	28.156	59.52	60	0.8
7.6277	10.013	10	0.1	33.328	73.90	80	7.6*
11.114	15.005	15	0.0	39.452	92.71	100	7.3*
14.400	19.979	20	0.1	Isotherm $T = 600$ K			
25.826	39.600	40	1.0	1.595	4.008	4	0.2
35.055	58.685	60	2.2	2.376	6.015	6	0.2
42.694	77.280	80	3.4	3.147	8.026	8	0.3
49.195	95.568	100	4.4	3.908	10.04	10	0.4
Isotherm $T = 350$ K				4.659	12.05	12	0.5
2.7137	4.005	4	0.1	6.133	16.09	16	0.6
4.0320	6.016	6	0.3	7.569	20.13	20	0.6
5.3165	8.017	8	0.2	11.010	30.23	30	0.8
6.5775	10.02	10	0.2	14.252	40.32	40	0.8
9.6183	15.04	15	0.2	20.215	60.38	60	0.6

Table 7. (Contd.)

ρ , g/cm ³ · 1000	<i>P</i> , MPa; calculated by formulas (1), (6), (7)	<i>P</i> , MPa; tabulated data [12, 14]	$ \Delta P /P$, %	ρ , g/cm ³ · 1000	<i>P</i> , MPa; calculated by formulas (1), (6), (7)	<i>P</i> , MPa; tabulated data [12, 14]	$ \Delta P /P$, %
Isotherm <i>T</i> = 600 K				17.349	102.11	100	2.1
22.968	70.32	70	0.5	20.274	122.60	120	2.2
25.587	80.21	80	0.3	23.060	143.03	140	2.2
28.082	90.02	90	0.0	25.717	163.3	160	2.1
Isotherm <i>T</i> = 800 K				Isotherm <i>T</i> = 1500 K			
1.200	4.008	4	0.2	0.803	5.011	5	0.2
1.790	6.014	6	0.2	1.595	10.039	10	0.4
2.375	8.026	8	0.3	3.148	20.146	20	0.7
2.954	10.041	10	0.4	6.138	40.53	40	1.3
3.527	12.058	12	0.5	8.986	61.08	60	1.8
4.656	16.097	16	0.6	11.704	81.74	80	2.2
5.764	20.15	20	0.7	14.305	102.46	100	2.5
8.441	30.28	30	0.9	Isotherm <i>T</i> = 1750 K			
10.999	40.44	40	1.1	0.689	5.009	5	0.1
15.789	60.72	60	1.2	1.370	10.03	10	0.3
20.201	80.91	80	1.1	2.709	20.12	20	0.6
24.286	100.93	100	0.9	5.303	40.44	40	1.1
28.088	120.76	120	0.6	7.791	60.90	60	1.5
Isotherm <i>T</i> = 1000 K				10.181	81.45	80	1.8
1.200	5.012	5	0.2	12.482	102.05	100	2.1
2.375	10.040	10	0.4	Isotherm <i>T</i> = 2000 K			
4.657	20.15	20	0.7	0.603	5.006	5	0.1
8.965	40.50	40	1.1	1.201	10.04	10	0.4
12.972	60.91	60	1.5	2.378	20.12	20	0.6
16.716	81.32	80	1.7	4.668	40.44	40	1.1
20.229	101.66	100	1.7	6.876	60.93	60	1.6
23.536	121.88	120	1.6	9.009	81.53	80	1.9
26.661	141.97	140	1.4	11.071	102.21	100	2.2
29.620	161.90	160	1.1	Isotherm <i>T</i> = 2500 K			
Isotherm <i>T</i> = 1200 K				0.483	5.006	5	0.1
1.002	5.012	5	0.2	0.963	10.03	10	0.3
1.986	10.038	10	0.4	1.911	20.12	20	0.6
3.907	20.149	20	0.7	3.766	40.44	40	1.1
7.569	40.52	40	1.1	5.568	60.92	60	1.5
11.015	61.02	60	1.7	7.321	81.56	80	2.0
14.268	81.56	80	2.0	9.028	102.05	100	2.3

* Probably, a misprint in tabulated data from [12].

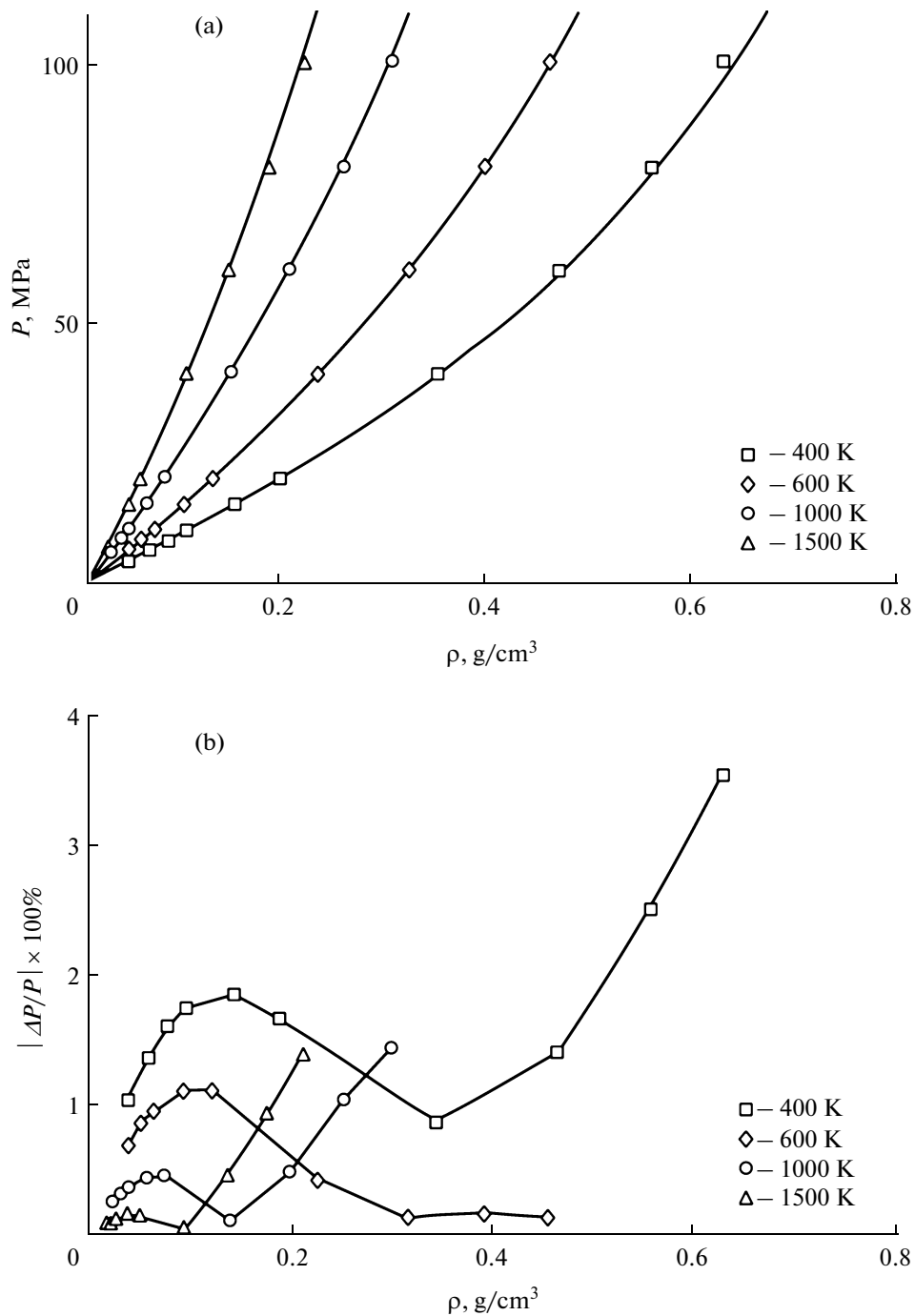


Fig. 1. (a) Dependences of the pressure on the density of oxygen at various isotherms: the symbols and curves represent, respectively, the reference data and results of calculations by thermal equation of state (1); (b) the error of approximation of the reference data for these isotherms as a function of the oxygen density.

carbon monoxide, and carbon dioxide, the mean deviation modulus ranging from tenths of a percent to one percent, with the maximum error reaching $\sim 2\text{--}3\%$. At temperatures near room temperature and a pressure of ~ 20 MPa, the error is markedly higher, but this range of thermodynamic parameters corresponds to cold

compression, being of no interest for gas dynamics, combustion, and detonation. The same applies to near-critical temperatures of the gases under consideration, where the error in the predictions of state equation (1), (6), (7) can reach tens of percent. The only exception is water vapor. The critical temperature

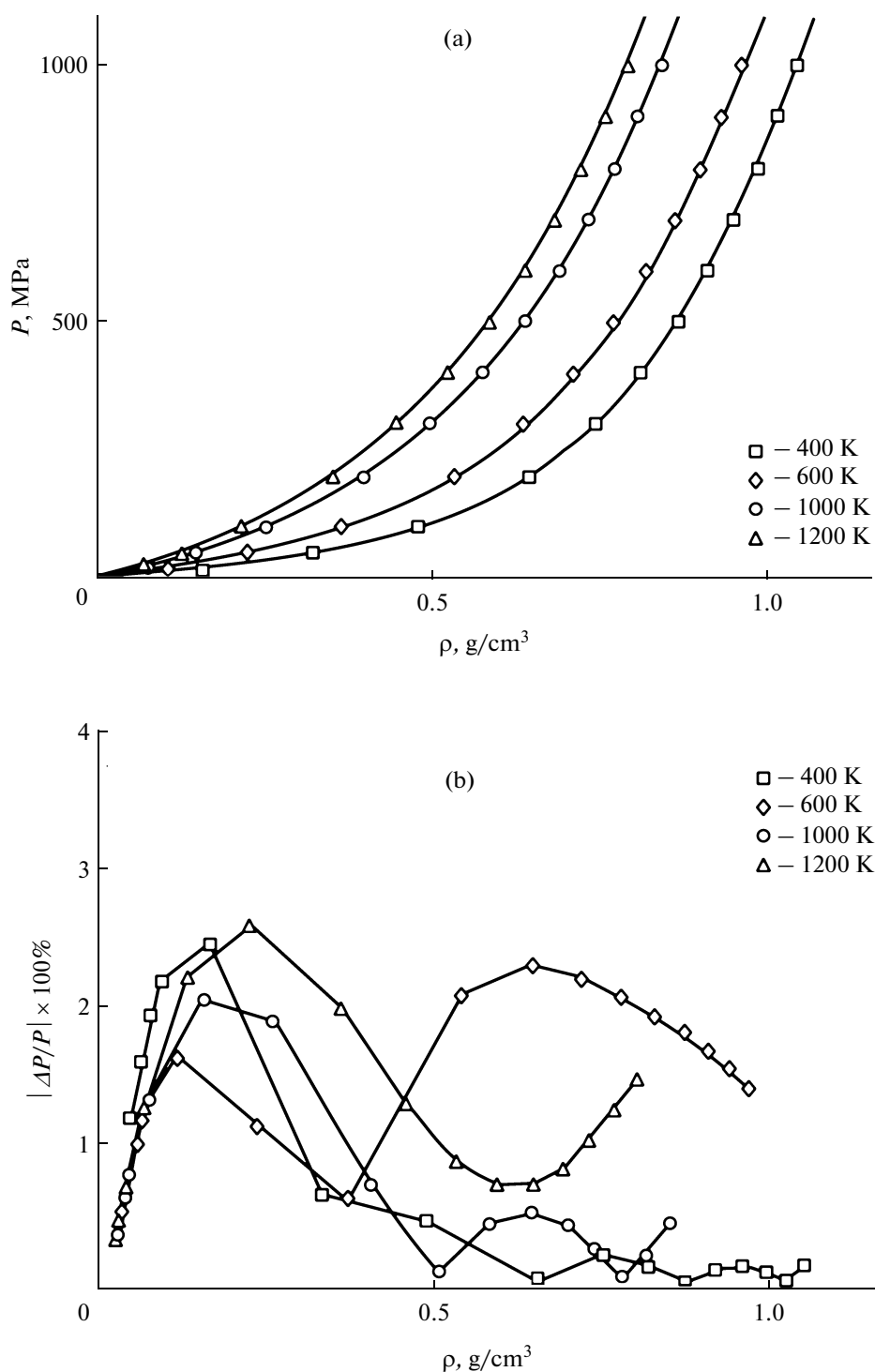


Fig. 2. (a) Dependences of the pressure on the density of nitrogen at various isotherms: the symbols and curves represent, respectively, the reference data and results of calculations by thermal equation of state (1); (b) the error of approximation of the reference data for these isotherms as a function of the nitrogen density.

of water is 647.14 K. The error of the equation of state of water vapor at temperatures ranging from critical to T_{\max} is approximately 1–2%. At lower temperatures, at some points, it can be as high as 5–6%.

On the Error of the Equation of State over a Wider Range of Pressures

The maximum pressure covered by the reference data with which it is possible to compare the calcula-

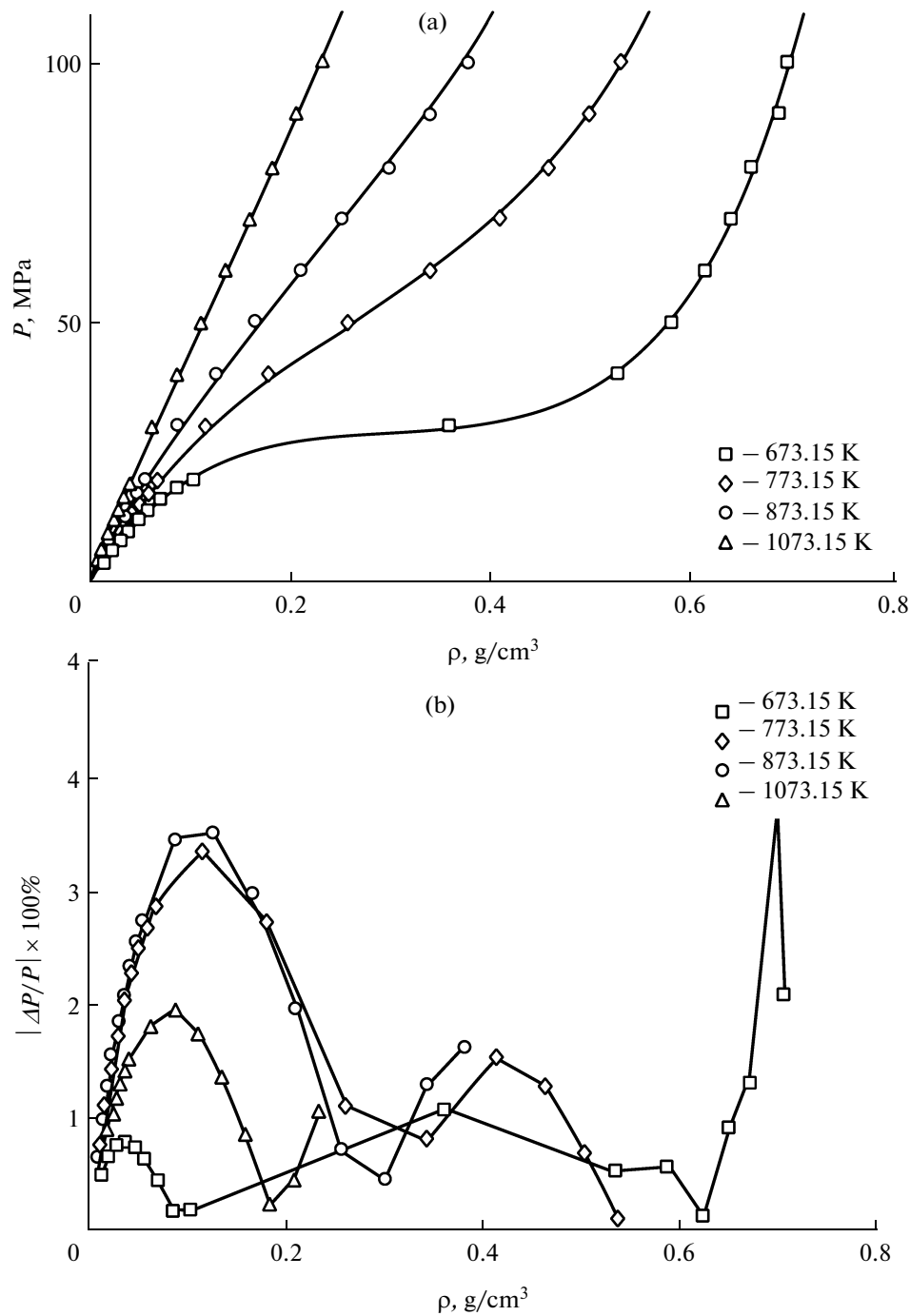


Fig. 3. (a) Dependences of the pressure on the density of water vapor at various isotherms: the symbols and curves represent, respectively, the reference data and results of calculations by thermal equation of state (1); (b) the error of approximation of the reference data for these isotherms as a function of the water vapor density.

tion results is 100 MPa for water and 60 MPa for carbon dioxide. Bearing in mind the physically sound form of equation of state (1), (6) (7), we can assume that it is applicable at higher pressures, when the density exceeds the critical value, being close to the density of the liquid phase under normal conditions (for water, for example, 1 g/cm³). The error in the pressure

can probably rise to 10–15%, but it may be less than that. For example, for oxygen, carbon monoxide, and hydrogen, for which the reference (experimental) data extend up to 100 MPa (Tables 2, 5, and 7), and for nitrogen (up to 1000 MPa, Table 3), the error in the pressure at $T \geq 500$ K is small (within 2.0–2.5%) over the entire range of pressures.

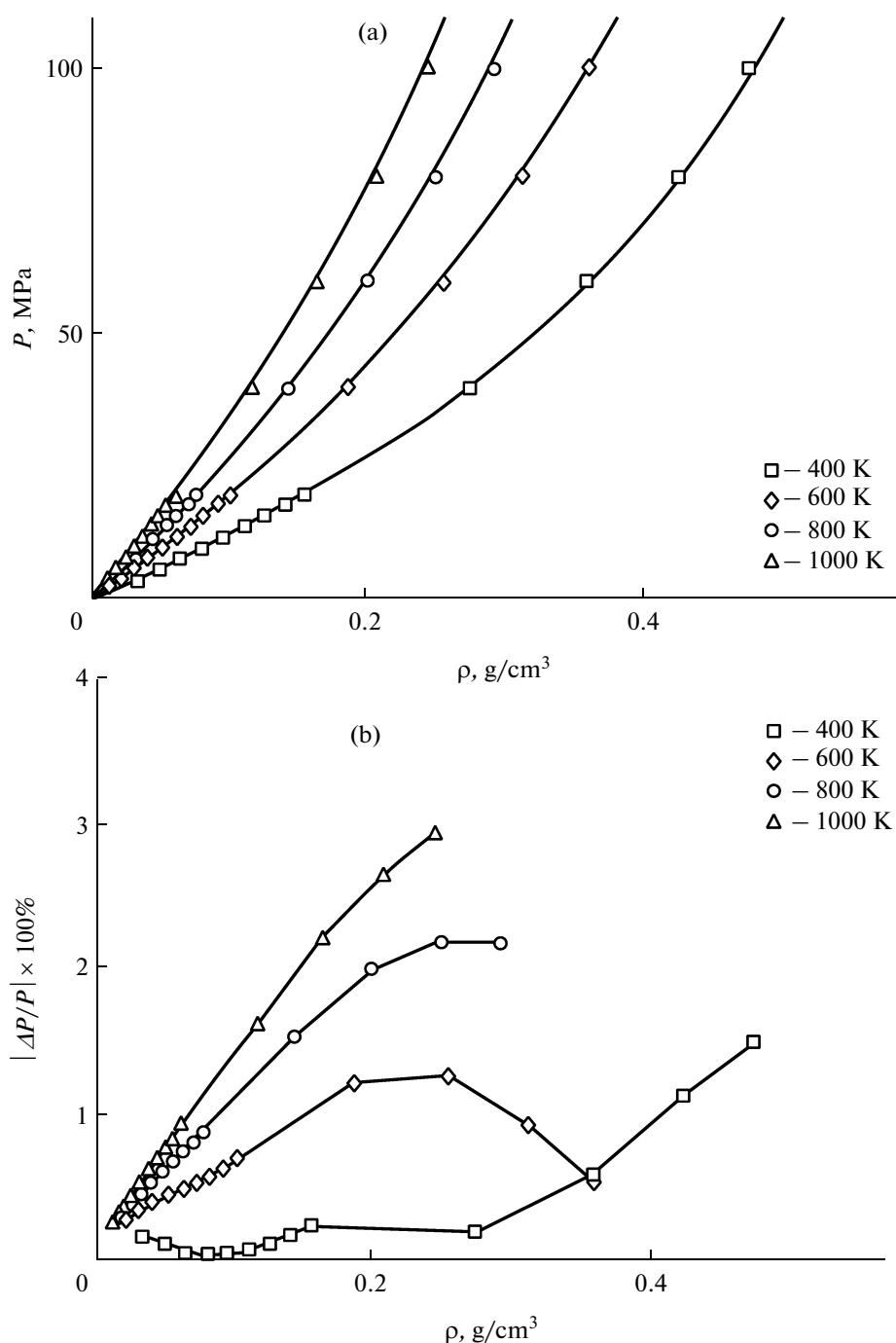


Fig. 4. (a) Dependences of the pressure on the density of carbon monoxide at various isotherms: the symbols and curves represent, respectively, the reference data and results of calculations by thermal equation of state (1); (b) the error of approximation of the reference data for these isotherms as a function of the carbon monoxide density.

CALORIC EQUATION OF STATE

Internal energy E , Heat Capacity at Constant Volume c_V , Enthalpy H , and Heat Capacity at Constant Pressure c_P of Individual Substances

Internal energy and heat capacity at constant volume. The internal energy of the gas E consists of the

energy of an ideal gas E_{id} and the so-called excess energy E_{exc} :

$$E = E_{id} + E_{exc}. \quad (11)$$

The excess energy is defined by the integral

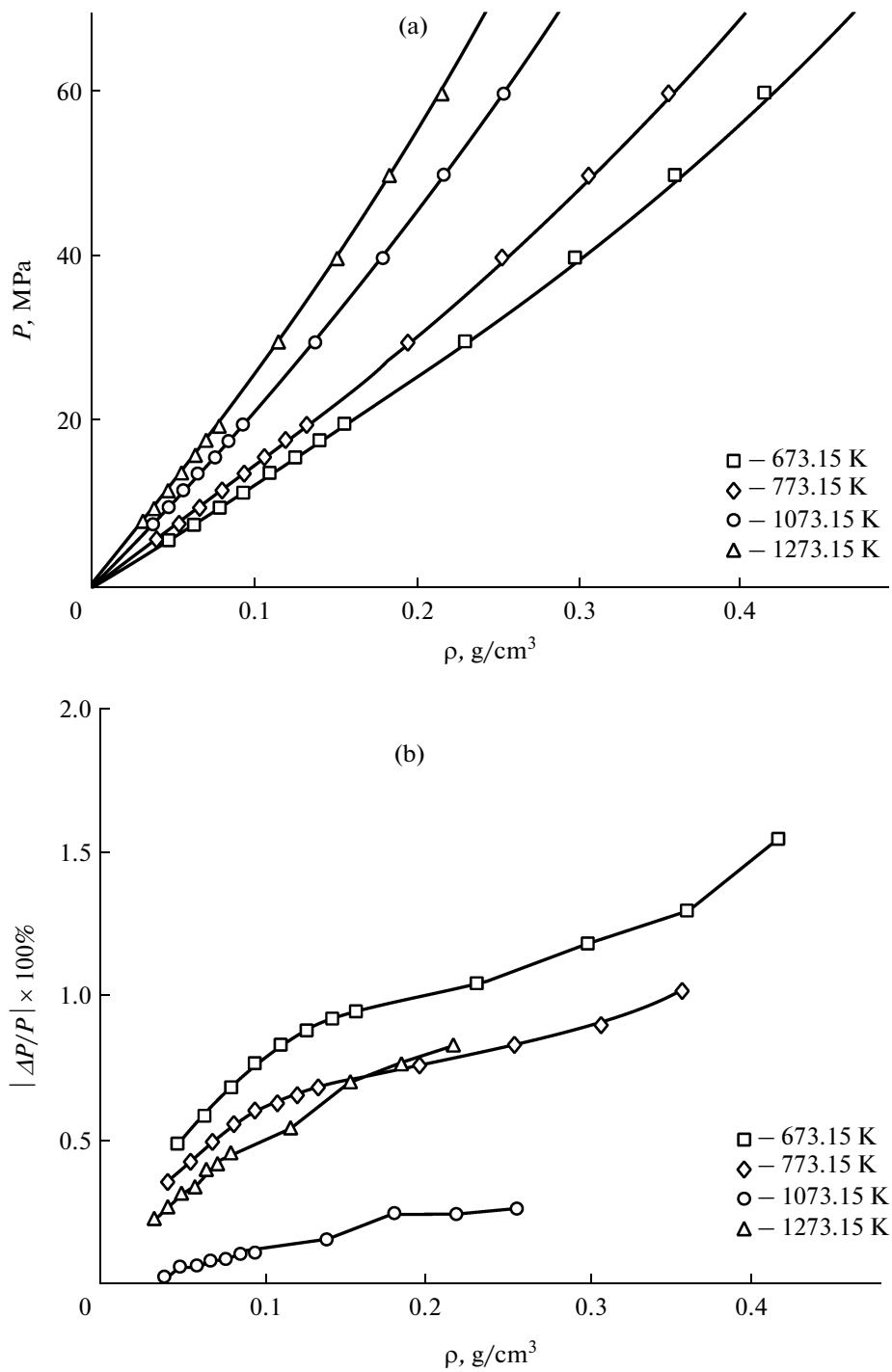


Fig. 5. (a) Dependences of the pressure on the density of carbon dioxide at various isotherms: the symbols and curves represent, respectively, the reference data and results of calculations by thermal equation of state (1); (b) the error of approximation of the reference data for these isotherms as a function of the carbon dioxide density.

$$E_{exc} = \int_0^{\rho} [p - T(\partial p / \partial T)_{\rho}] \rho^{-2} d\rho. \quad (12)$$

Due to the linear dependence of the pressure on the temperature in equation of state (1), its substitution into (12) gives

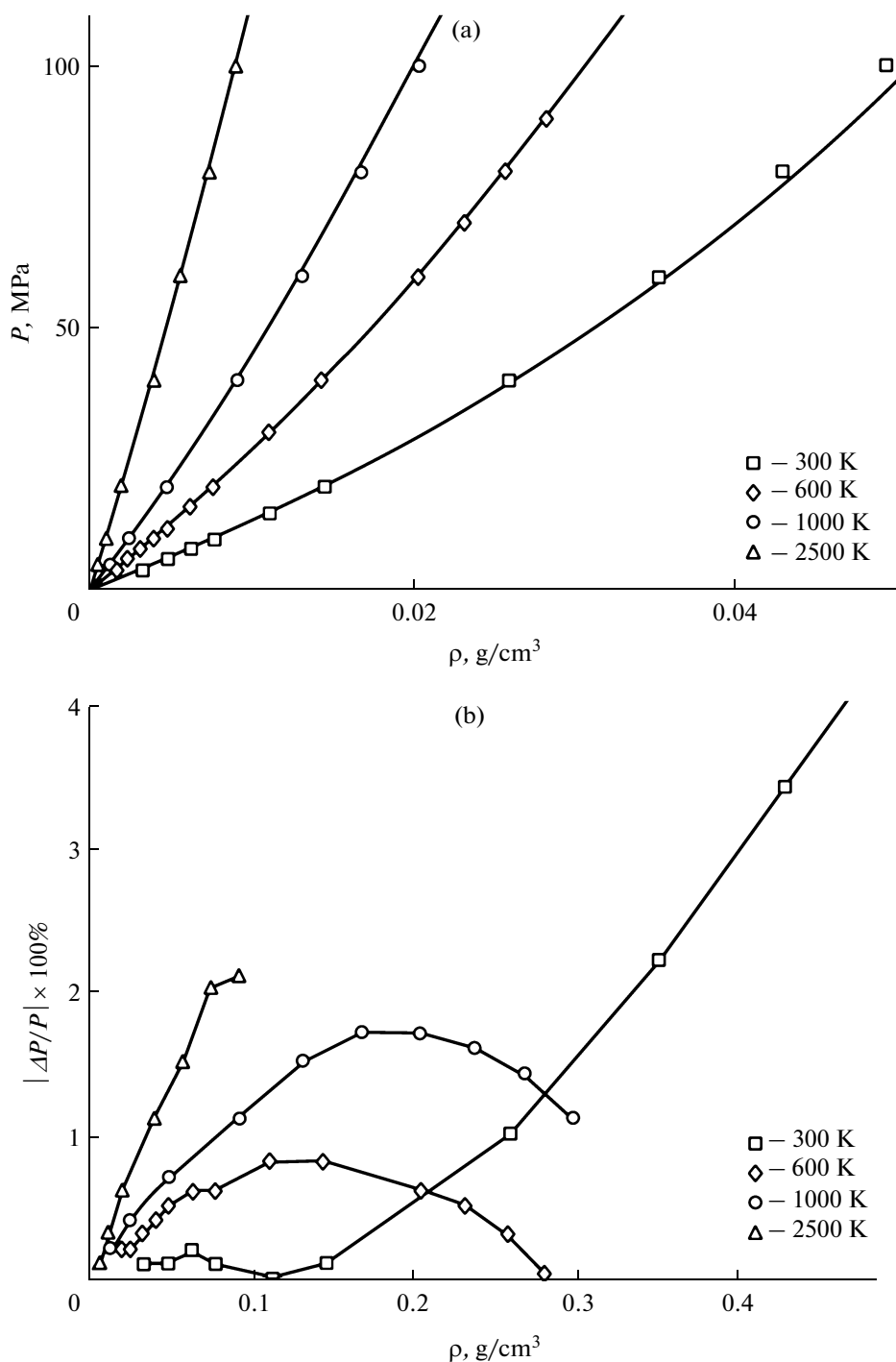


Fig. 6. (a) Dependences of the pressure on the density of hydrogen at various isotherms: the symbols and curves represent, respectively, the reference data and results of calculations by thermal equation of state (1); (b) the error of approximation of the reference data for these isotherms as a function of the hydrogen density.

$$E_{exc} = \int_0^{\rho} p_c(\rho) \rho^{-2} d\rho \quad (13)$$

$$= a\rho + b\rho^2/2 + c\rho^3/3 + d\rho^4/4.$$

From (13) it follows that E_{exc} is temperature-independent, and, accordingly, the excess heat capacity at constant volume $(c_V)_{exc} = 0$. In other words, the heat capacities c_V of all substances obeying equation of state (1) are identical to that of an ideal gas. Formulas for the internal energy and heat capacity c_V of the ideal

gases of the substances under consideration, sufficiently accurate and yet simple and convenient in practical calculations, were derived in [15, 16].

Enthalpy and heat capacity at constant pressure. By definition, the enthalpy H of one mole is related to the internal energy as

$$H = E + PV, \quad (14)$$

where V is the molar volume.

Combining the thermodynamic relationship $c_p = (\partial H/\partial T)_p$ with (14) yields the following expression for the molar heat capacity:

$$c_p = (\partial E/\partial T)_p + P(\partial V/\partial T)_p. \quad (15)$$

Representing in (15) the energy and pressure as the sum of the thermal and “cold” components, we can recast (15) as

$$c_p = [dE_{exc}/dV + P_c + P_T](\partial V/\partial T)_p + c_V,$$

where P_T is the thermal pressure and P_c is the “cold” component of the pressure that depends only on the density. Since $dE_{exc}/dV = -P_c$, we finally obtain

$$c_p = P_T(\partial V/\partial T)_p + c_V. \quad (16)$$

Recall that here c_p and c_V are the molar heat capacities. The specific heats are also related by (16) upon replacement of the molar volume V by the specific volume v .

Note that formula (16) is valid even when the pressure (internal energy) is composed of two components, “cold” and thermal, with the thermal component being proportional to the temperature.

The general relation between the heat capacities c_p and c_V , which is valid for an arbitrary equation of state, is given by the well-known thermodynamic relationship [3]

$$c_p = -T(\partial P/\partial T)_V^2/(\partial P/\partial V)_T + c_V. \quad (17)$$

Applying this formula to equation of state (1) and noting that, in this case

$$P_T = (\rho RT/\mu)f(\rho) \quad \text{and} \quad (\partial P/\partial T)_V = P_T/T,$$

we can rewrite (17) as

$$c_p = -P_T(\partial P/\partial T)_V/(\partial P/\partial V)_T + c_V. \quad (18)$$

If we now take into account the known formula for the partial derivatives of a function relating three variables (in our case, P , T , and V),

$$(\partial P/\partial T)_V(\partial V/\partial P)_T(\partial T/\partial V)_P = -1,$$

the equivalence of (17) and (18) becomes apparent.

CONCLUSIONS

Thus, we have developed the thermal and caloric EOS for the major components of gas mixtures typically used in calculations of gas dynamic processes, including combustion and detonation, as well as in

solving the problems of internal ballistics. The EOS obtained contains seven parameters and have an average error of less than 1% at temperatures from 500 to 2000–2500 K and at densities up to the critical. The effects of dissociation and ionization, important near the upper temperature limit at low densities, can be accounted for separately.

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