THE THERMODYNAMIC SIMILARITY OF NITROGEN, OXYGEN, AND AIR

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The thermodynamic similarity of nitrogen, oxygen, and air is established. The data for nitrogen are used to calculate the thermodynamic properties of oxygen at pressures of (1-1500) $\cdot$ 10^5 N/m^2 and temperatures of 170-1000 deg K. Tables of specific volume, enthalpy, entropy, and heat capacity of oxygen are given.

A knowledge of the thermophysical properties of nitrogen, oxygen, and air in a wide range of temperature and pressure is presently of great practical interest. Thus, there have been a number of investigations of the properties of these substances [1-5].

There are no experimental data on the compressibility of oxygen at pressures up to 1500 $\cdot$ 10^5 N/m^2 and temperatures 170-1000°K, hence this problem has been solved by the method of thermodynamic similarity.

It is known that equality of the critical numbers $k = P_c V_c / RT_c$ of different substances is one of the most important necessary conditions for the validity of the law of corresponding states. Table 1 gives the critical parameters of nitrogen, oxygen, and air. The close agreement of the critical numbers of these substances suggests that they are thermodynamically similar.

Table 1

Substance	T_c, °K	$P_c \cdot 10^{-5}$, N/m^2	d_c, g/cm^3	$k = \frac{P_c V_c}{RT_c}$
Nitrogen.	126.2	33.94	0.311	0.2914
Oxygen	154.8	50.81	0.433	0.2917
Air	132.4	37.75	0.328	0.3029

To verify this hypothesis we reduced the experimental PVT data for N_2, O_2, and air to the dimensionless parameters z, ω, and τ and compared them with one another.

We found that in corresponding states (equal values of ω and τ) the compressibility z for nitrogen and oxygen agreed to within 0.2-0.5%. The differences between these data and the corresponding values of z for air were greater. This can be attributed to the fact that the critical number of air differs slightly from the practically equal values of k for oxygen and nitrogen. To attain sufficient accuracy for fulfillment of the law of corresponding states for all three investigated substances, we decided to correct the critical density d_c for air.

We found that the best agreement between the compressibility z in the reduced coordinates z, ω, τ for all three substances was obtained when we took the value d_c = 0.3392 g/cm^3 for air (in this case k = 0.2927 and differs from the adopted values of the critical coefficients for oxygen and nitrogen by 0.3-0.4%).

This is clearly illustrated in Fig. 1. We found good agreement of the compared values on all the experimental isotherms of oxygen (τ = 1.009-3.0559). At low and medium densities (ω = 0-1.4) the compressibility z for each of the three substances agreed to within 0.2-0.3%. At larger values of ω the deviations of the compressibility of oxygen and air from that of nitrogen were 0.3-0.6%. The greatest differences (0.8-0.9%) were observed at very high densities (ω = 2.2-2.3). It should be noted that such differences in z (at high densities)

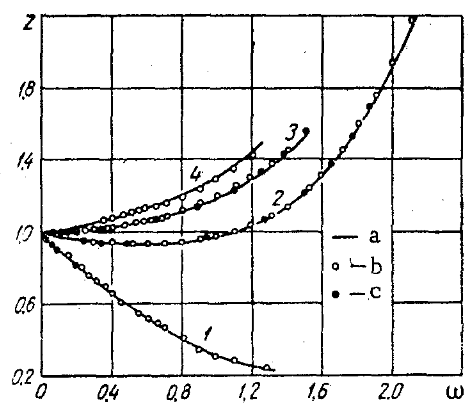

Fig. 1. Compressibility isotherms for N_2 (a), O_2 (b), and air (c) in relation to density for equal values of the reduced temperatures: 1) τ = 1.0285, t_{O_2} = = −113.97°C, t_{N_2} = −143.35°C, and t_{air} = = −137.00°C; 2) 1.7648, 0, −50.43, and −39.55; 3) 2.4007, 99.50, 30.7, and 45.69; 4) 3.0559, 199.50, and 112.50.

lead to errors of not more than 0.3-0.4% in the specific volume. Since the dimensionless group z is connected with the reduced parameters ω, π, and τ by the relationship $z = k\pi/\omega\tau$, agreement of z at equal ω and τ should read to agreement of the reduced pressures π, since the critical numbers of the investigated substances are practically equal ($k_{N_2} = 0.2914$; $k_{O_2} = 0.2917$; $k_{air} = 0.2927$).

We can infer from the above analysis that in the indicated temperature range the law of corresponding states is valid for the three substances for densities up to $\omega = 2.3$.

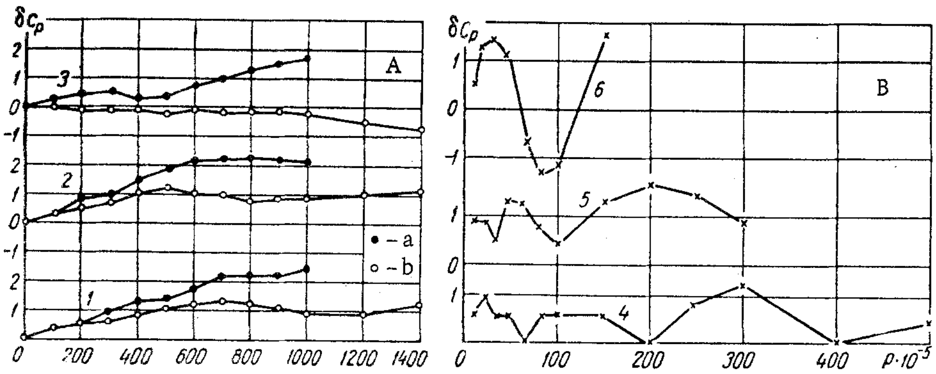

Fig. 2. Comparison of true heat capacity of air (A) with data of [3] (a) and [4] (b) and of true heat capacity of oxygen (B) with the data of [6] at t(°C): 1) 800; 2) 699; 3) 200; 4) 225; 5) 0; 6) −75.

Thus, within the above-indicated range of accuracy the thermodynamic behavior of N_2, O_2, and air can be predicted by a single reduced equation of state

$$z = f(\omega, t)$$

which is the same for the three investigated substances.

Thus we can use the equation of state of nitrogen (taken as a standard) to obtain the corresponding thermodynamic values for oxygen in the indicated range of parameters. There are, however, experimental compressibility data for nitrogen in a wider range of temperatures (up to t = 800°C, corresponding to $\tau = 8.5$).

As will be shown below, there is every reason to assume that at higher temperatures, outside the region in which oxygen has been investigated experimentally, the investigated substances are thermodynamically similar.

To verify this hypothesis we calculated the thermodynamic values of air on the basis of the equation of state of nitrogen [1] for the ranges of parameters $\tau = 1$-8.5 and $\omega = 0$-2.3. The obtained theoretical thermal and caloric values for air were compared with the corresponding data published in [3] and [4].

Table 2

Specific Volume of Oxygen at Different Temperatures and Pressures

$P \cdot 10^{-5}$ N/m²	Specific volume of oxygen, cm³/g, at temperature (°K).									
	170	200	300	400	500	600	700	800	900	1000
0.9807	446.8	528.8	795.4	1061	1327	1592	1858	2123	2388	2654
49.03	6.295	8.915	15.50	21.28	26.82	32.26	37.65	43.04	48.40	53.75
98.07	1.782	3.714	7.614	10.70	13.58	16.36	19.10	21.82	24.53	27.23
196.1	1.297	1.759	3.799	5.476	6.993	8.438	9.845	11.23	12.61	13.97
294.2	1.180	1.428	2.636	3.784	4.828	5.816	6.773	7.712	8.639	9.560
392.3	1.114	1.289	2.113	2.969	3.763	4.517	5.245	5.957	6.659	7.355
490.3	1.069	1.207	1.826	2.497	3.136	3.744	4.332	4.907	5.473	6.033
588.4	1.034	1.151	1.645	2.193	2.724	3.234	3.727	4.210	4.664	5.153
686.5	1.006	1.108	1.521	1.982	2.434	2.872	3.297	3.713	4.121	4.451
784.5	—	1.074	1.430	1.827	2.220	2.603	2.976	3.341	3.700	4.054
882.6	—	1.046	1.360	1.708	2.055	2.394	2.727	3.052	3.373	3.688
980.7	—	1.022	1.304	1.614	1.924	2.220	2.528	2.822	3.111	3.396
1079	—	1.001	1.258	1.537	1.817	2.094	2.386	2.633	2.897	3.157
1177	—	—	1.219	1.473	1.729	1.982	2.231	2.476	2.718	2.957
1275	—	—	1.186	1.419	1.654	1.887	2.117	2.343	2.586	2.788
1373	—	—	1.156	1.373	1.591	1.806	2.019	2.230	2.438	2.643
1471	—	—	1.131	1.332	1.535	1.735	1.934	2.131	2.326	2.518

The comparison showed satisfactory agreement among the compared values in the temperature range 0-850°C and at pressures up to 1500 · 10^5 N/m^2. In particular, the average enthalpy differences lay in the range 4-8 kJ/kg. The greatest differences (about 20 kJ/kg) were obtained at t = 850°C and pressures (1000-1200) · 10^5 N/m^2.

Table 3

Enthalpy of Oxygen at Different Temperatures and Pressures

P · 10^{-5} N/m^2	Entropy (kJ/kg) at temperature (°K).									
	170	200	300	400	500	600	700	800	900	1000
0.9807	153.7	180.9	273.0	365.9	461.8	560.6	662.4	766.6	873.4	981.4
49.03	111.8	151.6	260.4	359.8	458.9	559.4	661.9	767.0	874.2	982.6
98.07	46.05	118.5	246.7	352.2	455.9	558.1	661.9	767.4	875.2	983.5
196.1	16.75	75.36	229.4	345.0	451.8	556.8	662.2	768.7	877.1	985.9
294.2	14.23	61.96	216.0	338.3	448.8	556.2	663.2	770.7	879.2	988.2
392.3	15.91	60.29	208.6	334.1	447.4	556.6	665.1	773.3	881.7	990.6
490.3	19.52	61.55	205.2	331.6	447.2	557.7	667.4	776.6	884.4	993.1
588.4	24.28	64.31	203.9	331.2	448.0	559.8	670.2	780.0	887.2	995.4
686.5	29.00	67.41	204.8	332.0	449.7	562.3	673.2	783.4	890.1	997.8
784.5	—	71.59	206.9	334.1	452.0	565.2	676.6	786.9	893.0	1000
882.6	—	76.44	209.8	336.7	455.0	568.8	680.4	790.5	896.0	1003
980.7	—	81.22	213.5	340.0	458.4	572.8	684.5	794.4	899.0	1005
1079	—	85.83	217.7	343.7	462.6	576.9	688.7	798.4	901.9	1007
1177	—	—	222.2	347.9	467.2	581.5	692.9	802.6	904.9	1010
1275	—	—	226.9	352.7	472.0	586.2	697.1	806.8	907.8	1012
1373	—	—	231.9	357.6	476.9	591.2	701.4	811.1	910.7	1015
1471	—	—	236.9	362.2	481.9	596.6	705.9	815.4	913.6	1017

Table 4

Entropy of Oxygen at Different Temperatures and Pressures

P · 10^{-5} N/m^2	Enthalpy (kJ/kg) at temperature (°K).									
	170	200	300	400	500	600	700	800	900	1000
0.9807	5.8770	6.0466	6.4184	6.6859	6.8982	7.0795	7.2348	7.3759	7.5011	7.6154
49.03	4.7072	4.9241	5.3671	5.6543	5.8737	6.0575	6.2161	6.3564	6.4824	6.5967
98.07	4.1768	4.6189	5.1544	5.4592	5.6852	5.8724	6.0319	6.1734	6.2995	6.4146
196.1	3.9653	4.2747	4.9186	5.2523	5.4757	5.6823	5.8448	5.9780	6.1148	6.2304
294.2	3.8816	4.1416	4.7730	5.1251	5.3658	5.5680	5.7330	5.8774	6.0055	6.1215
392.3	3.8242	4.0637	4.6708	5.0330	5.2837	5.4855	5.6526	5.7983	5.9272	6.0436
490.3	3.7798	4.0076	4.5950	4.9609	5.2168	5.4206	5.5894	5.7363	5.8657	5.9829
588.4	3.7426	3.9628	4.5351	4.9027	5.1615	5.3671	5.5375	5.6852	5.8155	5.9331
686.5	3.7099	3.9247	4.4866	4.8542	5.1150	5.3214	5.4931	5.6417	5.7728	5.8864
784.5	—	3.8916	4.4455	4.8119	5.0740	5.2821	5.4546	5.6044	5.7355	5.8417
882.6	—	3.8623	4.4100	4.7755	5.0384	5.2473	5.4206	5.5710	5.7024	5.8230
980.7	—	3.8351	4.3786	4.7432	5.0057	5.2159	5.3901	5.5404	5.6731	5.7920
1079	—	3.8100	4.3505	4.7143	4.9773	5.1879	5.3624	5.5132	5.6459	5.7652
1177	—	—	4.3250	4.6880	4.9513	5.1623	5.3369	5.4885	5.6216	5.7409
1275	—	—	4.3015	4.6637	4.9279	5.1385	5.3147	5.4654	5.5990	5.7188
1373	—	—	4.2802	4.6415	4.9057	5.1167	5.2921	5.4441	5.5776	5.6978
1471	—	—	4.2601	4.6210	4.8852	5.0966	5.2720	5.4244	5.5584	5.6786

As regards the specific heat C_p, which is most senstive to change in the equation of state, the differences between our data and those of [3] and [4] lie in the range 1-2% (Fig. 2). In the whole investigated pressure range up to 1500 · 10^5 N/m^2 the obtained heat capacity data for air agree to within 1-1.2% with the data of [4] and to within 2-2.2% with the data of [3]. Such differences are permissible.

The analysis conducted confirms the expressed hypothesis of the validity of the law of corresponding states for the investigated substances in a wider temperature range. On the other hand, we can also assume that the caloric values obtained by the method of thermodynamic similarity from the data for nitrogen are reliable.

Table 5

True Specific Heat of Oxygen at Different Temperatures and Pressures

$P \cdot 10^{-5}$, N/m^2	Specific heat (kJ/kg · deg) at temperature (°K).									
	170	200	300	400	500	600	700	800	900	1000
0.9807	0.913	0.913	0.921	0.942	0.971	1.005	1.030	1.059	1.076	1.093
49.03	1.670	1.206	1.020	0.984	0.995	1.017	1.038	1.063	1.079	1.095
98.07	3.404	1.817	1.110	1.026	1.017	1.030	1.046	1.066	1.083	1.097
196.1	1.733	1.964	1.256	1.093	1.055	1.051	1.061	1.074	1.088	1.101
294.2	1.398	1.641	1.340	1.141	1.083	1.070	1.074	1.083	1.095	1.105
392.3	1.202	1.478	1.361	1.173	1.105	1.087	1.086	1.091	1.100	1.110
490.3	1.038	1.377	1.365	1.193	1.122	1.100	1.096	1.098	1.105	1.114
588.4	0.908	1.298	1.352	1.206	1.135	1.111	1.105	1.105	1.112	1.118
686.5	0.779	1.235	1.338	1.212	1.144	1.119	1.112	1.110	1.118	1.122
784.5	—	1.181	1.324	1.214	1.151	1.126	1.118	1.114	1.120	1.126
882.6	—	1.130	1.310	1.214	1.156	1.130	1.122	1.118	1.123	1.130
980.7	—	1.088	1.295	1.214	1.160	1.135	1.125	1.122	1.126	1.133
1079	—	1.047	1.280	1.214	1.162	1.137	1.128	1.124	1.130	1.135
1177	—	—	1.264	1.214	1.164	1.139	1.131	1.126	1.133	1.137
1275	—	—	1.250	1.212	1.164	1.141	1.135	1.130	1.136	1.139
1373	—	—	1.236	1.211	1.164	1.142	1.138	1.134	1.139	1.141
1471	—	—	1.223	1.210	1.164	1.143	1.141	1.138	1.141	1.143

Adopting the equation of state of nitrogen [1] as a basis, we calculated the thermodynamic properties of oxygen. A comparison of the obtained values with the data of [6], obtained on the basis of the accurate equation of state of oxygen for the range ω = 0-1.4 showed good agreement of the specific volumes and of the caloric values. In particular, the differences in specific volumes were 0.2-0.4%, in enthalpy 2-3 J/kg, and in specific heat not more than 1-1.5%.

We give tables of specific volume, enthalpy, entropy, and specific heat of oxygen (Tables 2-5). These tables are sufficiently accurate for use in various practical heat-engineering calculations.

NOTATION

$z = PV/RT$ – compressibility; $\tau = T/T_c$, $\omega = d/d_c$, and $\pi = P/P_c$ – reduced temperature, density, and pressure, respectively.

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