

SIMPLE EMPIRICAL EQUATION OF STATE FOR GASEOUS NITROGEN
IN THE HIGH-PRESSURE RANGE

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A two-parameter equation of state is presented for dense gases, which describes the available experimental data for nitrogen to a high accuracy over a wide temperature range.

Nitrogen is one of the most important technological gases, widely used as a pressure transfer medium in various high-pressure equipment. Design calculations for such equipment and for processes using such equipment require a knowledge of the equation of state of the gas used at high pressure over a wide temperature range.

The statistical theory of the equation of state together with computer methods for simulating dense gases [1, 2] have now been developed to a high degree, but their use in practical applications requires an extremely large volume of computations. This forces recourse to another type of empirical or semiempirical equation of state for such calculations, e.g., the Tate equation [3]

$$\frac{\rho - \rho_0}{\rho} = C \ln \frac{B + P}{B + P_0} \quad (1)$$

the logarithmic equation [3]

$$\rho = \rho_0 + A \ln(P/P_0) \quad (2)$$

or the equation of state proposed in [4]

$$\rho^* = A + BP. \quad (3)$$

Equations (1)-(3) are recommended for the temperature range 300-700°K, and their coefficients (unique to each equation) are defined for this range.

In the present study we will present a simple two-parameter equation of state for nitrogen, which describes its volume parameters at pressures above 2 kbar and temperatures from 100 to 2000°K with high accuracy. The equation is based on the observed fact that all known experimental nitrogen isotherms measured by various authors [5-10] at pressures above 2 kbar are described with high accuracy by straight lines in the coordinates $\sqrt{\rho} - \ln P$. As a result, the equation of the nitrogen isotherm at high pressures can be written in the form

$$\sqrt{\rho} = a + b \ln P. \quad (4)$$

The coefficients a and b are functions of temperature and can be determined by processing available experimental data, e.g., by the method of least squares.

The values of these coefficients for all known experimental nitrogen isotherms are presented in Table 1. Also shown there are the relative mean and maximum deviations (δ) of nitrogen density values calculated with equation of state (4) from experimental data on each isotherm, together with the same deviations for Eqs. (1)-(3) over their recommended temperature ranges.

It is evident from the table that the deviations of calculations with Eq. (4) from the experimental data are practically within the range of the experimental uncertainties. Moreover, in the comparable temperature range, this equation gives better results than Eqs. (1)-(3).

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TABLE 1. Values of Coefficients for Equation of State (4) for Nitrogen and Deviations of Nitrogen Density Values, as Calculated with Eqs. (1)-(4), from Experimental Data on Isotherms

Iso-therm, °K	Max. pres- sure on isotherm, kbar	Litera- ry source	Coefficients of Eq. (4)		δ , % (numerator, mean deviation; de- nominator; maximum deviation)			
			a	b	(1)	(2)	(3)	(4)
115,66	2,950		0,9221	0,0714	—	—	—	0,02/0,04
145,08	5,325		0,8884	0,0854	—	—	—	0,06/0,19
175,83	8,346		0,8611	0,0943	—	—	—	0,10/0,20
205,52	9,988		0,8351	0,1018	—	—	—	0,08/0,13
252,56	10,554	[5]	0,8005	0,1105	—	—	—	0,04/0,10
280,93	10,567		0,7815	0,1157	0,30/0,73	—	—	0,06/0,15
308,79	10,512		0,7647	0,1201	0,28/0,57	—	—	0,09/0,42
247,5	16,0		0,7959	0,1167	—	—	—	0,12/0,22
273,3	20,0	[6]	0,7765	0,1213	0,77/2,16	—	—	0,15/0,60
294,4	22,0		0,7628	0,1243	0,93/2,64	—	—	0,15/0,62
320,8	22,0		0,7501	0,1268	1,07/2,76	1,10/2,95	—	0,15/0,41
294,65	6,586		0,7710	0,1203	0,19/0,33	—	—	0,13/0,21
453,15	5,066	[7]	0,6797	0,1467	0,14/0,26	0,61/0,80	0,21/0,64	0,09/0,16
473,15	8,106		0,6719	0,1471	0,57/0,96	0,16/0,48	0,17/1,01	0,30/0,73
573,15	10,132		0,6357	0,1517	—	0,33/0,65	0,41/4,10	0,37/1,14
673,15	10,132		0,5981	0,1594	0,75/1,14	0,36/0,76	0,29/1,58	0,46/1,00
308,15	10,0		0,7630	0,1216	0,40/0,73	—	—	0,05/0,32
373,15	10,0	[8]	0,7255	0,1313	0,22/0,34	0,85/1,12	0,16/0,73	0,15/0,47
473,15	10,0		0,6828	0,1395	0,23/0,64	0,68/1,06	0,19/1,03	0,25/0,79
573,15	10,0		0,6389	0,1519	0,58/0,97	0,38/1,04	0,30/2,15	0,19/0,68
673,15	10,0		0,6022	0,1595	0,86/1,44	0,62/1,64	0,65/4,91	0,23/0,61
473,15	4,938		0,6722	0,1473	0,15/0,23	0,31/0,37	0,09/0,34	0,15/0,49
573,15	4,807		0,6279	0,1594	0,34/0,61	0,13/0,20	0,20/0,81	0,16/0,38
673,15	4,813	[9]	0,5905	0,1679	0,34/0,60	0,60/0,87	0,65/2,62	0,12/0,34
773,15	4,802		0,5549	0,1764	—	—	—	0,25/0,70
973,15	4,801		0,4920	0,1942	—	—	—	0,14/0,30
1073,15	4,853		0,4658	0,2004	—	—	—	0,17/0,36
1173,15	4,817		0,4448	0,2039	—	—	—	0,21/0,55
1273,15	4,803		0,4243	0,2072	—	—	—	0,33/0,73
400	3,0		0,7007	0,1495	—	0,24/0,35	0,36/0,67	0,23/0,32
500	3,5		0,6538	0,1569	0,72/0,72	0,21/0,47	0,04/0,06	0,26/0,30
600	4,0		0,6122	0,1658	0,86/0,96	0,16/0,34	0,36/0,76	0,25/0,38
700	5,0		0,5815	0,1685	—	—	0,77/2,76	0,17/0,45
800	5,5		0,5501	0,1744	—	—	—	0,18/0,50
900	6,0	[10]	0,5221	0,1792	—	—	—	0,33/0,75
1000	6,5		0,5011	0,1808	—	—	—	0,31/0,69
1100	7,0		0,4802	0,1832	—	—	—	0,28/0,73
1200	8,0		0,4606	0,1865	—	—	—	0,32/0,70
1300	8,0		0,4428	0,1884	—	—	—	0,28/0,58
1400	7,5		0,4292	0,1887	—	—	—	0,28/0,72
1500	7,0		0,4155	0,1892	—	—	—	0,27/0,43
1600	6,5		0,4028	0,1899	—	—	—	0,22/0,41
1700	6,0		0,3900	0,1913	—	—	—	0,23/0,48
1800	5,5		0,3735	0,1960	—	—	—	0,36/1,04

Note: Pressure in Eq. (4) expressed in kbar, density in g/cm^3 .

Another important quality characterizing any equation of state is the possibility of using the equation to extrapolate isotherms to higher pressures.

To evaluate the suitability of Eq. (4) for long-range extrapolation and compare the results with other equations of state, two experimental isotherms were used: 273.3 and 320.8°K, measured at pressures from 3 to 20 kbar [6]. To do this, the coefficients of all the equations, (1)-(4), were initially determined using experimental data for pressures up to 10 kbar, and these values were then used to calculate density values at the higher pressures. The results showed that the maximum relative deviation calculated from experimental data in such an extrapolation was as follows: on the 273.3°K isotherm for Eq. (1), 2.16%; Eq. (2), 2.55%; Eq. (3), 1.40%; Eq. (4), 0.92%, and on the 320.8°K isotherm, 2.74, 2.95, 1.14, and 0.85%, respectively. Thus, Eq. (4) also gives the best results in extrapolation.

Thus, the proposed equation of state (4) can be recommended for practical calculations of the volume behavior of nitrogen at high pressures over a wide temperature range, including extrapolation of known data to higher pressures.

NOTATION

ρ , gas density; P , pressure; ρ_0 , gas density at pressure P_0 .

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APPLICATION OF STATISTICAL APPROACHES TO SOLVE IMPURITY

PROPAGATION PROBLEMS

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The Cauchy problem for an equation of hyperbolic type describing impurity diffusion at a finite velocity is solved by the Monte Carlo method.

In connection with the appearance of high-speed electronic computers, interest in the Monte Carlo method has increased considerably at the present time. Its simplicity and universality permit extension of the circles of problems that can be solved by this method. In particular, this refers to problems allowing probabilistic treatment.

Let us examine a problem associated with impurity propagation in an unbounded space.

As is known, the description of passive impurity propagation processes in a turbulent medium by a semiempirical turbulent diffusion equation has the disadvantage that the velocity of impurity propagation is infinite. Hence, it can be detected at any instant at any distance from the source. This results in substantial errors when determining the impurity concentration near a cloud boundary.

Certain authors ([1] and the bibliography therein) proposed extensions of the diffusion equations by giving them a hyperbolic character (in this case the impurity propagation velocity is finite). In this connection, the stochastic models based on the random walk method merit special attention.

Let us consider the simplest one-dimensional model of continuous motion of impurity par-

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