EQUATION OF STATE OF NITRIC OXIDE OVER THE TEMPERATURE RANGE 190—2000° K AT DENSITIES OF 0—20 kmole/m³

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Experimental P, V, T data for nitric oxide are reviewed. An equation for the second virial coefficient is given together with the equation of state of NO over the temperature range 190–2000° K at densities 0–20 kmole/m³.

In the present investigation the method of comparing the densities of the experimental substance and some reference substance, whose properties have been well studied at the same reduced temperature τ and reduced pressure π [5], is used to correlate the experimental material and to obtain a reference network of P, V, T data. The virtue of this method is that on plotting the density of one substance as a function of the density of another having similar physical properties, a single curve is obtained over a fairly wide temperature range.

This is advantageous for a number of reasons. Firstly, it enables the available experimental data to be correlated very simply, while at the same time all the peculiarities of the thermodynamic surface of the real gas can be observed. Secondly, it provides the possibility of obtaining isotherms for the same range of volumes. This is very important when constructing equations of state based on experimental data derived from rounded pressure values. Thirdly, the relationship $\gamma_1 = f(\gamma_2)_{\tau,\pi = \text{idem}}$ is very close to a straight line, which enables the isotherms to be extrapolated fairly reliably with respect to densities. In our investigation we made use of this to extend the experimental data to $\gamma = 20$ kmole/m³.
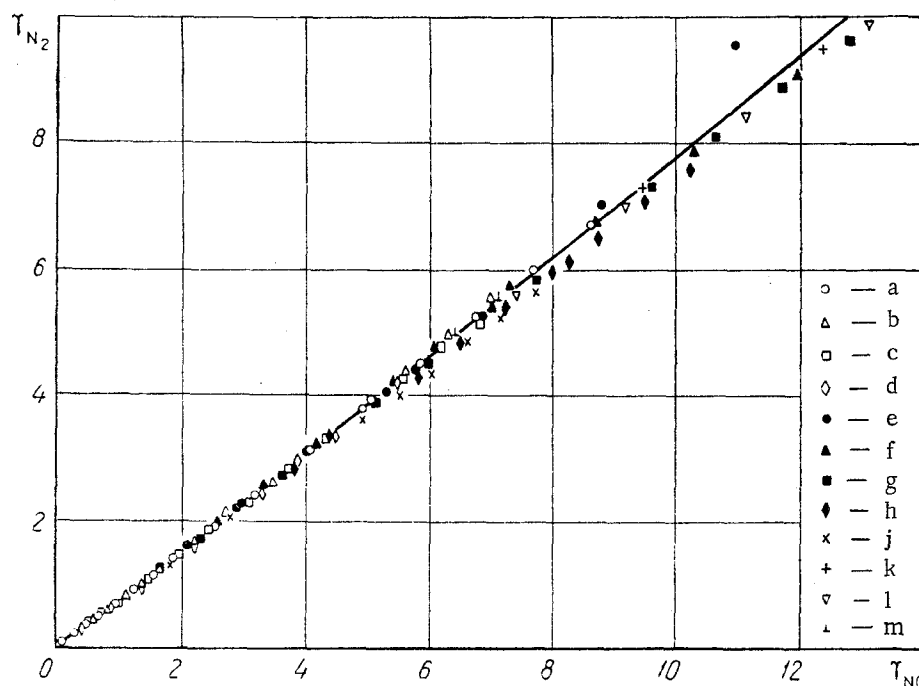

Fig. 1. Graph of γ_{NO} vs. γ_{N_2} for the same π and τ: data of [3] [a) $\tau = 1.54$; b) 1.73; c) 1.91; d) 2.10]; data of [2] [e) 1.08; f) 1.18; f) 1.18; g) 1.29; h) 1.41; i) 1.57]; data of [10] [k) 1.17; l) 1.26; m) 1.73]. Continuous line—authors' equation.

Nitrogen, which is close to NO in a number of respects* and for which an equation of state valid over a wide range of temperatures (up to $\tau = 8$) is available [6], was chosen as the reference substance. Using the equation of state for

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*In speaking of the similarity of the properties of NO and N_2, we have in mind that the gases are diatomic and that both belong to the group of low-boiling substances ($T_{cN_2} = 126°$ K; $T_{cNO} = 180.15°$ K). From the point of view of a comparison of macro-properties, this is more important than the differences in the properties of the molecules (low dipole moment for NO, unpaired electron in outer shell, etc.).

nitrogen [6], we determined the densities γ for τ and π equal to the reduced temperatures and pressures of nitric oxide from the experimental data in [2] and [3], and plotted the graph of the relationship $\gamma_{NO} = f(\gamma_{N_2})$ for $\pi, \tau =$ idem (Fig. 1).*

The critical state parameters of nitric oxide were taken from [7]: $T_c = 180.15°$ K, $P_c = 64.8 \times 10^5$ N/m².

As may be seen from the graph, the data of [3] for the isotherms $\tau = 1.54$, 1.91, and 2.10 lie on one curve. Certain deviations from this curve by the data of [3] for the $\tau = 1.73$ isotherm and by the data of [2] are attributable to the inconsistency of the experimental results, of which Fig. 2 gives some idea.
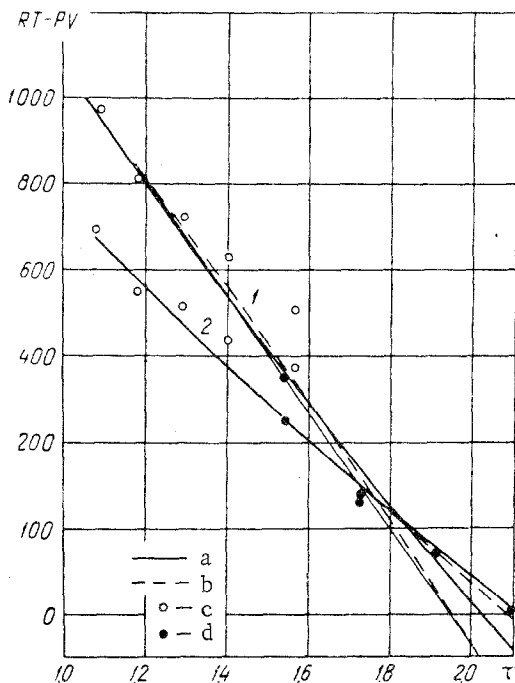
Fig. 2. Isochores for (1) $\gamma = 7$ and (2) $\gamma = 5$: a) from authors' equation; b) from the equation in [10]; c and d) experimental data from [2] and [3].
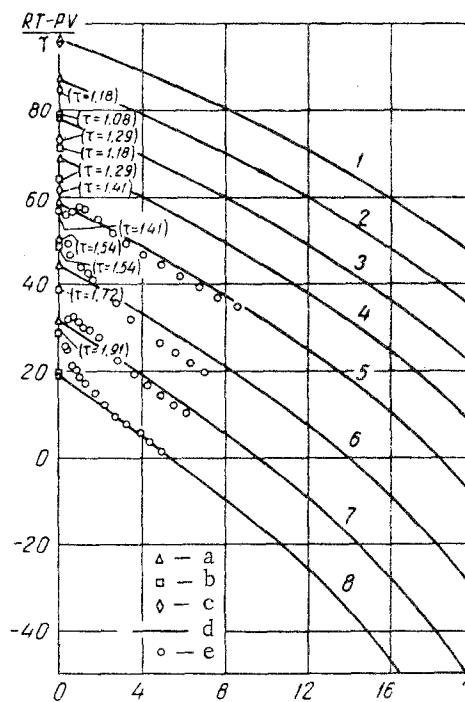
Fig. 3. Isolation of coefficient B': 1) $\tau =$ = 1.08; 2) 1.18; 3) 1.29; 4) 1.41; 5) 1.54; 6) 1.72; 7) 1.91; 8) 2.1; a) authors' data; b) from [4]; c) from [1]; d) from authors' equation; e) data from [3].

Through the experimental points plotted in γ_{NO}, γ_{NO_2} coordinates a smooth curve was drawn. This enabled us to obtain the reference network of P, V, T data, required to compare the equations of state, for round values of the density over the temperature range $\tau = 1.07$–2.1.

For practical purposes, the thermodynamic properties of NO are required over a considerably wider pressure range than that for which experimental data are available. Consequently, in this investigation we extrapolated the $\gamma_{NO} =$ = $f(\gamma_{N_2})_{\pi, \tau =}$idem relationship to $\gamma = 20$ kmole/m³. As already noted, the proximity of the relationship used to a linear relationship makes such an extrapolation sufficiently reliable. For further verification, the network of P, V, T reference data obtained was compared with compressibility coefficients determined from the generalized graphs of Nelson and Obert [8]. Systematic deviations were discovered on the isotherms. These increase with increase in density from 0 to about 7% at $\gamma = 20$ kmole/m³. If it is taken into account that deviations of up to 3–4% are also observed in the region covered by experiment, then it becomes clear that using our method of extrapolation gives more reliable results than using the generalized relationship $z = z(\pi, \tau)$, as most authors now do. The graphs of $z = z(\pi, \tau)$ are certain averagings of the compressibility coefficients for different substances, which deviate within wide limits from the law of corresponding states, and, of course, make no claim to high accuracy. However, they obviously reflect the configuration of the isotherms correctly, so that the presence of regularly increasing deviations over the whole range of densities (including direct comparison of experimental data) gives reason to suppose that the P, V, T data obtained for high densities are fairly close to the true values.

The equation of state was constructed by successive isolation, tying in, and temperature extrapolation of the virial

*For comparison, the data in [7] have also been plotted.

coefficients, as described in detail in [9]. For convenience the equation was constructed in the form

$$PV = RT + B'\gamma + C'\gamma^2 + \ldots, \tag{1}$$

where the coefficients B', C', etc. are connected with the virial coefficients B, C, etc. by the relations: $B' = RT \cdot B$, $C' = RT \cdot C$, etc.

The coefficients in Eq. (1) were isolated by constructing isotherms in the coordinates

$$\frac{1}{\gamma}(RT - PV), \ \gamma$$

$$\frac{1}{\gamma^2}(RT - PV + B'\gamma), \ \gamma$$

$$\cdot \ \cdot \ \cdot \ \ \cdot \ \cdot \ \cdot \ \cdot \ \ \cdot \ \cdot \ \cdot$$

and extrapolating to $\gamma = 0$ to determine, respectively, the coefficients B', C', etc.

Analysis showed that in $\gamma^{-4}(RT - PV + B'\gamma + C'\gamma^2)$, γ^2 coordinates the isotherms lie on straight lines with acceptable accuracy up to a density of $\gamma = 20$ kmole/m^3. Hence it follows that over the range of density variation 0–20 kmole/m^3 the equation of state may be put in the form

$$PV = RT + B'\gamma + C'\gamma^2 + D'\gamma^4 + E'\gamma^6. \tag{2}$$

On isolating the coefficient B' it was found that the second virial coefficients calculated from Johnston's equation [1] and presented in [4] show poor agreement with the general nature of the isotherms in $(RT - PV)/\gamma, \gamma$ coordinates (Fig. 3).

Since the virial coefficients from [1] and [4] also show poor agreement (Fig. 4), it was decided to take the second virial coefficient over the temperature range $\tau = 1.07-2.1$ from the network of P, V, T reference data. At the same time, new parameters of the Lennard-Jones potential were determined: $\varepsilon/k = 126°$ K, $b_0 = 53.3$ cm^3/mole.

As a result of an analytical representation of the second virial coefficient, calculated from the new potential parameters, by the method of least squares, we constructed an equation valid over the temperature range 190–10 000° K:

$$B = 23.9 + 212.3\frac{1}{\vartheta} - 3732.8\frac{1}{\vartheta^2} + 18976.8\frac{1}{\vartheta^3} -$$

$$- 52512.6\frac{1}{\vartheta^4} + 73102.2\frac{1}{\vartheta^5} - 40212.7\frac{1}{\vartheta^6}, \tag{3}$$

where $\vartheta = T/100$.

Fig. 4. Second virial coefficient B(cm^3/mole): 1) from authors, calculations; 2) from [4]; 3) from [1].

Going over to the form of Eq. (2), we obtain

$$B' = 176.5 + 19.87\vartheta + \psi, \tag{4}$$

where

$$\psi = -3103.6\frac{1}{\vartheta} + 15778.1\frac{1}{\vartheta^2} - 43661.1\frac{1}{\vartheta^3} +$$

$$+ 60780.0\frac{1}{\vartheta^4} - 33434.4\frac{1}{\vartheta^5}. \tag{5}$$

The coefficients C', D', and E', determined by the method described above, were represented analytically by the method of least squares:

$$C' \cdot 10^3 = 1865 + 715.3\vartheta + 4.203\psi,$$

$$D' \cdot 10^5 = -13426 + 838.5\vartheta - 38.33\psi, \tag{6}$$

$$E' \cdot 10^7 = 2680 - 142.38\vartheta + 7.7316\psi.$$

A comparison with the experimental data of [3] showed that the mean deviation of the compressibility, calculated from the equation of state, from the experimental data of [3] is 0.3% for the isotherms $\tau = 1.54$, 1.91, and 2.10, the maximum deviation not exceeding 0.5%. A comparison with the data of [2] and [3] for the isotherm $\tau = 1.73$ would be meaningless in view of their obvious inaccuracy.

To test the equation at high temperatures, we compared the compressibilities calculated from the equation of state with those determined from the relationship $\gamma_{NO} = f(\gamma_{N_2})_{\pi,\tau=\mathrm{idem}}$ at $\tau = 3$, 4, 6, 8, and 10. The discrepancies over the pressure range $(0-1000) \times 10^5$ N/m^2, for which experimental data are available for nitrogen, did not exceed 0.7%. This confirms both the weak temperature dependence of the function $\gamma_{NO} = f(\gamma_{N_2})_{\pi,\tau=\mathrm{idem}}$ and the validity of extrapolating the equation of state with respect to temperatures.

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