Thermodynamic Properties of Nitrogen Tetroxide

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The thermodynamic properties of nitrogen tetroxide were derived from available experimental data and from thermodynamic correlations. Temperature-entropy, temperature-enthalpy, and temperature-pressure-volume diagrams are presented. These thermodynamic properties are needed to predict accurately the physical behavior of nitrogen tetroxide when it is used as an oxidizer in missile and space propulsion applications as well as in propellant manufacture. In the computation of the thermodynamic and physical property data, dissociation of nitrogen tetroxide into nitrogen dioxide, nitric oxide, and oxygen has been taken into account.

Nomenclature

c_p = heat capacity at constant pressure, Btu/lb-°R
d = differential operator
∂ = partial differential operator
h = enthalpy, Btu/lb
H = enthalpy, Btu/lb-mole
$(H_i - H)$ = correction factor for perfect to real gas enthalpy at constant temperature and pressure, derived in Ref. 4
K_p = equilibrium constant
$\mathfrak{M}$ = molecular weight, lb/lb-mole
$j \ldots m$ = species in the mixture
n_j = pound-moles of component identified by subscript
N = total number of pound-moles of mixture
p = partial pressure of component, psia
P = total pressure, psia
P_r = reduced pressure, P/P_c
Q = quality of vapor-liquid or vapor-solid mixture, weight fraction vapor
R = gas constant, 1.9865 Btu/lb-mole-°R
s = entropy, Btu/lb-°R
S = entropy, Btu/lb-mole-°R
Δs_v = entropy of vaporization, Btu/lb
$(S_i - S)$ = correction factor for perfect to real gas entropy at constant temperature and pressure, derived in Ref. 4
T = temperature, °R
T_r = reduced temperature, T/T_c
v = specific volume, ft^3/lb
Z = compressibility factor
α = degree of dissociation of N_2O_4 to NO_2
β = degree of dissociation of NO_2 to NO and O_2
Δ = delta change in property

Subscripts

1 = reference condition
2 = final condition
c = critical
f = fusion
g = real gas
i = ideal gas
$j \ldots m$ = species in the mixture
l = liquid
mix = gaseous mixture of N_2O_4, NO_2, NO, and O_2
P_1 = reference pressure
P_2 = final pressure
Q = quality
r = reduced
R = reference substance
sl = saturated liquid
T = temperature
v = vaporization
x = refers to one of the components: N_2O_4, NO_2, NO, O_2
α = refers to the equilibrium of $N_2O_4 \rightleftharpoons 2NO_2$
β = refers to the equilibrium of $NO_2 \rightleftharpoons NO + \frac{1}{2}O_2$

Introduction

THE thermodynamic properties of propellants play an important role in the performance of rocket propulsion systems. The propellants themselves, as well as the ignition and combustion processes, are affected by the prevailing temperature and pressure conditions. In high-altitude and space operations, thermodynamic processes, such as phase changes that occur when liquid propellants are introduced into evacuated lines and thrust chambers, must be taken into account in system design and operation. Heat soakback from prolonged engine firing can cause premature propellant vaporization. Upon engine shutdown, the expansion of residual propellant may result in unpredicted tailoff impulse.

Nitrogen tetroxide has found increasing use in recent years in missile and space vehicle applications because of its high oxygen content, storability, and desirable physical properties. In order to predict accurately the physical behavior of N_2O_4 under the unusual conditions of temperature and pressure to which some of our present propulsion systems are subjected, it is necessary to develop temperature-entropy, enthalpy-temperature, and pressure-volume-temperature diagrams of the type shown in Figs. 1–4.§ For example, in the determination of propellant tank ullage pressure excursions during changes in the thermal environment of a spacecraft or missile, Figs. 3 and 4 are required. Computations needed to derive these diagrams are complicated by the fact that N_2O_4 contains various amounts of NO_2, NO, and O_2, depending upon the operating temperature and pressure.

Temperature-Entropy Relations

The temperature-entropy diagram, as well as the other figures derived herein, were based on experimental data, thermodynamic theory, empirical correlations, and generalized tables. The development of the curves given in Fig. 1 can be divided into portions that can be derived separately.

The entropy of the solid phase was obtained from the Joint Army-Navy-Air Force (JANAF) tables[1] and from a calorimetric study by Giauque and Kemp[2]; the enthalpy and entropy of fusion were also taken from Giauque and Kemp.[2] For entropy values at elevated temperatures in the liquid or

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§ Full-size copies of the figures are available on request from the authors.

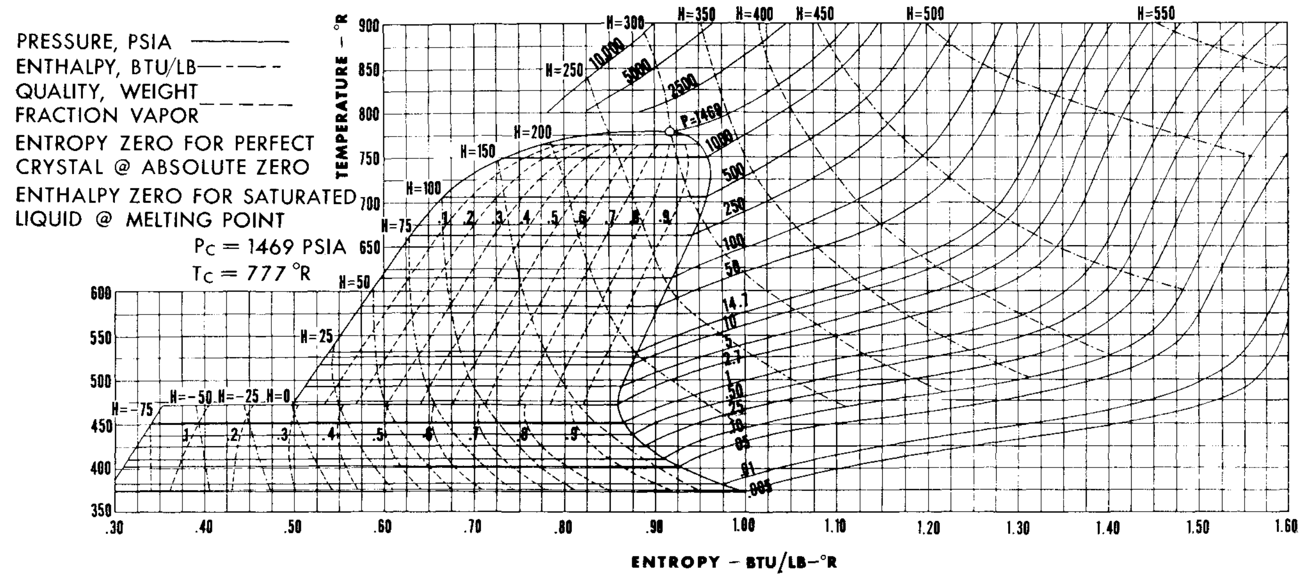

Fig. 1 Temperature-entropy diagram of nitrogen tetroxide.

vapor regions, the composition of an equilibrium mixture of N_2O_4, NO_2, NO, and O_2 was calculated. For the solid phase and the liquid phase at or below ambient temperatures, the dissociation effects were neglected, since, according to Gray and Rathbone,[3] the liquid dissociation is only 0.038%, 0.078%, and 0.12% at the freezing point, at 492°R, and at the normal boiling point, respectively. The vapor, however, is dissociated at all temperatures and pressures, even below the melting point.

In Fig. 1, the entropy of fusion at the melting-point temperature (472°R) is represented by the triple-point line between the saturated solid and saturated liquid curves; the entropy of vaporization at this temperature is represented by the line between the saturated liquid and the saturated vapor curves. Extension of the triple-point line yields the isobaric curve representing the entropy of superheated vapor at 2.7 psia. This constant pressure line, as well as the other isobars from 0.005 to 10,000 psia, was derived from the following relations. For a single real gas, the molar entropy, as shown by Hougen, Watson, and Ragatz,[4] can be expressed as

$$S_g = S_{iP_1} - R\ln(P_2/P_1) - (S_i - S)_{P_2,\,T} \tag{1}$$

where the correction factor for nonideality in terms of re-

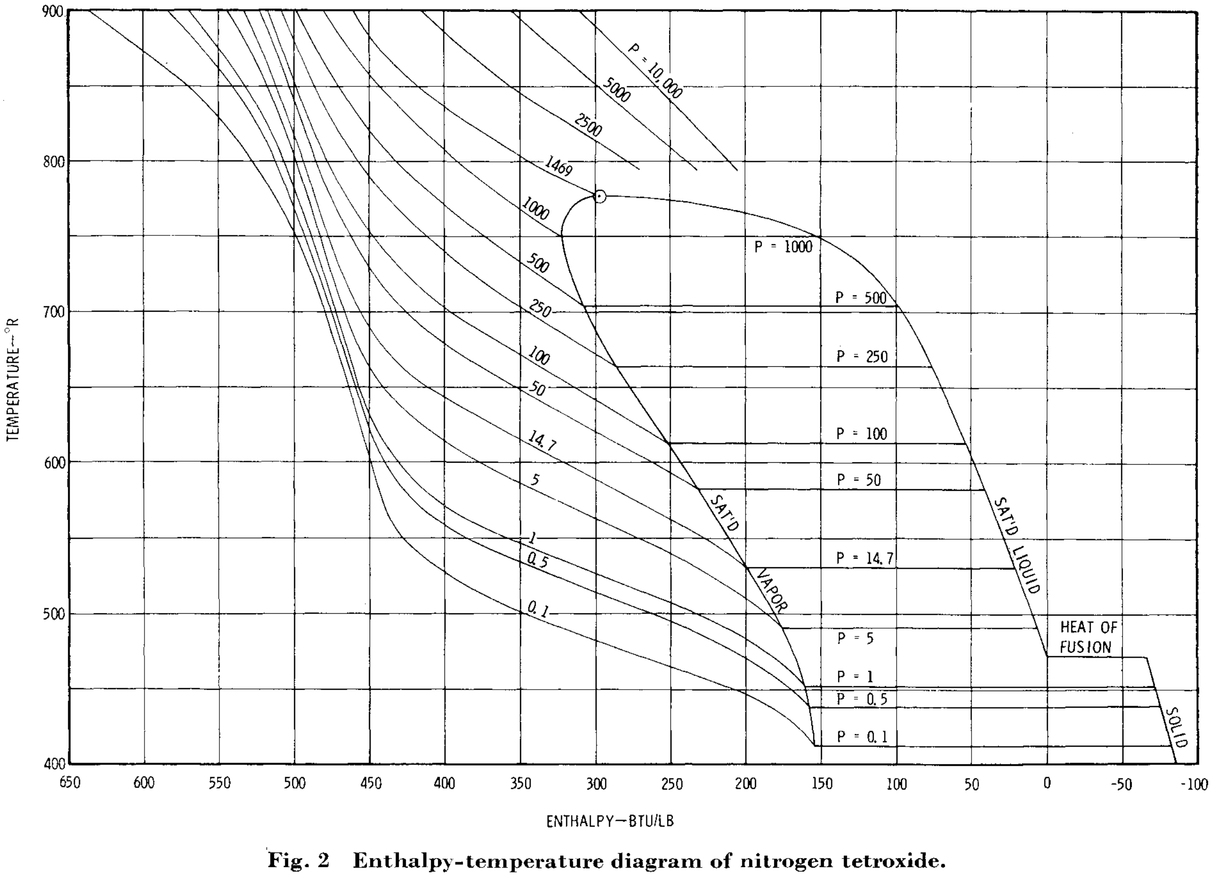

Fig. 2 Enthalpy-temperature diagram of nitrogen tetroxide.

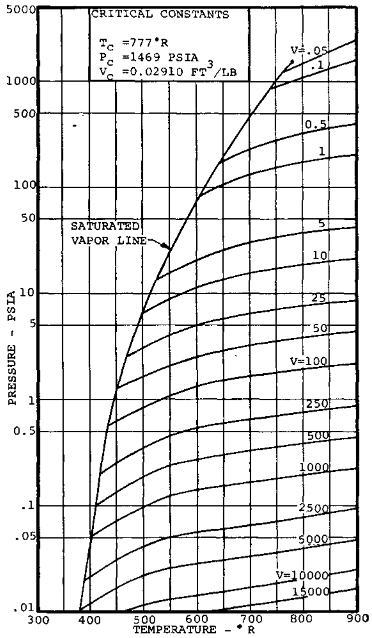

Fig. 3 Specific volume-temperature-pressure diagram of nitrogen tetroxide vapor.

duced properties is

$$(S_i - S)_{P_2,T} = -R\int_0^{P_r}\frac{(1-Z)\,dP_r}{P_r} + RT_r\int_0^{P_r}\left(\frac{\partial Z}{\partial T_r}\right)_{P_r}\frac{dP_r}{P_r} \tag{2}$$

Modifying Eq. (1) for a gaseous mixture and using moles of originally undissociated substance as the reference amount,

$$s_{\text{mix}} = \frac{1}{\mathfrak{M}_R}\left\{\sum_{j=1}^{m}\left(\frac{n_j}{n_R}S_{ij}\right) - R\sum_{j=1}^{m}\left[\frac{n_j}{n_R}\ln\left(\frac{n_j}{N}\right)\right] - \frac{N}{n_R}R\ln\left(\frac{P_2}{P_1}\right) - \sum_{j=1}^{m}\left(\frac{n_j}{n_R}(S_i - S)_j\right)\right\} \tag{3}$$

For the nitrogen tetroxide system, only four molecular species are found in appreciable quantities within the temperature and pressure limits investigated in this study. Expanding Eq. (3) to include these gases and using one mole of undissociated N_2O_4 as the reference, we then have

$$s_{\text{mix}} = (1/92.02)\{[(1-\alpha)S_{N_2O_4} + 2\alpha(1-\beta)S_{NO_2} + 2\alpha\beta(S_{NO} + \tfrac{1}{2}S_{O_2})] + [-R(1-\alpha)\ln((1-\alpha)/N) - R2\alpha(1-\beta)\ln(2\alpha(1-\beta)/N) - R2\alpha\beta\ln(2\alpha\beta/N) - R\alpha\beta\ln(\alpha\beta/N)] - NR\ln(P_2/P_1) - [(1-\alpha)(S_i - S)_{N_2O_4} + 2\alpha(1-\beta)(S_i - S)_{NO_2} + 2\alpha\beta(S_i - S)_{NO} + \alpha\beta(S_i - S)_{O_2}]\} \tag{4}$$

In Eq. (4), the first three terms represent the ideal entropy (S_i) of each gaseous ingredient[1]; the next four terms represent the entropy of mixing; the next separate term allows for the entropy change in proceeding from standard pressure (1 atm) to the desired pressure; and finally, the last four terms correct for deviations from ideal gas behavior.[4,5]

The composition of gaseous N_2O_4 at various temperatures and pressures was derived from consideration of the dissociation reactions

$$N_2O_4 \rightleftharpoons 2NO_2 \tag{5}$$

$$2NO_2 \rightleftharpoons 2NO + O_2 \tag{6}$$

The fractions (α, β) of N_2O_4 and NO_2 dissociated were calculated from the readily derivable equilibrium expressions:

$$K_{P(\alpha)} = \frac{[2\alpha(1-\beta)]^2P}{(1+\alpha+\alpha\beta)(1-\alpha)} \tag{7}$$

$$K_{P(\beta)} = \frac{\beta^{3/2}}{(1-\beta)}\left(\frac{\alpha P}{1+\alpha+\alpha\beta}\right)^{1/2} \tag{8}$$

Values of $K_{P(\alpha)}$ vs temperature and $K_{P(\beta)}$ vs temperature were taken from Hisatsune[6] and Giauque and Kemp,[2] respectively. Solution of Eqs. (7) and (8) for α and β was accomplished by an iterative process using an IBM 7094 computer. Using the values of α and β calculated in Eqs. (7) and (8), the equilibrium composition of the gaseous mixture at any temperature and pressure can be expressed by the equation

$$N = 1 + \alpha + \alpha\beta \tag{9}$$

The saturated vapor line up to the critical point and the superheated vapor curves, showing the effect of pressure on entropy at various temperatures in the region to the left and above the two-phase region, were also obtained using Eq. (4).

The saturated liquid line was determined by graphical integration of the specific heat using the standard relation

$$s_{slT_2} = s_{slT_1} + \int_{T_1}^{T_2}\frac{c_p dT}{T} \tag{10}$$

where s_{slT_1} and c_p values were taken from Giauque and Kemp[2] and Sage and Hough.[7] Since experimental data were not available for the portion of the saturated liquid line above 690°R, they were obtained by interpolation. The qualities of the vapor-liquid region and the vapor-solid region were found by linear interpolation between saturated liquid and saturated vapor line and between saturated solid and saturated vapor

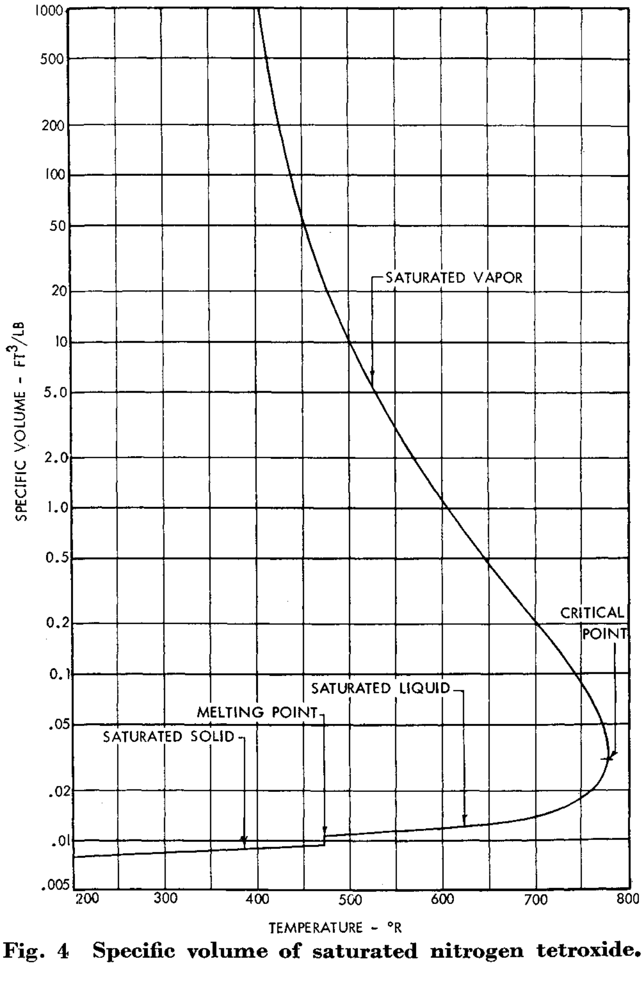

Fig. 4 Specific volume of saturated nitrogen tetroxide.

line, respectively. The entropy values presented herein are based on the most current information available and include some interpolations. The inaccuracies of the data in Fig. 1 are estimated to be about 2.0%.

Enthalpy-Temperature Relations

The isenthalpic lines in the two-phase region of Fig. 1 were derived from numerical integration of the liquid heat capacity and the entropies of vaporization, using the relation

$$h_{QT_2} = \int_{T_1}^{T_2} c_p dT + Q(\Delta s_v)_{T_2} \cdot T_2 \qquad (11)$$

This procedure was carried out to 690°R in the liquid-vapor and solid-vapor regions; the lack of heat capacity data required extrapolation of the liquid line beyond this temperature. Enthalpy curves for the superheated vapor were derived from JANAF ideal gas enthalpy values,[1] heats of dissociation,[2,6] and the real-gas correction factors of Hougen and Watson[4] using the equation based on one mole of originally undissociated N_2O_4 as the reference:

$$\begin{aligned} h_{\text{mix}} = {} & (1/92.02)\{(1-\alpha)H_{N_2O_4} + 2\alpha(1-\beta)H_{NO_2} + \\ & 2\alpha\beta(H_{NO} + 0.5H_{O_2}) + \alpha\Delta H_\alpha + 2\alpha\beta\Delta H_\beta - (1-\alpha) \times \\ & [(H_i - H)/T_c]_{N_2O_4} T_c(_{N_2O_4}) + 2\alpha\,(1-\beta) \times \\ & [(H_i - H)/T_c]_{NO_2} T_c(_{NO_2}) + 2\alpha\beta[(H_i - H)/T_c]_{NO} T_c(_{NO}) + \\ & \alpha\beta[(H_i - H)/T_c]_{O_2} T_{c(O_2)}\} + C \qquad (12) \end{aligned}$$

In the ideal gas portion of Eq. (12), ideal gas data[1] were utilized. A correction factor, C, was calculated and utilized to take into account the difference in the base value used in this report and that used by the JANAF tables.

Equation (11) was used to find the saturated liquid and solid enthalpies setting Q equal to zero. In Fig. 2, enthalpy is plotted vs temperature independently of entropy to illustrate this relation with greater clarity and to facilitate its usage. The error for the enthalpy values is approximately the same as the error in the entropy values, ±2.0%.

Pressure-Volume-Temperature (P-V-T) Relation

The P-V-T relation for gaseous dissociated N_2O_4 was calculated using a modification of the Wohl equation[8]:

$$P = \frac{RT}{v - B} - \frac{A}{T_r v(v - B)} + \frac{C}{v^3 T_r^{4/3}} \qquad (13)$$

where $A = 6v_c^2 \cdot P_c$, $B = 0.25v_c$, $C = 4v_c^3 \cdot P_c$, and $R = 10.73$ lb-ft^3/in.^{2}-lb-mole-°R, with other symbols as defined in the Nomenclature. This equation of state is basically of the Van der Waals form with another term that allows for the attractive and repulsive forces between molecules. For this application, the Wohl equation has adequate accuracy,[9] except in the region close to the saturation line near the critical point. In this region experimental data[10,11] were used.

The effect of dissociation on the molecular weight and thence upon the gas constant R was obtained from Eq. (9) and the relation

$$R = 10.73/\mathfrak{M}_R = 10.73\, N/92.02 \qquad (14)$$

As a result of the dissociation, the molecular weight was found to vary from 92.02 down to 36.9 lb/lb-mole in the temperature and pressure regions covered by this report. The P-V-T relation was found for the superheated region by use of Eqs. (7–9, 13, and 14), assuming a temperature and specific volume, solving for α and β and then for pressure. An iterative technique was used upon an IBM 7094 digital computer to effect the actual solutions, since α and β are functions of temperature and pressure.

A plot of saturation pressure vs temperature is shown in Fig. 3; the P-V-T data from the computer program and from Schlinger and Sage[10] and Reamer and Sage[11] were used for the superheated vapor region. Figure 4 is a diagram of temperature vs saturation specific volume, derived from data in Refs. 10–12.

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