Thermodynamic Properties of the System $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$

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Thermodynamic properties of the chemically reactive system $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$ have been evaluated over a pressure range of 0.005 to 200.0 atm. and a temperature range of 200° to 900°K. by making use of Lennard-Jones potential. In these calculations, the dissociation of nitrogen tetroxide to nitrogen dioxide, nitric oxide and oxygen, and the effect of pressure on the equilibrium constants for the system of reactions $N_2O_4 \rightleftharpoons 2NO_2$ and $2NO_2 \rightleftharpoons 2NO + O_2$ have been taken into account.

The system $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$ is a classical one in that $N_2O_4 \rightleftharpoons 2NO_2$ exists in reversible equilibrium even under ordinary conditions. The nitrogen tetroxide and dioxide are very good oxidizing agents and are materials in the manufacture of nitric acid. The advent of space science and the technological advancements made in the space research is pointing increasingly to the oxides of nitrogen to be used as oxidizers. The use of these oxides in rocketry demands a knowledge of the thermodynamic properties for the calculation of adiabatic temperatures, design of nozzle, etc. Hence this work was undertaken to present tables and graphs of thermodynamic properties of this system.

Furgason and Smith (*8*) have evaluated the heat capacity and enthalpy of the system $N_2O_4 \rightleftharpoons 2NO_2$ up to a pressure of about 2 atm. and a temperature of 395°K.

Thermodynamic and transport properties of the system $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$ have been evaluated up to a temperature of 1,100°K. at a pressure of 1 atm. by Fan and Mason (*7*).

Recently, while this investigation was in progress, the thermodynamic properties of $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$ have been reported by Stai et al. (*29*), Nesterenko et al. (*21*), and Svehla and Brokaw (*30*).

The data of Stai et al (*29*) extends up to a temperature of 500°K. and a pressure of about 333 atm. Svehla and Brokaw (*30*) evaluated the thermodynamic properties of the system $N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons 2NO + O_2$ up to a temperature of 1,280°K. and a pressure of 100 atm. In these two investigations, the effect of pressure on the equilibrium constants of the system of reactions $N_2O_4 \rightleftharpoons 2NO_2$ and $2NO_2 \rightleftharpoons 2NO + O_2$ was not considered. In addition to this, Svehla and Brokaw (*30*) did not make any corrections owing to the nonideality of the gas at higher pressures.

PRESENT INVESTIGATION

Heat Capacity

The heat capacity of nitrogen tetroxide in the ideal gaseous state have been evaluated up to a temperature of 1,500°K. by Hisatsune (*14*). These data were fitted to the equation

$$C_p{}^* = a + bT + cT^2 + dT^3 \qquad (1)$$

over two temperature ranges, namely, 200° to 400°K. and 250° to 1,500°K. The constants of Equation (1) along with the average absolute and maximum deviations are presented in Table 1.

For oxygen, nitric oxide, and nitrogen dioxide for the temperature range of 273 to 1,500°K., constants of Equation (1) are available (*16*). For nitrogen dioxide, the heat capacity data of Altschuller (*1*) and for oxygen and nitric oxide the data of API (2) were fitted over a temperature range of 150° to 400°K. to Equation (1). The constants of the heat capacity equation and the deviations are presented in Table 1.

The equilibrium constants K_1 and K_2 for the system of reactions $N_2O_4 \rightleftharpoons 2NO_2$ and $2NO_2 \rightleftharpoons 2NO + O_2$ were evaluated over a temperature range of 240° to 900°K. by using the constants of the heat capacity equation given in Table 1, the heats of reactions at 298.16°K., namely 13,756 and 27,124 cal./mole, respectively, and by making use of the equation

$$\Delta F_T{}^\circ = -RT \ln K \qquad (2)$$

where the reactants and the products are taken at unit fugacity and at reaction temperature.

Equilibrium Constants at Higher Pressures

The mole fractions and partial pressures of the constituent species in a reacting mixture are different at different pressures. For the standard state chosen as above, and using Lewis and Randall's rule, we have

$$K = K_p\, K_\alpha \qquad (3)$$

where K_p is the equilibrium constant defined in terms of mole fractions and K_α is the ratio of the fugacity coefficients of products and reactants. K is the true equilibrium constant, and K_p and K_α change in such a way as to keep K constant.

The critical constants for nitrogen tetroxide and nitrogen dioxide were assumed to be identical as they exist together at all temperatures up to the critical temperature. The critical temperature for nitrogen tetroxide was calculated by using a value of 294.25°K. for the boiling point and by employing group contribution methods. By using this calculated critical temperature for nitrogen tetroxide and by employing Kay's rule, the critical temperature of nitrogen dioxide was calculated at various mole fractions of nitrogen dioxide in nitrogen tetroxide-nitrogen dioxide mixtures. In employing Kay's rule, the critical temperature of 431.36°K. given by Schlinger and Sage (*27*) was used as the critical temperature of the mixture. This revealed that the deviation in the critical temperature of nitrogen dioxide at mole fractions below 0.2 was only 4%, with the deviation decreasing with increase of mole fraction of nitrogen dioxide. Furthermore, the mole fraction of nitrogen dioxide at temperatures above 300°K. is invariably above 0.4. Above 600°K., the mole fraction of nitrogen dioxide is in the range of 0.5 to 0.8. Thus, if the critical temperatures calculated from Kay's rule is accepted, then the critical temperature of nitrogen dioxide computed will be in error by 1% or less from the assumed value of

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431.36°K. The values of critical constants used in the present investigation are:

$$T_c = 431.36°\text{K.}$$
$$P_c = 100.0 \text{ atm.}$$
$$d_c = 0.560 \text{ g./cc.}$$

For oxygen and nitric oxide, the critical constants used are:

$$T_c = 154.78°\text{K.}$$
$$P_c = 50.10 \text{ atm.}$$
$$d_c = 0.43 \text{ g./cc.}$$

and

$$T_c = 180.0°\text{K.}$$
$$P_c = 65.0 \text{ atm.}$$
$$d_c = 0.52 \text{ g./cc.}$$

respectively.

With the assumption that the critical constants of nitrogen tetroxide and nitrogen dioxide are same, the equilibrium constant K_{p1} for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ can be evaluated from

$$K_{p1} = \frac{K_1}{(f/p)_{NO_2}} \tag{4}$$

The equilibrium constant K_{p2} for the reaction $2NO_2 \rightleftharpoons 2NO + O_2$ can be evaluated from

$$K_{p2} = K_2 \left[\frac{[(f/p)_{NO_2}]^2}{[(f/p)_{NO}]^2 \, [(f/p)_{O_2}]} \right] \tag{5}$$

The fugacity coefficients of nitrogen dioxide, nitric oxide, and oxygen were calculated by making use of the generalized fugacity coefficients (*16*).

The equilibrium constants K_{p1} and K_{p2} were calculated up to a temperature of 900°K. and a pressure of 200 atm. by using Equations (4) and (5).

Calculation of Equilibrium Compositions

For the calculation of equilibrium composition, 1 mole of undissociated nitrogen tetroxide was taken as the basis. If ξ_1 is the moles of nitrogen tetroxide dissociated, and ξ_2 the moles of oxygen formed, then the total number of moles at any temperature and pressure is $(1 + \xi_1 + \xi_2)$.

By making use of the equilibrium constants K_{p1} and K_{p2} for the system of reactions

$$N_2O_4 \rightleftharpoons 2NO_2$$

and

$$2NO_2 \rightleftharpoons 2NO + O_2$$

ξ_1 and ξ_2 can be calculated from

$$K_{p1} = \frac{4(\xi_1 - \xi_2)^2 \, P}{(1 + \xi_1 + \xi_2)(1 - \xi_1)} \tag{6}$$

and

$$K_{p2} = \frac{\xi_2^3 \, P}{(1 + \xi_1 + \xi_2)(\xi_1 - \xi_2)^2} \tag{7}$$

ξ_1 and ξ_2 were evaluated by an iterative method on a digital computer.

The mole fractions x_1, x_2, and x_3 of nitrogen tetroxide, nitrogen dioxide, and nitric oxide, respectively, were calculated from

$$x_1 = \frac{1 - \xi_1}{1 + \xi_1 + \xi_2} \tag{8}$$

$$x_2 = \frac{2(\xi_1 - \xi_2)}{(1 + \xi_1 + \xi_2)} \tag{9}$$

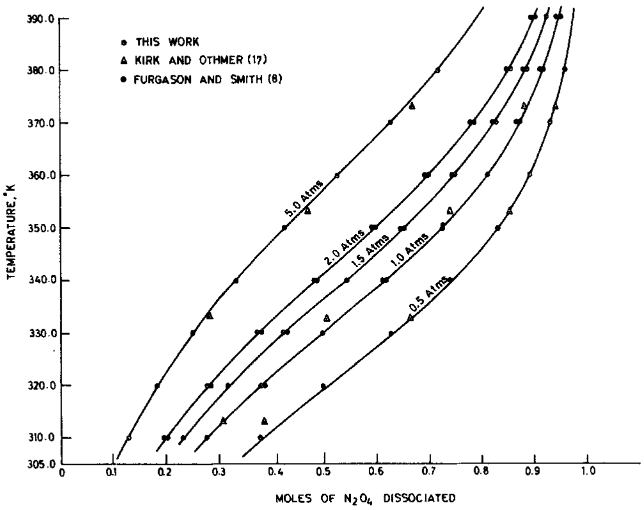

Fig. 1. Temperature vs. moles of nitrogen tetroxide dissociated.

$$x_3 = \frac{2\xi_1}{(1 + \xi_1 + \xi_2)} \tag{10}$$

Mole fraction x_4 of oxygen can be easily obtained by using the equation

$$x_4 = x_3/2 \tag{11}$$

The equilibrium molecular weight M of the nitrogen tetroxide-nitrogen dioxide-nitric oxide-oxygen system was calculated by using the calculated values of ξ_1 and ξ_2 from

$$M = \frac{92.016}{1 + \xi_1 + \xi_2} \tag{12}$$

A comparison of the calculated and the available (*8*, *17*) values of ξ_1 has been given in Figure 1. The plots of molecular weight vs. temperature and the mole fractions of nitrogen tetroxide, nitrogen dioxide, and oxygen vs. temperature for various pressures have been shown in Figures 2 to 4, respectively.

Calculation of Thermodynamic Properties

For the calculation of thermodynamic properties, an equation of state is necessary. For this work, virial equations of state, namely

$$Z = PV/RT = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} \tag{13}$$

where $B(T)$ and $C(T)$ are second and third virial coefficients, have been used. The second and third virial coefficients can be evaluated by the knowledge of a potential function.

Among the various potential functions available, Lennard-Jones potential (*18*), namely

$$\phi(r) = 4\epsilon \, [(\sigma/r)^{12} - (\sigma/r)^6] \tag{14}$$

has been chosen for the present work.

In the present case, $N_2O_4 \rightleftharpoons 2NO_2$ is treated as a single component system. This is mainly because of the fact that there is only the formation of a dimer or a monomer, and, therefore, such a formation and decomposition from a thermodynamic viewpoint is taken care of by the second virial coefficient. Furthermore, Ewald (*6*) has shown that a good expansion has to occur for the breakage of the N–N bonds, and the magnitude of the change in volume could not be attributed to the change in dimensions of nitrogen tetroxide and nitrogen dioxide.

A similar case of association and dissociation which occurs in the case of rare gases argon, krypton, neon, and

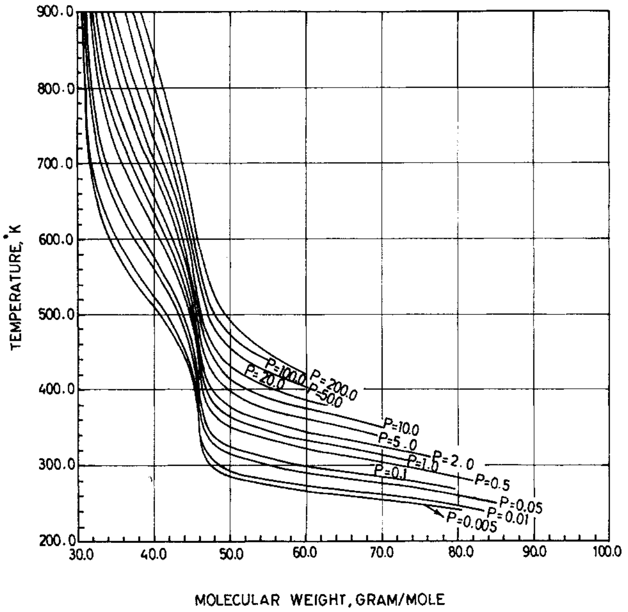

Fig. 2. Temperature vs. equilibrium molecular weight.

xenon has been treated recently by Buluggiu and Foglia (*4*) using Morse potential. The association or dissociation of monomers and dimers and their effect on the second virial coefficients are also treated by Hill (*13*).

Sinanoglu and Pitzer (*28*) following two approaches, namely, treatment of a gaseous mixture as if composed of different molecular species and treatment of a gaseous mixture as a monatomic assembly with imperfections given by second and third virial coefficient, have shown both the treatments to be identical. Svehla and Brokaw (*30*) have followed the first approach treating nitrogen dioxide and nitrogen tetroxide as different species and calculating the force constants for Lennard-Jones potential using viscosity data of Petkar and Mason (*22*). It is the second approach that is followed in this present work.

For the equilibrium mixture of nitrogen tetroxide and nitrogen dioxide, the dipole moment varies between 0.28 and 0.58 debye units (*10*). For nitric oxide, the dipole moment is 0.13 debye units. Thus, the effect of dipole moment which should be accounted can be neglected, as dipole moments greater than 1 debye unit affect the second and third virial coefficients. Oxygen and nitrogen tetroxide are planar, whereas nitrogen dioxide is triangular. These molecules approach spherical configuration because of rapid rotation.

For oxygen, the L-J potential parameters were evaluated by using the available (*14*) second virial coefficients from the method outlined by Hirschfelder et al. The parameters thus calculated are

$$\epsilon/K = 115.5°\text{K.} \quad \text{and} \quad \sigma = 3.52\ \text{Å}.$$

The calculated parameters were found to be better than the parameters available (*30, 12, 14*). For nitric oxide, the available parameters (*14*) $\epsilon/K = 131.0°$K. and $\sigma = 3.16$ Å. were used.

The L-J potential parameters for $N_2O_4 \rightleftharpoons 2NO_2$ were calculated as follows.

Approximate values of ϵ/K and b_0 were obtained by using the available correlations (*14*).

By using the values of ϵ/K and b_0, values of $B(T)$ and $C(T)$ were calculated by using the tabulated (*14*) values of the reduced second and third virial coefficients $B^*(T^*)$ and $C^*(T^*)$, respectively. Then the compressibility values were calculated from Equation (13) and compared with the experimental data of Schlinger and Sage (*27*). For different assumed values of ϵ/K and b_0, the same procedure was followed. For each set of values of ϵ/K and b_0, the average absolute deviation, maximum deviation, and the sum of squares of percentage deviation were obtained. A set of values of ϵ/K and b_0 which corresponds to a minimum in average absolute deviation and maximum percentage deviation was selected as the best value. The best values thus obtained are

$$\epsilon/K = 300.0°\text{K.} \quad \text{and} \quad \sigma = 4.147\ \text{Å}. \tag{15}$$

The calculated parameters predict the compressibility data up to a pressure of 136 atm. with average absolute and maximum deviations of 2.04 and 9.82%, respectively.

SPECIFIC VOLUME

Superheated Vapor

The specific volume of the nitrogen tetroxide-nitrogen dioxide-nitric oxide-oxygen system in the superheated vapor region was calculated by the equation

$$PV/RT = 1 + (B_{\text{mix.}}/V) + (C_{\text{mix.}}/V^2) \tag{16}$$

by an iterative method on a digital computer. $B_{\text{mix.}}$ and $C_{\text{mix.}}$ were evaluated by using the equations

$$B_{\text{mix.}} = \sum_i \sum_j x_i\, x_j\, B_{ij} \tag{17}$$

$$C_{\text{mix.}} = \sum_i \sum_j \sum_k x_i\, x_j\, x_k\, C_{ijk} \tag{18}$$

and by using the extension of the method of Prausnitz and Gunn (*23*) to a three-component system. The specific volumes thus calculated were converted to volume per gram by making use of the equilibrium molecular weight.

Specific Volume of Saturated Solid, Liquid and Vapor

The density of nitrogen tetroxide determined by Blitz et al. (*3*), by Vegard (*32*), and by Lorenz (*19*) were combined, smoothed, and used for this work.

Smoothed data of saturated liquid densities of Mittasch et al. (*20*), Reamer and Sage (*24*), Geuther (*9*), and Thorpe (*31*) were used for this work.

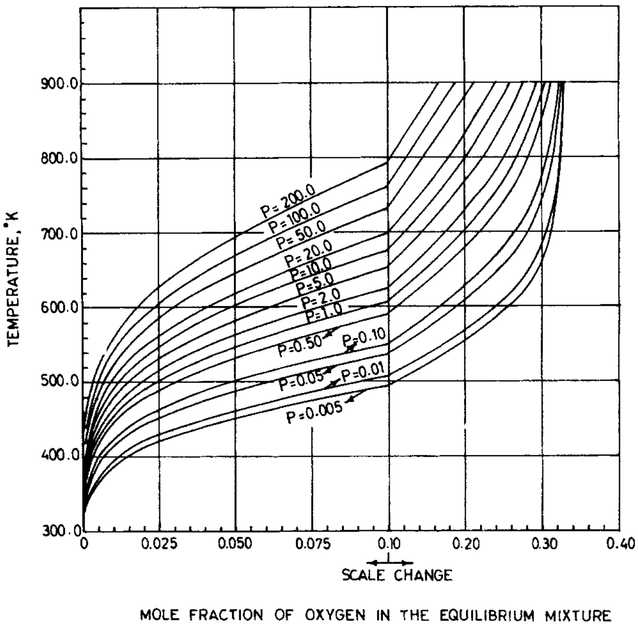

Fig. 3. Temperature vs. mole fraction of oxygen in the equilibrium mixture.

TABLE 1. CONSTANTS FOR THE SPECIFIC HEAT EQUATION

$$C_p{}^* = a + bT + cT^2 + dT^3$$

Substance		a	$b \times 10^2$	$c \times 10^5$	$d \times 10^9$	Temp. range, °K.	Deviation, % Avg.	Deviation, % Max.	Reference
N_2O_4	(a)	7.419	4.583	−3.30	8.39	250 to 1,500	0.36	0.71	This work
	(b)	4.8505	6.5382	−7.9331	44.509	200 to 400	0.013	0.022	This work
NO_2	(a)	5.48	1.365	−0.841	1.88	273 to 1,500	0.18	0.46	*16*
	(b)	8.0401	−0.4670	3.4389	−31.474	200 to 400	0.008	0.013	This work
NO	(a)	7.008	−0.02244	0.2328	−1.00	273 to 1,500	0.36	0.97	*16*
	(b)	8.5115	−1.0369	2.4649	−17.9044	150 to 400	0.02	0.041	This work
O_2	(a)	6.085	0.3631	−0.1709	0.3133	273 to 1,800	0.28	1.19	*16*
	(b)	6.9621	0.01971	−0.2976	9.8241	150 to 400	0.001	0.0016	This work

The density data for the saturated vapor used in this work are from Reamer and Sage (*24*). These were converted to volumes per gram by making use of the equilibrium molecular weights.

CALCULATION OF ENTROPY AND ENTHALPY

Entropy and Enthalpy of Saturated Vapor

The reference state as given by Canjar and Manning (*5*) names $H = 0$ and $S + R \ln P = 0$ for elements at 0°K. and zero pressure and was used for the computation of entropy and enthalpy of the nitrogen tetroxide-nitrogen dioxide, nitric oxide-oxygen system.

In the case of the virial equation of the type used in this work, expressions for entropy and enthalpy, as obtained by applying the equations given by Hirschfelder et al. (*14*) for a mixture, are

$$S_{\text{mix.}} = S^*{}_{\text{mix.}} + R \ln V/RT - R\left[(1/V)\left(B_{\text{mix.}} + T\frac{dB_{\text{mix.}}}{dT}\right) + (1/2V^2)\left(C_{\text{mix.}} + T\frac{dC_{\text{mix.}}}{dT}\right)\right] \quad (19)$$

and

$$H_{\text{mix.}} = H^*{}_{\text{mix}} + RT\left[(1/V)\left(B_{\text{mix.}} - T\frac{dB_{\text{mix.}}}{dT}\right) + (1/V^2)\left(C_{\text{mix.}} - \frac{T}{2}\,\frac{dC_{\text{mix.}}}{dT}\right)\right] \quad (20)$$

In these equations, $dB_{\text{mix.}}/dT$ and $dC_{\text{mix.}}/dT$ are the temperature derivatives of the second and third virial coefficients for the mixture, and V is the specific volume of saturated vapor. Values of $dB_{\text{mix.}}/dT$ and $dC_{\text{mix.}}/dT$ can be obtained by using the equations

$$dB/dT = (b_0/T)B_1{}^* \quad (21)$$

and

$$dC/dT = (b_0{}^2/T)C_1{}^* \quad (22)$$

along with Equations (17) and (18). Values of $B_1{}^*$ and $C_1{}^*$ were obtained from the tables of Hirschfelder et al. (*14*).

$S^*{}_{\text{mix.}}$ and $H^*{}_{\text{mix.}}$, the ideal gas entropy and enthalpy of the equilibrium mixture, were obtained from the values of ideal gas entropy and enthalpy of nitrogen tetroxide, nitrogen dioxide, nitric oxide, and oxygen by

$$S^*{}_{\text{mix.}} = \sum_{i=1}^{4} x_i S_i{}^* - R \sum_{i=1}^{4} x_i \ln x_i \quad (23)$$

$$H^*{}_{\text{mix.}} = \sum_{i=1}^{4} x_i H_i{}^* \quad (24)$$

Ideal gas entropy and enthalpy of nitrogen tetroxide, nitrogen dioxide, nitric oxide, and oxygen were obtained by making use of the heat capacity equations tabulated in Table 1. In these calculations, entropies at 298.16°K. and the heat of formation at 298.16°K. were used. Ideal gas entropy and enthalpy at 298.16°K. and the heat of formation at 0°K. for nitrogen tetroxide, nitrogen dioxide, nitric oxide, and oxygen are presented in Table 2.

Latent Heat of Vaporization

The heat of vaporization can be calculated by using the Clausius-Clapeyron equation, namely

$$\Delta H_v = T(dP/dT)(V_g - V_l) \quad (25)$$

The experimental vapor pressure data above 1 atm. (*26, 27, 20*) were smoothed and fitted to

$$\log P = A + B/T + C \log T + DT \quad (26)$$

by the least-squares method, where

$A = 2.0003314$

$B = -3263.31767$

$C = 1.39658235$

$D = 3.90625 \times 10^{-3}$

Equation (26) predicts vapor pressures with average absolute and maximum deviations of 0.41 and 1.25%, respectively.

Equation (26) was used to calculate dP/dT values above 1 atm. Below 1 atm. the vapor pressure equation constants given by Giauque and Kemp (*10*) were used for the calculation of dP/dT.

By using the values of dP/dT and the specific volumes of saturated liquid and vapor in Equation (25), latent heat of vaporization was evaluated up to the critical point. In

TABLE 2. IDEAL GAS ENTROPY AND ENTHALPY AT 298.16°K. AND THE HEAT OF FORMATION AT 0°K. AND 1 ATM.

Substance	$S^*{}_{298.16}$, cal./(mole,) (°K.)	$H^*{}_{298.16}$, cal./mole	$\Delta H_0{}^0$, cal./mole	Reference
N_2O_4	72.73	8,520.9	4,600.1	*15, 25, 2*
NO_2	57.32	11,197.0	8,758.0	*1, 25, 2*
NO	30.339	23,671.2	21,477.0	*2, 25*
O_2	49.003	2,069.8	0	*2, 25*

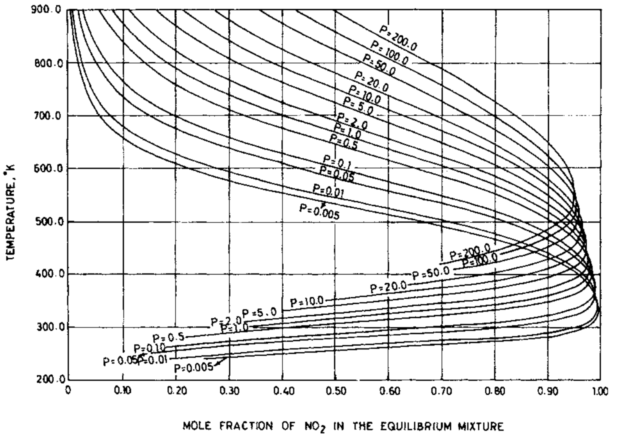

Fig. 4. Temperature vs. mole fraction of nitrogen dioxide in the equilibrium mixture.

these calculations, the specific volumes used are the values of volume of the equilibrium mixture. Hence, the dissociation of nitrogen tetroxide is taken care of by the increase in the volume of the saturated vapor.

Entropy and Enthalpy of the Saturated Liquid

These were obtained by making use of

$$S_l = S_g - \Delta S_v \tag{27}$$

$$H_l = H_g - \Delta H_v \tag{28}$$

by using the values of entropy and enthalpy of the saturated vapor and the heat of vaporization.

Entropy and Enthalpy of the Superheated Vapor

These were obtained by making use of the calculated specific volumes in Equations (19) and (20).

Specific volume, entropy, and enthalpy were calculated over a pressure range of 0.005 to 200 atm. and a temperature range of 240° to 900°K.

RESULTS AND DISCUSSION

The properties of saturated liquid and vapor and of superheated vapor are presented in Tables 3 and 4, respectively.* These are presented in graphical form as Figure 5. Comparison of entropy and enthalpy with those of Svehla and Brokaw (*30*) and Stai et al. (*29*) are presented in Table 5. Entropy values calculated in this work agree with the data of Svehla and Brokaw (*30*) with average absolute and maximum deviations of 0.21 and 1.94%, respectively, and with those of Stai et al. with average absolute and maximum deviations of 0.35 and 1.62%, respectively.

Enthalpy values calculated in this work agree with those of Svehla and Brokaw (*30*) with average absolute and maximum deviations of 0.52 and 5.49%, respectively, and with those of Stai et al. with average absolute and maximum deviations of 1.15 and 6.35%, respectively.

Svehla and Brokaw (*30*) have determined the L-J potential parameters for nitrogen dioxide and nitrogen tetroxide separately using the experimental viscosity data of Petkar and Mason (*22*) which covers a pressure range of 0.5 to 5 atm. and a temperature range of 298° to 443°K. The values of nitrogen dioxide and nitrogen tetroxide in equilibrium calculated by using the combining rules given by Hirschfelder et al. (*14*) are

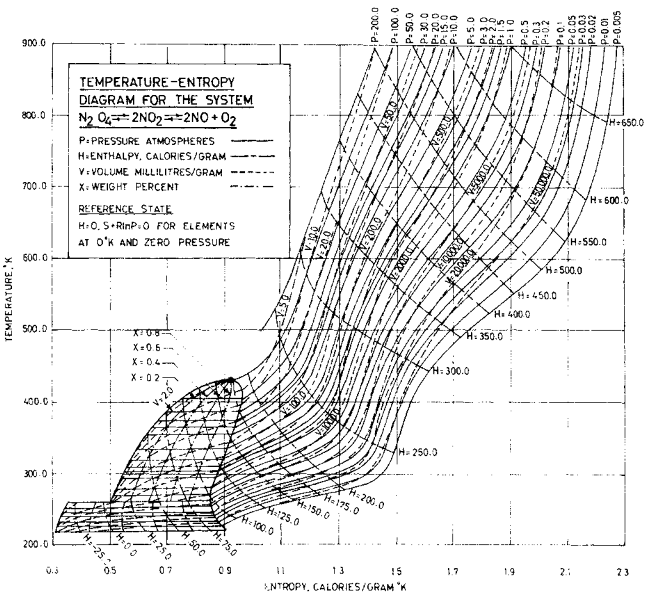

Fig. 5. Temperature-entropy diagram.

$$(\epsilon/K)_{NO_2\text{-}N_2O_4} = 270.0°K. \text{ and } \sigma)_{NO_2\text{-}N_2O_4} = 4.193 \text{ Å}.$$

The value of σ agrees with the value calculated in this work, namely 4.147 Å., but the values of ϵ/K differ. Svehla and Brokaw (*30*) used the transport property data, whereas in the present work PVT data have been used. The values of ϵ/K differ, the present value (ϵ/K = 300.0°K.) being higher than that reported by Svehla and Brokaw (*30*). This discrepancy and the present higher value may be because both long- and short-range forces are accounted. Also, the larger the ϵ/K value, the stronger is the binding, and possibly this is one of the reasons for higher ϵ/K values in the present work.

It can be seen from Figure 4 that at any particular pressure and a given mole fraction of nitrogen dioxide in the equilibrium mixture, there are two temperatures at which the system is stable. This can be seen easily, as the mole of nitrogen dioxide in the equilibrium mixture given by

$$x_2 = \frac{2(\xi_1 - \xi_2)}{1 + \xi_1 + \xi_2}$$

attains an extremum, thus giving two values of temperature for a given x_2.

NOTATION

A, B, C, D = constants in Equation (26)
a, b, c, d = constants in Equation (1)
$B(T)$ = second virial coefficient, cc./mole
B_1^*, C_1^* = reduced derivatives of the second and third virial coefficients, respectively
$C(T)$ = third virial coefficient, (cc.)^2/(mole)^2
C_p = heat capacity at constant pressure, cal./(g.)(mole)
d_c = critical density, g./cc.
H = enthalpy, cal./g.
$\Delta H_0°$ = heat of formation, cal./(g.)(mole)
ΔH_v = heat of vaporization, cal./g.
K, K_p, K_α = equilibrium constants
K_1, K_{p1} = equilibrium constants for the reaction $N_2O_4 \rightleftharpoons 2NO_2$
K_2, K_{p2} = equilibrium constants for the reaction $2NO_2 \rightleftharpoons 2NO + O_2$
M = molecular weight, g.

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* Tables 3 and 4 have been deposited as document 00776 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York 10001 and may be obtained for $1.00 for microfiche or $3.00 for photocopies.

TABLE 5. COMPARISON OF THE VALUES OF ENTROPY AND ENTHALPY

	Data of Svehla and Brokaw (*30*)				Data of Stai et al. (*29*)			
Pressure *P*, atm.	Range of temp., °K.	No. of points	Avg. abs. deviation, %	Max. deviation, %	Range of temp., °K.	No. of points	Avg. abs. deviation, %	Max. deviation, %
			(a) ENTROPY					
0.01	300-900	7	0.08	0.18	300-400	2	0.05	0.05
0.03	300-900	7	0.11	0.30	300-400	2	0.52	0.98
0.10	300-900	7	0.14	0.40	300-500	3	0.59	1.26
0.30	300-900	7	0.12	0.34	300-500	3	0.60	1.62
1.00	300-900	7	0.11	0.26	300-500	3	0.61	0.18
3.00	400-900	6	0.10	0.17	400-500	2	0.59	1.14
10.00	400-900	6	0.16	0.22	400-500	2	0.50	0.58
30.00	400-900	6	0.31	0.50	400-500	2	0.30	0.58
100.00	500-900	5	0.98	1.94	500	1	0.09	0.09
			(b) ENTHALPY					
0.01	300-900	7	0.15	0.34	300-500	3	1.44	2.26
0.03	300-900	7	0.21	0.59	300-500	3	2.52	3.78
0.10	300-900	7	0.24	0.74	300-500	3	0.74	1.16
0.30	300-900	7	0.24	0.72	300-500	3	0.89	1.58
1.00	300-900	7	0.24	0.61	300-500	3	1.45	2.98
3.00	400-900	6	0.22	0.38	400-500	2	0.57	0.96
10.00	400-900	6	0.32	0.59	400-500	2	0.20	0.23
30.00	400-900	6	0.93	1.46	400-500	2	0.69	1.00
100.00	500-900	5	2.72	5.49	500	1	0.78	0.78

P = pressure, atm.
R = universal gas constant, (liter)(atm.)/(g.)(mole)(°K.)
S = entropy, cal./(g.)(°K.)
T = temperature, °K.
V = specific volume, cc./g.
x_1, x_2, x_3, x_4 = mole fractions of nitrogen tetroxide, nitrogen dioxide, nitric oxide, and oxygen, respectively
$Z = PV/RT$ = compressibility factor, dimensionless

Greek Letters

$\phi(r)$ = potential energy function at a separation r
ξ_1 = moles of nitrogen tetroxide dissociated
ξ_2 = moles of oxygen formed
σ = collision diameter, Å.
ϵ = maximum energy of attraction, erg.

Superscript

* = properties referred to ideal gas

Subscripts

mix. = mixture
g = gas or vapor
i, j = i^{th} and j^{th} component, respectively
l = liquid
v = vapor

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