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GAS PHASE CHEMICAL EQUILIBRIUM IN DINITROGEN TRIOXIDE AND DINITROGEN TETROXIDE

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ABSTRACT

The ideal gas chemical thermodynamic properties for NO, NO_2, N_2O_3, and N_2O_4 for the temperature range 50 to 5000 K were evaluated by the statistical thermodynamic method using the most recent molecular parameters. In the calculations for NO and NO_2, the effects of anharmonicity and vibration–rotation interaction were included. The contributions due to centrifugal distortion were also included for NO_2. For evaluation of the thermodynamic properties for N_2O_3 and N_2O_4 molecules, the rigid-rotor and harmonic-oscillator model were adopted. A free internal rotation was assumed for N_2O_3 and an internal rotation barrier height (V_2) of 1.58 kcal mol^{-1} was derived for N_2O_4. The thermodynamic properties due to hindered internal rotation were calculated using a partition function formed by summation of internal rotation energy levels. The thermodynamic properties for two equilibrium mixtures: NO_2–N_2O_4 and N_2O_3–NO–NO_2–N_2O_4 were also calculated. The effects of temperature and pressure on heat capacities and compositions of these two mixtures are illustrated graphically and the calculated heat capacities and equilibrium constants are in good agreement with available experimental values.

INTRODUCTION

The nitrogen oxides are important compounds in air pollution, rocket propulsion, and chemical industries. Due to the recent revision of fundamental constants[1] and the availability of new molecular and spectroscopic data for some of these nitrogen oxides, their chemical thermodynamic properties in the ideal gaseous state in the temperature range 50 to 5000 K were evaluated by the statistical thermodynamic method. For all calculations the atomic weights[2] N = 14.0067 and O = 15.9994 and the new physical constants recommended by Taylor et al.[1] in 1969 were employed.

The thermodynamic properties of N_2O_3 and N_2O_4 were calculated based on the rigid-rotor and harmonic-oscillator (RRHO) models. A free internal rotation was assumed for N_2O_3 and a hindered internal rotation with a barrier height of 1.58 kcal mol^{-1} was evaluated for the N_2O_4 molecule*. The contributions from anharmonic

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*Throughout this paper 1 cal = 4.184 J; 1 atm = 101.325 k N m^{-2}; 1 Å = 0.1 nm.

vibrations, vibration–rotation interactions and centrifugal distortions, which were derived from appropriate spectroscopic data, were included in the calculation of thermodynamic properties for NO and NO_2. The method of Pennington and Kobe[3] was followed for the calculation of these effects in NO_2.

It is well known that at room temperature the NO_2 species exist as a mixture of monomers and dimers and the compound N_2O_3 is unstable at all temperatures and forms a mixture containing NO, NO_2, N_2O_4, and N_2O_3 at temperatures below 600 K, and at temperatures above 600 K the mixture contains only NO and NO_2. Because of these facts, we have also evaluated the thermodynamic properties for two equilibrium mixtures, i.e., NO_2–N_2O_4 and N_2O_3–NO–NO_2–N_2O_4.

MOLECULAR AND THERMAL DATA

Nitrogen oxide (NO)

The electronic configuration of NO molecule in the ground state is of the type $^2\pi$ where the two substates $^2\pi_{1/2}$ and $^2\pi_{3/2}$ are separated by about 121 cm^{-1}. The ground state is connected with seven excited states and for many years the presence of such a great number of electronic states in a comparatively narrow range caused difficulties and confusion in analyzing and interpreting the electronic spectra of NO. The vibrational levels of the ground state were obtained in investigation of the vibration-rotation spectrum of NO in the infrared range[4–9] and the vibrational constants were derived[4,9]. The rotational levels of NO were studied by many investigators in the infrared[10] and microwave regions of the spectrum[11–16]. The results of important research work on the determination of the rotational constants were summarized by Gillett and Eyster[4]. Investigations were also made of the isotopic molecules: $^{15}N^{16}O$[13,17] and $^{15}N^{18}O$[18].

Olman et al.[19] have analyzed the high resolution spectra of the first and second overtone vibration rotation bands of ^{14}NO and ^{15}NO. Their reported values of rotational (B_e), vibrational (ω_e), anharmonicity ($\omega_e x_e$) and vibrational-rotation coupling (α_e) constants were adopted and calculated for the natural isotopic mixture for evaluation of the thermodynamic properties. The standard enthalpy of formation ΔH_f°(NO(g), 298.15 K) = 21.57 kcal mol^{-1} was obtained from the National Bureau of Standards[20].

Nitrogen dioxide (NO_2)

The molecular structure of NO_2 has been elucidated by electronic diffraction[21,22], microwave[23] and infrared spectroscopy[24]. The molecular parameters determined by Bird[24] were employed. Based on this structure the product of the three principal moments of inertia ($I_A I_B I_C$) was derived as 1.54158×10^{-116} g^3 cm^6.

The vibration–rotation band of nitrogen dioxide was studied extensively[25–32,64,65]. Bird et al.[30] reviewed the reported microwave spectra for NO_2 in the literature and assigned corrected infrared harmonic wavenumbers from a combined microwave–infrared calculation. They suggested that the harmonic wavenumbers obtained exclusively from infrared needed revision due to discovery of a minor error in the published infrared analyses of NO_2 by Arakawa and Nielsen[31] and Bird et al.[32]. The harmonic zero-order vibrational wavenumbers assigned for $^{14}N^{16}O_2$ and $^{15}N^{16}O_2$ by Bird et al.[30] were adopted. The fundamental vibrational wavenumbers for natural isotopic mixture ($^{14}N^{16}O_2$, 99.6%; $^{15}N^{16}O_2$, 0.37%) were evaluated as 1320.6, 749.6 and 1617.0 cm^{-1}.

The anharmonicity constants for the $^{14}NO_2$ molecule have been reported by Moore[23] and Weston[33] based on results of Brown and Wilson[27] and Keller and Nielsen[28,34]. Arakawa and Nielsen[31] studied the spectra of $^{14}NO_2$ and $^{15}NO_2$ with high precision in the range 670 to 5900 cm^{-1}. They analyzed the rotational structure and derived the rotational and vibrational constants for these two species. Their reported values of anharmonicity and vibration–rotation coupling constants were adopted.

The centrifugal distortion constants have been obtained from fine-structure measurements of several bands of NO_2[23,27,28,34–36]. Those derived by Danti and Lord[36] were employed for calculation. The following additional molecular data: point group $= C_{2v}$; symmetry number, $\sigma = 2$; electronic level and statistical weight in the ground state $\varepsilon_0 = 0$ and $g_0 = 2$ were used for statistical thermodynamical calculation. The ΔH_f° (NO_2(g), 298.15 K) was adopted as 7.93 kcal mol^{-1} (ref. 20).

Dinitrogen trioxide (N_2O_3)

The molecular parameters for N_2O_3 have not been completely determined and reported in the literature. Kuczkowski[37] determined the three principal moments of inertia for each of the following species $O^{14}N^{14}NO_2$, $O^{15}N^{14}NO_2$, $O^{14}N^{15}NO_2$, and $O^{15}N^{15}NO_2$ from microwave spectrum and found that the N_2O_3 molecule has a planar structure. He established the N–N bond distance in N_2O_3 to be 1.85 ± 0.03 Å. Using additional estimated N–O bond distance and ∢ONO as 1.180 Å and 134°, respectively, we derived $I_A I_B I_C = 3.5478 \times 10^{-114}$ $g^3\,cm^6$ which is in reasonable agreement with Kuczkowski's experimental value 3.5649×10^{-114} $g^3\,cm^6$. The reduced moment (I_r) was obtained as 1.0582×10^{-39} g cm^2. Devlin and Hisatsune[38] calculated from Urey–Bradley force constants eight fundamental vibrational wavenumbers (in cm^{-1}): 1863, 1589, 1297, 783, 627, 407, 313 and 253 for N_2O_3 which were adopted tentatively. A free internal rotation was assumed[39,40] and the following data: point group C_s, $\sigma = 1$, $\varepsilon_0 = 1$, $g_0 = 1$ were employed for evaluation of ideal gas thermodynamic functions for N_2O_3.

The Gibbs energy change, ΔG_r° (298.15 K) for reaction (1) was derived to be -0.364 kcal mol^{-1} (refs. 41, 42)

$$N_2O_3(g) = NO(g) + NO_2(g) \qquad (1)$$

Based on the entropies, S° (298.15 K), for the species in the above equation from the present work, we calculated the entropy change ΔS_r° (298.15 K) = 34.03 cal K^{-1} mol^{-1}. Using the values of ΔG_r° and ΔS_r° thus obtained and the relationship

$$\Delta H_r^\circ = \Delta G_r^\circ + T\,\Delta S_r^\circ \qquad (2)$$

the enthalpy change ΔH_r° (298.15 K) for reaction (1) was calculated as 9.78 kcal mol^{-1}. Based on this ΔH_r° (298.15 K) value and ΔH_f° (g, 298.15 K) = 21.57 kcal mol^{-1} for NO and 7.93 kcal mol^{-1} for NO_2[20], we derived ΔH_f° (N_2O_3(g), 298.15 K) = 19.72 kcal mol^{-1}. This value was calculated to be consistent with the experimental equilibrium constant determined by Beattie and Bell[41] for reaction (1) and was adopted.

Dinitrogen tetroxide (N_2O_4)

The molecular structure of dinitrogen tetroxide has been investigated extensively by many researchers for many years. The stable form of this compound is known to be planar and symmetric (D_{2h} symmetry) as O_2N–NO_2[43,45,48]. Its molecular parameters have been determined by Broadley and Robertson[44], Smith and Hedberg[43], Groth[49], Cartwright and Robertson[50], and McClelland et al.[51]. The existence of N_2O_4 molecules with the same configuration but staggered (symmetry D_{2d}) and molecules with the configuration O_2N–ONO in the crystal state has been reported in the literature[46,47]. For the present work, the new molecular parameters determined recently by McClelland et al. by gaseous electron diffraction were adopted. The values of $I_A I_B I_C$ and I_r were evaluated as $1.0515_2 \times 10^{-113}$ g^3 cm^6 and 1.6102×10^{-39} g cm^2, respectively.

Hisatsune et al.[47] and Snyder and Hisatsune[45] investigated the infrared spectrum of N_2O_4 and assigned the following fundamental vibrational wavenumbers (in cm^{-1}): 1373, 812, 260, 50, 1710, 480, 430, 675, 1748, 385, 1261, and 750 which were used for calculation except the value 50 cm^{-1} for ν_4, the torsional frequency. This torsional frequency was not observed in the infrared spectrum and the value 50 cm^{-1} was estimated from entropy calculation[45] based on the molecular structure determined by Smith and Hedberg[44]. Since this work adopted the molecular parameters reported by McClelland et al.[51] for calculation of thermodynamic properties for N_2O_4, the value of ν_4 was recalculated as follows. The Gibbs energy change ΔG_r° (298.15 K) for reaction (3) was derived as 1.138 kcal mol^{-1} from the equilibrium constant $\log_{10} K = -0.834$ at 298.3 K reported by Giauque and Kemp[52] which was obtained from reevaluation of the equilibrium data measured by Wourtzel[53].

$$N_2O_4(g) = 2NO_2(g) \tag{3}$$

From the adopted values of ΔH_f° (g, 298.15 K) = 7.93 kcal mol^{-1} for NO_2 and 2.19 kcal mol^{-1} for N_2O_4[20] we obtained ΔH_r° (298.15 K) = 13.67 kcal mol^{-1}. By using the values of ΔG_r° (298.15 K) and ΔH_r° (298.15 K), and eqn (2), the entropy change ΔS_r° (298.15 K) of reaction (3) was computed as 42.03 cal K^{-1} mol^{-1}. Based on this ΔS_r° (298.15 K) and S° (NO_2(g), 298.15 K) = 57.42 cal K^{-1} mol^{-1} (this work), the S° (N_2O_4(g), 298.15 K) was calculated to be 72.81 cal K^{-1} mol^{-1}. Using this entropy for N_2O_4(g) and $I_r = 1.6102 \times 10^{-39}$ g cm^2, we evaluated the internal rotation potential barrier height[54] as $V_2 = 1.58 \pm 0.10$ kcal mol^{-1} for N_2O_4. From the values of I_r and V_2 thus obtained we generated 187 internal rotation energy levels up to 15280 cm^{-1} (ref. 55) of which the torsional wavenumber $(\nu_4)_{1-0}$

was found to be 60 cm^{-1}. The internal rotation contributions to the thermodynamic properties were calculated by the usual statistical thermodynamic method using a partition function formed by summation of these internal rotation energy levels. For evaluation of the other contributions to the thermodynamic properties for N_2O_4 (g), the following additional molecular data: point group $= D_{2h}$ (or V_h), $\sigma = 4$, $\varepsilon_0 = 0$, $g_0 = 1$ and molecular weight $= 92.011$ were used.

NO_2–N_2O_4 equilibrium mixture

As mentioned previously, at room temperature nitrogen dioxide exists as a mixture of monomers (NO_2) and dimers (N_2O_4). The composition of this equilibrium mixture changes with temperature and pressure, which can be calculated from known equilibrium constants (or Gibbs energy changes for reaction (3)) at given values of T and P. Based on the calculated equilibrium compositions and the thermodynamic functions for NO_2 (g) and N_2O_4 (g) from the present work, the thermodynamic properties for NO_2–N_2O_4 mixtures at temperatures of 50 to 5000 K were derived. These mixture properties were calculated as per mole of pure NO_2 which was arbitrarily chosen.

N_2O_3–NO–NO_2–N_2O_4 equilibrium mixture

Pure gaseous dinitrogen trioxide is unstable at temperatures higher than 100 K. The decomposition products are NO, NO_2, and N_2O_4. The compositions of the equilibrium mixture at different temperatures and pressures were obtained by solving four simultaneous equations by iteration. These four equations include two chemical equilibrium, reactions (1) and (3), and two mass balances for elements O and N. From the known equilibrium compositions and the thermodynamic functions for N_2O_3, NO, NO_2 and N_2O_4 from the present work, the ideal gas thermodynamic properties for the equilibrium mixtures at temperatures of 50 to 5000 K were evaluated. The results were calculated based on one mole of pure N_2O_3 before formation of equilibrium mixture.

CALCULATION RESULTS AND DISCUSSION

Employing the above selected molecular, spectroscopic and thermochemical constants for NO, NO_2, N_2O_3, and N_2O_4, the thermodynamic functions, C_p°, S°, $(H^\circ - H_0^\circ)/T$, $-(G^\circ - H_0^\circ)/T$, and $H^\circ - H_0^\circ$, for these species were evaluated by the statistical thermodynamic method[56]. From the adopted ΔH_f° (298.15 K) for each of these oxides and $H^\circ - H_0^\circ$ and $-(G^\circ - H_0^\circ)/T$ for O_2[57], N_2[57], and respective nitrogen oxides (this work), the ΔH_f°, ΔG_f°, and log K in the temperature range 50 to 5000 K for NO, NO_2, N_2O_3, and N_2O_4 were derived. Skeletal numerical results only for the range 0 to 2000 K are presented in Table 1. The contributions to C_p°, S°, and $H^\circ - H_0^\circ$ due to anharmonic vibrations, vibration–rotational interactions and centrifugal distortion effects, for NO and NO_2 at temperatures of 298.15, 500, and 1000 K are listed in Table 2. The complete tables of the thermodynamic properties for these four nitrogen oxides and other species, e.g. N, N_2, N_3, NO_3, N_2O, N_2O_2, and N_2O_5, will appear in the Thermodynamics Research Center Data Project tables[57]. The complete numerical results for the two equilibrium mixtures, NO_2–N_2O_4 and N_2O_3–NO–NO_2–N_2O_4, in the temperature range 50 to 5000 K are also available[57].

TABLE 1

IDEAL GAS THERMODYNAMIC FUNCTIONS AT 1 atm

T (*K*)	C_p° (*cal* K^{-1} *mol*$^{-1}$)	S° (*cal* K^{-1} *mol*$^{-1}$)	$H^\circ - H_0^\circ$ (*kcal mol*$^{-1}$)	ΔH_f° (*kcal mol*$^{-1}$)	ΔG_f° (*kcal mol*$^{-1}$)
Nitrogen oxide (*NO*)					
0	0	0	0	21.45	21.45
100	7.721	42.27	0.746	21.50	21.25
298.15	7.136	50.33	2.197	21.57	20.69
400	7.165	52.43	2.924	21.58	20.39
600	7.484	55.39	4.386	21.59	19.79
800	7.852	57.60	5.920	21.60	19.19
1000	8.142	59.38	7.521	21.62	18.58
1500	8.565	62.77	11.71	21.64	17.06
2000	8.769	65.27	16.05	21.64	15.53
Nitrogen dioxide (*NO*$_2$)					
0	0	0	0	8.591	8.591
100	7.971	48.40	0.796	8.346	9.554
298.15	8.991	57.42	2.450	7.930	12.24
400	9.823	60.17	3.405	7.807	13.74
600	11.28	64.42	5.514	7.721	16.73
800	12.28	67.79	7.864	7.761	19.74
1000	12.94	70.58	10.37	7.86	22.7
1500	13.83	75.99	17.06	8.24	30.1
2000	14.30	80.04	24.08	8.70	37.3
Dinitrogen trioxide (*N*$_2$*O*$_3$)					
0	0	0	0	21.34	21.34
100	10.35	59.70	0.927	20.53	24.59
298.15	15.68	73.72	3.566	19.72	33.30
400	17.38	78.58	5.253	19.61	37.96
600	19.82	86.12	8.991	19.70	47.13
800	21.39	92.05	13.12	20.00	56.22
1000	22.37	96.94	17.51	20.39	65.24
1500	23.6	106.0	29.1	21.5	87.4
2000	24.1	113.0	41.0	22.5	109.0
Dinitrogen tetroxide (*N*$_2$*O*$_4$)					
0	0	0	0	4.45	4.45
100	11.25	56.95	0.954	3.32	9.72
298.15	18.46	72.81	3.962	2.19	23.35
400	20.86	78.58	5.969	2.04	30.60
600	24.24	87.73	10.50	2.19	44.87
800	26.34	95.02	15.58	2.64	59.04
1000	27.65	101.0	20.99	3.24	73.07
1500	29.2	113.0	35.3	4.92	108.0
2000	29.9	121.0	50.1	6.59	142.0

TABLE 1 (*continued*)

T (K)	C_p° (cal K^{-1} mol^{-1})	S° (cal K^{-1} mol^{-1})	$H^\circ - H_0^\circ$ (kcal mol^{-1})	ΔH_f° (kcal mol^{-1})	ΔH_f° (kcal mol^{-1})
NO_2–N_2O_4 equilibrium mixture[a]					
0	0	0	0	2.225	2.225
100	5.623	28.48	0.477	1.66	4.86
200	8.09	33.1	1.15	1.29	8.22
298.15	57.1	41.1	3.27	2.38	11.56
300	59.7	41.5	3.37	2.47	11.62
400	20.0	59.6	9.52	7.56	13.72
500	10.8	62.4	10.78	7.74	15.23
600	11.3	64.4	11.88	7.72	16.73
N_2O_3–NO–NO_2–N_2O_4 equilibrium mixture[b]					
0	0	0	0	21.34	21.34
100	13.34	72.65	3.556	23.16	25.92
200	14.8	82.4	4.97	27.83	28.82
298.15	62.8	91.1	7.08	23.23	31.63
300	68.2	91.6	7.2	23.32	31.67
400	23.6	115.0	14.9	29.22	33.01
500	18.1	119.2	16.8	29.32	33.94
600	18.8	122.6	18.6	29.31	34.87

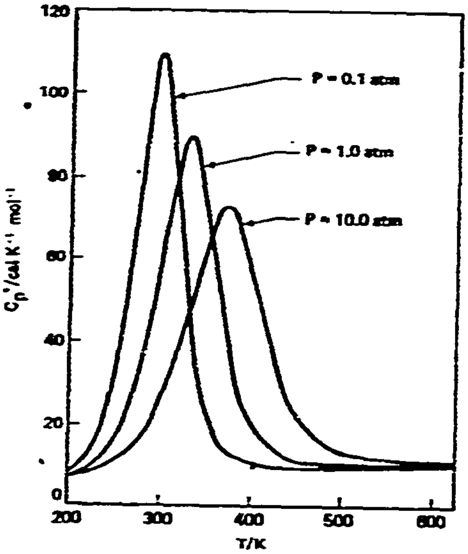
[a] The standard enthalpy and common logarithm of the equilibrium constant of formation for the reaction: $(1/2)N_2(g) + O_2(g) = nN_2O_4(g) + (1-n)NO_2(g)$ where n is the mole fraction of N_2O_4 species in the mixture at the given temperature. [b] The standard enthalpy and common logarithm of the equilibrium constant of formation for the reaction: $N_2(g) + (3/2)O_2(g) = nN_2O_3(g) + mNO(g) + kNO_2(g) + (1-n-m-k)N_2O_4(g)$ where n, m, and k are the mole fractions of N_2O_3, NO and NO_2 in the mixture at the given temperature.

TABLE 2

CONTRIBUTIONS TO THERMODYNAMIC PROPERTIES DUE TO ANHARMONIC VIBRATION, VIBRATION-ROTATIONAL INTERACTION AND CENTRIFUGAL DISTORTION EFFECTS

T (K)	NO_2			NO		
	C_p° (cal K^{-1} mol^{-1})	S° (cal K^{-1} mol^{-1})	$H^\circ - H_0^\circ$ (cal mol^{-1})	C_p° (cal K^{-1} mol^{-1})	S° (cal K^{-1} mol^{-1})	$H^\circ - H_0^\circ$ (cal mol^{-1})
298.15	0.117	0.067	12.4	0.004	0.003	0.5
500	0.197	0.124	38.2	0.009	0.006	1.6
1000	0.413	0.274	157.4	0.034	0.019	12.0

Part of the results obtained are shown in Table 1. The apparent heat capacities of the two equilibrium mixtures show the expected maximum in the range of 200 to 600 K for equilibrium involving chemically reacting species. The temperature and pressure dependences of C_p° and composition for NO_2–N_2O_4 equilibrium mixtures are shown in Figs. 1 and 2. Those for the other equilibrium mixture, N_2O_3–NO–NO_2–N_2O_4, are given in Figs. 3–5.



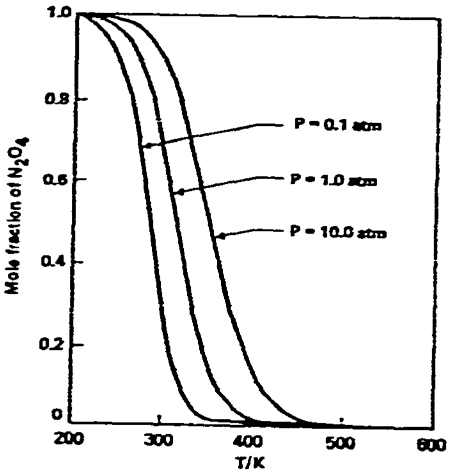


Fig. 1. Temperature and pressure dependence of heat capacities of NO_2–N_2O_4 equilibrium mixture

Fig. 2. Temperature and pressure dependence of composition of NO_2–N_2O_4 equilibrium mixture

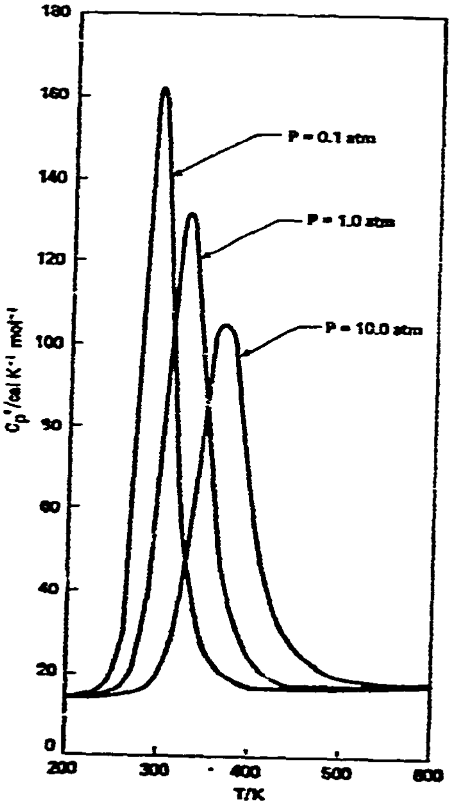
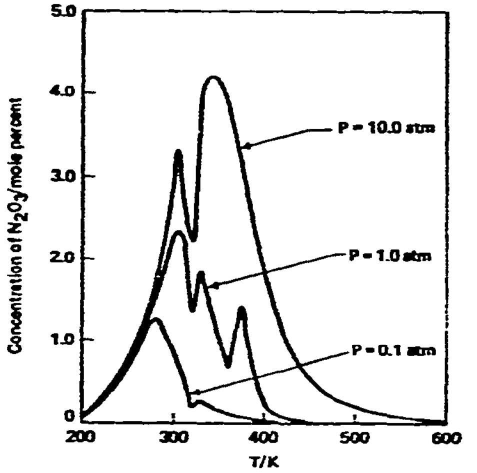


Fig. 3. Temperature and pressure dependence of heat capacities of N_2O_3–NO–NO_2–N_2O_4 equilibrium mixture.



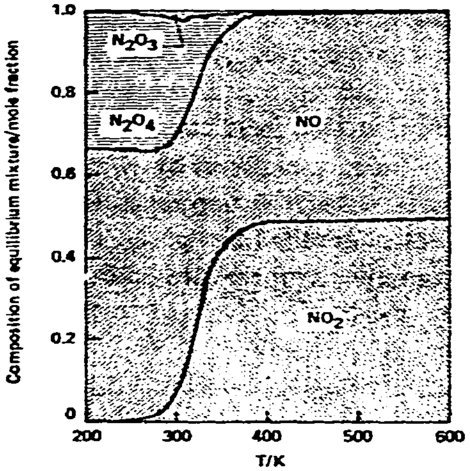


Fig. 4. Temperature and pressure dependence of concentration of N_2O_3 in N_2O_3–NO–NO_2–N_2O_4 equilibrium mixture.

Fig. 5. Composition of N_2O_3–NO–NO_2–N_2O_4 equilibrium mixture at various temperatures under one atmosphere total pressure.

It is interesting to note that Fig. 2 indicates the fact that higher total pressure favors the formation of dimer N_2O_4 from monomer NO_2 in the equilibrium mixtures. As dimerization of NO_2 is an exothermic reaction, -13.67 kcal mol^{-1} at 298.15 K, more N_2O_4 species formed in the equilibrium mixture means more dimerization energy being released, thus it decreases the enthalpy, $H^\circ - H_0^\circ$, of the mixture. Higher equilibrium pressure also brings down the corresponding C_p° and S° of the mixture at temperatures below 300 K; however, at temperatures above 370 K the reverse is true for C_p° of the NO_2–N_2O_4 system as indicated in Fig. 1. The situation for the equilibrium mixture of N_2O_3–NO–NO_2–N_2O_4 is very similar to that for the NO_2–N_2O_4

TABLE 3

COMPARISON OF EXPERIMENTAL AND CALCULATED HEAT CAPACITIES OF NO_2–N_2O_4 EQUILIBRIUM MIXTURE

T (K)	C_p° *(cal* K^{-1} *mol*$^{-1}$*)*	
	From ref. 58	*Calc. in this work*
306.88	63.0	69.1
314.15	73.0	78.6
317.15	77.0	82.0
328.18	88.0	89.9
334.05	89.0	90.0
336.48	89.5	89.1
343.85	84.0	83.1
354.04	71.5	69.8
370.66	46.5	44.2

equilibrium mixture. Figure 4 shows that the equilibrium concentration of N_2O_3 is a rather complex function of temperature and pressure, and that it never becomes large at pressures up to a few atmospheres.

The calculated heat capacities for the NO_2–N_2O_4 mixture at 1 atm were compared with those measured by McCollum[58]. Since the reported values are average heat capacities over the temperature range 1.2 to 4.4°C and for real gases while the calculated ones are for ideal gases, the agreement between the reported and calculated C_p° values in the temperature range from 307 to 471 K, as shown in Table 3, are reasonably good.

TABLE 4

COMPARISON OF EXPERIMENTAL AND CALCULATED EQUILIBRIUM CONSTANTS

$T(K)$	*Exp.*	*Calc.*
$N_2O_4 \rightleftharpoons 2NO_2$[a]		
273.1	0.0177 (ref. 53)	0.0176
281.82	0.0374 (ref. 59)	0.0384
298.1	0.136 (ref. 60)	0.146
298.3	0.147 (ref. 53)	0.148
297.44	0.140 (ref. 59)	0.138
308.1	0.302 (ref. 60)	0.308
318.1	0.628 (ref. 60)	0.621
323.4	0.863 (ref. 53)	0.885
326.0	1.076 (ref. 59)	1.048
359.6	7.499 (ref. 53)	7.487
374.68	16.18 (ref. 59)	16.111
403.93	59.43 (ref. 59)	60.354
$N_2O_3 \rightleftharpoons NO + NO_2$[b]		
278.15	0.595 (ref. 41)	0.568
281.28	0.539 (ref. 61)	0.692
288.15	1.082 (ref. 41)	1.055
298.15	1.916 (ref. 41)	1.860
	2.105 (ref. 60)	1.860
307.95	2.39 (ref. 61)	3.02
308.15	3.097 (ref. 41)	3.18
	3.673 (ref. 60)	3.18
318.15	5.193 (ref. 41)	5.25
	6.880 (ref. 60)	5.25

[a] The original experimental data were recalculated by Giauque and Kemp[52]. The values listed in this table are the recalculated ones. [b] The listed experimental values are obtained from Beattie and Bell[41].

Table 4 gives the comparison of experimental and calculated equilibrium constants (K_{eq}) for reactions (3) and (1). The calculated K_{eq} values for reaction (3) were derived from eqn (4); and those for reaction (1) were evaluated by use of eqn (5).

$$\log_{10} K_{eq} = -4.7040+6.9628+19^{-4}T-2691.09/T+9.981163\log T \\ -14.2840\left[(1+85/T)\log\left(1+\frac{T}{85}\right)\right]-6.6794\times10^{-8}T^2 \tag{4}$$

$$\log_{10} K_{eq} = -6.8331+4.4261\times10^{-4}T-1801.21/T+9.60957\log T \\ -12.8074\left[(1+85/T)\log\left(1+\frac{T}{85}\right)\right]-3.6968\times10^{-8}T^2 \tag{5}$$

The parameters in eqns (4) and (5) were evaluated by a least-squares fit to the equilibrium constants calculated from the data in Table 1 from 100 to 2000 K. The standard deviation between log K calculated from eqns (4) and (5) and log K calculated from Table 1 are 0.00056 and 0.00024, respectively. The maximum deviations are well within the uncertainties of these values. The good agreement between the calculated and experimental equilibrium constants listed in Table 4 indicates the fact that the values of the thermodynamic functions evaluated for these nitrogen oxides, as presented in Table 1, are internally consistent and reliable and may be used with confidence in thermodynamic calculations.

Novick et al.[62] reported the results of electric deflection of ultrasonic molecular beams of NO_2 and suggested that the NO_2 system shows extensive polymerization beyond that of the dimer. They showed that the trimer, $(NO_2)_3$, was non-polar and also proposed a cyclic planar C_{3h} structure. An alternative structure and a cycloaddition mechanism for the formation of $(NO_2)_3$ was discussed by Liebman[63].

Novick et al.[62] calculated the equilibrium constant for formation of NO_2 trimer from the monomer in the range 298.15 to 318.15 K. These values show that the equilibrium concentration of the trimer is no more than about 2–3 mole percent at pressures of 1 atm, but increases rapidly at higher pressures. The presence of a trimeric species may account for the differences between observed and calculated heat capacities reported in Table 3. However, due to the lack of more specific information about the trimer we did not include it in any of our calculations.

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REFERENCES

1 B. N. Taylor, W. H. Parker, and D. N. Langenberg, *Rev. Mod. Phys.*, 41 (1969) 375; also available in book form: *The Fundamental Constants and Quantum Electrodynamics* by the same authors. Academic Press, New York, 1969.

2 Commission on Atomic Weights, *Pure Appl. Chem.*, 21 (1970) 91.

3 R. E. Pennington and K. A. Kobe, *J. Chem. Phys.*, 22 (1954) 1442.

4 R. H. Gillet and E. H. Eyster, *Phys. Rev.*, 56 (1939) 1113.
5 N. L. Nichols, C. D. Hause and R. H. Noble, *J. Chem. Phys.*, 23 (1955) 57.
6 J. H. Shaw, *J. Chem. Phys.*, 24 (1956) 399.
7 H. W. Thompson and B. A. Green, *Spectrochim. Acta*, 8 (1956) 129.
8 E. Koczkas, *Acta Phys. Acad. Scient. Hung.*, 10 (1959) 117.
9 F. A. Jenkins, H. A. Barton and R. S. Mulliken, *Phys. Rev.*, 30 (1927) 150.
10 E. D. Palik and K. N. Rao, *J. Chem. Phys.*, 25 (1956) 1174.
11 C. A. Burrus and W. Gordy, *Phys. Rev.*, 92 (1953) 1437.
12 J. J. Gallagher, F. D. Bedard and C. M. Johnson, *Phys. Rev.*, 93 (1954) 729.
13 J. J. Gallagher and C. M. Johnson, *Phys. Rev.*, 103 (1956) 1727.
14 J. J. Gallagher, W. C. King and C. M. Johnson, *Phys. Rev.*, 98 (1955) 1551.
15 P. G. Favero, A. M. Mirri and W. Gordy, *Phys. Rev.*, 114 (1959) 1534.
16 P. G. Favero, A. M. Mirri and W. Gordy, *Bull. Amer. Phys. Soc.*, 4 (1959) 290.
17 W. H. Fletcher and G. M. Begun, *J. Chem. Phys.*, 27 (1957) 579.
18 J. L. Griggs, Jr. and K. N. Rao, *J. Mol. Spectrosc.*, 22 (1967) 383.
19 M. D. Olman, M. D. McNelis and C. D. Hause, *J. Mol. Spectrosc.*, 14 (1964) 62.
20 National Bureau of Standards, Washington, D.C., *U.S. Nat. Bur. Stand. Tech. Note, No. 270-3,* 1968.
21 L. R. Maxwell and V. M. Mosley, *J. Chem. Phys.*, 8 (1940) 738.
22 S. Claesson, J. Donohue and V. Schomaker, *J. Chem. Phys.*, 16 (1948) 207.
23 G. E. Moore, *J. Opt. Soc. Amer.*, 43 (1953) 1045.
24 G. R. Bird, *J. Chem. Phys.*, 25 (1956) 1040.
25 C. R. Bailey and A. B. D. Cassie, *Nature*, 131 (1933) 239 and 910.
26 R. Schaffert, *J. Chem. Phys.*, 1 (1933) 507.
27 M. Brown and M. K. Wilson, *J. Chem. Phys.*, 22 (1954) 955.
28 F. L. Keller and A. H. Nielsen, *J. Chem. Phys.*, 24 (1956) 636.
29 F. L. Keller and A. H. Nielsen, *J. Chem. Phys.*, 29 (1958) 252.
30 G. R. Bird, J. C. Baird, A. W. Jache, J. A. Hodgeson, R. F. Curl, Jr., A. C. Kunkle, J. W. Bransford, J. Rastrup-Anderson and J. Rosenthal, *J. Chem. Phys.*, 40 (1964) 3378.
31 E. T. Arakawa and A. H. Nielsen, *J. Mol. Spectrosc.*, 2 (1958) 413.
32 G. R. Bird, E. K. Plyler and G. R. Hunt, *Spectrochim. Acta*, 18 (1962) 1371.
33 R. E. Weston, *J. Chem. Phys.*, 26 (1957) 1248.
34 F. L. Keller and H. A. Nielsen, *Phys. Rev.*, 99 (1955) 1624.
35 G. R. Bird, A. Danti and R. C. Lord, *Spectrochim. Acta*, 12 (1958) 247.
36 A. Danti and R. C. Lord, *J. Chem. Phys.*, 30 (1959) 1310.
37 R. L. Kuckowski, *J. Amer. Chem. Soc.*, 87 (1965) 5259.
38 J. P. Devlin and I. C. Hisatsune, *Spectrochim. Acta*, 17 (1961) 218.
39 I. C. Hisatsune and J. P. Devlin, *Spectrochim. Acta*, 16 (1960) 401.
40 I. C. Hisatsune, *J. Phys. Chem.*, 65 (1961) 2249.
41 I. R. Beattie and S. W. Bell, *J. Chem. Soc.*, (1957) 1681.
42 *JANAF Thermochemical Tables*, Dow Chemical Co., Midland, Mich., 1964.
43 D. W. Smith and K. Hedberg, *J. Chem. Phys.*, 25 (1956) 1282.
44 J. S. Broadley and J. M. Robertson, *Nature*, 164 (1949) 915.
45 R. G. Snyder and I. C. Hisatsune, *J. Mol. Spectrosc.*, 1 (1957) 139.
46 W. G. Fately, H. A. Bent and B. Crawford, *J. Chem. Phys.*, 31 (1959) 204.
47 I. C. Hisatsune, J. P. Devlin and Y. Wada, *J. Chem. Phys.*, 33 (1960) 714.
48 G. M. Begun and W. H. Fletcher, *J. Mol. Spectrosc.*, 4 (1960) 388.
49 P. Groth, *Acta Chem. Scand.*, 17 (1963) 2419.
50 B. S. Cartwright and J. H. Robertson, *Chem. Commun.*, (1966) 82.
51 B. W. McClelland, G. Gundersen and K. Hedberg, *J. Chem. Phys.*, 56 (1972) 4541.
52 W. F. Giauque and J. D. Kemp, *J. Chem. Phys.*, 6 (1938) 40.
53 E. Wourtzel, *C. R. Acad. Sci. (Paris)*, 169 (1919) 1397.
54 K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, 10 (1942) 428.
55 J. D. Lewis, T. B. Malloy, Jr., T. H. Chao and J. Laone, *J. Mol. Struct.*, 12 (1972) 427.
56 J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, John Wiley & Sons, New York, 1940.
57 B. J. Zwolinski *et al.*, *Selected Values of Properties of Chemical Compounds*, Thermodynamics Research Center Data Project, Texas A & M University, College Station, Texas, 1971.

58 E. D. McCollum, *J. Amer. Chem. Soc.*, 49 (1927) 28.
59 M. Bodenstein and F. Boës, *Z. Phys. Chem.*, 100 (1922) 75.
60 F. H. Verhoek and F. Daniels, *J. Amer. Chem. Soc.*, 53 (1931) 1250.
61 E. Abel and J. Proisl, *Z. Electrochem.*, 35 (1929) 712.
62 S. E. Novick, B. J. Howard and W. Klemperer, *J. Chem. Phys.*, 57 (1972) 5619.
63 J. F. Liebman, *J. Chem. Phys.*, 60 (1974) 2944.
64 R. M. Lees, R. F. Curl, Jr. and J. G. Baker, *J. Chem. Phys.*, 45 (1966) 2037.
65 P. A. Baron, P. D. Godgrey and D. O. Harris, *J. Chem. Phys.*, 60 (1974) 3723.