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

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THERMAL PROPERTIES such as heat capacity, thermal conductivity, and coefficient of thermal expansion of equilibrium-type reacting systems are usually large, nonmonotonic functions of temperature (*3*). Accordingly, in convective heat transfer to such systems, large heat transfer coefficients are observed (*2, 12, 15, 17*). In correlating heat transfer data in reacting systems it is necessary to have available information on the pertinent properties of the system. N_2O_4 gas represents a convenient equilibrium-type system for studying at relatively low temperatures, the effects of reaction on heat transfer processes. Properties such as molecular weight, density, diffusion coefficient, viscosity, thermal conductivity, isobaric specific heat capacity, specific enthalpy, and coefficient of thermal expansion are calculated for the systems

$$N_2O_4 \rightleftarrows 2NO_2 \qquad (\Delta H_1)_{25^\circ\,C.} = 13{,}743\ \frac{\text{Calories}}{\text{gram-mole } N_2O_4} \tag{1}$$

$$2NO_2 \leftrightarrows 2NO + O_2 \qquad (\Delta H_2)_{25^\circ\,C.} = 27{,}020\ \frac{\text{Calories}}{\text{gram-mole } O_2} \tag{2}$$

Three conditions are assumed for thermal properties:

That chemical equilibrium prevails in both Equations 1 and 2.

That chemical equilibrium exists in Equation 1 with Equation 2 nonexistent,

That both Equations 1 and 2 are in frozen equilibrium.

The term frozen equilibrium is used to denote the system having at a given temperature and pressure an equilibrium composition which does not shift with a displacement in temperature at constant pressure. Equation 1 is much more likely to be at equilibrium for most processes than Equation 2, since kinetic measurements indicate reaction times for Equation 1 of the order of a microsecond at 25° C. (*6*), whereas Equation 2 is relatively slow (*16*). Properties of the N_2O_4-NO_2 system excluding the effects of Equation 2 have been presented (*3*).

NONTHERMAL PROPERTIES

To be considered first are nonthermal properties which do not involve a temperature derivative.

Equilibrium Composition. In the consecutive Equations 1 and 2 for a system consisting initially of 1 gram-mole of N_2O_4, let N_1, = total moles of N_2O_4 dissociated and N_2 = total moles of O_2 formed for 1 initial mole of N_2O_4. The degree of advancement of Equations 1 and 2 is given by $\xi_1 = N_1$ and $\xi_2 = N_2$, respectively. Thus the moles of NO_2 formed = $2\xi_1 - 2\xi_2$ and the moles of NO formed = $2\gamma_2$. If the restriction of chemical equilibrium is imposed, the degree of advancement of Equations 1 and 2, ξ_1 and ξ_2, may be calculated by using values of the equilibrium constants K_{P_1} and K_{P_2} at 1 atm. (*7*) to solve the following equilibrium expressions

$$\xi_1 = \frac{\xi_2(8 - K_{P_1}) \pm [\xi_2^2(K_{P_1} - 8)^2 - 4(4 + K_{P_1})\ (4\xi_2^2 - \xi_2 K_{P_1} - K_{P_1})]^{1/2}}{2(4 + K_{P_1})} \qquad (e_1, e_2) \tag{3}$$

$$K_{P_2} = \frac{\xi_2^3}{(\xi_1 - \xi_2)^2\,(1 + \xi_1 + \xi_2)} \qquad (e_1/e_2) \tag{4}$$

The equilibrium values of ξ_1 and ξ_2 as a function of temperature at 1 atm. are presented in Table I.

Molecular Weight. The equilibrium molecular weight, M, of the N_2O_4–NO_2–NO-O_2 system is given by

$$M = \frac{M_{N_2O_4}}{1 + \xi_1 + \xi_2} \qquad (e_1, e_2) \tag{5}$$

Values of the molecular weight are presented in Table I.

Density. The density, ρ, was evaluated by assuming ideal gas and ideal mixture behavior in which case

$$\rho = \frac{M_{N_2O_4}}{(1 + \xi_1 + \xi_2)\ \dfrac{RT}{P}} \qquad (e_1, e_2) \tag{6}$$

In Table I, density is presented as a function of temperature at 1 atm.

Diffusion Coefficients. The self and binary diffusion coefficients D_i and D_{ij} were calculated by Equations 8, 2–46 and 8.2–44 of (*10*), respectively.

The Lennard-Jones potential parameters for O_2 and NO were from (*8*); for NO_2 and N_2O_4, from (*3*).

Values of D_i and D_{ij} are presented in Table II as a function of temperature at 1 atm.

Viscosity. The viscosity, μ, was computed by Equation 8.2–30 of (*10*)

$$\mu = \sum_{i=1}^{v} \frac{X_i^2}{\dfrac{X_i^2}{(\mu_i)} + 1.385 \displaystyle\sum_{\substack{k=1\\k\neq i}}^{v} X_i X_k\ \dfrac{RT}{PM_i(D_{ik})_1}} \qquad (e_1, e_2) \tag{7}$$

The viscosities of NO_2 and N_2O_4 had to be calculated with the first approximation formula for $(\mu_i)_1$ (*10*). Experimental values of the viscosities of O_2 and NO were available (*8*) and thus the approximation formula was not used. The viscosity values at 1 atm. are presented in Table I.

THERMAL PROPERTIES

To be considered here are properties which involve in their definition a temperature derivative.

Isobaric Specific Heat Capacity. The total enthalpy, H, of a reacting system can be expressed as a function of the temperature T, pressure P, and the degrees of advancement (*14*) of all the j reactions ξ_j, where $j = 1, 2, \text{---} n$.

Under isobaric conditions

$$dH = \left(\frac{\partial H}{\partial T}\right)_{\xi_j, P} dT + \sum_{j=1}^{n} \left(\frac{\partial H}{\partial \xi_j}\right)_{T, P} d\xi_j \tag{8}$$

In the second term, $(\partial H/\partial \xi_j)_{T,P}$ represents the molal enthalpy of reaction, ΔH_j. Thus, by definition the isobaric heat capacity

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_{\xi_j, P} + \sum_{j=1}^{n} \Delta H_j \left(\frac{\partial \xi_j}{\partial T}\right)_P \quad (9)$$

For a closed system in which successive reactions of the type

$$M_o \leftrightarrows \nu_1 M_1 + \cdots + \nu_s M_s \leftrightarrows \nu_{s-1} M_{s+1} + \cdots + \nu_n M_n \quad (10)$$

occur and by assuming the system has a mass and atomic composition corresponding to M_0, the isobaric specific heat capacity may be written

$$C_P = \frac{C_P}{M_0} = \frac{1}{M_0} \left\{\left(\frac{\partial H}{\partial T}\right)_{\xi_j P} + \sum_{j=1}^{n} \Delta H_j \left(\frac{\partial \xi_i}{\partial T}\right)_P\right\} \quad (11)$$

Assuming an ideal mixture with additive heat capacities

$$C_P = \frac{1}{M_{N_2O_4}}\left\{(1 - \xi_1) C_{P, N_2O_4} + 2(\xi_1 - \xi_2)\, C_{P, NO_2} + 2\xi_2 C_{P, NO} + \xi_2 C_{P, O_2} + \Delta H_1 \left(\frac{\partial \xi_1}{\partial T}\right)_P + \Delta H_2 \left(\frac{\partial \xi_2}{\partial T}\right)_P\right\} \quad (12)$$

Assuming chemical equilibrium and using van't Hoff's relationship (*14*) for the temperature dependence of the equilibrium constant, expressions may be obtained for $(\partial \xi_1/\partial T)_P$ and $(\partial \xi_2/\partial T)_P$ which when substituted into Equation 12 give

$$C_P = \frac{1}{M_{N_2O_4}}\Big\{(1 - \xi_1) C_{P, N_2O_4} + 2(\xi_1 - \xi_2) C_{P, NO_2} + 2\xi_2 C_{P, NO} + \xi_2 C_{P, O_2} + \frac{\Delta H_1 \xi_1 (1 - \xi_1)}{6RT^2} \{\alpha(2 + 3\xi_1 + \xi_2)\Delta H_2 + (3 + 3\xi_1 - \alpha + \xi_2)\Delta H_1\} + \frac{\Delta H_2 \xi_2 (1 - \alpha)}{6RT^2} \{(2 + \xi_2)\Delta H_2 - (1 - \xi_1)\Delta H_1\} + \frac{\Delta H_2 \xi_2 (1 - \xi_1)}{6RT^2} \{\alpha(2 + 3\xi_1 + \xi_2)\Delta H_2 + (3 + 3\xi_1 - \alpha + \xi_2)\Delta H_1\}\Big\} \quad (e_1, e_2) \quad (13)$$

The sum of the first group of terms in Equation 13 not containing ΔH is called the frozen equilibrium heat capacity, $C_{P,\xi}$ and the sum of the second group of terms containing ΔH_1 and ΔH_2 is called the equilibrium reaction heat capacity, $C_{P,r}$. The net heat capacity is called the equilibrium heat capacity, $C_P = C_{P,\xi} + C_{P,r}$.

At frozen equilibrium by definition $(\partial \xi_1/\partial T)_P = 0$ and $(\partial \xi_2/\partial T)_P = 0$ so that $C_{P,r} = 0$.

In computing values of C_P from Equation 13, isobaric specific heat capacities of each individual molecular species were taken from the literature: C_{P, N_2O_4} from Giauque and Kemp (*7*), C_{P, NO_2} form Altshuller (*1*), and both $C_{P, NO}$ and C_{P, O_2} from Masi (*13*). Values of ΔH_1 were obtained from Brokaw (*3*) and values of ΔH_2 were from Altshuller (*1*).

Since rates of the forward and reverse steps of Equation 2 are relatively low below 500° K. (*16*), it can be assumed in many processes that only Equation 1 contributes to properties below 500° K. The specific heat expression then simplifies to

$$C_P = (1 - \xi_1) C_{P, N_2O_4} + 2\xi_1 C_{P, NO_2} + \frac{\Delta H_1^2}{RT^2 M_{N_2O_4}} \frac{\xi_1 (1 - \xi_1^2)}{2} \quad (e_1) \quad (14)$$

Table I. Summary of Properties of N_2O_4-NO_2-NO-O_2 System at 1 Atm.

Temp., ° K.	ξ_1[a]	ξ_2[a]	M[b]	ρ[c]	μ[d]	$C_{P,\xi}$[e]	$C_P(e_1)$[e]	$C_P(e_1, e_2)$[e]	$H(e_1)$[f]	$H(e_1, e_2)$[f]	k_ξ[g]	$k(e_1)$[g,h]	$k(e_1, e_2)$[g]	β_ξ, ° K.$^{-1}$	$\beta(e_1)$, ° K.$^{-1}$	$\beta(e_1, e_2)$, ° K.$^{-1}$
300	0.2007	0.0000324	76.63	3.113	0.0001176	0.2033	1.307	1.309	29.92	29.92	3.34	25.67	25.82	0.003333	0.009492	0.009500
350	0.7256	0.000754	53.45	1.864	0.0001594	0.2066	1.644	1.656	118.2	118.7	4.66	29.09	28.43	0.002857	0.008461	0.008483
400	0.9642	0.004882	46.73	1.424	0.0001909	0.2109	0.4269	0.4704	163.9	165.6	5.70	9.478	10.62	0.002500	0.003244	0.003317
450	0.9947	0.01790	45.72	1.238	0.0002135	0.2187	0.2457	0.3660	179.3	185.7	6.615	7.147	11.70	0.002222	0.002315	0.002514
500	0.9989	0.04910	44.93	1.095	0.0002348	0.2267	0.2340	0.4949	191.3	206.8	7.563	...	19.35	0.002000	0.002027	0.002447
550	0.9997	0.1100	43.61	0.9663	0.0002562	0.2342	0.2348	0.7071	203.0	236.6	8.60	...	28.63	0.001818	0.001824	0.002569
600	0.9999	0.2083	41.68	0.8465	0.0002789	0.2412	0.2406	0.9425	214.8	277.7	9.692	...	40.56	0.001667	0.001669	0.002728
700	...	0.488	36.99	0.6439	0.0003272	0.2515	...	1.132	...	386.3	12.02	...	50.56	0.001429	...	0.002610
800	...	0.7388	33.60	0.5118	0.0003742	0.2584	...	0.8309	...	486.5	14.00	...	39.03	0.001250	...	0.001948
900	...	0.8752	32.01	0.4333	0.0004143	0.2634	...	0.5319	...	553.3	15.90	...	28.03	0.001111	...	0.001423
1000	...	0.938	31.32	0.3817	0.0004491	0.2674	...	0.3857	...	598.2	17.46	...	23.04	0.001000	...	0.001134
1100	...	0.965	31.03	0.3437	0.0004829	0.2709	...	0.3270	...	633.5	18.89	...	21.71	0.0009091	...	0.0009734

[a] Gram-mole.
[b] Gram/gram-mole.
[c] Gram/liter.
[d] Gram/cm. second.
[e] Calories/gram ° K.
[f] Calories/gram.
[g] Calories/cm. second ° K. × 10^5.
[h] Taken from (*3*).

Table II. Diffusion Coefficients for the N_2O_4-NO_2-NO-O_2System at 1 Atm.

Temp., ° K.	Self-diffusion Coefficients, Cm.²/Sec.				Binary Diffusion Coefficients, Cm.²/Sec.					
	D_0	D_1	D_2	D_3	D_{01}	D_{02}	D_{03}	D_{12}	D_{13}	D_{23}
300	0.03884	0.10407	0.20766	0.20738	0.06532	0.0974	0.09797	0.14974	0.15046	0.20777
325	0.04567	0.12144	0.23962	0.23901	0.07643	0.1135	0.1142	0.1739	0.1744	0.2395
350	0.05301	0.14007	0.27345	0.27227	0.08843	0.1308	0.1312	0.1993	0.1996	0.2730
375	0.06089	0.15956	0.30892	0.30708	0.10124	0.1489	0.1491	0.2262	0.2263	0.3081
400	0.06918	0.18032	0.3459	0.3434	0.1147	0.1678	0.1680	0.2543	0.2541	0.3449
450	0.08726	0.22449	0.4250	0.4204	0.1437	0.2086	0.2085	0.3143	0.3134	0.4231
500	0.10717	0.27244	0.50992	0.5035	0.1757	0.2529	0.2523	0.3788	0.3773	0.5068
550	0.12891	0.32423	0.6005	0.5920	0.2099	0.3007	0.2993	0.4481	0.4459	0.5967
600	0.15223	0.3793	0.6969	0.6859	0.2467	0.3507	0.3487	0.5218	0.5183	0.6916
700	...	0.4989	0.9048	0.8895	0.3271	0.4629	0.4576	0.6814	0.6758	0.8977
800	...	0.6310	1.1338	1.1111	0.4161	0.5847	0.5769	0.8567	0.8488	1.1228
900	...	0.7744	1.3803	1.3547	0.5126	0.7167	0.7060	1.0467	1.0363	1.3672
1000	...	0.9288	1.6468	1.6152	0.6173	0.8588	0.8457	1.2514	1.2381	1.6317
1100	...	1.0937	1.9325	1.8952	0.7291	1.0107	0.9938	1.4694	1.4527	1.9127

Table III. Detailed Values of Equilibrium Thermal Properties of the N_3O_4-NO_2-NO-O_2 System at 1 Atm.

Temp., ° K.	$C_P(e_1, e_2)$[a]	$\beta(e_1, e_2)$, ° K.$^{-1}$	$k(e_1, e_2)$[b]
300	1.309	0.009500	25.82
310	1.605	0.01053	31.12
315	1.739	0.01089	...
320	1.860	0.01112	34.92
324	1.916	...	...
325	1.941	0.01114	35.79
326	1.952	...	...
330	1.983	0.01096	35.83
332	1.988	...	...
334	1.979	...	...
336	1.964	0.01048	...
338	1.942	...	...
340	1.911	0.009997	33.38
345	1.797	...	...
350	1.656	0.008483	28.43
355	1.495	...	...
360	1.323	0.006897	22.87
365	1.148	...	...
370	1.000	0.005516	...
375	0.8629	...	15.85
380	0.7494	0.004487	...
390	0.5792	0.003787	11.92
400	0.4704	0.003317	10.62
410	0.4071	0.003011	10.06
420	0.3727	0.002805	10.02
430	0.3580	...	10.16
440	0.3549	...	10.80
450	0.3660	0.002514	11.70
470	0.4038	...	13.91
500	0.4949	0.002447	18.53
530	0.6147	...	24.44
550	0.7071	0.002569	28.63
580	0.8464	...	35.89
600	0.9425	0.002728	40.56
620	1.023	...	44.57
640	1.086	...	47.73
650	1.110	0.002768	48.91
660	1.128	...	49.85
670	1.138	...	50.46
680	1.143	...	50.78
690	1.141	...	50.79
700	1.132	0.002610	50.56
710	1.118	...	50.03
720	1.098	...	49.30
730	1.074	...	48.40
750	1.014	0.002297	46.10
770	0.9433	...	43.37
800	0.8309	0.001948	39.03
820	0.7605	...	36.37
850	0.6602	0.001649	32.61
870	0.6054	...	30.67
900	0.5319	0.001423	28.03
920	0.4938	...	26.70
950	0.4419	0.001256	24.88
1000	0.3857	0.001134	23.04
1050	0.3498	0.001044	22.13
1100	0.3270	0.0009734	21.71

[a] Calories/gram ° K.

[b] Calories/cm. second ° K. × 10^5.

However, values of C_P based on both Equation 13 and 14, one including Equation 2 at temperatures below 500° K. and the other not, as well as values of $C_{P,\xi}$ are presented in Table I.

Specific Enthalpy. Although the equilibrium specific enthalpy of the system is a property not defined by a temperature derivative, it is presented in this section, since it can be obtained by graphically integrating the C_P *vs.* T curve. The enthalpy of the species N_2O_4 was considered zero at 25° C.

Values of the equilibrium specific enthalpy H are given in Table I. It is noteworthy that H is a monotonic function of temperature, whereas the thermal property C_P reaches a maximum value with temperature.

Thermal Conductivity. For a reacting mixture, the equilibrium thermal conductivity, k, consists of three parts (*3*). First the contribution from collisional kinetic energy transport, k_c; second, the contribution from the diffusional transport of internal energy, k_i; third, the contribution from chemical dissociation, k_r. The effect of thermal diffusion was neglected and it was assumed that the remaining contributions are linearly additive (*9*).

$$k = k_c + k_i + k_r = k_\xi + k_r \qquad (15)$$

The expression used for k_c was the one proposed in (*5*); k_i was calculated using Equation 77 of (*9*), and k_r was calculated using the rather elaborate Equation 12 of (*4*).

The thermal equilibrium conductivity of the system $N_2O_4 \rightleftarrows 2NO_2$ has been computed up to 490° K. (*3*) neglecting the dissociation of NO_2 of Equation 2. Included in the present set of computations is the effect of the second reaction.

In Table I are presented values of k and k_ξ as a function of temperature at 1 atm. Equilibrium in both Equations 1 and 2 and in Equation 1 alone was considered as was the case with the isobaric heat capacity.

Coefficient of Thermal Expansion. The coefficient of thermal expansion $\beta = 1/V(\partial V/\partial T)_P$, assuming perfect gas behavior, is given for this system by

$$\beta = \frac{1}{T} + \frac{\left(\frac{\partial \xi_1}{\partial T}\right)_P + \left(\frac{\partial \xi_2}{\partial T}\right)_P}{1 + \xi_1 + \xi_2} \qquad (e_1, e_2) \qquad (16)$$

If Equations 1 and 2 are at frozen equilibrium $\beta_\xi = 1/T$. If Equation 2 is absent,

$$\beta = \frac{1}{T} + \frac{\left(\frac{\partial \xi_1}{\partial T}\right)_P}{1 + \xi_1} \qquad (e_1) \qquad (17)$$

Equilibrium values of β computed by both Equations 16 and 17 at 1 atm. are presented in Table I. Included for comparison are values of β_ξ for frozen equilibrium in Equations 1 and 2.

CONCLUSIONS

Thermal properties were calculated on the assumption of either chemical equilibrium or frozen equilibrium and are thus limited to these two extreme cases. The equilibrium thermal properties are seen from Table I to be nonmonotonic functions of temperature and in Figure 1 is shown graphically the behavior of the isobaric heat capacity under a variety of assumed conditions.

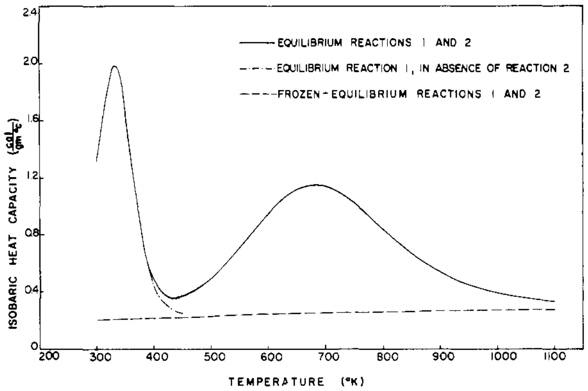

Figure 1. Isobaric heat capacity as a function of temperature at 1 atm.

For the dissociation of NO_2, the rate of the reaction is low—for example, at 500° K. the reaction goes only to half completion in approximately 200 seconds (*16*). Thus thermal properties C_P and k for this system are controlled by kinetics and could lie between the extremes given.

The nonthermal properties, density, viscosity, and diffusion coefficient have the same values whether calculated on an equilibrium or frozen equilibrium basis. However, they will be affected by the fact that if kinetics retard the reaction, the composition of the system will be influenced. The present calculation was done on the assumption of extremes of frozen or true chemical equilibrium.

It is of particular interest to calculate the effect of reactions kinetics on the properties of reacting systems and the work of previous investigators (*9*, *18*) in this field is being extended.

NOMENCLATURE

C_P = isobaric specific heat, calories/gram ° C.
D_i = self-diffusion coefficient of i th species, cm.^{2}/sec.
D_{ij} = binary diffusion coefficient, cm.^{2}/sec.
H = specific enthalpy of equilibrium mixture, calories/gram
ΔH = enthalpy or reaction (Equations 1 and 2), calories/gram-mole
k = thermal conductivity, calories/cm.-sec. ° C.
K_P = equilibrium constant ---
M = molecular weight, gram/gram-mole
n = upper limits in a series ---
N = number of moles, gram-mole
P = pressure, atmosphere
R = universal gas constant, calories/gram-mole ° C.
T = absolute temperature, ° K.
V = specific volume, liter/gram
α = the ratio, (ξ_2/ξ_1) ---
β = coefficient of thermal expansion, ° K.$^{-1}$
μ = viscosity, gram/cm. sec.
ξ_j = degree of advancement of reaction j, gram-mole
ρ = density, gram/liter

Extensive properties are underlined.
Restraints are shown in parentheses to the right of an equation.

Subscripts

i = i th species
j = j th species
o = reactant species
p = isobaric path
r = contribution due to the chemical reaction at equilibrium
ξ = thermal property at frozen equilibrium or at constant degree of advancement of reaction

Subnumerals

0 = reactant (N_2O_4)
1 = Equation 1 or species NO_2
2 = Equation 2 or species NO
3 = Equation 3 or species O_2

The restraint of equilibrium with respect to Equation 1 is designated by (e_1); with respect to Equation 2, by (e_2); with respect to both Equations 1 and 2 by (e_1, e_2).

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