Enthalpy and Heat Capacity of N_2O_4-NO_2 at Pressures Above One Atmosphere

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INTEREST in the thermodynamic properties of the nitrogen tetroxide-nitrogen dioxide system has increased during the past few years. This system is especially useful in the study of the effects of chemical reaction on heat transfer. The rate of the reaction is sufficiently rapid that chemical equilibrium can be assumed to be reached at the specified temperature and pressure. At 1 atm. and 70° F., the fraction N_2O_4 dissociated is 0.163, while at the same pressure and 250° F., α is 0.954. Thus, a wide range of dissociation can be obtained at conditions easily established in the laboratory. Nitrogen tetroxide is of interest also as an oxidizer for rocket propulsion and a nitrating and oxidizing agent for chemical reactions.

Most of the data published in the literature for the nitrogen tetroxide–nitrogen dioxide system are for a pressure of 1 atm. or lower. The thermodynamic properties such as enthalpy are sensitive to both temperature and pressure because the composition of the system is a function of both variables. It seemed worthwhile, therefore, to present values of the heat capacity and enthalpy of the equilibrium mixture over a range of pressure and temperature. Specifically, the fraction N_2O_4 dissociated, α, the heat capacity, C_{p_e}, and the enthalpy, H, were evaluated from existing data for pressures from 12 to 30 p.s.i.a. and temperatures from 70° to 250° F. The vapor pressure of the system at 70° F. is 14.8 p.s.i.a. Hence for temperatures above 70° F. the calculations extend only to the appropriate vapor pressure.

FRACTION OF N_2O_4 DISSOCIATED

The fraction of N_2O_4 dissociated at equilibrium has been studied experimentally by Bodenstein and Boës (*1*), Wourtzel (*8*) and Verhoek and Daniels (*7*). The first work is the culmination of several investigations of the N_2O_4-NO_2 system by Bodenstein and represents an experienced study. Volumetric data were measured over a range of temperatures and pressures from 0.29 to 0.76 atm. The fraction dissociated α was evaluated from the data by utilizing a Berthelot-type equation of state, $PV = RT(1 + \lambda P)$ to take account of deviations from the ideal gas law. The data of Wourtzel were obtained at 0.1 to 0.2 atm. where these deviations could be safely neglected, while the Verhoek and Daniels work covered a narrow temperature range of 25°–45° C., but at pressures up to 0.8 atm.

Giaque and Kemp (*4*) analyzed the three sets of data and found excellent agreement between them. These authors were particularly interested in the heat of dissociation, and this was evaluated using the equilibrium constant obtained from the α results. Using the Berthelot equation to evaluate the fugacities, this relationship between K and α can be shown, by standard thermodynamic methods, to be

$$K = \frac{4P\lambda_2}{1 - \lambda^2}\, e^{(2\lambda_{NO_2} - \lambda_{N_2O_4})P} \tag{1}$$

It was found by Bodenstein and Boës and later checked by Giaque and Kemp, that the experimental *P-V-T* data were well represented by choosing the relationship

$$2\lambda_{NO_2} = \lambda_{N_2O_4} = \lambda = -0.01\,(294/T)^3 \tag{2}$$
$$\lambda = \text{atm.}^{-1}$$

This simplifies Equation 1 to the same form as that obtained by assuming ideal gases:

$$K = \frac{4P\alpha^2}{1 - \alpha^2} \tag{3}$$

(This does not mean that α can be calculated by neglecting deviations from the ideal gas law; it means that the form of Equation 3 is the same. The deviation from ideality is involved in obtaining α from experimental data as shown by Equation 4.) Giague and Kemp tabulated values of K evaluated from the extensive *P-V-T* data of Bodenstein and Boës. The calculation of α is carried out from the following equation

$$(PV)_{\text{Exp}} = (1 + \alpha + \lambda P)RT \tag{4}$$

$(PV)_{\text{Exp}}$ refers to the equilibrium volume corresponding to 1 mole of undissociated N_2O_4. Equation 4 is based upon the Berthelot equation of state and Equation 2.

Equation 3 is believed to provide the most accurate means available for calculating the fraction dissociated. The deviation from ideality, which is particularly important for the present work, is taken into account through the Berthelot equation. This equation of state has been found, from experimental studies with several gases, to be of high accuracy at low pressures (up to several atmospheres). Accordingly, the table of K *vs.* temperature presented in the Giaque and Kemp paper along with Equation 3 was employed to calculate α values for pressure increments of 2 p.s.i.a. from 12 to 30 p.s.i.a. The results showing α as a function of temperature and pressure are given in Figure 1.

HEAT CAPACITY AND ENTHALPY

The heat capacity of the equilibrium mixture consists of: a frozen contribution, corresponding to an inert mixture of NO_2 and N_2O_4, and a reaction contribution to take into account the heat of dissociation. Thus C_{p_e} is given by

$$C_{p_e} = C_{p_f} + C_{p_r} \tag{5}$$

The reaction contribution C_{p_r} is approximately 5 to 10 times the inert contribution. Brokaw (*2*) has calculated C_{p_f} from the molecular parameters (vibration frequencies, bond distances, and angles). These results apply exactly only to ideal gas conditions. However, up to pressures of several atmospheres the effect of pressure on C_p is very small. Hence the frozen heat capacities given by Brokaw were used in this investigation in the calculations up to 30 p.s.i.a. The justification for neglecting the effect of pressure on C_{p_f} is enhanced in this case because the frozen contribution is a small part of the desired equilibrium heat capacity. The reacting contribution, sensitive to both temperature and pressure, was determined from the equation

$$C_{p_r} = \frac{(\Delta H_T^0)^2}{2RT^2} \quad \frac{\alpha(1 - \alpha)}{M} \tag{6}$$

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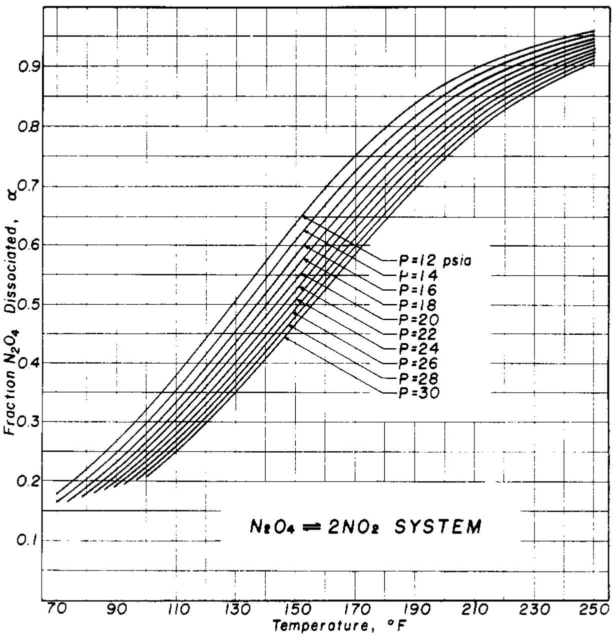

Figure 1. Degree of dissociation of N_2O_4

where ΔH_T^0 is the standard-state heat of reaction at $T°\ K$. Equation 6 can be derived from heat transfer, or thermodynamic considerations as described in the literature (5).

The heat of reaction was evaluated from the expression

$$\Delta H_T^0 = 12{,}875 + 3.345\ T \qquad (7)$$

This linear equation was so chosen to agree with the following results presented by the Bureau of Standards (6).

$$\Delta H_0^0 = 12{,}875 \text{ cal./(gram mole)}$$

$$\Delta H_{298}^0 = 13{,}873 \text{ cal./(gram mole)}$$

These results are essentially the same as those recommended by Giaque and Kemp (4).

The heat capacities computed from Equations 5-7 are illustrated in Figure 2.

At each pressure large-scale plots of C_{p_e} *vs.* T were integrated graphically to obtain the enthalpy of the equilibrium mixture. The results, (Figure 3) are based upon $H = 0$ at 70° F., 14.7 p.s.i.a. and $\alpha = 0.163$. Complete tables (3) of α, C_{p_e}, and H are available.

Figure 1 shows that the change in α with temperature is greatest at temperatures from 130-160° F. Hence the contribution of the heat of reaction to the equilibrium heat capacity is largest in this temperature range. It is for this reason that the curves in Figure 2 show a maximum in C_{p_e} at each pressure.

ACKNOWLEDGMENT

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NOMENCLATURE

α = fraction N_2O_4 dissociated
λ = parameter in Berthelot equation of state $[PV = RT(1 + \lambda P)]$; λ_{NO_2} = value of λ for NO_2, atm.$^{-1}$
C_{p_e} = equilibrium heat capacity, cal./g.)(° K.) or B.t.u./-(lb.)(° F.)
C_{p_f} = frozen heat capacity
C_{p_r} = reacting heat capacity contribution
H = enthalpy, B.t.u./(lb. of equilibrium mixture)
ΔH_T^0 = standard heat of reaction at temperature T, cal./(g. mole)
K = equilibrium constant
M = molecular weight of the equilibrium mixture, g./mole

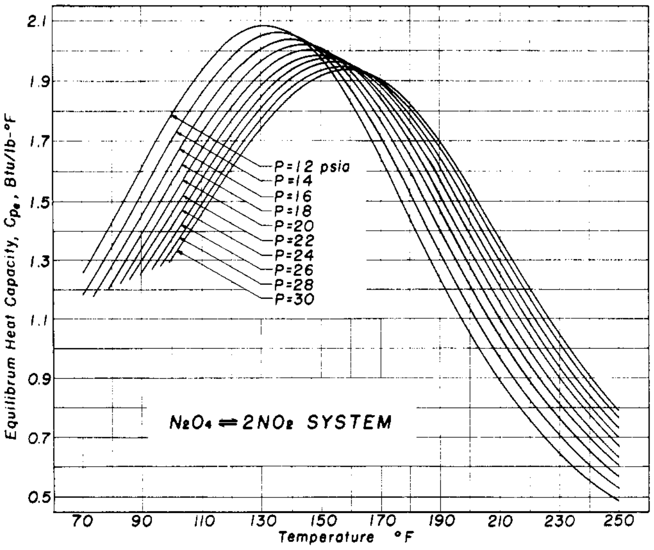

Figure 2. Equilibrium heat Capacity of N_2O_4

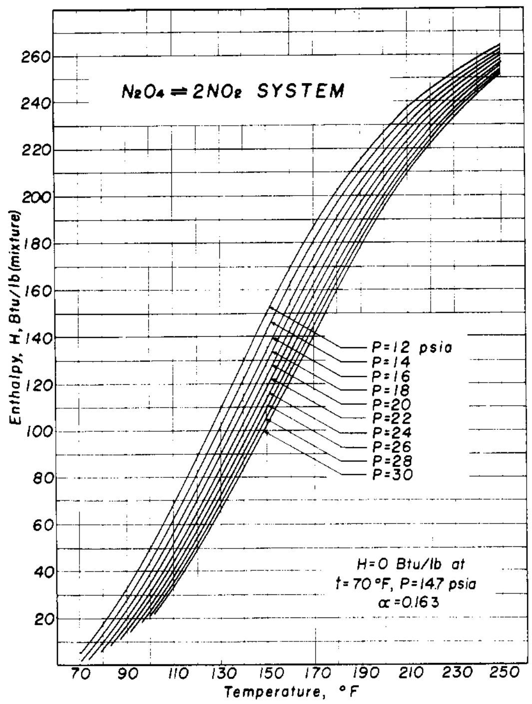

Figure 3. Enthalpy of N_2O_4

P = pressure, atm.
R = gas constant, cal./(g. mole)(° K.) or (cc.) (atm.)/(g. mole) (° K.)
T = Temperature, ° K.
V = volume, cc./g. mole

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