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Nitric Oxide Equilibrium

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I. SYNOPSIS

In earlier work, the equilibrium of ammonia was treated extensively [1]. As is common, the notational difficulties, which preclude writing a protoypical chemical reaction's $\Delta G(\zeta)$ expression in transparent enough terms for comprehension, tends to obscure the content when dealing with three substances and a change in the number of moles of -2 ($\Delta\nu = -2$ in this case). For this reason, treating a simpler case is warranted.

The explicit derivation of the form of the chemical equilibrium equation is found for the reaction of NO_2 reacting to form N_2O_4.

II. INTRODUCTION

For the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

the molar Gibbs free energy of the two components are

$$\mu_{NO_2} = \mu^o_{NO_2} + RT\ell n P_{NO_2} \tag{2.1}$$

$$\mu_{N_2O_4} = \mu^o_{N_2O_4} + RT\ell n P_{N_2O_4} \tag{2.2}$$

so $G_{mixture}$, the Gibbs Free Energy of a mixture of n_{NO_2} moles of NO_2 and $n_{N_2O_4}$ moles of N_2O_4 would be

$$G_{mixture} = n_{NO_2}\mu_{NO_2} + n_{N_2O_4}\mu_{N_2O_4} \tag{2.3}$$

III. DEFINING THE EXTENT OF REACTION

We define the extent of reaction, ζ, as

$$\zeta = \frac{n_{NO_2} - n^o_{NO_2}}{2} \tag{3.1}$$

and

$$-\zeta = \frac{n_{N_2O_4} - n^o_{N_2O_4}}{1} \tag{3.2}$$

where the denominators are the stoichiometric [2] coëfficients taken from the balanced chemical equation. These equations can be inverted to solve for the number of moles of each component as a function of the starting number of moles of that component and the extent of reaction. One has from Equation 3.1

$$n_{NO_2} = 2\zeta + n^o_{NO_2} \tag{3.3}$$

and, from Equation 3.2, one has

$$n_{N_2O_4} = -\zeta + n^o_{N_2O_4} \tag{3.4}$$

so, the mixture's Gibbs Free Energy must be (substituting Equations 3.3 and 3.4 not Equation 2.3)

$$G_{mixture} = \left(2\zeta + n^o_{NO_2}\right)\mu_{NO_2} + \left(-\zeta + n^o_{N_2O_4}\right)\mu_{N_2O_4} \tag{3.5}$$

which is

$$G_{mixture} = \left(2\zeta + n^o_{NO_2}\right)\left(\mu^o_{NO_2} + RT\ell n P_{NO_2}\right) + \left(-\zeta + n^o_{N_2O_4}\right)\left(\mu^o_{N_2O_4} + RT\ell n P_{N_2O_4}\right) \tag{3.6}$$

We wish to take the derivative of $G_{mixture}$ with respect to ζ, with the intent of setting the result equal to zero, searching for an extremum in $G_{mixture}$ (which we suspect is a minimum). Wishing to do this at constant pressure, we need to write each partial pressure in terms of the total pressure and the mole fraction, using Dalton's Law. We have:

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$$G_{mixture} = \left(2\zeta + n^o_{NO_2}\right)\left(\mu^o_{NO_2} + RT\ell n[x_{NO_2}P_{total}]\right) + \left(-\zeta + n^o_{N_2O_4}\right)\left(\mu^o_{N_2O_4} + RT\ell n[x_{N_2O_4}P_{total}]\right) \tag{3.7}$$

where we recognize that each mole fraction is itself a function of the extent of reaction, ζ. From here, the calculus becomes a bit messy, but the result is worth it. What we know is that

$$x_{NO_2} = \frac{n_{NO_2}}{n_{NO_2} + n_{N_2O_4}}$$

and

$$x_{N_2O_4} = \frac{n_{N_2O_4}}{n_{NO_2} + n_{N_2O_4}}$$

which is a little harder than the equimolar cases where Δn is zero. We will do this work in parts, so that the differentiation can be explicitly followed, line by line. First, we attempt taking the derivative of $G_{mixture}$ with respect to ζ, i.e.,

$$\frac{dG_{mixture}}{d\zeta} = \frac{d}{d\zeta}\left(2\zeta\mu^o_{NO_2} + 2\zeta RT\ell n(x_{NO_2}P_{total}) + n^o_{NO_2}\mu^o_{NO_2} + n^o_{NO_2}RT\ell n(x_{NO_2}P_{total}) - \zeta\mu^o_{N_2O_4} - \zeta RT\ell n(x_{N_2O_4}P_{total}) + n^o_{N_2O_4}\mu^o_{N_2O_4} + n^o_{N_2O_4}RT\ell n(x_{N_2O_4}P_{total})\right) \tag{3.8}$$

$$\frac{dG_{mixture}}{d\zeta} = 2\mu^o_{NO_2} + 2RT\ell n(x_{NO_2}P_{total}) + 2\zeta RT\frac{d\ell n(x_{NO_2}P_{total})}{d\zeta} + n^o_{NO_2}RT\frac{d\ell n(x_{NO_2}P_{total})}{d\zeta} - \mu^o_{N_2O_4} - RT\ell n(x_{N_2O_4}P_{total}) - \zeta RT\frac{d\ell n(x_{N_2O_4}P_{total})}{d\zeta} + n^o_{N_2O_4}RT\frac{d\ell n(x_{N_2O_4}P_{total})}{d\zeta} \tag{3.9}$$

where we need to just evaluate the remaining partial derivatives.

$$\frac{dx_{NO_2}}{d\zeta} = \frac{d\left(\frac{2\zeta + n^o_{NO_2}}{2\zeta + n^o_{NO_2} - \zeta + n^o_{N_2O_4}}\right)}{d\zeta} = \frac{d\left(\frac{2\zeta + n^o_{NO_2}}{\zeta + n^o_{NO_2} + n^o_{N_2O_4}}\right)}{d\zeta} \tag{3.10}$$

and

$$\frac{dx_{N_2O_4}}{d\zeta} = \frac{d\left(\frac{-\zeta + n^o_{N_2O_4}}{2\zeta + n^o_{NO_2} - \zeta + n^o_{N_2O_4}}\right)}{d\zeta} = \frac{d\left(\frac{-\zeta + n^o_{N_2O_4}}{\zeta + n^o_{NO_2} + n^o_{N_2O_4}}\right)}{d\zeta} \tag{3.11}$$

so, doing the dirty deed, we have

$$\frac{dx_{NO_2}}{d\zeta} = \frac{2}{\zeta + n^o_{NO_2} + n^o_{N_2O_4}} + \frac{(-1)(2\zeta + n^o_{NO_2})}{\left(\zeta + n^o_{NO_2} + n^o_{N_2O_4}\right)^2} \tag{3.12}$$

$$\frac{dx_{N_2O_4}}{d\zeta} = \frac{(-1)}{\zeta + n^o_{NO_2} + n^o_{N_2O_4}} + \frac{(-1)(-\zeta + n^o_{N_2O_4})}{\left(\zeta + n^o_{NO_2} + n^o_{N_2O_4}\right)^2} \tag{3.13}$$

Bringing these two equations separately over a common denominator, one has

$$\frac{dx_{NO_2}}{d\zeta} = \frac{(2)(\zeta + n^o_{NO_2} + n^o_{N_2O_4}) - (2\zeta + n^o_{NO_2})}{\left(\zeta + n^o_{NO_2} + n^o_{N_2O_4}\right)^2} \tag{3.14}$$

$$\frac{dx_{N_2O_4}}{d\zeta} = \frac{(-1)(\zeta + n^o_{NO_2} + n^o_{N_2O_4}) - (-\zeta + n^o_{N_2O_4})}{\left(\zeta + n^o_{NO_2} + n^o_{N_2O_4}\right)^2} \tag{3.15}$$

which become, again sequentially,

$$\frac{dx_{NO_2}}{d\zeta} = \frac{(n_{NO_2} + 2n^o_{N_2O_4})}{\left(\zeta + n^o_{NO_2} + n^o_{N_2O_4}\right)^2} \tag{3.16}$$

$$\frac{dx_{N_2O_4}}{d\zeta} = -\frac{n^o_{NO_2} + 2n^o_{N_2O_4}}{\left(\zeta + n^o_{NO_2} + n^o_{N_2O_4}\right)^2} \tag{3.17}$$

Taking the derivatives of logarithms in Equation 3.9 appropriately, we obtain

$$\frac{dG_{mixture}}{d\zeta} = 2\mu^o_{NO_2} + 2RT\ell n[x_{NO_2}P_{total}] + (2\zeta RT + 2n^o_{NO_2}RT)\frac{dx_{NO_2}}{d\zeta}\frac{1}{x_{NO_2}}$$

$$-\mu^o_{N_2O_4} + RT\ell n[x_{N_2O_4}P_{total}] + (-\zeta RT + 2n^o_{N_2O_4}RT)\frac{dx_{N_2O_4}}{d\zeta}\frac{1}{x_{N_2O_4}} \tag{3.18}$$

which is, upon substitution of Equations 3.16 and 3.17 yields,

$$\frac{dG_{mixture}}{d\zeta} = 2\mu^o_{NO_2} + 2RT\ell n[x_{NO_2}P_{total}] + (2\zeta RT + 2n^o_{NO_2}RT)\frac{(n^o_{NO_2} + 2n^o_{N_2O_4})}{\left(\zeta + n^o_{NO_2} + n^o_{N_2O_4}\right)^2}\frac{1}{x_{NO_2}}$$
$$-\mu^o_{N_2O_4} - RT\ell n[x_{N_2O_4}P_{total}] - (-\zeta RT + n^o_{N_2O_4}RT)\frac{n^o_{NO_2} + 2n^o_{N_2O_4}}{\left(\zeta + n^o_{NO_2} + n^o_{N_2O_4}\right)^2}\frac{1}{x_{N_2O_4}} \tag{3.19}$$

which is

$$\frac{dG_{mixture}}{d\zeta} = 2\mu^o_{NO_2} + 2RT\ell n(x_{NO_2}P_{total})$$
$$+(2\zeta RT + n^o_{NO_2}RT)\frac{(n^o_{NO_2} + 2n^o_{N_2O_4})}{\left(\zeta + n^o_{NO_2} + n^o_{N_2O_4}\right)^2}\frac{\zeta + n^o_{NO_2} + n^o_{N_2O_4}}{(2\zeta + n^o_{NO_2})}$$
$$-\mu^o_{N_2O_4} - RT\ell n(x_{N_2O_4}P_{total})$$
$$-(-\zeta RT + n^o_{N_2O_4}RT)\frac{n^o_{NO_2} + 2n^o_{N_2O_4}}{\left(\zeta + n^o_{NO_2} + n^o_{N_2O_4}\right)^2}\frac{\zeta + n^o_{NO_2} + n^o_{N_2O_4}}{(-\zeta + n^o_{N_2O_4})} \tag{3.20}$$

$$\frac{dG_{mixture}}{d\zeta} = 2\mu^o_{NO_2} + 2RT\ell n(P_{NO_2})$$
$$+RT\frac{(n^o_{NO_2} + 2n^o_{N_2O_4})}{(\zeta + n^o_{NO_2} + n^o_{N_2O_4})}$$
$$-\mu^o_{N_2O_4} - RT\ell n(P_{N_2O_4})$$
$$-RT\frac{n^o_{NO_2} + 2n^o_{N_2O_4}}{(\zeta + n^o_{NO_2} + n^o_{N_2O_4})} = 0 \tag{3.21}$$

$$\frac{dG_{mixture}}{d\zeta} = 0 = 2\mu^o_{NO_2} - \mu^o_{N_2O_4} + RT\ell n(P^2_{NO_2}) - RT\ell n(P_{N_2O_4}) \tag{3.22}$$

$$\frac{dG_{mixture}}{d\zeta} = 0 = \Delta G^o_{reaction} + RT\ell n K_p \tag{3.23}$$

Q.E.D.

[1] J. Chem. Ed., 65, 407 (1988); J. Chem. Ed., 66, A237 (1989)

[2] Greek "stoicheio" $\longmapsto$ component, and -metry $\equiv$ measure