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 prototypical 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

$$\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$$

the molar Gibbs free energy of the two components are

$$\mu_{\text{NO}_2} = \mu_{\text{NO}_2}^o + RT \ln P_{\text{NO}_2} \quad (2.1)$$

$$\mu_{\text{N}_2\text{O}_4} = \mu_{\text{N}_2\text{O}_4}^o + RT \ln P_{\text{N}_2\text{O}_4} \quad (2.2)$$

so $G_{\text{mixture}}$, the Gibbs Free Energy of a mixture of $n_{\text{NO}_2}$ moles of NO$_2$ and $n_{\text{N}_2\text{O}_4}$ moles of N$_2$O$_4$ would be

$$G_{\text{mixture}} = n_{\text{NO}_2} \mu_{\text{NO}_2} + n_{\text{N}_2\text{O}_4} \mu_{\text{N}_2\text{O}_4} \quad (2.3)$$

We wish to take the derivative of $G_{\text{mixture}}$ with respect to $\zeta$, with the intent of setting the result equal to zero, searching for an extremum in $G_{\text{mixture}}$ (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:

III. DEFINING THE EXTENT OF REACTION

We define the extent of reaction, $\zeta$, as

$$\zeta = \frac{n_{\text{NO}_2} - n_{\text{NO}_2}^o}{2} \quad (3.1)$$

and

$$-\zeta = \frac{n_{\text{N}_2\text{O}_4} - n_{\text{N}_2\text{O}_4}^o}{1} \quad (3.2)$$

where the denominators are the stoichiometric [2] coefficients 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]

$$n_{\text{NO}_2} = 2\zeta + n_{\text{NO}_2}^o \quad (3.3)$$

and, from Equation [3.2] one has

$$n_{\text{N}_2\text{O}_4} = -\zeta + n_{\text{N}_2\text{O}_4}^o \quad (3.4)$$

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

$$G_{\text{mixture}} = (2\zeta + n_{\text{NO}_2}^o) \mu_{\text{NO}_2} + (-\zeta + n_{\text{N}_2\text{O}_4}^o) \mu_{\text{N}_2\text{O}_4} \quad (3.5)$$

which is

$$G_{\text{mixture}} = (2\zeta + n_{\text{NO}_2}^o) (\mu_{\text{NO}_2}^o + RT \ln P_{\text{NO}_2}) + (-\zeta + n_{\text{N}_2\text{O}_4}^o) (\mu_{\text{N}_2\text{O}_4}^o + RT \ln P_{\text{N}_2\text{O}_4}) \quad (3.6)$$

Typeset by REVTeX
\[ G_{\text{mixture}} = (2\zeta + n_{N_2O_2}^o) \left( \mu_{N_2O_2}^o + RT \ln(x_{NO_2} P_{\text{total}}) \right) + (-\zeta + n_{N_2O_4}^o) \left( \mu_{N_2O_4}^o + RT \ln(x_{N_2O_4} P_{\text{total}}) \right) \] (3.7)

where we recognize that each mole fraction is itself a function of the extent of reaction, \( \zeta \). 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

\[
x_{N_2O_4} = \frac{n_{N_2O_4}}{n_{NO_2} + n_{N_2O_4}}
\]

so, doing the dirty deed, we have

\[
\frac{dG_{\text{mixture}}}{d\zeta} = \frac{d}{d\zeta} \left( 2\zeta \mu_{N_2O_2}^o + 2\zeta RT \ln(x_{NO_2} P_{\text{total}}) + n_{N_2O_2}^o \mu_{N_2O_2}^o + n_{N_2O_4}^o RT \ln(x_{NO_2} P_{\text{total}}) \right)
\]

\[
-\zeta \mu_{N_2O_4}^o - \zeta RT \ln(x_{N_2O_4} P_{\text{total}}) + n_{N_2O_4}^o \mu_{N_2O_4}^o + n_{N_2O_4}^o RT \ln(x_{N_2O_4} P_{\text{total}})
\] (3.8)

\[
\frac{dG_{\text{mixture}}}{d\zeta} = 2\mu_{N_2O_2}^o + 2RT \ln(x_{NO_2} P_{\text{total}}) + 2\zeta RT \frac{d\ln(x_{NO_2} P_{\text{total}})}{d\zeta} + n_{N_2O_4}^o RT \frac{d\ln(x_{NO_2} P_{\text{total}})}{d\zeta}
\]

\[
-\mu_{N_2O_4}^o - RT \ln(x_{N_2O_4} P_{\text{total}}) - \zeta RT \frac{d\ln(x_{N_2O_4} P_{\text{total}})}{d\zeta} + n_{N_2O_4}^o RT \frac{d\ln(x_{N_2O_4} P_{\text{total}})}{d\zeta}
\] (3.9)

where we need to just evaluate the remaining partial derivatives.

\[
\frac{dx_{NO_2}}{d\zeta} = \frac{d}{d\zeta} \left( \frac{2\zeta + n_{N_2O_2}^o}{\zeta + n_{NO_2}^o + n_{N_2O_4}^o} \right) = \frac{d}{d\zeta} \left( \frac{2\zeta + n_{N_2O_2}^o}{\zeta + n_{NO_2}^o + n_{N_2O_4}^o} \right)
\] (3.10)

and

\[
\frac{dx_{N_2O_4}}{d\zeta} = \frac{d}{d\zeta} \left( \frac{-\zeta + n_{N_2O_4}^o}{2\zeta + n_{NO_2}^o - \zeta + n_{N_2O_4}^o} \right) = \frac{d}{d\zeta} \left( \frac{-\zeta + n_{N_2O_4}^o}{2\zeta + n_{NO_2}^o - \zeta + n_{N_2O_4}^o} \right)
\] (3.11)

so, doing the dirty deed, we have

\[
\frac{dx_{NO_2}}{d\zeta} = \frac{2}{\zeta + n_{NO_2}^o + n_{N_2O_4}^o} + \frac{(-1)(2\zeta + n_{N_2O_2}^o)}{(\zeta + n_{NO_2}^o + n_{N_2O_4}^o)^2}
\] (3.12)

\[
\frac{dx_{N_2O_4}}{d\zeta} = \frac{(-1)}{\zeta + n_{N_2O_2}^o + n_{N_2O_4}^o} + \frac{(-1)(-\zeta + n_{N_2O_4}^o)}{(\zeta + n_{NO_2}^o + n_{N_2O_4}^o)^2}
\] (3.13)

which is a little harder than the equimolar cases where \( \Delta n \) 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 \( G_{\text{mixture}} \) with respect to \( \zeta \), i.e.,

\[
\frac{dG_{\text{mixture}}}{d\zeta} = 2\mu_{N_2O_2}^o + 2RT \ln[x_{NO_2} P_{\text{total}}] + (2\zeta RT + 2n_{NO_2}^o RT) \frac{dx_{NO_2}}{d\zeta} \frac{1}{x_{NO_2}}
\]

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

\[
\frac{dx_{NO_2}}{d\zeta} = \frac{(2\zeta + n_{N_2O_2}^o + n_{N_2O_4}^o) - (2\zeta + n_{N_2O_2}^o)}{(\zeta + n_{NO_2}^o + n_{N_2O_4}^o)^2}
\] (3.14)

\[
\frac{dx_{N_2O_4}}{d\zeta} = \frac{(-1)(\zeta + n_{N_2O_2}^o + n_{N_2O_4}^o) - (-\zeta + n_{N_2O_4}^o)}{(\zeta + n_{NO_2}^o + n_{N_2O_4}^o)^2}
\] (3.15)

which become, again sequentially,

\[
\frac{dx_{NO_2}}{d\zeta} = \frac{(n_{NO_2}^o + 2n_{N_2O_4}^o)}{(\zeta + n_{NO_2}^o + n_{N_2O_4}^o)^2}
\] (3.16)

\[
\frac{dx_{N_2O_4}}{d\zeta} = -\frac{n_{N_2O_2}^o + 2n_{N_2O_4}^o}{(\zeta + n_{NO_2}^o + n_{N_2O_4}^o)^2}
\] (3.17)

Taking the derivatives of logarithms in Equation 3.9 appropriately, we obtain
\[ -\mu_{N_2O_4}^{o} + RT \ln [x_{N_2O_4}P_{total}] + (-\zeta RT + 2n_{N_2O_4}^{o}RT) \frac{dx_{N_2O_4}}{d\zeta} \frac{1}{x_{N_2O_4}} \]  

(3.18)

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

\[
\frac{dG_{mixture}}{d\zeta} = 2\mu_{NO_2}^{o} + 2RT \ln [x_{NO_2}P_{total}] + (2\zeta RT + 2n_{NO_2}^{o}RT) \frac{(n_{NO_2}^{o} + 2n_{N_2O_4}^{o})}{(\zeta + n_{NO_2}^{o} + n_{N_2O_4}^{o})^2 x_{NO_2}} \]

\[
-\mu_{N_2O_4}^{o} - RT \ln [x_{N_2O_4}P_{total}] - (-\zeta RT + n_{N_2O_4}^{o}RT) \frac{n_{NO_2}^{o} + 2n_{N_2O_4}^{o}}{(\zeta + n_{NO_2}^{o} + n_{N_2O_4}^{o})^2 x_{N_2O_4}} \]

(3.19)

which is

\[
\frac{dG_{mixture}}{d\zeta} = 2\mu_{NO_2}^{o} + 2RT \ln (x_{NO_2}P_{total})
\]

\[
+ (2\zeta RT + n_{NO_2}^{o}RT) \frac{(n_{NO_2}^{o} + 2n_{N_2O_4}^{o})}{(\zeta + n_{NO_2}^{o} + n_{N_2O_4}^{o})^2} \frac{\zeta + n_{NO_2}^{o} + n_{N_2O_4}^{o}}{(2\zeta + n_{N_2O_4}^{o})}
\]

\[
-\mu_{N_2O_4}^{o} - RT \ln (x_{N_2O_4}P_{total})
\]

\[
- (-\zeta RT + n_{N_2O_4}^{o}RT) \frac{n_{NO_2}^{o} + 2n_{N_2O_4}^{o}}{(\zeta + n_{NO_2}^{o} + n_{N_2O_4}^{o})^2} \frac{\zeta + n_{NO_2}^{o} + n_{N_2O_4}^{o}}{(-\zeta + n_{N_2O_4}^{o})}
\]

(3.20)

\[
\frac{dG_{mixture}}{d\zeta} = 2\mu_{NO_2}^{o} + 2RT \ln (P_{NO_2})
\]

\[
+ RT \frac{(n_{NO_2}^{o} + 2n_{N_2O_4}^{o})}{(\zeta + n_{NO_2}^{o} + n_{N_2O_4}^{o})}
\]

\[
-\mu_{N_2O_4}^{o} - RT \ln (P_{N_2O_4})
\]

\[
- RT \frac{n_{NO_2}^{o} + 2n_{N_2O_4}^{o}}{(\zeta + n_{NO_2}^{o} + n_{N_2O_4}^{o})} = 0
\]

(3.21)

Q.E.D.

\[
\frac{dG_{mixture}}{d\zeta} = 0 = 2\mu_{NO_2}^{o} - \mu_{N_2O_4}^{o} + RT \ln (P_{NO_2}) - RT \ln (P_{N_2O_4})
\]

(3.22)

\[
\frac{dG_{mixture}}{d\zeta} = 0 = \Delta G_{reaction}^{o} + RT \ln K_p
\]

(3.23)


