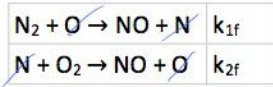


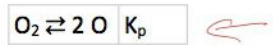
# SSA problem

Thursday, September 21, 2017 2:59 PM

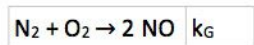
A famous chain mechanism is the Zeldovich, or thermal, mechanism for the formation of nitric oxide from atmospheric nitrogen:



Because the second reaction is much faster than the first, the steady state approximation can be used to evaluate the N-atom concentration. Furthermore, in high-temperature systems, the NO formation reaction is typically much slower than other reactions involving  $O_2$  and O. Thus,  $O_2$  and O can assumed to be in equilibrium.



Construct a global mechanism

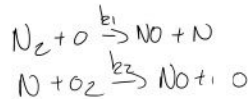


Represented as

$k_1 \ll k_2$

$d[NO]/dt = k_G [N_2]^m [O_2]^n$

i.e., determine  $k_G$ , m, and n using the elementary rate coefficients, etc. from the detailed mechanism.



$\frac{d[NO]}{dt} = k_1 [N_2][O] + k_2 [N][O_2]$

$[N]: \frac{d[N]}{dt} = k_1 [N_2][O] - k_2 [N][O_2]$

SSA:  $\frac{d[N]}{dt} \rightarrow 0 \quad k_1 \ll k_2$

$0 = k_1 [N_2][O] - k_2 [N][O_2]$

$[N]_{ss} = \frac{k_1 [N_2][O]}{k_2 [O_2]}$

$\hookrightarrow \frac{d[NO]}{dt} = k_1 [N_2][O] + k_2 [O_2] \frac{k_1 [N_2][O]}{k_2 [O_2]}$   
 $= 2 k_1 [N_2][O]$

$[O]: \quad O_2 \rightleftharpoons 2O$   
 $K_p = \frac{(P_O/P^\circ)^2}{(P_{O_2}/P^\circ)} = \frac{P_O^2}{P_{O_2} P^\circ} = K_c \left( \frac{R_0 T}{P^\circ} \right)^{2-1}$   
 $= (R_0 T)^{2-1} P^{\circ-1}$

$$K_p = \frac{[O]^2}{[O_2]} \left( \frac{R_0 T}{P^0} \right) \Rightarrow [O] = \left( K_p [O_2] \left( \frac{P^0}{R_0 T} \right) \right)^{1/2}$$

$$\begin{aligned} \frac{d[NO]}{dt} &= 2k_1 [N_2] [O] \\ &= 2k_1 [N_2] K_p^{1/2} [O_2]^{1/2} \left( \frac{P^0}{R_0 T} \right)^{1/2} \end{aligned}$$

$$\begin{aligned} \frac{d[NO]}{dt} &= k_G [N_2]^m [O_2]^n \\ k_G &= 2k_1 \left( \frac{P^0}{R_0 T} \right)^{1/2} K_p^{1/2} \end{aligned}$$

$$m = 1$$

$$n = 1/2$$

## Continuation: Shock Heating NO<sub>x</sub>

Monday, September 25, 2017 5:48 PM

Consider the shock heating of air to 2500 K and 3 atm. Use the results of the previous problem to determine the initial nitric oxide formation rate in ppm/s.

$$\begin{aligned} \rightarrow k_{1f} &= 1.82 \times 10^{17} \text{ cm}^3/\text{kmol}\cdot\text{s} * e^{-(38370 \text{ K}/T)} \\ g^{\circ}_{f, O, 2500 \text{ K}} &= 88203 \text{ kJ/kmol} \\ g^{\circ}_{f, O_2, 2500 \text{ K}} &= 0 \text{ kJ/kmol} \end{aligned}$$

$$\begin{aligned} \frac{d[\text{NO}]}{dt} &= k_g [\text{N}_2] [\text{O}_2]^{1/2} \\ \text{N}_2 + \text{O} &\xrightarrow{k_1} \text{NO} + \text{N} \\ \text{N} + \text{O}_2 &\xrightarrow{k_2} \text{NO} + \text{O} \\ \text{O}_2 &\rightleftharpoons 2\text{O} \quad K_p \end{aligned}$$

$$K_p = \exp\left(\frac{-\Delta G^{\circ}_{R, T}}{R_0 T}\right) = \exp\left(\frac{-1}{R_0 T} (2\bar{g}^{\circ}_{f, O} - \bar{g}^{\circ}_{f, O_2})_{2500}\right)$$

$$= 2.063 \times 10^{-11} \text{ atm}$$

$$= 20.90 \text{ Pa}$$

$$P[\text{N}_2] = \frac{P}{\sigma} X_{N_2} = 3.671 \times 10^{-2} \text{ kmol/m}^3$$

$$[\text{O}_2]_i = \frac{P}{R_0 T} X_{O_2} = 1.155 \times 10^{-2} \text{ kmol/m}^3$$

$$k_1 = 3.93 \times 10^{-4} \text{ m}^3/\text{kmol}\cdot\text{s}$$

$$\frac{d[\text{NO}]}{dt} = 6.0505 \frac{\text{kmol}}{\text{m}^3\cdot\text{s}}$$

$$\text{ppm} = \frac{\text{part (moles)}}{\text{mol total}} = \frac{\text{mol}[\text{NO}]}{\text{mol total}}$$

$$\begin{aligned} \frac{dX_{\text{NO}}}{dt} &= V \frac{d[\text{NO}]}{dt} = \frac{R_0 T}{P} \frac{d[\text{NO}]}{dt} \\ &= \frac{\text{kmol}[\text{NO}]}{\text{kmol total}} \frac{1}{s} \\ &= 3.45 \times 10^6 \text{ ppm/s} \end{aligned}$$