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:

$N_2 + \cancel{O} \rightarrow NO + \cancel{N}$	k_{1f}
$\cancel{N} + O_2 \rightarrow NO + \cancel{O}$	k_{2f}

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.

$O_2 \rightleftarrows 2\,O$	K_p

Construct a global mechanism

$N_2 + O_2 \rightarrow 2\,NO$	k_G

Represented as

$$\underline{d[NO]/dt = k_G[N_2]^m[O_2]^n}$$

$k_1 << k_2$

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

$$N_2 + O \xrightarrow{k_1} NO + N$$
$$N + O_2 \xrightarrow{k_2} NO + O$$

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

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

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

$$0 = k_1[N_2][O] - k_2[N]_{ss}[O_2]$$

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

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

$$= 2k_1[N_2][O]$$

$[O]$: $O_2 \Leftrightarrow 2O$

$$K_p = \frac{(P_O/P^\circ)^2}{(P_{O_2}/P^\circ)} = \frac{P_O^2}{P_{O_2}P^\circ} = K_c\left(\frac{R_u T}{P^\circ}\right)^{2-1}$$

$$= \frac{}{[O_2]}\left(\frac{}{p^\circ}\right)$$

$$K_p = \frac{[O]^2}{[O_2]}\left(\frac{R_uT}{p^o}\right) \Rightarrow \underline{[O] = \left(K_p[O_2]\left(\frac{p^o}{R_uT}\right)\right)^{1/2}}$$

$$\frac{d[NO]}{dt} = 2k_1[N_2][O]$$

$$= 2k_1[N_2]K_p^{1/2}[O_2]^{1/2}\left(\frac{p^o}{R_uT}\right)^{1/2}$$

$$\frac{d[NO]}{dt} = k_G[N_2]^m[O_2]^n$$

$$k_G = 2k_1\left(\frac{p^o}{R_uT}\right)^{1/2}K_p^{1/2}$$

$$m = 1$$

$$n = 1/2$$

Continuation: Shock Heating NO$_x$

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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.

$\Rightarrow k_{1f} = 1.82 \times 10^{17}$ cm^3/kmol-s * $e^{(-38370\text{ K}/T)}$
$g^o_{f,\,O,\,2500\,K} = 88203$ kJ/ kmol
$g^o_{f,\,O2,\,2500\,K} = 0$ kJ/ kmol

$$\frac{d[NO]}{dt} = k_G [N_2][O_2]^{1/2}$$

$$N_2 + O \xrightarrow{k_1} NO + N$$

$$N + O_2 \xrightarrow{k_2} NO + O$$

$$O_2 \rightleftarrows 2O \quad K_p$$

$$K_p = \exp\left(\frac{-\Delta G^\circ_{R,T}}{R_uT}\right) = \exp\left(\frac{-1}{R_uT}\left(2\bar{g}^\circ_{f,O} - \overset{0}{\cancel{\bar{g}_{f,O_2}}}\right)_{2500}\right)$$

$$= 2.663 \times 10^{-4}\ \text{atm}$$

$$\overset{A}{i} \quad = 20.90\ \text{Pa}$$

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

$$[O_2]_i = \frac{P}{R_uT} X_{O_2} \rightsquigarrow .21 = 1.155 \times 10^{-2}\ \text{kmol/m}^3$$

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

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

parts (moles)

ppm $\quad \dfrac{\text{mol }[NO]}{\text{mol total}}$

$$\frac{dX_{NO}}{dt} = V\frac{d[NO]}{dt} = \frac{R_uT}{P}\frac{d[NO]}{dt}$$

$$= \frac{\text{kmol }[NO]}{\text{kmol total}}\,\frac{1}{s}$$

$$= 3.45 \times 10^{6}\ \text{ppm/s}$$