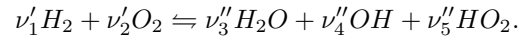


1. Find the most general stoichiometric balance for the reaction



Solution

Let us take $\nu_i = \nu''_i - \nu'_i$ so

$$\nu_1 H_2 + \nu_2 O_2 + \nu_3 H_2O + \nu_4 OH + \nu_5 HO_2 = 0.$$

We have $N = 5$, $L = 2$, and $J = 1$. Take $l = 1, 2$ to correspond to (H, O) for elements. For species take, $i = 1, \dots, 5$ to correspond to $(H_2, O_2, H_2O, OH, HO_2)$. The stoichiometric matrix ϕ_{li} is

$$\phi_{li} = \begin{pmatrix} 2 & 0 & 2 & 1 & 1 \\ 0 & 2 & 1 & 1 & 2 \end{pmatrix}.$$

Element balance is enforced by

$$\sum_{i=1}^N \phi_{li} \nu_i = 0.$$

So we have

$$\begin{pmatrix} 2 & 0 & 2 & 1 & 1 \\ 0 & 2 & 1 & 1 & 2 \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}.$$

Let us take $\nu_3 = r$, $\nu_4 = s$, and $\nu_5 = t$ and get

$$\begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \end{pmatrix} = \begin{pmatrix} -2r - s - t \\ -r - s - 2t \end{pmatrix}.$$

So

$$\begin{pmatrix} \nu_1 \\ \nu_2 \end{pmatrix} = \begin{pmatrix} -r - \frac{1}{2}s - \frac{1}{2}t \\ -\frac{1}{2}r - \frac{1}{2}s - t \end{pmatrix}.$$

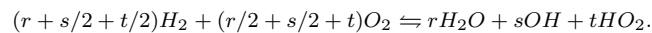
So

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \end{pmatrix} = \begin{pmatrix} -r - \frac{1}{2}s - \frac{1}{2}t \\ -\frac{1}{2}r - \frac{1}{2}s - t \\ r \\ s \\ t \end{pmatrix} = r \begin{pmatrix} -1 \\ -\frac{1}{2} \\ 1 \\ 0 \\ 0 \end{pmatrix} + s \begin{pmatrix} -\frac{1}{2} \\ -\frac{1}{2} \\ 0 \\ 1 \\ 0 \end{pmatrix} + t \begin{pmatrix} -\frac{1}{2} \\ -1 \\ 0 \\ 0 \\ 1 \end{pmatrix}.$$

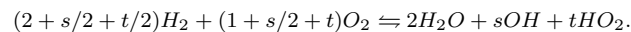
So we can say our most general balanced equation is

$$-(r + s/2 + t/2)H_2 - (r/2 + s/2 + t)O_2 + rH_2O + sOH + tHO_2 = 0.$$

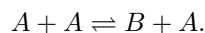
In more standard chemistry notation, we could say



Taking $r = 2$, we get an even more standard representation,



2. Species A and B have identical molecular masses and undergo a reversible reaction described by



The reaction is adiabatic and isobaric. At $t = 0$, $T = T_o$, $\bar{p}_A = \bar{p}_{Ao}$, and $\bar{p}_B = 0$. The reaction has $\mathcal{E} = 0$ and $\beta = 0$. It has collision frequency factor a , constant c_P , and is exothermic.

- (a) Write appropriate simple ordinary differential equations for the change of $\bar{\rho}_A$ and T with respect to time. Define any additional appropriate constants you might need.
- (b) Find the equilibrium concentration of A .
- (c) Find the time scales of relaxation near equilibrium.
- (d) Make as much progress as possible in finding $\bar{\rho}_A(t)$ and $T(t)$.

Solution

There's a variety of ways to go about this problem. For the reaction we have

$$\frac{d}{dt} \left(\frac{\bar{\rho}_A}{\rho} \right) = -\frac{r}{\rho}.$$

$$\frac{d}{dt} \left(\frac{\bar{\rho}_B}{\rho} \right) = \frac{r}{\rho}.$$

Let us recognize that V varies while the total mass m remains constant, and that $\rho = m/V$. We can restate our reaction laws in terms of number of moles n_A , n_B as

$$\frac{d}{dt} \left(\frac{n_A/V}{m/V} \right) = -\frac{r}{m/V}.$$

$$\frac{d}{dt} \left(\frac{n_B/V}{m/V} \right) = \frac{r}{m/V}.$$

So we have

$$\frac{dn_A}{dt} = -Vr,$$

$$\frac{dn_B}{dt} = Vr.$$

Adding the two, we get

$$\frac{d}{dt} (n_A + n_B) = 0.$$

Integrating, we get

$$n_A + n_B = n_{A_0},$$

recalling that $n_{B_0} = 0$.

Our energy conservation relation gives a constant total enthalpy H , which retains its initial value:

$$H = n_A \bar{h}_A + n_B \bar{h}_B = n_{A_0} \bar{h}_{A,T_0}^o.$$

Substituting, we get

$$n_A (\bar{c}_P (T - T_0) + \bar{h}_A^o) + (n_{A_0} - n_A) (\bar{c}_P (T - T_0) + \bar{h}_{B,T_0}^o) = n_{A_0} \bar{h}_{A,T_0}^o.$$

$$n_A (\bar{c}_P (T - T_0) + \bar{h}_A^o) + (n_{A_0}) (\bar{c}_P (T - T_0) + \bar{h}_{B,T_0}^o) - n_A (\bar{c}_P (T - T_0) + \bar{h}_{B,T_0}^o) = n_{A_0} \bar{h}_{A,T_0}^o.$$

$$n_A (\bar{h}_A^o - \bar{h}_{B,T_0}^o) + n_{A_0} (\bar{c}_P (T - T_0) + \bar{h}_{B,T_0}^o) = n_{A_0} \bar{h}_{A,T_0}^o.$$

$$\frac{n_A}{n_{A_0}} (\bar{h}_A^o - \bar{h}_{B,T_0}^o) + \bar{c}_P (T - T_0) = \bar{h}_{A,T_0}^o - \bar{h}_{B,T_0}^o.$$

$$\bar{c}_P (T - T_0) = (\bar{h}_{A,T_0}^o - \bar{h}_{B,T_0}^o) \left(1 - \frac{n_A}{n_{A_0}} \right).$$

$$T = T_0 + \frac{\bar{h}_{A,T_0}^o - \bar{h}_{B,T_0}^o}{\bar{c}_P} \left(1 - \frac{n_A}{n_{A_0}} \right).$$

Now the ideal gas law gives us

$$PV = (n_A + n_B) \bar{R}T.$$

Since $n_A + n_B = n_{A_0}$ and since $P = P_0$, we get

$$P_0 V = n_{A_0} \bar{R}T.$$

Solving for V , we get

$$V = \frac{n_{A_0} \bar{R}}{P_0} T.$$

Substituting from energy conservation, we get

$$V = \frac{n_{A_0} \bar{R} T_0}{P_0} \left(1 + \frac{\bar{h}_{A,T_0}^o - \bar{h}_{B,T_0}^o}{\bar{c}_P T_0} \left(1 - \frac{n_A}{n_{A_0}} \right) \right).$$

With $V_o = n_{A_o} \bar{R} T_o / P_o$, we can say

$$V = V_o \left(1 + \frac{\bar{h}_{A,T_o}^o - \bar{h}_{B,T_o}^o}{\bar{c}_P T_o} \left(1 - \frac{n_A}{n_{A_o}} \right) \right).$$

Now we have

$$r = a \bar{\rho}_A^2 \left(1 - \frac{1}{K_c} \frac{\bar{\rho}_B}{\bar{\rho}_A} \right) = a \frac{n_A^2}{V^2} \left(1 - \frac{1}{K_c} \frac{n_B}{n_A} \right).$$

$$r = a \frac{n_A^2}{V^2} \left(1 - \frac{1}{K_c} \frac{n_{A_o} - n_A}{n_A} \right).$$

So, we get

$$\frac{dn_A}{dt} = -Vr = -a \frac{n_A^2}{V} \left(1 - \frac{1}{K_c} \frac{n_{A_o} - n_A}{n_A} \right).$$

$$\frac{dn_A}{dt} = -a \frac{n_A^2}{V_o \left(1 + \frac{\bar{h}_{A,T_o}^o - \bar{h}_{B,T_o}^o}{\bar{c}_P T_o} \left(1 - \frac{n_A}{n_{A_o}} \right) \right)} \left(1 - \frac{1}{K_c} \frac{n_{A_o} - n_A}{n_A} \right).$$

Now recall that for the reaction with no net mole change

$$K_c = \exp \left(\frac{-\Delta G^o}{RT} \right).$$

$$K_c = \exp \left(\frac{-(\bar{g}_B^o - \bar{g}_A^o)}{RT} \right).$$

$$K_c = \exp \left(\frac{\bar{g}_A^o - \bar{g}_B^o}{RT} \right).$$

$$K_c = \exp \left(\frac{(\bar{h}_A^o - T\bar{s}_A^o) - (\bar{h}_B^o - T\bar{s}_B^o)}{RT} \right).$$

$$K_c = \exp \left(\frac{\bar{h}_A^o - \bar{h}_B^o}{RT} \right) \exp \left(\frac{\bar{s}_B^o - \bar{s}_A^o}{R} \right).$$

$$K_c = \exp \left(\frac{\bar{h}_{A,T_o}^o - \bar{h}_{B,T_o}^o}{RT} \right) \exp \left(\frac{\bar{s}_{B,T_o}^o - \bar{s}_{A,T_o}^o}{R} \right).$$

$$K_c = \exp \left(\frac{\bar{h}_{A,T_o}^o - \bar{h}_{B,T_o}^o}{RT_o \left(1 + \frac{\bar{h}_{A,T_o}^o - \bar{h}_{B,T_o}^o}{\bar{c}_P T_o} \left(1 - \frac{n_A}{n_{A_o}} \right) \right)} \right) \exp \left(\frac{\bar{s}_{B,T_o}^o - \bar{s}_{A,T_o}^o}{R} \right).$$

Let us simplify to ease the analysis. Take $y_A = n_A/n_{A_o}$. Take $\bar{s}_{B,T_o}^o = \bar{s}_{A,T_o}^o$. Take $q = (\bar{h}_{A,T_o}^o - \bar{h}_{B,T_o}^o)/\bar{c}_P T_o$. Take $\gamma = \bar{c}_P/\bar{c}_v$. Take $\tau = an_{A_o}t/V$. Then we get

$$K_c = \exp \left(\frac{\gamma}{\gamma - 1} \frac{q}{1 + q(1 - y_A)} \right).$$

We also get

$$\frac{dy_A}{d\tau} = - \frac{y_A^2}{1 + q(1 - y_A)} \left(1 - \frac{1}{K_c} \frac{1 - y_A}{y_A} \right).$$

This has equilibrium when

$$K_c = \frac{1 - y_A}{y_A}.$$

So this becomes

$$\exp \left(\frac{\gamma}{\gamma - 1} \frac{q}{1 + q(1 - y_A)} \right) = \frac{1 - y_A}{y_A}.$$

This has no closed form solution.

Let us assume that $K_c \rightarrow \infty$. Thus

$$\frac{dy_A}{d\tau} = - \frac{y_A^2}{1 + q(1 - y_A)}.$$

There is an equilibrium at $y_A = 0$. This is the limit of irreversible reaction. Near this equilibrium, Taylor series expansion reveals no linear term. There is a quadratic term, and the local behavior is dictated by

$$\frac{dy_A}{d\tau} \sim - \frac{y_A^2}{1 + q}.$$

If we take $y_A(0) = y_{A_o} > 0$, we find local solution

$$y_A(\tau) = \frac{y_{A_o}(1 + q)}{1 + qy_{A_o}\tau}.$$

As $\tau \rightarrow \infty$, $y_A \rightarrow 0$, as long as $y_{A_o} > 0$. In the physical domain, this equilibrium is stable.
