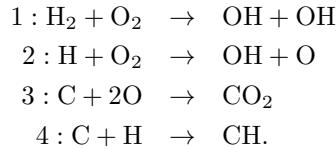


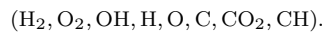
1. (40) Consider the irreversible reaction mechanism



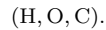
- Identify the number of species N , reactions J , and elements L .
- Find the $L \times N$ species-element matrix ϕ .
- Find the $N \times J$ stoichiometric reaction matrix ν .
- Demonstrate $\phi \cdot \nu = \mathbf{0}$.
- For isothermal, isochoric kinetics, write an ordinary differential equation for the evolution of the concentration of H; define any necessary constants.

Solution

We have $N = 8$ species. We can take them to be ordered as



We have $J = 4$ reactions, as numbered in the problem statement. We have $L = 3$ elements and take them to be ordered as



With this ordering, we have

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

And with this ordering, we get

$$\nu = \begin{pmatrix} -1 & 0 & 0 & 0 \\ -1 & -1 & 0 & 0 \\ 2 & 1 & 0 & 0 \\ 0 & -1 & 0 & -1 \\ 0 & 1 & -2 & 0 \\ 0 & 0 & -1 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

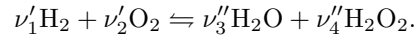
Element conservation is assured because

$$\phi \cdot \nu = \begin{pmatrix} 2 & 0 & 1 & 1 & 0 & 0 & 0 & 1 \\ 0 & 2 & 1 & 0 & 1 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 & 0 \\ -1 & -1 & 0 & 0 \\ 2 & 1 & 0 & 0 \\ 0 & -1 & 0 & -1 \\ 0 & 1 & -2 & 0 \\ 0 & 0 & -1 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

We see that

$$\frac{d\bar{\rho}_\text{H}}{dt} = -k_2\bar{\rho}_\text{H}\bar{\rho}_{\text{O}_2} - k_4\bar{\rho}_\text{H}\bar{\rho}_\text{C}$$

2. (20) Find the most general stoichiometric balance for the reaction



Solution

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

$$\nu_1 \text{H}_2 + \nu_2 \text{O}_2 + \nu_3 \text{H}_2\text{O} + \nu_4 \text{H}_2\text{O}_2 = 0.$$

We have $N = 4$, $L = 2$, and $J = 1$. Take $l = 1, 2$ to correspond to (H, O) for elements. For species take, $i = 1, \dots, 4$ to correspond to ($\text{H}_2, \text{O}_2, \text{H}_2\text{O}, \text{H}_2\text{O}_2$). The stoichiometric matrix ϕ_{li} is

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

Element balance is enforced by

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

So we have

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

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

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

So

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

So

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

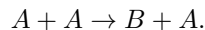
So we can say our most general balanced equation is

$$(-r - s) \text{H}_2 + \left(-\frac{1}{2}r - s\right) \text{O}_2 + r \text{H}_2\text{O} + s \text{H}_2\text{O}_2 = 0.$$

Set $r = 2$, and rearrange to get

$$(2 + s) \text{H}_2 + (1 + s) \text{O}_2 = 2 \text{H}_2\text{O} + s \text{H}_2\text{O}_2.$$

3. (40) Species A and B have identical molecular masses and identical specific heats and undergo an irreversible reaction described by



The reaction is *adiabatic* and *isochoric*. The fixed volume is V , and no mass enters or exits the volume. 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 \bar{c}_v , and is exothermic.

- Write an appropriate simple ordinary differential equations for the change of \bar{p}_A with respect to time.
- Find the equilibrium concentration of A .
- Find $\bar{p}_A(t)$ and $T(t)$.

Solution

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

$$\frac{d\bar{\rho}_A}{dt} = -r.$$

$$\frac{d\bar{\rho}_B}{dt} = r.$$

For the isochoric reaction, volume V , total mass m , and $\rho = m/V$, remain constant. We can restate our reaction laws in terms of number of moles n_A, n_B as

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

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

Adding the two, we get

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

Integrating, we get

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

recalling that $n_{Bo} = 0$.

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

$$E = n_A \bar{e}_A + n_B \bar{e}_B = n_{Ao} \bar{e}_{A, T_o}^o.$$

Substituting, we get

$$n_A (\bar{c}_v (T - T_o) + \bar{e}_{A, T_o}^o) + (n_{Ao} - n_A) (\bar{c}_v (T - T_o) + \bar{e}_{B, T_o}^o) = n_{Ao} \bar{e}_{A, T_o}^o.$$

Solving, we find

$$T = T_o + \frac{\bar{e}_{A, T_o}^o - \bar{e}_{B, T_o}^o}{\bar{c}_v} \left(1 - \frac{n_A}{n_{Ao}} \right).$$

Now the ideal gas law gives us

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

Because $n_A + n_B = n_{Ao}$ we get

$$PV = n_{Ao} \bar{R}T.$$

Solving for P , we get

$$P = \frac{n_{Ao} \bar{R}}{V} T.$$

Here T will be time-dependent, and thus P will also be time-dependent. Substituting from energy conservation, we get

$$P = \frac{n_{Ao} \bar{R} T_o}{V} \left(1 + \frac{\bar{e}_{A, T_o}^o - \bar{e}_{B, T_o}^o}{\bar{c}_v T_o} \left(1 - \frac{n_A}{n_{Ao}} \right) \right).$$

Now we have

$$r = a \bar{\rho}_A^2 = a \frac{n_A^2}{V^2}.$$

So, we get

$$\frac{dn_A}{dt} = -Vr = -a \frac{n_A^2}{V}.$$

The solution that satisfies the initial condition is

$$n_A(t) = n_{Ao} \frac{1}{1 + a \frac{n_{Ao}}{V} t}.$$

As $t \rightarrow \infty$, $n_A \rightarrow 0$, as long as $n_{Ao} > 0$. In the physical domain, this equilibrium is stable. We also see

$$\bar{\rho}_A(t) = \bar{\rho}_{Ao} \frac{1}{1 + a \bar{\rho}_{Ao} t}.$$

So

$$T(t) = T_o + \frac{\bar{e}_{A, T_o}^o - \bar{e}_{B, T_o}^o}{\bar{c}_v} \left(\frac{a n_{Ao} t}{V + a n_{Ao} t} \right).$$
