AME 60636
Examination 1: Solution
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23 February 2022

1. (40) Consider the irreversible reaction mechanism

$$
\begin{aligned}
1 : H_2 + O_2 &\rightarrow OH + OH \\
2 : H + O_2 &\rightarrow OH + O \\
3 : C + 2O &\rightarrow CO_2 \\
4 : C + H &\rightarrow CH.
\end{aligned}
$$

   (a) Identify the number of species N, reactions J, and elements L.
   (b) Find the $L \times N$ species-element matrix $\boldsymbol{\phi}$.
   (c) Find the $N \times J$ stoichiometric reaction matrix $\boldsymbol{\nu}$.
   (d) Demonstrate $\boldsymbol{\phi} \cdot \boldsymbol{\nu} = \mathbf{0}$.
   (e) 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

$$(H_2, O_2, OH, H, O, C, CO_2, CH).$$

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

$$(H, O, C).$$

With this ordering, we have

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

And with this ordering, we get

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

Element conservation is assured because

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

We see that

$$\frac{d\overline{\rho}_H}{dt} = -k_2 \overline{\rho}_H \overline{\rho}_{O_2} - k_4 \overline{\rho}_H \overline{\rho}_C$$

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

$$\nu_1' H_2 + \nu_2' O_2 \leftrightharpoons \nu_3'' H_2O + \nu_4'' H_2O_2.$$

Solution

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

$$\nu_1 H_2 + \nu_2 O_2 + \nu_3 H_2O + \nu_4 H_2O_2 = 0.$$

We have $N = 4$, $L = 2$, and $J = 1$. Take $l = 1, 2$ to correspond to (H, O) for elements. For species take, $i = 1, \ldots, 4$ to correspond to (H_2, O_2, H_2O, H_2O_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

$$(-r - s)\, H_2 + \left(-\frac{1}{2}r - s\right) O_2 + r H_2O + s H_2O_2 = 0.$$

Set $r = 2$, and rearrange to get

$$(2 + s) H_2 + (1 + s) O_2 = 2 H_2O + s H_2O_2.$$

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

$$A + A \rightarrow B + A.$$

The reaction is *adiabatic* and *isochoric*. The fixed volume is V, and no mass enters or exits the volume. At $t = 0$, $T = T_o$, $\overline{\rho}_A = \overline{\rho}_{Ao}$, and $\overline{\rho}_B = 0$. The reaction has $\mathcal{E} = 0$ and $\beta = 0$. It has collision frequency factor a, constant $\overline{c}_v$, and is exothermic.

(a) Write an appropriate simple ordinary differential equations for the change of $\overline{\rho}_A$ with respect to time.

(b) Find the equilibrium concentration of A.

(c) Find $\overline{\rho}_A(t)$ and $T(t)$.

Solution

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

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

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

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:

$$E = n_A\overline{e}_A + n_B\overline{e}_B = n_{Ao}\overline{e}^o_{A,T_o}.$$

Substituting, we get

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

Solving, we find

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

Now the ideal gas law gives us

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

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

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

Solving for P, we get

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

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

$$P = \frac{n_{Ao}\overline{R}T_o}{V}\left(1 + \frac{\overline{e}^o_{A,T_o} - \overline{e}^o_{B,T_o}}{\overline{c}_vT_o}\left(1 - \frac{n_A}{n_{Ao}}\right)\right).$$

Now we have

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

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

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

So

$$T(t) = T_o + \frac{\overline{e}^o_{A,T_o} - \overline{e}^o_{B,T_o}}{\overline{c}_v}\left(\frac{an_{Ao}t}{V + an_{Ao}t}\right).$$