AME 60636
Examination 1: Solution
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1. A simple isothermal, isochoric one-step reversible kinetics system is modelled by

$$\frac{d\lambda}{dt} = k(1-\lambda)\left(1 - \frac{1}{K_c}\frac{\lambda}{1-\lambda}\right), \qquad \lambda(0) = 0.$$

Here λ is the reaction progress variable, k, and K_c are constants. Analyze the stability of any and all equilibria and find the associated time constants.

Solution

The kinetics equation expands to

$$\frac{d\lambda}{dt} = k\left(1 - \lambda - \frac{1}{K_c}\lambda\right), \qquad \lambda(0) = 0.$$

$$\frac{d\lambda}{dt} = k\left(1 - \left(1 + \frac{1}{K_c}\right)\lambda\right), \qquad \lambda(0) = 0.$$

The equation is purely linear, and by inspection the equilibrium is at

$$\boxed{\lambda = \frac{1}{1+\frac{1}{K_c}}.}$$

Also by inspection, the time constant is

$$\tau = \boxed{\frac{1}{k\left(1+\frac{1}{K_c}\right)}}.$$

2. The following three step model is a common surrogate for more complex kinetics:

$$\begin{aligned} F &\rightarrow I \\ F + I &\rightarrow 2I, \\ I &\rightarrow P. \end{aligned}$$

Here F, I, and P are fuel, intermediate, and product respectively. Each are assumed to have the same molecular mass. Assume the reactions to be isochoric and isothermal, with isothermal reaction rate constants known to be k_1, k_2, and k_3, respectively.

(a) Write an appropriate set of differential equations for the evolution of each species.

(b) Find any and all combinations that are conserved.

(c) If the initial mass fraction of F is unity, find the final mass fractions of each species at equilibrium.

Solution

We have

$$\frac{d\overline{\rho}_F}{dt} = -r_1 - r_2$$

$$\frac{d\overline{\rho}_I}{dt} = r_1 + r_2 - r_3,$$
$$\frac{d\overline{\rho}_P}{dt} = r_3.$$

Here we can say

$$r_1 = k_1 \overline{\rho}_F,$$
$$r_2 = k_2 \overline{\rho}_F \overline{\rho}_I,$$
$$r_3 = k_3 \overline{\rho}_I.$$

In matrix form, we have

$$\frac{d}{dt}\begin{pmatrix} \overline{\rho}_F \\ \overline{\rho}_I \\ \overline{\rho}_P \end{pmatrix} = \begin{pmatrix} -1 & -1 & 0 \\ 1 & 1 & -1 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$$

Let us seek a row echelon form. Add the first two equations to get

$$\frac{d}{dt}\begin{pmatrix} \overline{\rho}_F \\ \overline{\rho}_I + \rho_F \\ \overline{\rho}_P \end{pmatrix} = \begin{pmatrix} -1 & -1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$$

Add the second two to get

$$\frac{d}{dt}\begin{pmatrix} \overline{\rho}_F \\ \overline{\rho}_I + \rho_F \\ \overline{\rho}_I + \overline{\rho}_F + \overline{\rho}_P \end{pmatrix} = \begin{pmatrix} -1 & -1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$$

Thus, the third equation is conservative:

$$\frac{d}{dt}\left(\overline{\rho}_I + \overline{\rho}_F + \overline{\rho}_P\right) = 0.$$

Since at $t = 0$, we have all F, we can say

$$\boxed{\overline{\rho}_I + \overline{\rho}_F + \overline{\rho}_P = \overline{\rho}_{Fo}}.$$

By inspection, at equilibrium, we must have

$$\overline{\rho}_F = 0, \qquad \overline{\rho}_I = 0, \qquad \overline{\rho}_P = \overline{\rho}_{Fo}.$$

3. Consider an inert ideal mixture of N calorically perfect ideal gases undergoing a single reaction described by

$$\sum_i \nu_i \chi_i = 0,$$

under adiabatic, isochoric conditions. The reaction occurs at rate r. Find an expression for dT/dt. Use all necessary notions as developed in class.

Solution

See course notes, Sec. 4.6.3, where it is shown

$$\frac{dT}{dt} = -\frac{r\Delta E}{\rho c_v}.$$