AME 598t
Examination 1: **Solution**
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1. Consider the reaction kinetics law using the notation described in class

$$\frac{dc_i}{dt} = \sum_{j=1}^{J} \nu_{ij} \underbrace{\underbrace{\alpha_j T^{\beta_j} \exp\left(\frac{-E_j}{\Re T}\right)}_{\equiv k_j(T)} \prod_{k=1}^{N} c_k^{\nu'_{kj}} \left(1 - \frac{1}{K_{c,j}} \prod_{k=1}^{N} c_k^{\nu_{kj}}\right)}_{=r_j}.$$

   (a) Taking $K_{c,j}$, $j = 1, \ldots, J$, as having known values, give a simple sufficient condition, or set of conditions, for the ith species to be in equilibrium.

   (b) Using appropriate notation as described in class, show that element mass fractions remain constant with time.

By inspection, a *sufficient* condition, which may not be necessary, for equilibrium is that *each* of the J reactions be in equilibrium. This will exist when

$$1 - \frac{1}{K_{c,j}} \prod_{k=1}^{N} c_k^{\nu_{kj}} = 0, \tag{1}$$

$$1 = \frac{1}{K_{c,j}} \prod_{k=1}^{N} c_k^{\nu_{kj}}, \tag{2}$$

$$K_{c,j} = \frac{1}{K_{c,j}} \prod_{k=1}^{N} c_k^{\nu_{kj}}. \tag{3}$$

A less likely, and less interesting, condition for equilibrium would be to have *at least one* of the $c_k = 0,\ k = 1, \ldots, N$ when $\nu'_{kj} \neq 0$, for each of the J reactions. This simply implies that for each reaction, a necessarry reactant is totally absent, thus suppressing that reaction and inducing a state which is formally in equilibrium. Other sufficient conditions which are not very interesting include $\alpha_j = 0,\ j = 1, \ldots, J$; $\nu_{ij} = 0,\ i = 1, \ldots, N; j = 1, \ldots, J;\ T = 0$.

For the second part, one can begin with the equation for reaction kinetics and carry out a series of operations, as done in class, utilizing definitions described in class:

$$\frac{dc_i}{dt} = \sum_{j=1}^{J} \nu_{ij} r_j, \qquad i = 1, \ldots, N, \tag{4}$$

$$\phi_{li} \frac{dc_i}{dt} = \phi_{li} \sum_{j=1}^{J} \nu_{ij} r_j, \qquad i = 1, \ldots, N;\ j = 1, \ldots, L, \tag{5}$$

$$\frac{d}{dt}(\phi_{li} c_i) = \sum_{j=1}^{J} \phi_{li} \nu_{ij} r_j, \qquad i = 1, \ldots, N;\ l = 1, \ldots, L, \tag{6}$$

$$\sum_{i=1}^{N} \frac{d}{dt}(\phi_{li} c_i) = \sum_{i=1}^{N} \sum_{j=1}^{J} \phi_{li} \nu_{ij} r_j, \qquad l = 1, \ldots, L, \tag{7}$$

$$\frac{d}{dt}\left(\sum_{i=1}^{N} \phi_{li} c_i\right) = \sum_{j=1}^{J} r_j \sum_{i=1}^{N} \underbrace{\phi_{li} \nu_{ij}}_{=0}, \qquad l = 1, \ldots, L, \tag{8}$$

$$\frac{d}{dt}\left(\sum_{i=1}^{N} \phi_{li} c_i\right) = 0, \qquad l = 1, \ldots, L \tag{9}$$

The term $\sum_{i=1}^{N} \phi_{li} c_i$ represents the number of moles of element l per unit volume, by the following analysis

$$\sum_{i=1}^{N} \phi_{li} c_i = \sum_{i=1}^{N} \frac{moles\ element\ l}{moles\ species\ i} \frac{moles\ species\ i}{volume} = \frac{moles\ element\ l}{volume} \equiv {c_l}^e. \tag{10}$$

So

$$\frac{dc_l^e}{dt} = 0, \qquad , l = 1, \ldots, L. \tag{11}$$

Now, since the atomic mass of element l, $\mathcal{M}_l$, is a constant.

$$\mathcal{M}_l \frac{dc_l^e}{dt} = 0, \qquad , l = 1, \ldots, L, \tag{12}$$

$$\frac{d}{dt}\left(\mathcal{M}_l c_l^e\right) = 0, \tag{13}$$

$$\frac{d}{dt} \rho_l^e = 0. \tag{14}$$

That is, the element mass density, ρ_l^e, of element l is constant with time.

2. Species A and B have identical molecular masses and undergo an irreversible decomposition described by

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

The reaction is isothermal and isochoric. At $t = 0$, $c_A = c_{Ao}$, and $c_B = 0$.

(a) Write an appropriate simple ordinary differential equation for the change in concentration of species A with respect to time. Define any appropriate constants.

(b) Find the equilbrium concentration of A.

(c) Find $c_A(t)$.

From kinetics of the irreversible reaciton, one gets

$$\frac{dc_A}{dt} = -kc_A^2, \qquad c_A(0) = c_{Ao}. \tag{15}$$

Separate variables to get

$$\frac{dc_A}{c_A^2} = -kdt. \tag{16}$$

Integrate to get

$$-\frac{1}{c_A} + \frac{1}{c_{Ao}} = -kt. \tag{17}$$

Solve for c_A:

$$c_A(t) = \frac{1}{\frac{1}{c_{Ao}} + kt}. \tag{18}$$

As $t \rightarrow +\infty$, one finds

$$\lim_{t \rightarrow \infty} c_A(t) = 0. \tag{19}$$

3. Find the most general stoichiometric balance for the reaction

$$\nu_1' H_2 + \nu_2' O_2 \leftrightharpoons \nu_3'' H_2O + \nu_4'' OH + \nu_5' O.$$

Rearranging, one writes

$$\nu_1 H_2 + \nu_2 O_2 + \nu_3 H_2O + \nu_4 OH + \nu_5 O = 0. \tag{20}$$

Taking $l = 1$ to correspond to H and $l = 2$ to correspond to O, one solves the equation

$$\boldsymbol{\phi} \cdot \boldsymbol{\nu} = 0. \tag{21}$$

Here $\boldsymbol{\phi}$ is the matrix of elements in each species and $\boldsymbol{\nu}$ is the vector of stoichiometric coefficients. Leaving out the details, one finds

$$\begin{pmatrix} 2 & 0 & 2 & 1 & 0 \\ 0 & 2 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{22}$$

In row echelon form, this becomes

$$\begin{pmatrix} 1 & 0 & 1 & 1/2 & 0 \\ 0 & 1 & 1/2 & 1/2 & 1/2 \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{23}$$

So, ν_3, ν_4, and ν_5 are free variables. Take $\nu_3 = r$, $\nu_4 = s$, and $\nu_5 = t$, so that

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \end{pmatrix} = \begin{pmatrix} -r - s/2 \\ -r/2 - s/2 - t/2 \end{pmatrix} \tag{24}$$

So

$$\begin{pmatrix} \nu_1 \\ \nu_2 \\ \nu_3 \\ \nu_4 \\ \nu_5 \end{pmatrix} = \begin{pmatrix} -r - s/2 \\ -r/2 - s/2 - t/2 \\ r \\ s \\ t \end{pmatrix} = r \begin{pmatrix} -1 \\ -1/2 \\ 1 \\ 0 \\ 0 \end{pmatrix} + s \begin{pmatrix} -1/2 \\ -1/2 \\ 0 \\ 1 \\ 0 \end{pmatrix} + t \begin{pmatrix} 0 \\ -1/2 \\ 0 \\ 0 \\ 1 \end{pmatrix} \tag{25}$$

So the most general balance is given by

$$-(r + s/2)H_2 - (r/2 + s/2 + t/2)O_2 + rH_2O + sOH + tO = 0. \tag{26}$$

Slightly more traditionally, one might say

$$(r + s/2)H_2 + (r/2 + s/2 + t/2)O_2 \leftrightharpoons rH_2O + sOH + tO \tag{27}$$

Taking even more traditionally $r = 2$, one gets

$$(2 + s/2)H_2 + (1 + s/2 + t/2)O_2 \leftrightharpoons 2H_2O + sOH + tO. \tag{28}$$

So when $s = 0$ and $t = 0$, one gets the traditional simple balance.