MAE 770 Written Preliminary Exam #1

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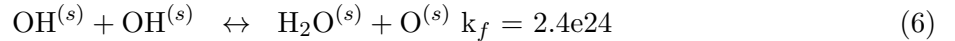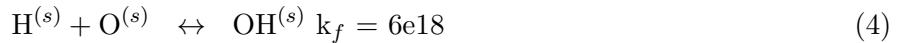
I. Catalytic reaction processes may be modeled by imposing the boundary condition

$$\rho D_k \frac{\partial Y_k^{(g)}}{\partial x_j} \cdot \hat{n}_j = M_k \dot{s}_k \tag{1}$$

in place of the non-catalytic condition

$$\rho D_k \frac{\partial Y_k^{(g)}}{\partial x_j} \cdot \hat{n}_j = 0$$

In this, M_k is the molecular weight and $\dot{s}$ is a source term for surface reactions, which will be a function of concentrations of gas-phase species (g) and surface species (s). The reaction rates for surface reactions are formulated using the law of mass action in the same way as is done for gas-phase reactions, except that concentrations for surface-adsorbed species (s) are expressed as moles/area^2 as opposed to moles/area^3. Concentrations of surface-adsorbed species are also generally expressed as the product of a surface coverage Θ_i and a surface site density Γ (usually a constant). The surface coverage of species i is usually interpreted as the fraction of sites occupied by species i. Now consider the following system of reactions

$$
\begin{align}
\mathrm{H_2}^{(g)} &\leftrightarrow 2\mathrm{H}^{(s)} \ \mathrm{k}_f = 1.9e19 \tag{2} \\
\mathrm{O_2}^{(g)} &\leftrightarrow 2\mathrm{O}^{(s)} \ \mathrm{k}_f = 3e21 \tag{3} \\
\mathrm{H}^{(s)} + \mathrm{O}^{(s)} &\leftrightarrow \mathrm{OH}^{(s)} \ \mathrm{k}_f = 6e18 \tag{4} \\
\mathrm{H}^{(s)} + \mathrm{OH}^{(s)} &\leftrightarrow \mathrm{H_2O}^{(s)} \ \mathrm{k}_f = 1e7 \tag{5} \\
\mathrm{OH}^{(s)} + \mathrm{OH}^{(s)} &\leftrightarrow \mathrm{H_2O}^{(s)} + \mathrm{O}^{(s)} \ \mathrm{k}_f = 2.4e24 \tag{6} \\
\mathrm{H_2O}^{(s)} &\leftrightarrow \mathrm{H_2O}^{(g)} \ \mathrm{k}_f = 1e5 \tag{7}
\end{align}
$$

a.) What are the units of $\dot{s}_k$ and Γ?

b.) Formulate the source terms $\dot{s}_k$ for $k =$gas species and $k =$surface species.

c.) Eq. 1 only holds for gas-phase species participating in surface reactions. In general, what equation holds for surface species participating in surface reactions if the time variation of the surface coverage is held to be zero?

d.) If the forward rate coefficients listed above were determined using a cm, mol, s basis, determine what the forward and backward rate coefficients would be in an SI basis (m, kmol, s).

e.) Explain in detail how one would couple the surface-catalytic equations with a gas-phase CFD code that solves the species conservation equations

$$\frac{\partial \rho Y_k^{(g)}}{\partial t} + \frac{\partial (\rho Y_k^{(g)} u_j - \rho D_k \frac{\partial Y_k^{(g)}}{\partial x_j})}{\partial x_j} = \dot{\omega}_k$$

, where $\dot{\omega}_k$ is the species production rate for gas-phase reactions, using a finite volume method. Would one expect $\sum_{k=\text{gas species}} \dot{\omega}_k$ to be zero everywhere in the computational domain?

(a) The units can be determined from the left hand side of the equation

$$\rho D_k \frac{\partial Y_k^{(g)}}{\partial x_j} \cdot \hat{n}_j = M_k \dot{s}_k \qquad (1)$$

The units of the variables on the left hand side of 1 are

$$\rho = \frac{(mass)}{(length)^3}$$

$$D_k = \frac{(length)^2}{(time)}$$

$$x_j = (length)$$

The mass fraction, $Y_k^{(g)}$, is unitless, as well as the unit normal vector, $\hat{n}_j$. Since the units of molecular weight are, $M_k = (mass)/(mole)$, we can rearrange Eq. (1) and solve for the units of $\dot{s}_k$

$$\begin{aligned}
\dot{s}_k &= \frac{\rho D_k}{M_k} \frac{\partial Y_k^{(g)}}{\partial x_j} \cdot \hat{n}_j \\
&= \frac{(mass)}{(length)^3} \frac{(moles)}{(mass)} \frac{(length)^2}{(time)} \frac{1}{(length)} \\
&= \frac{(moles)}{(length)^2(time)}
\end{aligned} \qquad (2)$$

Expressing surface coverage, Θ_i, as the fraction of sites occupied by species i implies that it is unitless. The concentration of surface-absorbed species, C_k, has units $(moles)/(length)^2$ and must be equivalent to the product of surface coverage and surface site density, Γ; therefore, the units of surface site density must be $(moles)/(length)^2$. Thus, the units for $\dot{s}_k$ and Γ, expressed in the same basis as the problem was posed, are

$$\boxed{\dot{s}_k = \frac{moles}{area^2 - sec}}$$

$$\boxed{\Gamma = \frac{moles}{area^2}}$$

(b) The formulation of the source terms $\dot{s}_k$ for $k =$ gas species and $k =$ surface species can be expressed as

$$\dot{s}_k = \sum_{r=1}^{N_r} \left[(\nu_{k,r}'' - \nu_{k,r}')(R_{f,r} - R_{b,r}) \right]$$

$$R_{f,r} = k_{f,r} \prod_{i=1}^{N_k} (C_i^{\nu_{i,r}'}), \quad R_{b,r} = k_{b,r} \prod_{i=1}^{N_k} (C_i^{\nu_{i,r}''}) \qquad (3)$$

where $\nu_{k,r}'$ is the stoichometric coefficient for species k in reaction r as a reactant in the forward reaction, and $\nu_{k,r}''$ is for that species as a product in the forward reaction. N_k denotes the number of species and N_r denotes the number of reactions. Additionally, the backward rate coefficient $k_{b,r}$ is usually determined from the forward rate coefficient $k_{f,r}$ and the equilibrium constant $k_{c,r}$. Both $k_{f,r}$ and $k_{c,r}$ are often available as functions of temperature. Thus, using Eq. (3) the $\dot{s}_k$ source

terms can be expressed as

$$\dot{s}_{H_2}^{(g)} = -\left(k_{f,1}C_{H_2}^{(g)} - \frac{k_{f,1}}{k_{c,1}}C_H^{(s)2}\right) \tag{4}$$

$$\dot{s}_{O_2}^{(g)} = -\left(k_{f,2}C_{O_2}^{(g)} - \frac{k_{f,2}}{k_{c,2}}C_O^{(s)2}\right) \tag{5}$$

$$\dot{s}_{H_2O}^{(g)} = \left(k_{f,6}C_{H_2O}^{(s)} - \frac{k_{f,6}}{k_{c,6}}C_{H_2O}^{(g)}\right) \tag{6}$$

$$\dot{s}_H^{(s)} = 2\left(k_{f,1}C_{H_2}^{(g)} - \frac{k_{f,1}}{k_{c,1}}C_H^{(s)2}\right)$$
$$- \left(k_{f,3}C_H^{(s)}C_O^{(s)} - \frac{k_{f,3}}{k_{c,3}}C_{OH}^{(s)}\right) \tag{7}$$
$$- \left(k_{f,4}C_H^{(s)}C_{OH}^{(s)} - \frac{k_{f,4}}{k_{c,4}}C_{H_2O}^{(s)}\right)$$

$$\dot{s}_O^{(s)} = 2\left(k_{f,2}C_{O_2}^{(g)} - \frac{k_{f,2}}{k_{c,2}}C_O^{(s)2}\right)$$
$$- \left(k_{f,3}C_H^{(s)}C_O^{(s)} - \frac{k_{f,3}}{k_{c,3}}C_{OH}^{(s)}\right) \tag{8}$$
$$+ \left(k_{f,5}C_{OH}^{(s)\,2} - \frac{k_{f,5}}{k_{c,5}}C_{H_2O}^{(s)}C_O^{(s)}\right)$$

$$\dot{s}_{OH}^{(s)} = \left(k_{f,3}C_H^{(s)}C_O^{(s)} - \frac{k_{f,3}}{k_{c,3}}C_{HO}^{(s)}\right)$$
$$- \left(k_{f,4}C_H^{(s)}C_{OH}^{(s)} - \frac{k_{f,4}}{k_{c,4}}C_{H_2O}^{(s)}\right) \tag{9}$$
$$- 2\left(k_{f,5}C_{OH}^{(s)\,2} - \frac{k_{f,5}}{k_{c,5}}C_{H_2O}^{(s)}C_O^{(s)}\right)$$

$$\dot{s}_{H_2O}^{(s)} = \left(k_{f,4}C_H^{(s)}C_{OH}^{(s)} - \frac{k_{f,4}}{k_{c,4}}C_{H_2O}^{(s)}\right)$$
$$+ \left(k_{f,5}C_{OH}^{(s)\,2} - \frac{k_{f,5}}{k_{c,5}}C_{H_2O}^{(s)}C_O^{(s)}\right) \tag{10}$$
$$- \left(k_{f,6}C_{H_2O}^{(s)} - \frac{k_{f,6}}{k_{c,6}}C_{H_2O}^{(g)}\right)$$

(c) By characterizing the concentrations of surface species as

$$C_i = \theta_i\Gamma \tag{11}$$

and differentiating in time

$$\frac{\partial C_i}{\partial t} = \frac{\partial \theta_i}{\partial t}\Gamma = \dot{s}_i^{(s)} \tag{12}$$

Thus, if the time variation of the surface coverage is held to be zero

$$\frac{\partial \theta_i}{\partial t} = \frac{\dot{s}_i^{(s)}}{\Gamma} = 0 \tag{13}$$

For i=surface species. This reduces Eq.s (7-10) to an algebraic system to be solved for all surface species concentrations. The algebraic system is nonlinear, and it can be solved by a Newton or quasi-Newton iteration in practice.

(d) Determining the units for the forward and backward rate coefficients, k_f and k_b, begins with looking at the units of $\dot{s}_k$. Since the source term was found to have units of $moles/(area^2\text{-}sec)$, in the generic sense, it would have proper units of $mol/(cm^2\text{-}s)$ using a cm, mol, s basis. The units

of k_f and k_b will vary for each reaction, but must ultimately conform to the fact that $R_{f,r}$ and $R_{b,r}$ in Eq. (3) must have units of $mol/(cm^2\text{-}s)$. For the first reaction

$$k_{f,1} = 1.9e19 \quad \frac{cm}{s} \tag{14}$$

which satisfies

$$R_{f,1} = k_{f,1} C_{H_2}^{(g)} = \frac{cm}{s}\frac{mol}{cm^3} = \frac{mol}{cm^2\text{-}s} \tag{15}$$

More generally, the units for k_f can be expressed as

$$k_{f,r} = \frac{mol}{(cm^2)(s) \prod_{i=1}^{N_k} \left(\left(\frac{mol}{cm^3}\right)^{\nu_{i,r}'^{(g)}} \left(\frac{mol}{cm^2}\right)^{\nu_{i,r}'^{(s)}} \right)} \tag{16}$$

where $\nu_{i,r}'^{(g)}$ is the stoichiometric coefficient of gas-phase reactant species i in reaction r, and $\nu_{i,r}'^{(s)}$ is the stoichiometric coefficient of surface reactant species i in reaction r. Since $R_{b,r}$ must also have units of $mol/(cm^2\text{-}s)$, the same reasoning can be used to derive

$$k_{b,r} = \frac{mol}{(cm^2)(s) \prod_{i=1}^{N_k} \left(\left(\frac{mol}{cm^3}\right)^{\nu_{i,r}''^{(g)}} \left(\frac{mol}{cm^2}\right)^{\nu_{i,r}''^{(s)}} \right)} \tag{17}$$

where $\nu_{i,r}''^{(g)}$ and $\nu_{i,r}''^{(s)}$ are the are the stoichiometric coefficients of gas-phase and surface product species i in reaction r, respectively. Using Eq.s (16-17), the units of $k_{f,r}$ and $k_{b,r}$ (using a cm, mol, s basis) are

$$
\begin{aligned}
k_{f,1} &= 1.9e19 \quad \frac{cm}{s} & k_{b,1} &= \frac{k_{f,1}}{k_{c,1}}\frac{cm^2}{mol\text{-}s} \\
k_{f,2} &= 3e21 \quad \frac{cm}{s} & k_{b,2} &= \frac{k_{f,2}}{k_{c,2}}\frac{cm^2}{mol\text{-}s} \\
k_{f,3} &= 6e18 \quad \frac{cm^2}{mol\text{-}s} & k_{b,3} &= \frac{k_{f,3}}{k_{c,3}}\frac{1}{s} \\
k_{f,4} &= 1e7 \quad \frac{cm^2}{mol\text{-}s} & k_{b,4} &= \frac{k_{f,4}}{k_{c,4}}\frac{1}{s} \\
k_{f,5} &= 2.4e24 \quad \frac{cm^2}{mol\text{-}s} & k_{b,5} &= \frac{k_{f,5}}{k_{c,5}}\frac{cm^2}{mol\text{-}s} \\
k_{f,6} &= 1e5 \quad \frac{1}{s} & k_{b,6} &= \frac{k_{f,6}}{k_{c,6}}\frac{cm}{s}
\end{aligned}
\tag{18}
$$

Converting $k_{f,r}$ in Eq. (18) to an SI basis (m, $kmol$, s), using $m = 100\,cm$ and $kmol = 1000\,mol$, yields

$$
\boxed{
\begin{aligned}
k_{f,1} &= 1.9e17 \quad \frac{m}{s} \\
k_{f,2} &= 3e19 \quad \frac{m}{s} \\
k_{f,3} &= 6e17 \quad \frac{m^2}{kmol\text{-}s} \\
k_{f,4} &= 1e6 \quad \frac{m^2}{kmol\text{-}s} \\
k_{f,5} &= 2.4e23 \quad \frac{m^2}{kmol\text{-}s} \\
k_{f,6} &= 1e5 \quad \frac{1}{s}
\end{aligned}
}
\tag{19}
$$

Using this and Eq. (17), $k_{b,r}$ can also be defined in an SI basis

$$
\begin{aligned}
k_{b,1} &= \frac{1.9e17}{k_{c,1}} \quad \frac{m^2}{kmol\text{-}s} \\[4pt]
k_{b,2} &= \frac{3e19}{k_{c,2}} \quad \frac{m^2}{kmol\text{-}s} \\[4pt]
k_{b,3} &= \frac{6e17}{k_{c,3}} \quad \frac{1}{s} \\[4pt]
k_{b,4} &= \frac{1e6}{k_{c,4}} \quad \frac{1}{s} \\[4pt]
k_{b,5} &= \frac{2.4e23}{k_{c,5}} \quad \frac{m^2}{kmol\text{-}s} \\[4pt]
k_{b,6} &= \frac{1e5}{k_{c,6}} \quad \frac{m}{s}
\end{aligned}
\tag{20}
$$

It should be noted that the equilibrium constants $k_{c,r}$ must be in an SI basis for the units in Eq. (20) to be the correct units of $k_{b,r}$. If they in a another basis, then another conversion will be necessary. The conversion of $k_{c,r}$ from a cm, mol, s basis to a m, $kmol$, s basis can be derived from Eq.s (16-17) as

$$
k_{c,r}^{(cgs)} = \frac{k_{f,r}^{(cgs)}}{k_{b,r}^{(cgs)}} = \frac{\prod_{i=1}^{N_k}\left(\left(\frac{mol}{cm^3}\right)^{\nu_{i,r}^{''(g)}}\left(\frac{mol}{cm^2}\right)^{\nu_{i,r}^{''(s)}}\right)}{\prod_{i=1}^{N_k}\left(\left(\frac{mol}{cm^3}\right)^{\nu_{i,r}^{'(g)}}\left(\frac{mol}{cm^2}\right)^{\nu_{i,r}^{'(s)}}\right)}
\tag{21}
$$

$$
= \frac{(mol)^a}{(cm)^b}
$$

$$
a = \sum_{i=1}^{N_k}\left(\nu_{i,r}^{''} - \nu_{i,r}^{'}\right)
$$

$$
b = \sum_{i=1}^{N_k}\left(3(\nu_{i,r}^{''} - \nu_{i,r}^{'})^{(g)} + 2(\nu_{i,r}^{''} - \nu_{i,r}^{'})^{(s)}\right)
\tag{22}
$$

$$
k_{c,r}^{(mks)} = k_{c,r}^{(cgs)}\left(\frac{kmol}{1000\,mol}\right)^a\left(\frac{100\,cm}{m}\right)^b
\tag{23}
$$

(e) The coupling of the catalytic boundary condition specified in Eq. (1) can be accomplished by first examining the finite volume (FV) method used. By integrating and applying the Green-Gauss theorem, the species conservation equation can written as

$$
\frac{\partial}{\partial t}\int_\Omega \rho Y_k^{(g)}d\Omega + \int_\Gamma\left(\rho Y_k^{(g)}u_j - \rho D_k\frac{\partial Y_k^{(g)}}{\partial x_j}\right)\cdot\hat{n}_j d\Gamma = \int_\Omega \dot{w}_k d\Omega
\tag{24}
$$

Where Ω is a cell volume domain and Γ is the interface/boundaries of that cell. For a first order FV scheme, $\rho Y_k^{(g)}$ and $\dot{w}_k$ become cell averaged quantities

$$
\overline{\rho Y_k^{(g)}} = \frac{1}{V}\int_\Omega \rho Y_k^{(g)}d\Omega
\tag{25}
$$

$$
\overline{\dot{w}_k} = \frac{1}{V}\int_\Omega \dot{w}_k d\Omega
\tag{26}
$$

where V is the volume of the cell. The fluxes at the cell interfaces are discontinuous; therefore, a flux function $\vec{F} = \vec{F}(\vec{q}_L, \vec{q}_R)$ is used evaluate fluxes at the cell interface. The vectors $\vec{q}_{L,R}$ denote the interface left and right states used in evaluating the flux. If Eq. (24) is integrated explicitly in time, $\overline{\rho Y_k^{(g)}}$ can be updated via

$$
(\overline{\rho Y_k^{(g)}})_i^{n+1} = (\overline{\rho Y_k^{(g)}})_i^n - \Delta t(R_k)_i
\tag{27}
$$

Where the superscript n denotes the time level, the subscript i denotes the node or cell number, and $(R_k)_i$ is the residual of species k flux at node or cell i computed by summing the fluxes/sources at each cell face. For a node-centered FV method a dual control volume is constructed around each node, enabling the residual to be formulated in an edge-based fashion. An advantage of using a node-centered FV method is that it is easy to implement the boundary condition posed in Eq. (1) via specifying the flux (weak enforcement). By looping over nodes on the boundary with the catalytic surface, the residual can be set by

$$(R_k)_{ibc} = \rho D_k \frac{\partial Y_k^{(g)}}{\partial x_j} \cdot \hat{n}_j - M_k \dot{s}_k \tag{28}$$

By this weak enforcement of the catalytic boundary condition, Eq. (1) is satisfied as the solution of $Y_k^{(g)}$ converges to steady state and $R_k = 0$.

Since it was previously shown that $\dot{s}_k$ is a function of both the gas phase and surface species concentrations, a decision must be made as to how to couple updating the surface-absorbed species. One option is to update the surface species at the same time level as the gas phase species have been updated. While admittedly overly simplistic, here is what an implementation of solving one iteration of this loosely coupled scheme might look like this

Listing 1: Simple Implementation

```
do timestep = 1, n_timesteps

   ! Form the residual at all nodes
   call add_inviscid_fluxes(q, grid, residual)
   call add_viscous_flux(q, grid, residual)

   ! Set other non-surface boundary conditions
   call set_nonsurface_bc(q, grid, residual)

   ! Set the catalytic boundary condition
   do inode = 1, nsurface_nodes
      bc_node = get_node_on_surface(inode)
      residual(:, bc_node) = set_catalytic_bc(q(:, bc_node), &
                             surface_species(:, bc_node))

      ! Update the surface species concentrations
      sdot = get_surface_source_term(q(:, bc_node))
      surface_species(:, bc_node) = surface_species(:, bc_node) &
                             + sdot*dt
   end do

   ! Update the conserved (gas-phase) quantities
   do node = 1, nnodes
      q(:, node) = q(:, node) - dt*residual(:, node)
   end do

end do
```

In this simple illustration, the source term vector used to update the system is evaluated with all concentrations at the same time level. The surface concentrations are then updated via

$$C_k^{(s)^{n+1}} = C_k^{(s)^n} + (\Delta t)\left(\dot{s}_k(C^{(g)^n}, C^{(s)^n})\right) \tag{29}$$

for k=surface species. Eq. (29) can also be expressed in terms of surface coverage $C_k^{(s)} = \theta_k \Gamma$

$$\theta_k^{n+1} = \theta_k^n + \left(\frac{\Delta t}{\Gamma}\right)\left(\dot{s}_k(C^{(g)^n}, C^{(s)^n})\right) \tag{30}$$

As was previously shown, if the time variation of the surface coverage is held to be zero, then $\dot{s}_k = 0$ for k=surface species. This results in an algebraic system of equations to be solved for at the boundary nodes that can be solved via a Newton iteration to obtain the surface concentrations. In this case, the step of updating and storing the surface species concentrations can be handled in the routine "`set_catalytic_bc`" that calculates the boundary flux.

It is also worth noting that an implicit approach can also be derived using a "loosely coupled" approach for updating the gas phase and surface species. Recasting Eq. (24) as

$$\mathbf{A}\Delta(\overline{\rho Y_k^{(g)}})_i = -(R_k)_i \tag{31}$$

Where $\mathbf{A}$ is the jacobian matrix of the residual fluxes, with the time derivative terms on the diagonal. This becomes a Newton method (or quasi-Newton method, depending of the exactness of $\mathbf{A}$), as the system is solved for the state update and marched forward to steady state. Since there is still a need to account for the surface species in this formulation, the surface concentrations can be updated with the gas concentrations in the overall system; however, this drastically increases the number of equations to solve. This is impractical, since the surface concentrations will be zero everywhere other than on the catalytic surface. A better approach is to loosely couple the gas-phase system to the surface concentrations, where only $\Delta(\overline{\rho Y_k^{(g)}})_i$ is solved for at a given timestep and the law of mass action can be used to enforce elemental conservation in updating the surface concentrations. In practice, this could be done as

$$\theta_k^{n+1} = \theta_k^n + \left(\frac{\Delta t}{\Gamma}\right)\left(\dot{s}_k'(C^{(g)^{n+1}}, C^{(s)^n})\right) \tag{32}$$

For k = surface species and $\dot{s}_k'$ are the source terms from Eq.s (7-10) evaluated such that $\dot{s}_k$ for k = gas species is zero.

Determining whether the source term components sum to zero is based on elemental conservation. $\sum_{k=\text{gas species}} \dot{w}_k$ will only be zero everywhere in the computational domain if $\sum_{k=\text{surface species}} \dot{w}_k = 0$. If there is production or destruction of surface species, then the source terms of the gas-phase species will not sum to zero, because this would violate elemental conservation. For example, the absorbtion of atomic hydrogen is accounted for in the entire chemical species source term, $\sum_{k=\text{all species}} \dot{w}_k$, but not in just $\sum_{k=\text{gas species}} \dot{w}_k$; therefore, $\sum_{k=\text{gas species}} \dot{w}_k \neq 0$ at the catalytic surface boundary.