

# MAE 770 Written Preliminary Exam #1

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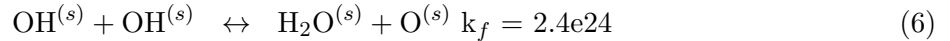
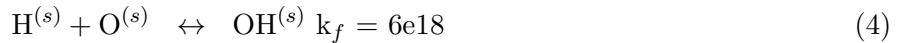
I. Catalytic reaction processes may be modeled by imposing the boundary condition

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

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<sup>2</sup> as opposed to moles/area<sup>3</sup>. Concentrations of surface-adsorbed species are also generally expressed as the product of a surface coverage  $\Theta_i$  and a surface site density  $\Gamma$  (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



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

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

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

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

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

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

Using the following nomenclature:

$m$	mass
$N$	number of molecules
$l$	length
$t$	time

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

$$\begin{aligned} \rho &= \frac{m}{l^3} \\ D_k &= \frac{l^2}{t} \\ x_j &= l \end{aligned}$$

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

$$\begin{aligned} \dot{s}_k &= \frac{\rho D_k}{M_k} \frac{\partial Y_k^{(g)}}{\partial x_j} \cdot \hat{n}_j \\ &= \frac{m}{l^3} \frac{N}{m} \frac{l^2}{t} \frac{1}{l} \\ &= \frac{N}{l^2 t} \end{aligned} \quad (2)$$

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

$$\begin{aligned} \dot{s}_k &= \frac{\text{moles}}{\text{area}^2 \cdot \text{sec}} \\ \Gamma &= \frac{\text{moles}}{\text{area}^2} \end{aligned}$$

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

$$\begin{aligned} \dot{s}_k &= \sum_{r=1}^{N_r} \left[ (\nu_{k,r}'' - \nu_{k,r}') (R_{f,r} - R_{b,r}) \right] \\ R_{f,r} &= k_{f,r} \prod_{i=1}^{N_k} (C_i^{\nu_{i,r}'}), \quad R_{b,r} = k_{b,r} \prod_{i=1}^{N_k} (C_i^{\nu_{i,r}''}) \end{aligned} \quad (3)$$

where  $\nu_{k,r}'$  is the stoichiometric 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  $k_{c,r}$ . The later of these is often available as a curve fit function of temperature. Thus, using Eq. (3) the  $\dot{s}_k$

source terms can be expressed as

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

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

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

$$\begin{aligned} \dot{s}_H^{(s)} = & 2 \left( k_{f,1} C_{H_2}^{(g)} - \frac{k_{f,1}}{k_{c,1}} C_H^{(s)2} \right) \\ & - \left( k_{f,3} C_H^{(s)} C_O^{(s)} - \frac{k_{f,3}}{k_{c,3}} C_{OH}^{(s)} \right) \end{aligned} \quad (7)$$

$$- \left( k_{f,4} C_H^{(s)} C_{OH}^{(s)} - \frac{k_{f,4}}{k_{c,4}} C_{H_2O}^{(s)} \right)$$

$$\begin{aligned} \dot{s}_O^{(s)} = & 2 \left( k_{f,2} C_{O_2}^{(g)} - \frac{k_{f,2}}{k_{c,2}} C_O^{(s)2} \right) \\ & - \left( k_{f,3} C_H^{(s)} C_O^{(s)} - \frac{k_{f,3}}{k_{c,3}} C_{OH}^{(s)} \right) \end{aligned} \quad (8)$$

$$+ \left( k_{f,5} C_{OH}^{(s)2} - \frac{k_{f,5}}{k_{c,5}} C_{H_2O}^{(s)} C_O^{(s)} \right)$$

$$\begin{aligned} \dot{s}_{OH}^{(s)} = & \left( k_{f,3} C_H^{(s)} C_O^{(s)} - \frac{k_{f,3}}{k_{c,3}} C_{HO}^{(s)} \right) \\ & - \left( k_{f,4} C_H^{(s)} C_{OH}^{(s)} - \frac{k_{f,4}}{k_{c,4}} C_{H_2O}^{(s)} \right) \end{aligned} \quad (9)$$

$$- 2 \left( k_{f,5} C_{OH}^{(s)2} - \frac{k_{f,5}}{k_{c,5}} C_{H_2O}^{(s)} C_O^{(s)} \right)$$

$$\begin{aligned} \dot{s}_{H_2O}^{(s)} = & \left( k_{f,4} C_H^{(s)} C_{OH}^{(s)} - \frac{k_{f,4}}{k_{c,4}} C_{H_2O}^{(s)} \right) \\ & + \left( k_{f,5} C_{OH}^{(s)2} - \frac{k_{f,5}}{k_{c,5}} C_{H_2O}^{(s)} C_O^{(s)} \right) \end{aligned} \quad (10)$$

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

(c) By characterizing the concentrations of surface species as

$$C_i = \theta_i \Gamma \quad (11)$$

It becomes clear that

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

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

$$\left[ \frac{\partial \theta_i}{\partial t} = \frac{\dot{s}_i^{(s)}}{\Gamma} = 0 \right] \quad (13)$$

For  $i$ =surface species. This reduces Eq.s (7-10) to a set of linear equations to be solved for all surface species concentrations.

(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<sup>2</sup>-sec)*, in the generic sense, it would have proper units of *mol/(cm<sup>2</sup>-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<sup>2</sup>-s)*. For the first reaction

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

which satisfies

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

More generally, the units for  $k_f$  can be expressed as

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

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  $mol/(cm \cdot s)$ , the same reasoning can be used to derive

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

where  $\nu''_{i,r}(g)$  and  $\nu''_{i,r}(s)$  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

$$\begin{array}{ll} k_{f,1} = 1.9e19 & \frac{cm}{s} \\ k_{f,2} = 3e21 & \frac{cm}{s} \\ k_{f,3} = 6e18 & \frac{cm^2}{mol \cdot s} \\ k_{f,4} = 1e7 & \frac{cm^2}{mol \cdot s} \\ k_{f,5} = 2.4e24 & \frac{cm^2}{mol \cdot s} \\ k_{f,6} = 1e5 & \frac{1}{s} \end{array} \quad \begin{array}{ll} k_{b,1} = \frac{k_{f,1}}{k_{c,1}} \frac{cm^2}{mol \cdot s} \\ k_{b,2} = \frac{k_{f,2}}{k_{c,2}} \frac{cm^2}{mol \cdot s} \\ k_{b,3} = \frac{k_{f,3}}{k_{c,3}} \frac{1}{s} \\ k_{b,4} = \frac{k_{f,4}}{k_{c,4}} \frac{1}{s} \\ k_{b,5} = \frac{k_{f,5}}{k_{c,5}} \frac{cm^2}{mol \cdot s} \\ k_{b,6} = \frac{k_{f,6}}{k_{c,6}} \frac{cm}{s} \end{array} \quad (18)$$

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

$k_{f,1} = 1.9e17$	$\frac{m}{s}$
$k_{f,2} = 3e19$	$\frac{m}{s}$
$k_{f,3} = 6e17$	$\frac{m^2}{kmol \cdot s}$
$k_{f,4} = 1e6$	$\frac{m^2}{kmol \cdot s}$
$k_{f,5} = 2.4e23$	$\frac{m^2}{kmol \cdot s}$
$k_{f,6} = 1e5$	$\frac{1}{s}$

(19)

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

$$\boxed{\begin{array}{ll} k_{b,1} = \frac{1.9e17}{k_{c,1}} & \frac{m^2}{kmol \cdot s} \\ k_{b,2} = \frac{3e19}{k_{c,2}} & \frac{m^2}{kmol \cdot s} \\ k_{b,3} = \frac{6e17}{k_{c,3}} & \frac{1}{s} \\ k_{b,4} = \frac{1e6}{k_{c,4}} & \frac{1}{s} \\ k_{b,5} = \frac{2.4e23}{k_{c,5}} & \frac{m^2}{kmol \cdot s} \\ k_{b,6} = \frac{1e5}{k_{c,6}} & \frac{m}{s} \end{array}} \quad (20)$$

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

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

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

$$a = \sum_{i=1}^{N_k} (\nu''_{i,r} - \nu'_{i,r}) \quad (22)$$

$$b = \sum_{i=1}^{N_k} (3(\nu''_{i,r} - \nu'_{i,r})^{(g)} + 2(\nu''_{i,r} - \nu'_{i,r})^{(s)})$$

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

- (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

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

Where  $\Omega$  is a cell volume domain and  $\Gamma$  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

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

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

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

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

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

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

By this weak enforcement of the catalytic boundary condition, Eq. (1) is satisfied as the solution of  $\overline{Y_k^{(g)}}$  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. In this explicit formulation, it is plausible to adopt a “loosely coupled” approach, where the surface species are lagged and updated after the gas phase species have been updated. This introduces an added explicitness to the scheme, which may impact robustness, but it is very straightforward to program. While overly simplistic, an implementation of solving one iteration of this loosely coupled scheme might look like this

Listing 1: Loosely Coupled Implementation

```
! Form the residual at all nodes
do iedge = 1, nedges
  node1 = edge_to_node(1,iedge)
  node2 = edge_to_node(2,iedge)

  flux = get_flux(q(:,node1),q(:,node2))

  residual(:,node1) = residual(:,node1) + flux
  residual(:,node2) = residual(:,node2) - flux
end do

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

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

! Update the surface species concentrations
do inode = 1, nbc_nodes
  bc_node = get_node_on_surface(inode)
  sdot = get_surface_source_term(q(:,bc_node))
  surface_species(:,bc_node) = surface_species(:,bc_node) &
    + sdot*dt
end do
```

In this simple illustration, the gas-phase species mass fractions (or densities) are updated to the next time-level, and are in turn used to compute the source term vector used to update the surface species concentrations via

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

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

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

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 expression to be solved for at the boundary nodes that will evolve the gas-phase species concentrations, but not the surface species concentrations. In this case, the final step of updating the surface species concentrations is not needed; however, their quantities should still be stored in the routine “`set_catalytic_bc`” that calculates the boundary flux, as they are still needed to evaluate the source term  $\dot{s}_k$ .

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 absorption 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.