

# MAE 770 Written Preliminary Exam #1

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1. 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

$$\dot{s}_k = \frac{\text{moles}}{\text{area}^2 \cdot \text{sec}}$$

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

2. 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 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  $k_{b,r}$  can be determined from the forward rate coefficient  $k_{f,r}$  and the equilibrium constant  $K_{c,r}$ . This is much better, since the law of mass action enables the determination of  $K_{c,r}$  as a function of species concentrations, resulting in  $\dot{s}_k = \dot{s}_k(k_{f,r}, C_1, \dots, C_{N_k})$ . Thus, using Eq. (3) the  $\dot{s}_k$  source terms can be expressed as

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

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

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

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

$$\begin{aligned} & - \left( k_{f,4} C_H^{(s)} C_{OH}^{(s)} - \frac{k_{f,4}}{k_{c,4}} C_{H_2O}^{(s)} \right) \\ \dot{s}_O^{(s)} = & 2 \left( k_{f,2} C_{O_2}^{(g)} - \frac{k_{f,2}}{k_{c,2}} C_O^{(s)2} \right) \\ & - \left( k_{f,3} C_H^{(s)} C_O^{(s)} - \frac{k_{f,3}}{k_{c,3}} C_{OH}^{(s)} \right) \end{aligned} \quad (8)$$

$$\begin{aligned} & + \left( k_{f,5} C_{OH}^{(s)2} - \frac{k_{f,5}}{k_{c,5}} C_{H_2O}^{(s)} C_O^{(s)} \right) \\ \dot{s}_{OH}^{(s)} = & 2 \left( k_{f,3} C_{OH}^{(s)} - \frac{k_{f,3}}{k_{c,3}} C_H^{(s)} C_O^{(s)} \right) \\ & - \left( k_{f,4} C_H^{(s)} C_{OH}^{(s)} - \frac{k_{f,4}}{k_{c,4}} C_{H_2O}^{(s)} \right) \end{aligned} \quad (9)$$

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

3. 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  $moles/(area^2 \cdot sec)$ , in the generic sense, it would have proper units of  $mol/(cm^2 \cdot s)$  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  $mol/(cm^2-s)$ . For the first reaction

$$k_{f,1} = 1.9e19 \quad \frac{cm}{s} \quad (11)$$

which satisfies

$$R_{f,1} = k_{f,1} C_{H_2}^{(g)} = \frac{cm}{s} \frac{mol}{cm^3} = \frac{mol}{cm^2-s} \quad (12)$$

Much more generally, the units for  $k_f$  can be expressed as

$$k_{f,r} = \frac{mol}{(cm^2)(s) \prod_{i=1}^{N_k} \left( \left( \frac{mol}{cm^3} \right)^{\nu_{i,r}'^{(g)}} \left( \frac{mol}{cm^2} \right)^{\nu_{i,r}'^{(s)}} \right)} \quad (13)$$

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

$$k_{b,r} = \frac{mol}{(cm^2)(s) \prod_{i=1}^{N_k} \left( \left( \frac{mol}{cm^3} \right)^{\nu_{i,r}''^{(g)}} \left( \frac{mol}{cm^2} \right)^{\nu_{i,r}''^{(s)}} \right)} \quad (14)$$

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 (13-14), the units of  $k_{f,r}$  and  $k_{b,r}$  (using a  $cm$ ,  $mol$ ,  $s$  basis) are

$$\begin{array}{ll} k_{f,1} = 1.9e19 & \frac{cm}{s} \\ k_{f,2} = 3e21 & \frac{cm}{s} \\ k_{f,3} = 6e18 & \frac{cm^2}{mol-s} \\ k_{f,4} = 1e7 & \frac{cm^2}{mol-s} \\ k_{f,5} = 2.4e24 & \frac{cm^2}{mol-s} \\ k_{f,6} = 1e5 & \frac{1}{s} \end{array} \quad \begin{array}{ll} k_{b,1} = \frac{k_{f,1}}{k_{c,1}} \frac{cm^2}{mol-s} \\ k_{b,2} = \frac{k_{f,2}}{k_{c,2}} \frac{cm^2}{mol-s} \\ k_{b,3} = \frac{k_{f,3}}{k_{c,3}} \frac{1}{s} \\ k_{b,4} = \frac{k_{f,4}}{k_{c,4}} \frac{1}{s} \\ k_{b,5} = \frac{k_{f,5}}{k_{c,5}} \frac{cm^2}{mol-s} \\ k_{b,6} = \frac{k_{f,6}}{k_{c,6}} \frac{cm}{s} \end{array} \quad (15)$$

by the law of mass action, the equilibrium constant can be defined as

$$k_{c,r} = \frac{\prod_{i=1}^{N_k} (C_i^{\nu_{i,r}''})}{\prod_{i=1}^{N_k} (C_i^{\nu_{i,r}'})} \quad (16)$$

Converting  $k_{f,r}$  in Eq. (15) to an SI basis ( $m$ ,  $kmol$ ,  $s$ ), using  $m = 100 \text{ cm}$

and  $kmol = 1000\ mol$ , yields

$$\begin{aligned}
 k_{f,1} &= 1.9e17 \quad \frac{m}{s} \\
 k_{f,2} &= 3e19 \quad \frac{m}{s} \\
 k_{f,3} &= 6e17 \quad \frac{m^2}{kmol \cdot s} \\
 k_{f,4} &= 1e6 \quad \frac{m^2}{kmol \cdot s} \\
 k_{f,5} &= 2.4e23 \quad \frac{m^2}{kmol \cdot s} \\
 k_{f,6} &= 1e5 \quad \frac{1}{s}
 \end{aligned} \tag{17}$$