

MAE 770 Written Preliminary Exam #1

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February 21, 2016

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, 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 N/l^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 N/l^2 . Thus, the units for \dot{s}_k and Γ , 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 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 $k_{b,r}$ 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, C_i , 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

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

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

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

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

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

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

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

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

- 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

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

Using this and Eq. (16), $k_{b,r}$ can also be defined in an SI basis

$$\begin{array}{ll}
 k_{b,1} = 1.9e17 \left(\frac{C_{H_2}^{(g)}}{C_H^{(s)^2}} \right) & \frac{m^2}{kmol \cdot s} \\
 k_{b,2} = 3e19 \left(\frac{C_{O_2}^{(g)}}{C_O^{(s)^2}} \right) & \frac{m^2}{kmol \cdot s} \\
 k_{b,3} = 6e17 \left(\frac{C_H^{(s)} C_O^{(s)}}{C_{OH}^{(s)}} \right) & \frac{1}{s} \\
 k_{b,4} = 1e6 \left(\frac{C_H^{(s)} C_{OH}^{(s)}}{C_{H_2O}^{(s)}} \right) & \frac{1}{s} \\
 k_{b,5} = 2.4e23 \left(\frac{C_{OH}^{(s)^2}}{C_{H_2O}^{(s)} C_O^{(s)}} \right) & \frac{m^2}{kmol \cdot s} \\
 k_{b,6} = 1e5 \left(\frac{C_{H_2O}^{(s)}}{C_{H_2O}^{(g)}} \right) & \frac{m}{s}
 \end{array} \tag{18}$$

It should be noted that the species concentrations $C_i^{(g,s)}$ must be in an SI basis for the units in Eq. (18) to be the correct units of $k_{b,r}$. If the concentrations are in a another basis, then another conversion will be necessary.