MAE 770 Written Preliminary Exam #1

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1. The units can be determined from the left hand side of the equation

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

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

$$\rho = \frac{m}{l^3}$$

$$D_k = \frac{l^2}{t}$$

$$x_j = l$$

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 $\dot{s}_k$

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

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

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

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

2. 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 $k_{b,r}$ 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 $\dot{s}_k = \dot{s}_k(k_{f,r}, C_1, \ldots, C_{N_k})$. Thus, using Eq. (3) the $\dot{s}_k$ source terms can be expressed as

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

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

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

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

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

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

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

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 $moles/(area^2\text{-}sec)$, 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

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

which satisfies

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

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

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

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

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

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

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

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

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

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

and $kmol = 1000\,mol$, yields

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

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

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

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.

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