Reaction rate calculation and unit conversion

The notations are as follows:
A=pre-exponential in sec^{-1}
s=sticking coefficient (dimensionless)
σ=site density in $mol.cm^{-2}$
n=reaction order (dimensionless integer)
β=temperature exponent (dimensionless)
E=activation energy in $kcal.mol^{-1}$
R=ideal gas constant in $kcal.mol^{-1}.K^{-1}$
T=temperature in K
T_o=reference temperature in K (T_o=300 K)
M=molecular weight in $gm.mol^{-1}$
C_g=concentration of gas phase species in $mol.cm^{-3}$
C_s=concentration of surface species in $mol.cm^{-2}$
C_*=concentration of vacancies in $mol.cm^{-2}$
k=rate constant in $(cm^2.mol^{-1})^n.cm.sec^{-1}$ for adsorption and $(cm^2.mol^{-1})^{n-1}.sec^{-1}$ for desorption or surface reaction
r=rate of reaction in $mol.cm^{-2}.sec^{-1}$
P_{atm}=atmospheric pressure in $dyne.cm^{-2}$
k'=rate constant in sec^{-1}
$\sqrt{\frac{RT}{2\pi M}}$ has units of $cm.sec^{-1}$.

The following equations are used for rate calculation:

$$r=k\left(C_g\right)\left(C_*\right)^n \quad \text{for adsorption,} \quad (1)$$

$$r=k\left(C_s\right)^n \quad \text{for desorption,} \quad (2)$$

and

$$r=k\prod_{i=1}^{n}\left(C_s\right)_i \quad \text{for surface reaction.} \quad (3)$$

The following equations are used for rate constant (k) calculation:

$$k=\frac{s}{\sigma^n}\sqrt{\frac{RT}{2\pi M}}\left(\frac{T}{T_o}\right)^{\beta} e^{-E/RT} \quad \text{for adsorption} \quad (4)$$

and

$$k=\frac{A}{\sigma^{n-1}}\left(\frac{T}{T_o}\right)^{\beta} e^{-E/RT} \quad \text{for desorption or surface reaction.} \quad (5)$$

Illustrative examples:

1) **First order adsorption:**
Reaction: X + * → X* where n=1

$$r=k\left(C_g\right)\left(C_*\right)^1$$

$$\frac{\text{mol}}{\text{cm}^2\,\text{sec}} \equiv k\,\frac{\text{mol}}{\text{cm}^3}\,\frac{\text{mol}}{\text{cm}^2}$$

$$k \equiv \frac{\text{cm}^3}{\text{mol}}\,\frac{1}{\text{sec}}$$

$$k=\frac{s}{\sigma}\sqrt{\frac{RT}{2\pi M}}\left(\frac{T}{T_o}\right)^{\beta} e^{-E/RT}$$

2) **Second order adsorption:**

Reaction: $X_2 + 2^* \rightarrow 2X^*$ where n=2

$$r=k\left(C_g\right)\left(C_*\right)^2$$

$$\frac{\text{mol}}{\text{cm}^2\,\text{sec}} \equiv k\,\frac{\text{mol}}{\text{cm}^3}\left(\frac{\text{mol}}{\text{cm}^2}\right)^2$$

$$k \equiv \frac{\text{cm}^3}{\text{mol}}\,\frac{\text{cm}^2}{\text{mol}}\,\frac{1}{\text{sec}}$$

$$k=\frac{s}{\sigma^2}\sqrt{\frac{RT}{2\pi M}}\left(\frac{T}{T_o}\right)^{\beta} e^{-E/RT}$$

3) **First order desorption:**

Reaction: $X^* \rightarrow X + {}^*$ where n=1

$$r=k\left(C_s\right)^1$$

$$\frac{\text{mol}}{\text{cm}^2\,\text{sec}} \equiv k\,\frac{\text{mol}}{\text{cm}^2}$$

$$k \equiv \frac{1}{\text{sec}}$$

$$k=\frac{A}{\sigma^0}\left(\frac{T}{T_o}\right)^{\beta} e^{-E/RT} = A\left(\frac{T}{T_o}\right)^{\beta} e^{-E/RT}$$

4) **Second order desorption:**

Reaction: $2X^* \rightarrow X_2 + 2^*$ where n=2

$$r=k\left(C_s\right)^2$$

$$\frac{\text{mol}}{\text{cm}^2\,\text{sec}} \equiv k\left(\frac{\text{mol}}{\text{cm}^2}\right)^2$$

$$k \equiv \frac{\text{cm}^2}{\text{mol}}\,\frac{1}{\text{sec}}$$

$$k=\frac{A}{\sigma^1}\left(\frac{T}{T_o}\right)^{\beta} e^{-E/RT}$$

5) **Surface reaction:**

Reaction: $X^* + Y^* \rightarrow Z^* + W^*$ where n=2

$$r = k\left(C_s\right)_1\left(C_s\right)_2$$

$$\frac{\text{mol}}{\text{cm}^2\,\text{sec}} \equiv k\left(\frac{\text{mol}}{\text{cm}^2}\right)^2$$

$$k \equiv \frac{\text{cm}^2}{\text{mol}}\frac{1}{\text{sec}}$$

$$k = \frac{A}{\sigma^1}\left(\frac{T}{T_o}\right)^{\beta} e^{-E/RT}$$

To convert the units of rate constants (k) into sec^{-1} (denoted as k'), we employ the following equations:

$$k' = k\frac{P_{atm}}{RT}\sigma^{n-1} = \frac{s}{\sigma}\sqrt{\frac{RT}{2\pi M}}\left(\frac{T}{T_o}\right)^{\beta} e^{-E/RT}\frac{P_{atm}}{RT} \qquad \text{for adsorption} \qquad (6)$$

and $$k' = k\sigma^{n-1} = A\left(\frac{T}{T_o}\right)^{\beta} e^{-E/RT} \qquad \text{for desorption or surface reaction.} \qquad (7)$$