

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 $\text{kcal.mol}^{-1}.\text{K}^{-1}$

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 $(\text{cm}^2.\text{mol}^{-1})^n.\text{cm}.\text{sec}^{-1}$ for adsorption and $(\text{cm}^2.\text{mol}^{-1})^{n-1}.\text{sec}^{-1}$ for desorption or surface reaction

r=rate of reaction in $\text{mol.cm}^{-2}.\text{sec}^{-1}$

P_{atm} =atmospheric pressure in dyne.cm^{-2}

k' =rate constant in sec^{-1}

$\sqrt{\frac{RT}{2\pi M}}$ has units of $\text{cm}.\text{sec}^{-1}$.

The following equations are used for rate calculation:

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

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

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

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

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

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

Illustrative examples:

1) First order adsorption:

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

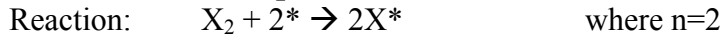
$$r=k(C_g)(C^*)^1$$

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

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

$$k = \frac{s}{\sigma} \sqrt{\frac{RT}{2\pi M}} \left(\frac{T}{T_0}\right)^\beta e^{-E/RT}$$

2) Second order adsorption:



$$r = k(C_g)(C_*)^2$$

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

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

$$k = \frac{s}{\sigma^2} \sqrt{\frac{RT}{2\pi M}} \left(\frac{T}{T_0}\right)^\beta e^{-E/RT}$$

3) First order desorption:



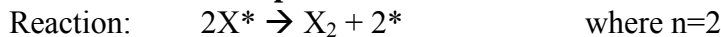
$$r = k(C_s)^1$$

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

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

$$k = \frac{A}{\sigma^0} \left(\frac{T}{T_0}\right)^\beta e^{-E/RT} = A \left(\frac{T}{T_0}\right)^\beta e^{-E/RT}$$

4) Second order desorption:



$$r = k(C_s)^2$$

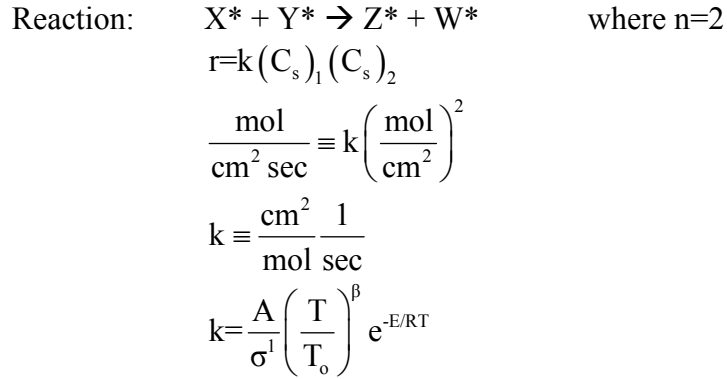
$$\frac{\text{mol}}{\text{cm}^2 \text{ sec}} \equiv k \left(\frac{\text{mol}}{\text{cm}^2}\right)^2$$

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

$$k = \frac{A}{\sigma^1} \left(\frac{T}{T_0}\right)^\beta e^{-E/RT}$$

5) Surface reaction:

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

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

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