

## Reaction rate calculation and unit conversion

The notations are as follows:

A=pre-exponential in  $\text{sec}^{-1}$

s=sticking coefficient (dimensionless)

$\sigma$ =site density in  $\text{mol.cm}^{-2}$

n=reaction order (dimensionless integer)

$\beta$ =temperature exponent (dimensionless)

E=activation energy in  $\text{kcal.mol}^{-1}$

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  $\text{gm.mol}^{-1}$

$C_g$ =concentration of gas phase species in  $\text{mol.cm}^{-3}$

$C_s$ =concentration of surface species in  $\text{mol.cm}^{-2}$

$C^*$ =concentration of vacancies in  $\text{mol.cm}^{-2}$

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  $\text{mol.cm}^{-2}.\text{sec}^{-1}$

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

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

$\sqrt{\frac{RT}{2\pi M}}$  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  $n=1$

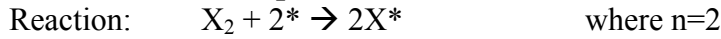
$$r=k(C_g)(C^*)^1$$

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

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

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

**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:**



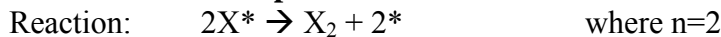
$$r = k(C_s)^1$$

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

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

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

**4) Second order desorption:**



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

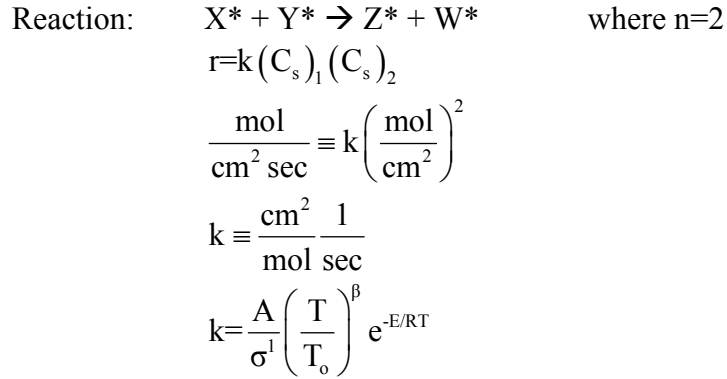
$$\frac{\text{mol}}{\text{cm}^2 \text{ sec}} \equiv k \left(\frac{\text{mol}}{\text{cm}^2}\right)^2$$

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

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

**5) Surface reaction:**

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

$$k' = k \frac{P_{\text{atm}}}{RT} \sigma^{n-1} = \frac{s}{\sigma} \sqrt{\frac{RT}{2\pi M}} \left( \frac{T}{T_0} \right)^\beta e^{-E/RT} \frac{P_{\text{atm}}}{RT} \quad \text{for adsorption} \quad (6)$$

$$\text{and} \quad k' = k \sigma^{n-1} = A \left( \frac{T}{T_0} \right)^\beta e^{-E/RT} \quad \text{for desorption or surface reaction.} \quad (7)$$