

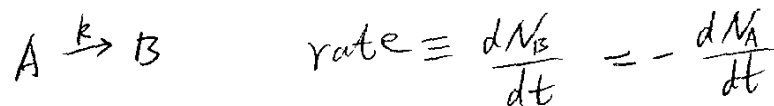
Course 565/665 Lecturer Prof. Cavagnero  
 Day 4.22.04 Date 9:55 am  
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## Kinetics and Reaction Rates (chapter 19)

$A \xrightleftharpoons[k_{-1}]{k_1} B$  what about the rate at which the equilibrium is reached?

$A \rightarrow B$  how fast is A converted to B in a rxn that never reaches equilibrium?

rate  $\equiv$  # of molecules converted to product per unit time.



or rate  $\equiv$  # of molecules of reactants disappearing per unit time

$$\text{rate} \equiv -\frac{dN_A}{dt} = \frac{dN_B}{dt} = k N_A \quad (\text{rate law})$$

↓  
rate coefficient

$k$ : probability that  $N_A$  molecules will convert to B per unit time.

Instead of using  $N$ , you can use any concentration units, e.g. mole fraction, molarity, molality.

$$\text{rate} = -\frac{dX_A}{dt} = \frac{-d(N_A/(N_A+N_B))}{dt} = k \frac{N_A}{N_A+N_B} = k X_A$$

↑  
mole fraction

Mental is also a fn. of T.?

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T-dependence of Rxn Rates

$T \uparrow \Rightarrow \text{rates} \uparrow$

Arrhenius:  $A \xrightarrow{k} B$   $\frac{d \ln k}{dT} = \frac{E_a'}{KT^2}$  at const P.   
activation energy.

integrate:  $k = A \cdot \exp\left(\frac{-E_a}{KT}\right)$

From transition-state theory:

$$k = \frac{k_B T}{h} e^{-\Delta H^\ddagger / RT} e^{\Delta S^\ddagger / R}$$

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