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

$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$ 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 ≡ # of molecules converted to product per unit time.

$A \xrightarrow{k} B$ $\text{rate} \equiv \frac{dN_B}{dt} = -\frac{dN_A}{dt}$

or rate ≡ # of molecules of reactants disappearing per unit time

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

k ↓ 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

(N_{total} is also a fn. of T?)

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T- dependence of Rxn Rates

$T \uparrow \Rightarrow$ rates $\uparrow$

Arrenhenis: $A \xrightarrow{k} B$ $\qquad \frac{d \ln k}{dT} = \frac{E_a}{kT^2}$ at const P. (E_a: activation energy.)

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

From transition-state thory:

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