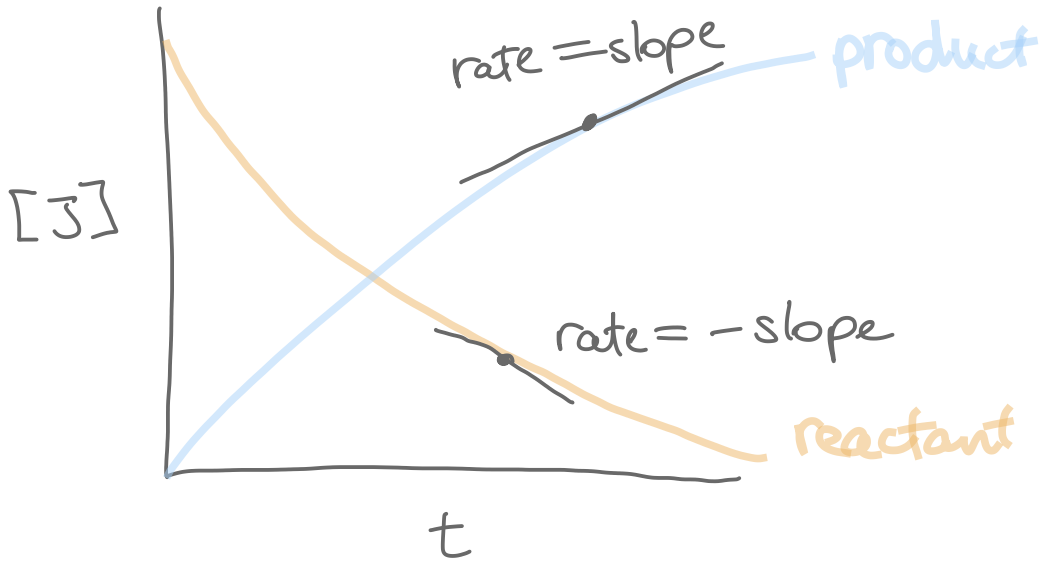
Lecture 17

Tuesday, November 12, 2024 10:08

Focus 17: Chemical Kinetics

Rates of Reactions



Instantaneous rate of consumption:

$$-\frac{d[R]}{dt}$$

Instantaneous rate of formation:

$$\frac{d[P]}{dt}$$

Example:

$$A + 2B \rightarrow 3C + D$$

$$\frac{d[D]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

Extent of reaction ξ (xi):

$$dn_J = \nu_J d\xi$$

Unique rate of reaction r

$$r = \frac{1}{V}\frac{d\xi}{dt}$$

$$d\xi = \frac{dn_J}{\nu_J}$$

$$r = \frac{1}{\nu_J} \cdot \frac{1}{V}\frac{dn_J}{dt}$$

$$r = \frac{1}{\nu_J}\frac{d[J]}{dt}$$

signed

Rate Laws and Rate Constants

$$r = k[A][B]$$

k: rate constant

$r = f([A], [B], \ldots)$ generally

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$$

$$r = \frac{k_1[H_2][Br_2]^{3/2}}{[Br_2] + k_2[HBr]}$$

Rate laws are generally not based on overall reaction!

k: $mol^{-1} \cdot dm^3 \cdot s^{-1}$

$r = k[A][B]$

$r = k[A][B]$

$mol \cdot dm^{-3}$ $\quad mol \cdot dm^{-3}$

$mol^2 \cdot dm^{-6}$

$mol \cdot dm^{-3} \cdot s^{-1}$

s^{-1}

$r = k[A]$ $\quad mol \cdot dm^{-3}$

$mol \cdot dm^{-3} \cdot s^{-1}$

Reaction Order

order WRT A

$r = k[A]^a[B]^b \ldots$

order WRT B

The power to which the concentr
of a species is raised in a rat
law is the order of the rea
WRT that species.

overall order $= a + b + \ldots$

half-order in A!

$r = k[A]^{\frac{1}{2}}[B]$

$r = k$ ← zeroth-order rate law

The Determination of the Rate Law

Isolation method: all reactants ex

one are present in large excess

$$r = k[A][B]^2$$

Keep [B] in large excess

At any point in time, $[B] \approx [B$

$r = k_{eff}[A]$, where $k_{eff} = k[B]_0^2$

$r = k_{eff}[A]$: pseudo-first order rate law

k_{eff}: effective rat constant

Keep [A] in large excess

At any point in time, $[A] \approx [A]_0$

$r = k_{eff}'[B]^2$, where $k_{eff}' = k[A]^a$

pseudo-second order rate law

Method of Initial Rates: measure instantaneous rate at the beginning of the reaction for several differe concentrations of the isolated react

$$r = k[A]^a$$

$$r_0 = k_{eff}[A]_0^a$$

$$\log r_0 = \log\left(k_{eff}[A]_0^a\right)$$

$$= \log k_{eff} + \log [A]_0^a$$

$$\log r_0 = a \log [A]_0 + \log k_{eff}$$

y mx b

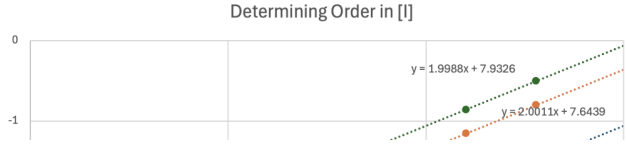
Example: find the rate law for the reaction $2I(g) + Ar(g) \rightarrow I_2(g) +$ in Excel.

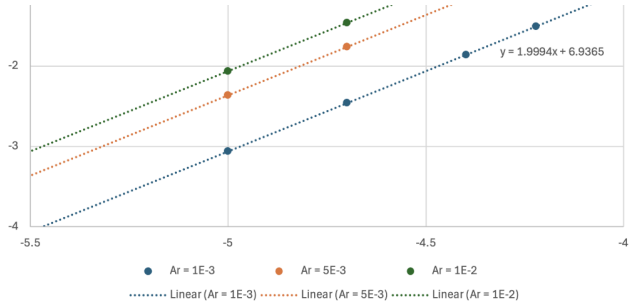
(Spreadsheet will be uploaded

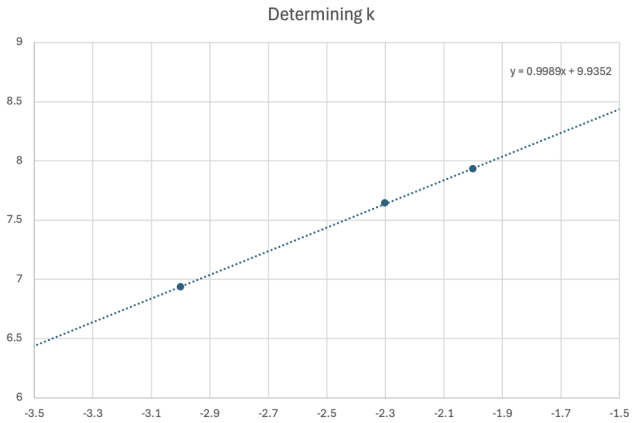
After doing linear fitting of the log/log data, we found the slope to be 2.

∴ The reaction is second - or in I.

Please see the attached Excel spreadsheet for our work in class. The initial data investigating different values of $[I]_0$ give us the reaction order (slope) and effective rate constant (intercepts), and by plotting k_{eff} vs. $[Ar]_0$, we can then extract the true rate constant k itself.







Initial Rates