

Chemistry 104, Dr. Batterton
REVIEW EXAM II; Tony Jacob

CHAPTER 15: KINETICS

Reaction Rate = $\frac{\Delta[A]}{\Delta t}$; negative sign used with reactants to make rxn rate positive; units of rate = M/time

From data of concentration reactant versus time:

Average Rate over a finite time is the slope $\rightarrow \Delta y/\Delta x = \Delta[A]/\Delta t$

Instantaneous Rate over an instant in time requires a derivative from calculus = $d[]/dt$;
however, an approximation can be made which is equivalent to an average rate

RELATIVE RATES: for $2A + B \rightarrow 3C$ the relative rates are: $-\frac{1}{2}\left[\frac{\Delta A}{\Delta t}\right] = -\left[\frac{\Delta B}{\Delta t}\right] = +\frac{1}{3}\left[\frac{\Delta C}{\Delta t}\right]$

Once rate of one chemical is determined, rate of any other chemical of the reaction at that point in time can be determined

RATE LAW or RATE EXPRESSION = $k[A]^x[B]^y$; k = rate constant; x = order with respect to A; y = order with respect to B; order of reaction = $x + y$

The rate expression is the differential rate law - function of concentration (often just called *the rate law*)

Integrated rate law - function of time

Units of k vary depending on the order of the reaction

DETERMINE RATE EXPRESSION: $A + 3B + 2C \rightarrow 3D$

- Initial rates:** $\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[A]_1^a[B]_1^b[C]_1^c}{k[A]_2^a[B]_2^b[C]_2^c}$ initial rates \rightarrow time = 0; 2 concentrations should be constant
- From description/words:** "When $[A]$ doubles, the rate increases by 4." $\rightarrow [B]$ and $[C]$ are constant
 $\frac{\text{rate}_1}{\text{rate}_2} = \frac{[A]_1^a}{[A]_2^a}$ this simplifies to: $\frac{4}{1} = \left(\frac{2}{1}\right)^a$ which implies $\rightarrow a = 2$
- From graphs – see below**
- From mechanisms**
- Raw data: Two rates + two concentrations:** Two average rates of reactants and the concentration at the same point in time when these average rates were determined

USING LOG OR LN:

$$\ln(xy) = \ln(x) + \ln(y)$$

$$\ln(x/y) = \ln(x) - \ln(y)$$

$$\ln(a^x) = x \ln(a)$$

INTEGRATED RATE LAWS

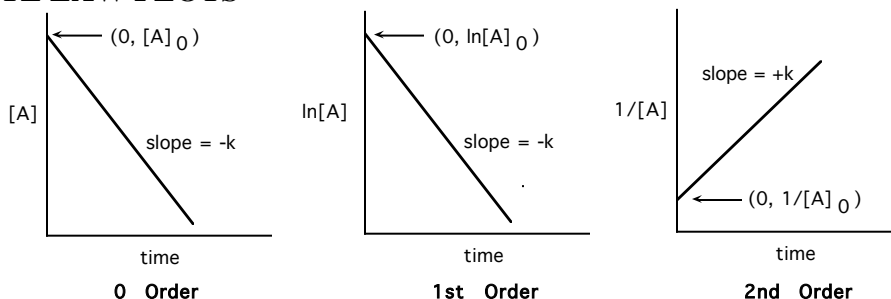
Order	Differential Rate Law	Integrated Rate Law	y-axis vs x-axis ($y = mx + b$)	Slope	y-intercept	$t_{1/2}$	units of k
0	$\Delta[A]/\Delta t = k[A]^0 = k$	$[A] = -kt + [A]_0$	$[A]$ vs t	$m = -k$	$[A]_0$	$t_{1/2} = [A]_0/2k$	$M s^{-1}$
1	$\Delta[A]/\Delta t = k[A]^1$	$\ln[A] = -kt + \ln[A]_0$	$\ln[A]$ vs t	$m = -k$	$\ln[A]_0$	$t_{1/2} = 0.693/k$	s^{-1}
2	$\Delta[A]/\Delta t = k[A]^2$	$1/[A] = kt + 1/[A]_0$	$1/[A]$ vs t	$m = k$	$1/[A]_0$	$t_{1/2} = 1/k[A]_0$	$M^{-1} s^{-1}$

HALF-LIFE $t_{1/2}$ – The time it takes for half the substance to react or decay; all *radioactive decays* are 1st order

$$t_{1/2} = 0.693/k \text{ for 1}^{\text{st}} \text{ order } (k = 0.693/t_{1/2}); [A]_t = [A]_0 \left(\frac{1}{2}\right)^{t/t_{1/2}}$$

1st order rate law: $\ln[A]_t = -kt + \ln[A]_0$ can also be written: $\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$ which is good for % consumed problems; $[A]_t$ is concentration of A that *remains*; can substitute % *that remains* in decimal form for $[A]_t/[A]_0$

INTEGRATED RATE LAW PLOTS



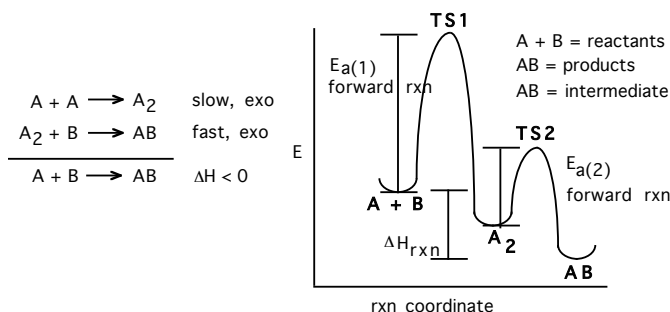
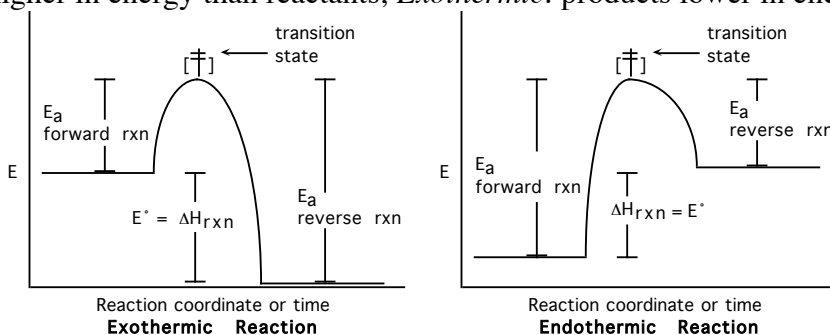
FACTORS THAT AFFECT RATE:

- Concentration** $\uparrow \rightarrow$ #collisions $\uparrow \rightarrow$ reaction rate \uparrow
- Temperature** $\uparrow \rightarrow$ KE $\uparrow \rightarrow$ $E_{\text{collisions}} \uparrow$ and more molecules have $E > E_a$ (i.e., sufficient energy) \rightarrow reaction rate \uparrow
- Catalyst** \rightarrow E_a is lowered; more molecules have $E > E_a$; (i.e., sufficient energy) \rightarrow reaction rate \uparrow (note: both forward and reverse reaction rate \uparrow)
- Particle size** $\downarrow \rightarrow$ #collisions \uparrow since there is more surface area for greater contact \rightarrow reaction rate \uparrow

REACTION COORDINATE DIAGRAMS: reactants, products, axes, transition state, $\Delta E^\circ_{\text{rxn}}$ (ΔH_{rxn}),

E_a forward, E_a reverse

Endothermic: products higher in energy than reactants; *Exothermic:* products lower in energy than reactants



For a reaction to proceed:

- Collision must occur
- Sufficient energy
- Correct molecular orientation

ARRHENIUS EQUATION: $\ln(k) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$

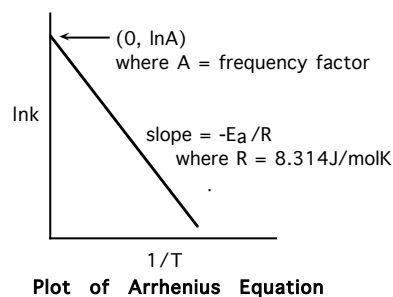
can be plotted with x-axis = $1/T$ and y-axis = $\ln(k)$,

slope = $-E_a/R$, y-intercept = $\ln A$

To find activation energy, E_a :

$$\ln k_2 - \ln k_1 = \ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$R = 8.314 \text{ J/molK}$; T in K; E_a will come out in J/mol; when T increases and reaction rate doubles but concentrations are unchanged $\rightarrow k_{(\text{higher } T)} = 2 \times k_{(\text{lower } T)}$



MECHANISMS

Series of chemical reactions also called *elementary* or *mechanistic* steps

Molecularity: number of species that collide

Unimolecular: $A \rightarrow$; *Bimolecular:* $A + B \rightarrow$ (or $2A \rightarrow$); *Termolecular:* $A + B + C \rightarrow$ (or $2A + B \rightarrow$)

The rate expression from *elementary* reaction: **Rate = $k[A]^n[B]^m$** ; where n and $m =$ *stoichiometric coefficients*;

this does not apply to overall reactions – overall reactions will just have unknown variables n and m

Intermediate: does not appear in the final reaction; appears 1st as a product, 2nd as a reactant

Catalyst: does not appear in the final reaction; appears 1st as a reactant, 2nd as a product

Rate-determining step = the slow step; rate-determining step used to determine rate law; all chemicals in the rate law must also appear in overall reaction or be a catalyst, **no intermediates are allowed in the rate law – if they are there then make a substitution using the steady-state approximation.**

TEMPERATURE: *changes both the rate of the reaction and k*

Temperature $\uparrow \rightarrow k \uparrow \rightarrow$ rate \uparrow ; for every 10°C increase in reaction temperature the reaction rate \sim doubles

CHAPTER 16: EQUILIBRIUM

EQUILIBRIUM EXPRESSION, EQUILIBRIUM CONSTANT (K)

$$aA + bB \rightarrow cC \rightarrow K_{eq} = \frac{[C]^c}{[A]^a[B]^b} \text{ where values in are in molarity (or atm)}$$

Solids and *liquids not* included in equilibrium expression because concentrations are constant

Forward rate = reverse rate at equilibrium; Dynamic equilibrium – microscopic forward and reverse reactions present; Macroscopic – no change in concentrations

K_c versus K_p

K_c uses M, K_p uses atm; $K_p = K_c (RT)^{\Delta n}$ where $\Delta n =$ *gaseous* moles product – *gaseous* moles reactant;

$R = 0.0821 \text{ Latm/molK}$

SIZE OF K

K large \rightarrow products favored; K small \rightarrow reactants favored;

K close to 1 \rightarrow reactants/products favored about the same

HOW K CHANGES AS THE REACTION CHANGES

1. Reverse: $K \rightarrow \frac{1}{K}$

2. Multiply a reaction by c : $K \rightarrow K^c$

3. Add reactions: $K_3 = K_1 \times K_2$

REACTION QUOTIENT (Q): a snapshot of reaction; used to determine which way reaction proceeds (L, R, no shift);

$Q > K \rightarrow$ left

$Q < K \rightarrow$ right

$Q = K \rightarrow$ at equilibrium (no shift)

CALCULATIONS:

- given equilibrium concentrations \rightarrow **find K**
 - given initial concentration + other information, first find equilibrium concentrations \rightarrow **find K**
- given K \rightarrow **find equilibrium concentrations**
- **approximations:** make them if needed and when $100 \times K_{eq} < [A]_0$
- **determine Q** - is system is at equilibrium; if not, **which way will reaction shift**

Le CHATELIER'S PRINCIPLE: reaction shifts to restore equilibrium (opposes stress on the system)

Factors **affecting** equilibrium:

1. **Concentration:** add or remove reactants or products that are part of K expression; pure liquids or solids usually do not affect equilibrium; sometimes water can cause shift but depends on K expressions
2. **Temperature** (heat/cool a system); endothermic reaction: heat written as a reactant; exothermic reaction: heat written as a product
3. **Pressure** (e.g., change V of system); an increase in P: alleviate by reducing number of gaseous moles; only gas moles are counted not aqueous, solid, or liquid substances

What is done to the system	What system "wants" to do	How system shifts
$[] \uparrow$	$[] \downarrow$	shift to consume chemical and $[] \downarrow$; solids and liquids (in general) will not shift equilibrium (water can shift reaction because of dilution effect)
$P \uparrow$	$P \downarrow$	From Ideal Gas Law: $n \downarrow \Rightarrow$ shift to $n(\text{gas}) \downarrow$ (only gaseous mol); fewer gas mole and $P \downarrow$; if equivalent number of gas moles on both sides \Rightarrow no shift
$T \uparrow$	$T \downarrow$	consume heat to $T \downarrow$; if exo (heat on the reactant/right side) \Rightarrow shift to L and heat is consumed

Factors **not affecting** equilibrium

1. **Catalyst** (reaction speeds up but no shift in equilibrium)
2. **Pure liquid or solid** added to system (since these don't appear in equilibrium expression, they don't shift reaction); water can affect equilibrium by changing concentrations of K expression components

TEMPERATURE: shifts the reaction (Le Chatelier's Principle) **and** changes the value of K

Exothermic reaction: $T \uparrow \Rightarrow K \downarrow$

Endothermic reaction: $T \uparrow \Rightarrow K \uparrow$

Quadratic equation: from $ax^2 + bx + c = 0 \rightarrow x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$