6.1 Rates of Reactions

Def: rate of change in [conc] ($mols\,dm^{-3}$) s^{-1}

rate measured in time = $\frac{1}{time} = \frac{1}{s} = s^{-1}$

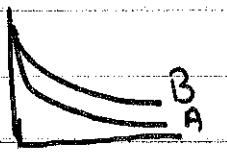
rate of rxn = how quickly a rxn happens
[R] ↓ : [P] ↑

ROR = $\frac{\uparrow [P]}{time}$ or $\frac{\downarrow [R]}{time}$ graphs

$\frac{\Delta [P]}{\Delta t}$ $\quad$ $\frac{-\Delta [R]}{\Delta t}$

showing [ ] ↓ (though rate is always positive)

given in graphical ~~representation~~ representation



- steepness (gradient) = measure of rate
  - due to curve → rate given at one pt. in time

★ Tangent graph

hint pg 214

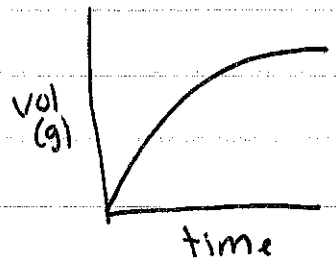
- take tangent at pt in time to measure rate
- usually take $t = 0$ to compare diff rxns

Curve shows rate is not constant
- greatest at start, slows w/ progression

Techniques for measuring rates

1. Change in vol of (g) produced

- good if product is a gas
- use: gas syringe or H_2O displacement (inverted eudiometer)
  - limitations: (g) may be soluble
- collect data at intervals (rate graph)

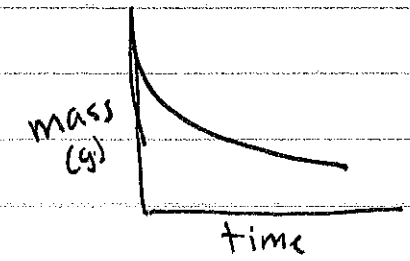


$Mg_{(s)} + 2\,HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$

H_2 → light gas

2. Change in mass

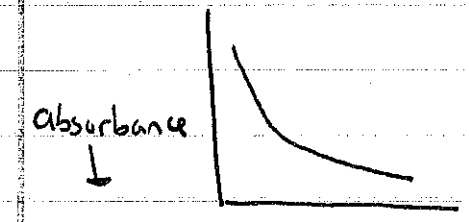
- good if heavy gas is produced (not H_2)
- continuous readings (rate graph)
- use: balance w/ rxn in flask on top



$CaCO_{3(s)} + HCl_{(aq)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$

CO_2 → heavy gas

3. Change in transmission of light : colorimetry / spectraphotometry
   - one of R or P is colored → give characteristic absorption in visible range (320-800nm)
   - can use an indicator (to provide color change)
   - use: pass specific λ of light through soln, light passed through is measured



Crystal violet + NaOH → colorless

$HI \rightarrow H_2 + I_2$

4. Change in [ ], measured by titration
   - titrate a rxn by known 'standard'
   - cannot be done continuously as rxn proceeds
   - ∴ take samples → quench → snapshot → repeat

↓

stopping agent

$H_2O_2(aq) + \underbrace{2H^+ + 2I^{-1}}_{\text{acidified KI}} \longrightarrow I_2 + 2H_2O$

- Na_2CO_3 (quench)
- $Na_2S_2O_3$ titrant

5. Change in [ ] measured by conductivity
   - total electrical conductivity: total [ ] of ions & charges
   - use: conductivity probe
     - either ↑ or ↓ [ions]; conductivity corresponds

$$BrO_{3(aq)} + 5Br^-_{(aq)} + 6H^+_{(aq)} \rightarrow 3Br_{2(aq)} + 3H_2O_{(l)}$$

6. non-continuous methods 'clock rxn'
   - make an arbitrary end pt → run rxn under diff. conditions & stop clock
   - avg rate over time

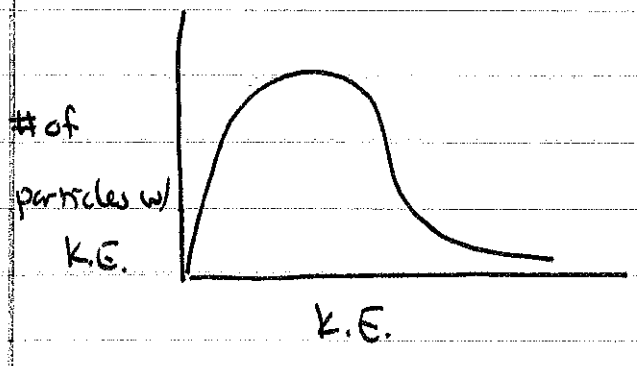
diff masses of $Mg_{(s)}$ in dilute $HCl_{(aq)}$

Collision Theory

- Kinetic energy & temperature
  - Kinetic molecular theory: particles in a substance move randomly as a result of k.e.
    - avg k.e. in relation to absolute temp

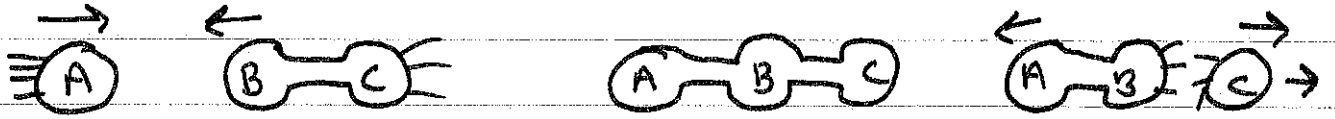
s l g → ↑ K.E. ↑ Temp

Maxwell-Boltzmann distribution curve (gas behavior)



- Shows # of particles that have particular K.E.
- area under curve = total # of particles in sample

How rxns happen



particles collide, some bonds broken, some formed

∴ rate of rxn = # of successful collisions → form products

Influence on rate (2 factors)

1. Energy of collision
   need to meet/exceed <u>activation energy</u> (min. KE needed for rxn)

↓

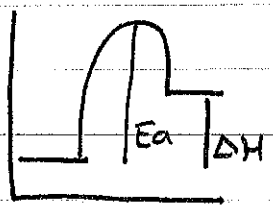
energy necessary for overcoming repulsion or breaking bonds before rxn

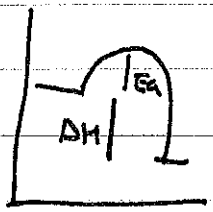
↓

energy barrier

↓

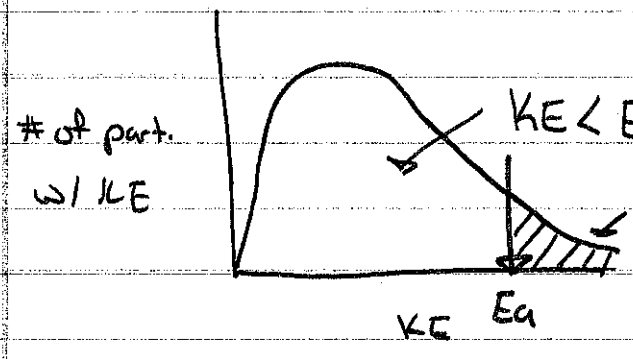
reactants achieve transition state → product formation





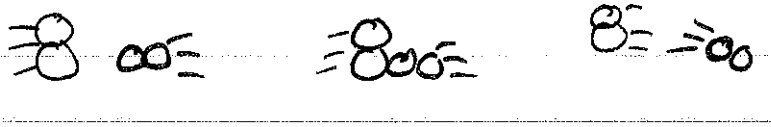
only particles w/ KE at/higher than Ea, do have successful collisions

rate: proportion of particles KE > Ea

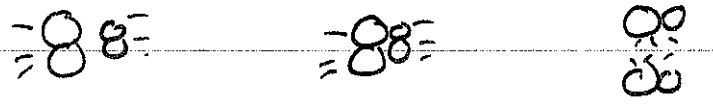


rxns w/ ↑ Ea slower than ↓ Ea

2. Geometry of Collision
- diff orientations → diff success rate of rxn

a) 

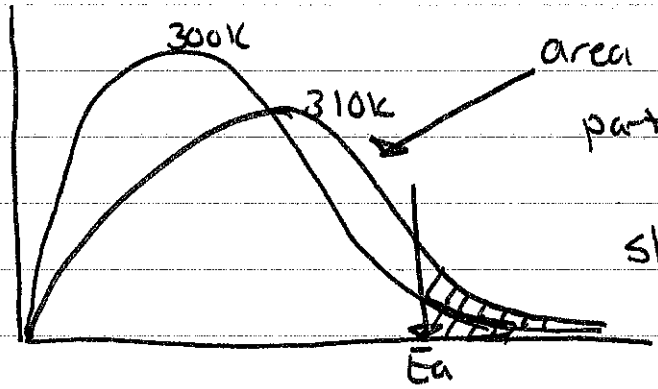
approach | ineffective collision | separate

b) 

correct collision geometry

Factors affecting rate

1. Temperature — ↑ Temp, ↑ avg KE



area under curve = more particles w/ ↑ KE (shifted graph)

shift in T, changes proportion of particles at Ea

∴ ↑ T, ↑ collision frequency, ↑ # of successful collisions → ↑ rxn rate

★ rule of thumb: double rxn rate every 10°C

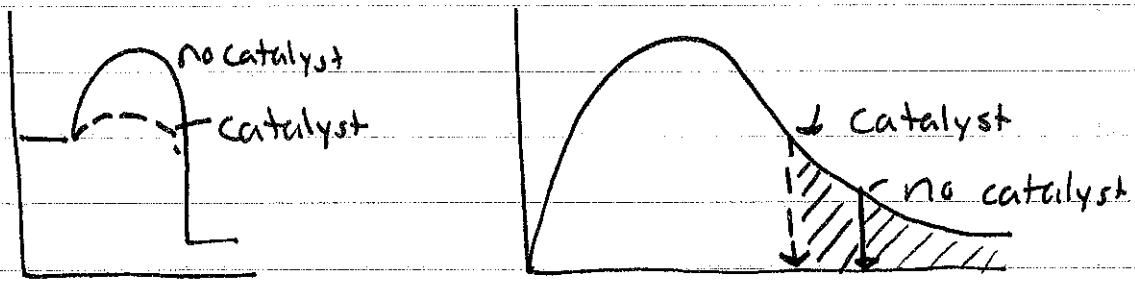
2. Concentration — ↑ [ ], ↑ rate due to frequency of collisions

3. Particle size — ↓ particle size, ↑ surface area, ↑ rate allows more contact & higher probability of collisions

4. Pressure (involving gases) ↑ Pa, ↑ rate
compress gas, ↑ [ ], ↑ collision frequency

5. Catalyst
def: substance that ↑ rate of rxn w/out itself undergoing rxn or being permanently changed

must provide alt route for rxn (↓ Ea)



catalyst affect forward & reverse rxns equally
do not affect overall yield, just time to get to yield

enzyme = biological catalyst

- Analysis of graphical & numerical data
- design lab (after bucket lab)
- calculation from tangents