Kinetics: Rates of Reaction

Inspired by Paul Groves   **A B L U F F E R' S G U I D E**

1. How to talk about Reaction Rate
    $$\text{rate} = \Delta[\text{chemical}]/\Delta\text{time}$$
    - Common Units: $\underline{M}$/s, mol·L^{-1}·s^{-1}
    - Rate of **disappearance** of reactant or Rate of **appearance** of product
    - Use **coefficients** to change one rate to another
        Reaction: 2A + 3B → 4C
        $$-\tfrac{1}{2}\frac{\Delta[A]}{\Delta t} = -\tfrac{1}{3}\frac{\Delta[B]}{\Delta t} = \tfrac{1}{4}\frac{\Delta[C]}{\Delta t}$$
    Watch your **signs** (-Δ[React.] = Δ[Prod.])
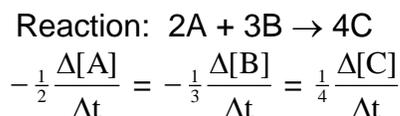
2. From a graph of [R] vs time
    Average rate is the **slope** of a **segment**.
    Instantaneous rate is **slope** of the **tangent**.
    Initial rate is often used.

3. How to **Speed Up** a Reaction
    Use Collision Theory and
    Kinetic Molecular Theory

    increase the **concentration** of reactants
    - increase **molarity** of solutions
    - increase partial **pressure** of gases
    collision model → more collisions

    more **surface area** between unlike phases
    collision model → more collisions

    increase the **temperature**
    collision model → more & <u>harder</u> collisions

    add a **catalyst**
    - homogeneous catalyst (used & reformed)
    - heterogeneous catalyst (surface catalyst)
    collision model → alternate mechanism/ pathway that needs lower energy collision and/or helps correct orientation

4. Because Rate depends on Concentration…
    we use Rate Laws
    - what they mean
    - how to determine them
    - how they relate to rate determining step
    - how they help you choose a mechanism

5. General Form:
    Equation: A + B → C
    Rate = k [A]^x[B]^y

    k is the "specific rate constant"
    Use experimental data to determine
   the values of x, y, and k.

6. The Rate Law **CANNOT** be determined from the overall reaction.
    - It MUST be determined **experimentally** because the rate law reflects only the "rate determining step."

7. Rate law can be determined from initial rates. *See your notes and worksheets!*
    - Hold [ ] of all chemicals except one constant.
    - Change [ ] of one chemical and see how it changes the rate.
    - Determine what the exponent order must be to result in that change.
    - If [A] doubles, and rate quadruples, then [A] must be raised to the 2nd power. [A]^2, it is second order with respect to A

8. Rate Law matches Molecularity of the Rate Determining Step in the Mechanism

    Examples for: 2A + 3B → C

 | Rate Law | Rate Determining Step in the mechanism |
    |---|---|
    | Rate = k [A][B] | A + B → X (slow) |
    | Rate = k [A]^2 | A + A → X (slow) |
    | Rate = k [A]^2[B] | A + A ⇆ X (fast)
B + X → Y (slow)
Each step is usually bimolecular. A 3rd order overall rxn often comes from a fast equilibrium before a slow step. |
    | Rate = k | This could be a mechanism that depends on a catalyst only. The concentrations would not matter. |

9. Determining the order by graphing

	order	straight-line plot	slope
C *Concentration*	0	$[A]_t$ vs. t	-k
N *Natural Log*	1	$\ln[A]_t$ vs. t	-k
R *Reciprocal*	2	$1/[A]_t$ vs. t	k

**10.** PE energy profile of a reaction
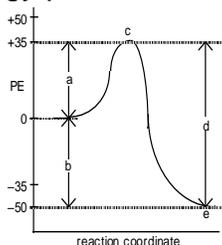
ΔH of the reaction relates reactant and product PE's / exo- or endothermic/ downhill, $-\Delta H$, or uphill, $+\Delta H$

11. Activation energy (E_a) = energy barrier
- Activated complex (transition state) is at the peak of the graph.
- Whether a rxn is fast or slow depends on the activation energy in the PE profile
- PE profile does not change with change in temperature of the reactants?
- Adding a catalyst lowers the E_a

12. The KE distribution of a substance
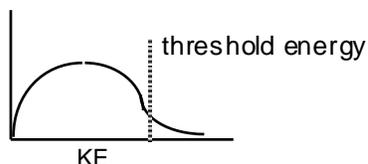
- Temperature is the **average** KE

- Increasing temperature spreads out curve to the right, increases average KE
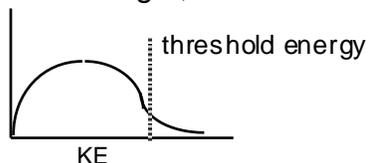
- Adding a catalyst moves the threshold energy to the left.
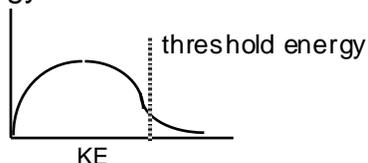
13. Reaction mechanisms how the reaction happens step by step

Overall reaction:
$$4\ HBr\ +\ O_2\ \rightarrow\ 2\ Br_2\ +\ 2\ H_2O$$

Mechanism:
$$HBr\ +\ O_2\ \rightarrow\ HOOBr$$
$$HOOBr + HBr\ \rightarrow\ 2\ HOBr$$
$$HOBr + HBr\ \rightarrow\ Br_2\ +\ H_2O$$
$$HOBr + HBr\ \rightarrow\ Br_2\ +\ H_2O$$
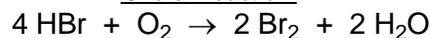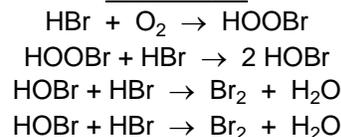
NOTE: HOOBr and HOBr are not in the overall rxn because they are not reactants or products, they are "intermediates." We don't like putting intermediates into our rate laws, we often will substitute things to make them not show up.

- Overall reaction is sum of steps
- Slowest step is **rate-determining step**

14. Half-Life
- relationship to radioactivity (a first order reaction)

Order	Half-Life
0	$\dfrac{[A]_0}{2k}$
1*	$\dfrac{0.693}{k}$
2	$\dfrac{1}{k[A]_0}$

This is the one that typically shows up on the AP exam.

15. Arrhenius Equation
$$k = Ae^{\frac{-E_a}{RT}}$$

Graphing to find E_a

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

$$\frac{-E_a}{R} = slope$$
ln(A) = y-intercept