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Organic chemistry



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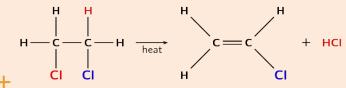


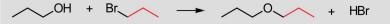


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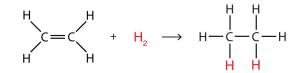


- Important reactions in organic chemistry
 - Substitution -
 - One functional group is replaced with another
 - Addition
 - Addition of one or more atoms to a molecule
 - Elimination
 - Removal of one or more atoms from adjacent carbons in a given molecule





substitutes for -H





Ethane







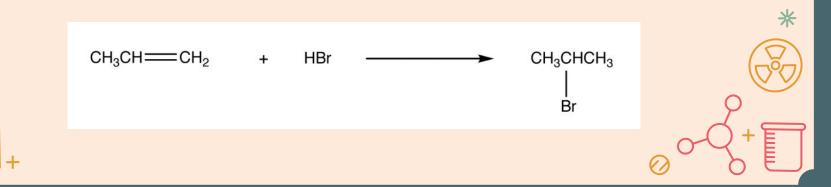
Markovnikov's rule



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Markovnikov's rule

- Describes how an addition reaction may proceed to form the most potentially stable organic molecule
- The least electronegative atom in a reaction will bond to the carbon with the highest number of alkyl groups





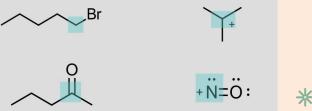
Nucleophiles and Electrophiles

- Nucleophiles
 - Attracted to positive charges
 - Includes:
 - Lone pairs
 - Multiple (i.e., double/triple) bonds
 - Negative charges
- Electrophiles

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- Attracted to e-
- Includes:
 - Positive charges
 - Positively polarized atoms
- Basis of most chemical reactions is the interaction between nucleophiles and electrophiles









Spontaneity





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Making sense of it all

- → Why does there seem to be a natural progression of events?
 - Change can be reasonably predicted based on a natural direction of change
 - I.e., Based on natural laws, an object will always fall toward another object with a stronger force of gravity (e.g., a waterfall)
 - The universe favours spontaneity
 - The universe being a system and its surroundings
 - I.e., Entropy (S)!!!



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→ What the heck is entropy?

- A thermodynamic principle
- Empirical measurement of the disorder or randomness as it relates to a given closed system
 - In this sense, it represents the amount of thermal energy in a closed system that is unavailable to perform work
 - If energy is not put into a system, the closed system will move closer to entropy, or true randomness, as time passes
- S = (kb)(ln)(W)









- S = entropy (SI unit measurement = J/K)
- kb = Boltzmann's constant
 - 1.38E-23 J/K
- In = a natural logarithm
- W = number of possible configurations of a state



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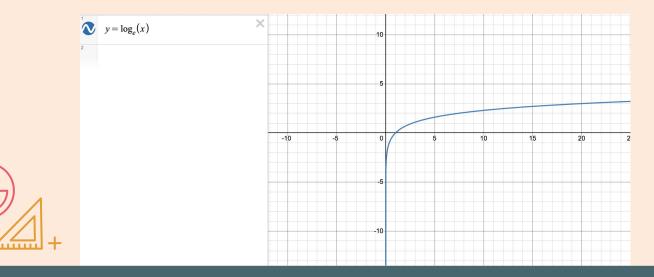
→ ln

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- Wait...what's ln?
 - ln =
 - a logarithm to the base of e
 - e = is an irrational number that is used in mathematics
 - ... ln (x) = log(e)(x) = y
 - The ln of a negative number is 'undefined' and therefore there is a vertical asymptote at (0,0)





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Spontaneous change

- Occurs when change happens in a system without any influence or input from the surroundings
- → Spontaneous processes release energy and are favourable
 - Doesn't mean that heat is always released when a reaction takes place
 - Heat = the transfer of thermal energy from one object to another



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Ok, back to entropy

→ Entropy

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- Recognized as a state function
 - The path and rate of a reaction are negligible here
 - This is thermodynamics, afterall!
 - We're not concerned with how quickly a reaction proceeds, just that it has taken place at all!

∴ S = S(final) - S(initial)

- △S > 0 → melting, vaporization, creating a solution, the outcome of a solution that increases the number of moles, and heating a substance
- .: AS > 0 is favourable



Entropy change?

- → Entropy decrease of a system
 - Can only occur if the entropy of a system's surroundings increases
- → \triangle S (universe) = \triangle S(system) + \triangle S(surroundings)
 - Considered spontaneous if △S(universe) > 0
 - Considered non-spontaneous if △S(universe) < 0</p>
 - "Non-spontaneous" refers to the fact that a process or reaction in a system will not occur without influence from its surroundings
 - By this logic...
 - A spontaneous rxn (A S > 0) carried out in a forward direction will, in turn, be non-spontaneous (A S < 0) in the opposite direction



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Energy Review

- → Enthalpy \rightarrow State function that describes the properties of a thermodynamic system
 - The
 - The path taken from reactants to products is irrelevant
 - The rate of a rxn is irrelevant
 - More concerned with whether the rxn will happen or not
- → Hess's law
 - For any multi-step rxn, the net enthalpy is equal to the sum of all of the enthalpies from each step of the rxn



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Gibbs free energy (^G)

- → A thermodynamic concept that empirically describes the maximum amount of work that can be carried out by a closed system with no external influence
 - Basically demonstrates the energy of a chemical reaction after taking into account entropy
 - Determines the spontaneity of a reaction
- $\Rightarrow \quad \triangle G = \triangle H T \triangle S$
 - △G = Gibbs free energy (expressed in: J, kJ, kJ/mol, etc...)
 - AH = enthalpy of a reaction
 - T = temperature in Kelvin
 - $\Delta S = entropy$
 - A reaction is said to be spontaneous if $\triangle G < 0$
 - Non-spontaneous if ${}^{\scriptscriptstyle riangle}G > 0$
 - At equilibrium if $\triangle G = 0$



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- Nonspontaneous reactions are said to be unfavourable as they do not favour the formation of products from reactants
- This obviously isn't ideal as this would prevent a ton of reactions from being carried forward. So, what gives??
 - Reaction coupling!! (a.k.a meet Biochemistry)
 - When an unfavourable, or nonspontaneous reaction, is paired with the energy produced from a favourable/spontaneous reaction
 - E.g., Most biological processes are unfavourable!
 - Solution: use a universal energy source to couple unfavourable reactions
 - ATP to the rescue!
 - The third inorganic phosphate of ATP is cleaved off and the energy released from ATP hydrolysis is used to drive unfavourable reactions forward







Kinetics



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Rate of reaction

→ Rate determining step

E.g.,

- The slowest reaction in a multi-step reaction
 - Therefore, the overall rate of a multi-step reaction = the rate determining step

$$O_3 + CI \rightarrow OCI + O_2 \quad (slow)$$
$$OCI + O \rightarrow CI + O_2 \quad (fast)$$
$$O_3 + O \rightarrow 2 O_2 \quad (overall)$$

rate of overall reaction = rate of first step



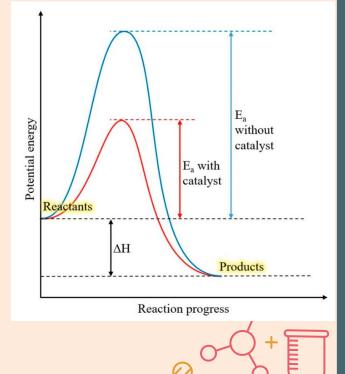


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Catalysts

- Most reactions (especially biological reactions) are too slow to effectively proceed on their own and require an extra boost!
 - A catalyst lowers the activation energy of a reaction by stabilizing the transition state, therefore making the reaction more favourable
- → Catalysts serve only a kinetic role, and therefore do not affect △G
 - Therefore, they speed up the reaction, but don't directly affect the thermodynamic properties of the reaction





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Chemical kinetics

→ What affects the rate of a reaction?

- $\bullet \quad \text{E.g., } A + B \rightarrow C$
 - The rate at which reactants A and B collide with each other
 - The fraction of molecules A and B having the correct orientation when they collide
 - The fraction of collisions between molecules A and B resulting in enough energy to cause a reaction to move forward





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Chemical kinetics

→ What affects the rate of a reaction?

- $\bullet \quad \mathsf{E.g., A} + \mathsf{B} \to \mathsf{C}$
 - The rate at which reactants A and B collide with each other
 - Collision rate = Z [A][B]
 - Therefore, if you increase the [] of reactants, there will be a higher collision rate



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Chemical kinetics



- $\bullet \quad \text{E.g., } A + B \rightarrow C$
 - The fraction of molecules A and B having the correct orientation when they collide
 - p = fraction of collisions with the correct orientation
 - ♦ 0









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Chemical kinetics

- → What affects the rate of a reaction?
 - $\bullet \quad \text{E.g., } \mathsf{A} + \mathsf{B} \to \mathsf{C}$
 - The fraction of collisions between molecules A and B resulting in enough energy to cause a reaction to move forward
 - $f = e^{-Ea/RT}$
 - Ea = activation energy
 - If energy of collisions > Ea, then there is a chance products may be formed from reactants





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Chemical kinetics

- → Put it all together!
 - Collision rate = Z [A][B]
 - ♦ 0
 - $f = e^{-Ea/RT}$
- → Therefore...
 - rate = (p)(f)(Z[A][B])
 - rate = (p)(Z)(e^-Ea/RT)
- → And finally Arrhenius stepped in and gave us:
 - Rate = Ae^-Ea/RT



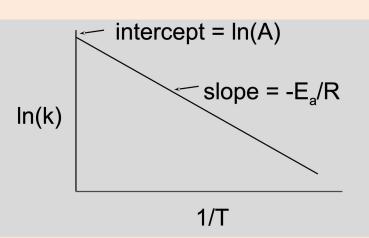


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Return of In

- → When values are unknown, you can rearrange Arrhenius' equation to solve for A or Ea
 - ...ln(k) = [-Ea/R][1/T] + ln(A)
- → Subsequent return of the linear equation!!
 - ♦ y= mx+b











Chemical equilibrium



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What is equilibrium?

When:

- 1. The [] of reactants and products are not changing
- 2. The forward rate = the reverse rate
- [C][D]/[A][B] = kf/kr
- \rightarrow Keq, the equilibrium constant
 - A function of temperature
 - Keq = [C]^c[D]^d/[A]^a[B]^b
 - The exponents are directly related to the stoichiometry of the equation!!
 - A.k.a make sure the equation is properly balanced!
 - Does not include pure liquids (e.g., H2O or solids)
 - For gases, use a partial pressure variation of the equation
 - Keq = $(pC^c)(pD^d)/(pA^a)(pB^b)$

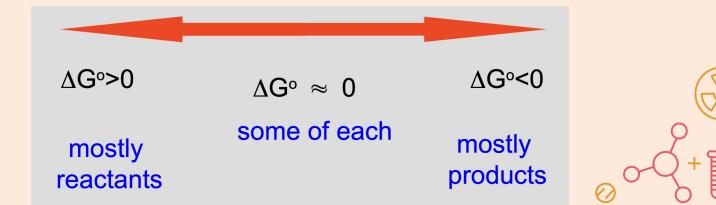






$\twoheadrightarrow \quad \mathsf{K} \text{ and } {\scriptscriptstyle \bigtriangleup} \mathsf{G} \text{ are related} \to \mathsf{K} \text{ is a function of } {\scriptscriptstyle \vartriangle} \mathsf{G}^{\mathsf{o}}$

- As a system gets closer to equilibrium, gibbs free energy decreases
 - Recall: $\triangle G = 0$ means that a reaction is at equilibrium!
 - Therefore, if you know the value of
 ^AG°, then you can determine the
 point of equilibrium for a given reaction





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Thanks!

Please email me if you need anything!



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