

The Saga Continues

- Exam Thurs-chapters 10,11, Second Law and Kinetics up to getting a rate law and rate constant from a table of kinetic data
- Two corrections from Thurs
 - $\text{rate} = -\frac{1}{2} \Delta[A] / \Delta t$
 - dimension of k and overall order-if the overall order is n then the dimensions of k are $M^{-(n-1)}\text{sec}^{-1}$ or $M^{(1-n)}\text{sec}^{-1}$

Comment on Raoult's Law

- A number of students have asked about the following sort of problem
- A mixture of ethanol($P^\circ=60.4\text{torr}$) and acetone($P^\circ=227\text{torr}$) both of which are volatile, has the property shown below. What is the total pressure(torr)?
ethanol: $X_{\text{vap}}=0.0906$
- It would seem to contain inadequate information, but is, in fact, solvable.
- Key idea: is there more than one possible result based upon the data provided?
- If not, then the data must be sufficient to solve it.
- Of use:
 - $X_B=1-X_A$
 - $P_t=P_A^\circ * X_{A(\text{liq})} + P_B^\circ * X_{B(\text{liq})} \Rightarrow P_A^\circ * X_{A(\text{liq})} + P_B^\circ * (1-X_{A(\text{liq})})$
 - $X_{B(\text{vap})} = P_B/P_t \Rightarrow P_B^\circ * (1-X_{A(\text{liq})}) / (P_A^\circ * X_{A(\text{liq})} + P_B^\circ * (1-X_{A(\text{liq})}))$
- Thus, any solution to such a problem, if both P° s are known, requires only any one of the four possible Xs. The mathematics is not as awkward as it might appear once one substitutes values for all known quantities.

More on 1st order processes

- $\ln([A]_t/[A]_0) = -kt$
- Always calculate the half-life since it's a useful signpost in any problem.
- When given $[A]_t$ and $[A]_0$, evaluate the \ln term immediately
- Pay close attention to wording: “remains” vs “consumed” are totally different problems
- If the question is in %, then set $[A]_0 = 100$

When t is given

- When t is given (and assuming k is known), the equation becomes, from a practical standpoint, $[A]_t/[A]_o=e^{-kt}$
- In this case, the right side should be fully evaluated, before proceeding.
- Generic:
- How much remains (is consumed) after...
- It is found that ... remains (is consumed) after..how much did you begin with?
- Again-pay very close attention to wording and to the time dimension.

Why do reactions have rates?

- We know that reactions take place at different rates and that a kinetics study allows us to determine the value of k , the rate constant, which tells us what the rate of the process will be.
- However, it does not tell us why.
- Consider a process such as $A+B \Rightarrow C$
- What fundamental requirements are there for this to occur?
- A and B must collide
- The collision must have the required orientation
 - $H\cdot + \cdot H \Rightarrow H_2$ any collision brings the atoms together correctly
 - $CH_3CH_2CH_2Cl + OH^- \Rightarrow CH_3CH_2CH_2OH + Cl^-$ only collisions of the OH^- on the carbon containing the Cl will have the chance of being productive.
- The collision factor, Z , is the product of the number of collisions and the fraction which are productive. Suppose you had 57 collisions/sec and 0.045 of those could be productive then $Z=2.65$ (these number are not real, just illustrative)

Does Temperature Matter?

- How do temperature changes affect reaction rates?
- In general, for every 10deg increase in T, the rate will double. This is a very useful “rule of thumb.”
- Increasing T increases k, but it is not a simple linear relationship. Rather $\ln k$ is related to T(K).
- There must be some minimum energy needed for the process to proceed (sound familiar?)
- This energy is called the activation energy E_a
- The rate constant, the collision factor and the activation energy are related by the Arrhenius equation:
 - $k = Z \cdot e^{-E_a/RT}$ or
 - $\ln(k_2/k_1) = (-E_a/R)(1/T_2 - 1/T_1)$ (this should look very familiar)
 - a plot of $\ln K$ vs $1/T$ permits determination of E_a
 - The actual use of the Arrhenius equation in calculations is a web only exercise.

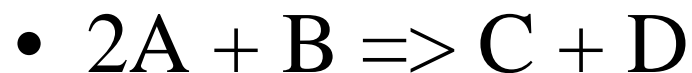
How many steps would it take

- $2A + 3B \Rightarrow C + 2D$
- What is the likelihood that 2As come together with 3Bs and in one great conflagration kick out a C and 2Ds?
- What's the alternative?
- Given that overwhelmingly, particularly in the gas phase, the most likely event is a two body collision, the reaction probably occurs as a result of a series of “bimolecular” steps.

Elementary Reactions and the mechanism

- A chemical reaction which describes two or more species directly reacting to produce product is called elementary.
- Not surprising, most elem. reactions have only two species reacting
- The step by step process consisting of a series of elementary reactions which yields the overall reaction is called a mechanism.
- In a reaction mechanism it is common for species to be produced (and then consumed) which don't appear in the overall reaction, These are called intermediates.

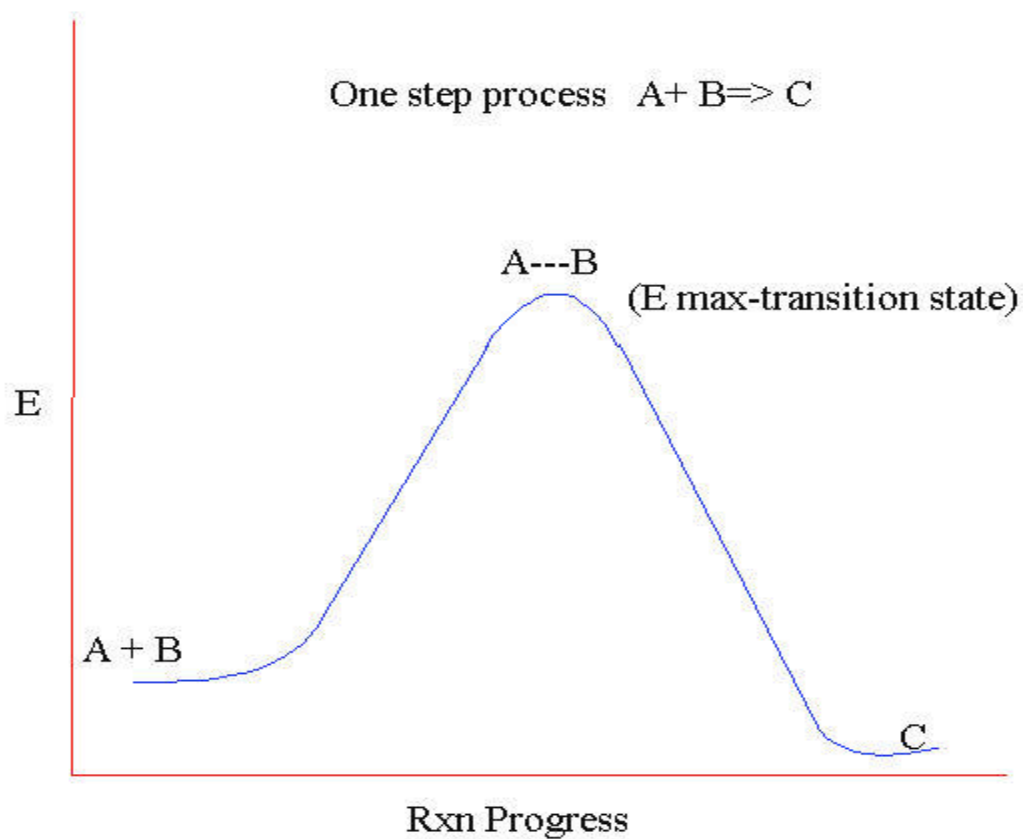
A sample mechanism



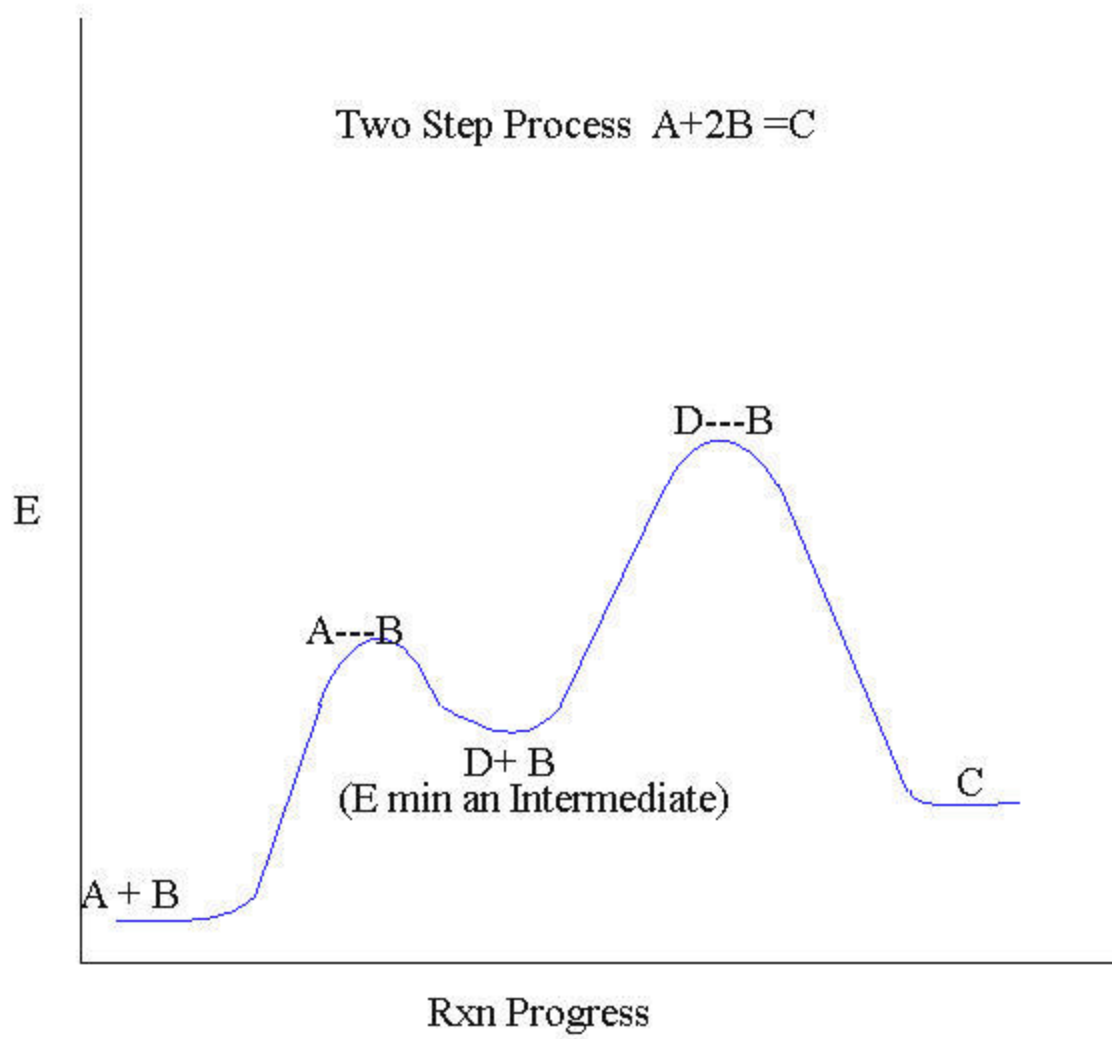
E, which is neither a product nor reagent, but a transitory species in the mechanism is called an intermediate.

The Reaction Progress Diagram

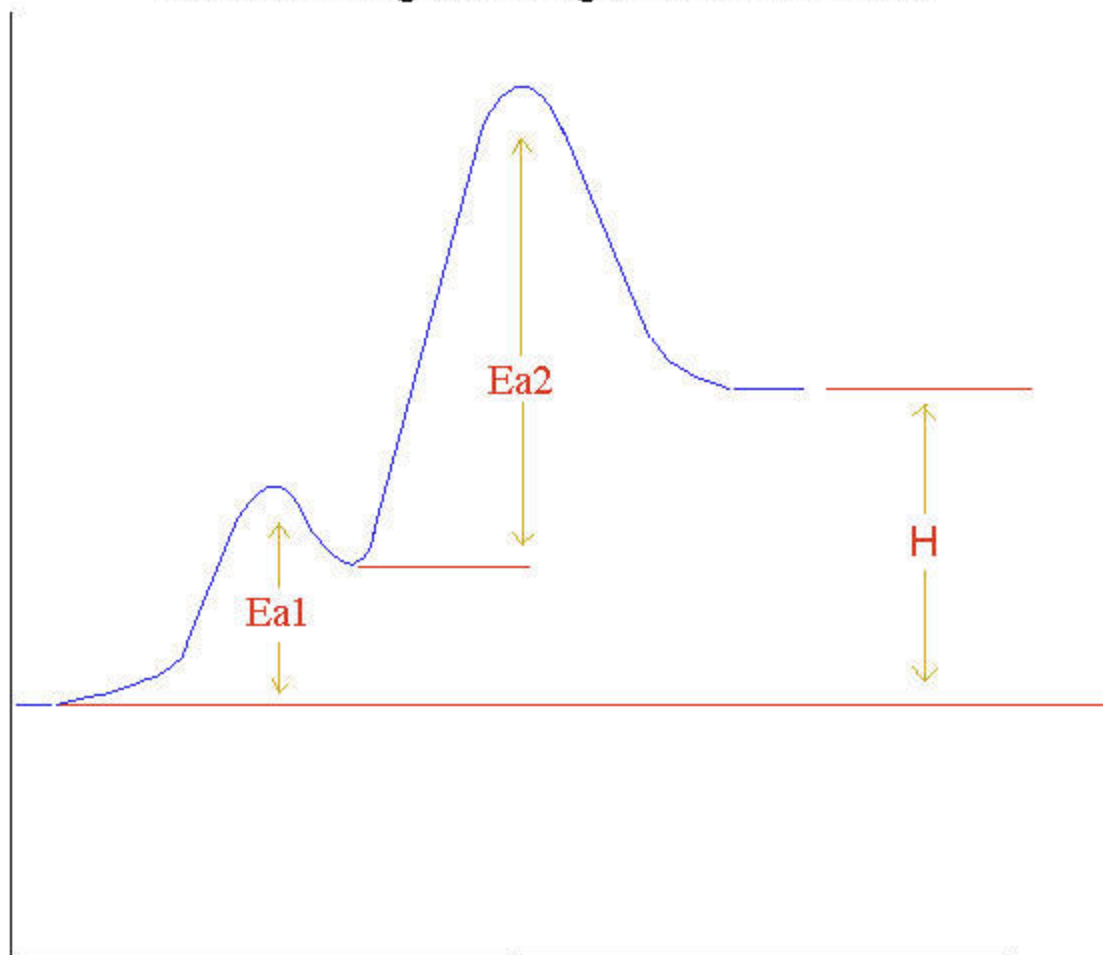
- It is often useful to depict the conversion of reactants into products as a plot of energy vs reaction progress.



Two Step Process $A+2B=C$



Reaction Progress Diagrams-some labels



Mechanism and rate laws

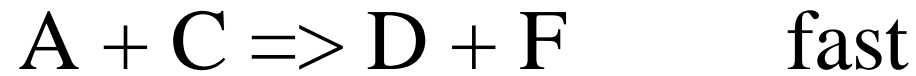
- Logically, each step in a series of elementary reactions is likely to have different individual rates due to differing activation energies
- The overall rate is the result of the slowest step. This is the step with the largest E_a and is called the rds.
- Only steps up to and including the rds affect the rate.
- The order of a species in the rate law will equal its appearances in the mechanism up to and including the rds.

Interpreting/using mechanisms

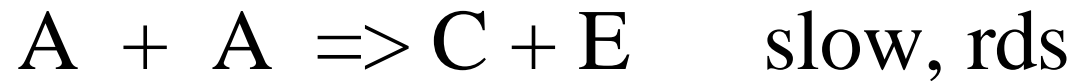
- You are not responsible for “creating” a mechanism for a reaction. Rather, you must be able to connect, in either direction, a rate law and its proposed mechanism
- Example 1-For the reaction $2A + B \Rightarrow 3C$, what rate law is consistent with the following mechanism



• Example 2: $A + 2B + C \Rightarrow D + E$



Example 3 $2A + B \Rightarrow C + D$



Catalysis

- What is a catalyst
- A species which affects the rate of a reaction without itself undergoing a net chemical change
- How does a catalyst work
- By influencing Z and E_a , often by providing an alternative mechanism. Enzymes-proteins which catalyze reactions are often capable of “causing” reactions which would otherwise be vanishing unlikely.
- Homogenous and heterogeneous catalysis-how do they differ?