

1. D (a) and (b) can both affect the amount activation energy required and (c) can provide activation energy.

2. A In only (a) are all reactants and all products one phase (homogeneous).

3. B The quantitative handle on reaction rate as a function of reactant concentrations is the rate law:

$$\text{rate} = k[A]^x[B]^y$$

The sum of the exponents (*which must be determined by experiment, if the exact reaction mechanism is unknown*) as I was saying, the sum of the exponents, x and y , is called the order of the reaction. We found in the experiment presented by this problem, that doubling the concentration of a reactant species quadrupled reaction rate. Its exponent in the rate expression would then be two, and the order of the reaction with respect to that reagent would then be two.

4. B It is not true because a catalyst speeds up both the forward and reverse reaction. It does not change the *thermodynamics* only the *kinetics*.

5. D The stoichiometry of the reaction will not reveal the rate expression (only experiment will) because the stoichiometry does not reveal which species are present in the rate determining step of the reaction.

6. C We know that our rate expression will be some form of the following:

$$\text{rate} = k[A]^x[B]^y$$

We need to determine what the order of the reaction is with respect to the concentrations of our reagents. Notice that in between trials #1 and #3 (through which $[A]$ is constant), the reaction rate triples when $[B]$ is tripled. Therefore the reaction is first order with regard to $[B]$:

$$\text{rate} = k[A]^x[B]^1$$

Between trials #1 and #2, the concentrations of both species are doubled. We know now that doubling $[B]$, doubles the rate. The actual rate is four times greater than even that. So the

reaction rate is second order with regard to $[A]$, quadrupling when $[A]$ is doubled:

$$\text{rate} = k[A]^2[B]^1$$

7. A With first order reactions, we can express the time for the concentration of reactant to be halved:

$$t_{1/2} = \frac{.693}{k}$$

We need the amount of time for our concentration to decrease to 1/30 of its original value:

$$\frac{1}{30} = \frac{1}{3^2} = \left(\frac{1}{2}\right)^5$$

So we are talking about approximately five half lives.

8. C The *Arrhenius equation* shows the rate constant to be a function of the activation energy and the temperature:

$$k = Ae^{-E_a/RT}$$

or

$$\log k = \log A + \left(\frac{-E_a}{2.303 R}\right)\left(\frac{1}{T}\right)$$

k = rate constant

A = frequency factor

E_a = activation energy

R = ideal gas constant

T = temperature

9. B The reaction is exothermic because the system loses energy over the entire reaction coordinate. It is unimolecular because the activated complex of the rate determining step involves only one species.

10. B This is the highest energy hurdle the reaction must cross, so the rate is dependent on particles obtaining such energy (activation energy).

11. A The SN1 mechanism proceeds by formation of the carbocation followed by capture by the nucleophile. As can be seen in the energy diagram, the first step requires greater activation energy and is thus rate determining.

12. A With a strong base, elimination would predominate (forming alkene) over substitution.