5.1 Reaction Rates.

5.1.A: Convert between the rate of appearance or disappearance of different species in a chemical reaction using ratios.

1. Determine the rate of appearance of B in the reaction $2A \rightarrow B$, if the rate of disappearance of A is 0.35 Ms^{-1}

Answer

$$0.35\ Ms^{-1}\ A \times \frac{1\ Ms^{-1}\ B}{2\ Ms^{-1}\ A} = 0.78\ Ms^{-1}\ B$$

The rate that B is being produced is 2x as fast as the rate A is being consumed. This information comes from the coefficients of the balanced chemical equation.

5.1.B: Justify how a change in conditions (surface area, concentration/pressure, temperature, presence of a catalyst) will affect the rate of the reaction.

1. Explain why increasing temperature generally increases the rate of reaction.

Answer: When the temperature of a sample is increased the average speed of the particles increases which increases the average kinetic energy of the sample. This increases:

1. the frequency of collisions and,
2. the fraction of collisions with sufficient energy to overcome the activation energy

Both factors lead to an increase in the frequency of efficient collisions so the rate is increased. (An understanding of the collision model (unit 5.5) is required for this answer)

5.2 Introduction to Rate Law.

5.2.A: Write a rate law for a reaction using initial rate data from multiple trials.

1. Determine the rate law for the reaction: X + Y → XY Using the lab data in the table below.

Trial	Initial[X] (M)	Initial[Y] (M)	Initial Rate of Appearance of XY (Ms^{-1})
1	0.010	0.010	0.0050
2	0.010	0.020	0.010
3	0.020	0.010	0.020

Answer: Comparing trials 1 and 2: The concentration of X has remained constant and the concentration of Y has doubled (x2), this caused the rate to double (x2). Therefore the reaction is 1st order with respect to [X] because $2^1=2$.

Comparing trials 1 and 3: The concentration of X doubled (x2) and the the concentration of Y remained constant, this caused the date to quadruple (x4). Therefore the rate is 2nd order with respect to [Y] because $2^2=4$

Putting the 2 individual orders together we get a rate law of: Rate = $k[X][Y]^2$

5.2.B: Determine the overall order of the reaction by adding the powers of the reactant concentrations in the rate law.

1. What is the overall order of the reaction with an experimentally determined rate law of: rate = $k[A]^2[B]$?

Answer: The overall order of the reaction is calculated by adding the exponents in rate law. In this case 2 + 1 = 3. The overall order of the reaction is 3rd order.

5.2.C: Calculate the value of the rate constant (k) and express it with the correct units.

1. The data below was used to determine the rate law of: rate = k[X][Y]. Determine the value of the rate constant (k) and its units.

Trial	Initial[X] (M)	Initial[Y] (M)	Initial Rate of Appearance of XY (Ms^{-1})
1	0.010	0.010	0.0050
2	0.010	0.020	0.010
3	0.020	0.010	0.010

Answer: We substitute values from any trial into the rate law and solve for k. Using values from trial 1:

rate = k[X][Y]

$0.0050 Ms^{-1} = k(0.01M)(0.01M)$

$$k = \frac{0.0050 Ms^{-1}}{(0.01M)(0.01M)} = 50.\ M^{-1}s^{-1}$$

5.2.D: Understand that the rate constant (k) is dependent on temperature and therefore specific to a temperature.

1. Predict whether the following changes would affect the value of the rate constant (k)?
    a) Increasing the temperature of the reactants from 300K to 400K.
    b) Increase the concentration of the reactants from 1.0M to 2.0M.
    c) Reducing the volume of a reaction container for gas phase reactants.

Answer:
a) Yes, the rate constant (k) will change as the temperature has changed. At equivalent initial concentrations the rate will not be greater therefore k will be greater.

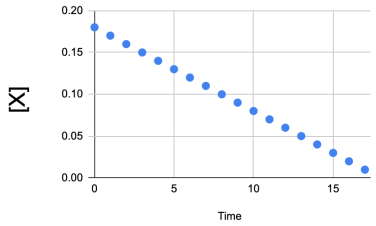
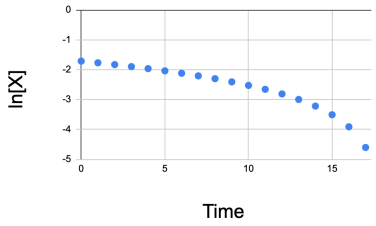
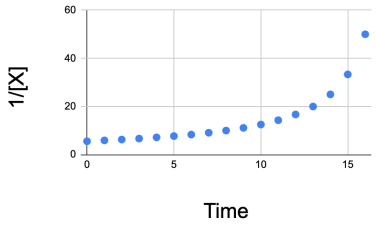
b) No, the rate constant (k) will not change because the temperature has not changed.

c) No, rate constant (k) will not change because the temperature has not changed. Also, changing the volume of the container at constant temperature is equivalent to changing the concentration. Therefore questions b and c required the same logic.

5.3 Concentration Changes Over Time.

5.3.A: Determine the order of a reaction by examining graphs of [A], ln[A] and 1/[A] vs time.

1. Identify the order of the reaction with respect to [X] based on the plots below.

[X] vs time.	ln[X] vs time.	1/[X] vs time.
		

Answer: The [X] vs time plot is linear while the other 2 plots are not. Therefore this reaction must be 0^{th} order with respect to [X].

Trick! Remember that the integrated rate laws on the Equation Sheet are in order (0^{th} order, 1^{st} order, 2^{nd} order). By looking at the sheet and seeing that the first formula uses [A] not ln[A] or 1/[A] you can see that this must be a 0^{th} order reaction with respect to [X].

5.3.B: Use the integrated rate law corresponding to the order of a reaction to determine the value of k with the appropriate units.

1. A student is studying a first order chemical reaction and collects the data shown in the table below. Determine the value and units of the rate constant (k) using the appropriate integrated rate law.

Time (sec)	[X] (M)
0.0	1.0
60.0	0.40

Answer: Use the first order integrated rate law from the Equation sheet (the 2nd equation in Kinetics).

$\ln[A]_t - \ln[A]_o = -kt$
$\ln(0.4) - \ln(1) = -k(60s)$

$$-k = \frac{\ln(0.4)-\ln(1)}{60s} = -0.01527s^{-1}$$

$k = 0.015\ s^{-1}$

Hint: natural log's (ln) are considered unitless.

5.3.C: Use the half-life equation to solve for the rate constant (k) or the half-life ($t_{1/2}$)

1. Calculate the half-life of a reaction with $k = 0.0030\ s^{-1}$.

Answer: Use the half-life equation from the Equation sheet (the 4nd equation in Kinetics).

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0030\ s^{-1}} = 2.3s$$

The concentration will be reduced by half every 2.3 seconds.

5.3.D Apply the fact: ***Only first order chemical reactions have consistent half-lives.***

1. Without graphing or using an integrated rate law, the data shown below gives evidence for the reaction being first order.

Time (sec)	[X] (M)
0	1.0
10	0.68
20	0.50
30	0.34
40	0.25
50	0.16
60	0.125

Answer: In the first 20 seconds [X] is halved, going from 1.0M to 0.50M. In the next 20 seconds [X] is again halved going from 0.050M to 0.25M. This proves that the reaction has a consistent half-life which is a feature of only 1st order reactions, proving this is a first order reaction.

5.4 Elementary Reactions.

5.4.A: Use coefficients of elementary steps to determine the rate law.

1. Write the rate law for the elementary step A + B → C.

Answer: rate= k[A][B]

The “invisible” coefficients in front A and B in the chemical equation become the “invisible” exponent on [A] and [B] in the rate law. Remember that we can only write rate laws using this method for elementary steps and never overall chemical equations.

5.4.B: Justify if a theorized elementary step is likely or not based on the number of particles colliding (its molecularity).

1. Explain why the elementary step 2A + 3B → A_2B_3 is not likely part of a true reaction mechanism.

This elementary step would require 5 particles (2A’s and 3B’s) to collide at the same time and with sufficient kinetic energy for an efficient collision. This would happen so rarely that the step would be extremely slow and not a good candidate for a true reaction mechanism.

5.5 Collision Model.

5.5.A: Apply the fact: *breaking and forming of bonds requires a collision that has sufficient energy and correct orientation.*

1. Explain why collisions between particles with very large kinetic energies are not always successful.

Answer: The collisions don't have correct orientation. Efficient collisions required both sufficient kinetic energy to overcome the activation energy and correct orientation. High energy collisions with improper orientation will not be successful.

5.5.B: Use the collision model to justify how reactant concentration, temperature, and surface area affects the frequency of successful collisions.

1. Use particle level reasoning to explain how the grinding of a solid reactant into a fine powder increases the rate of a chemical reaction.

Answer: When a solid is ground into a powder the surface area is increased. This exposes more particles to collisions with the other reactants increasing the frequency of efficient collisions and therefore increasing the rate of the reaction.

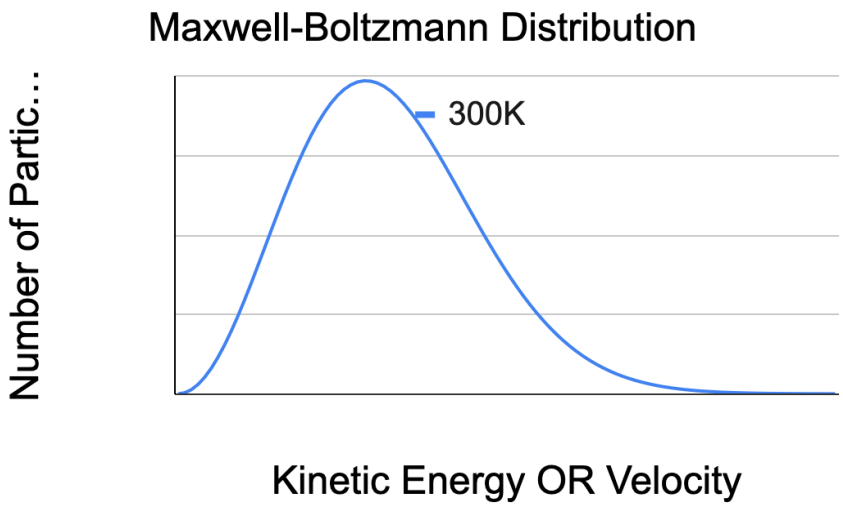
2. Use particle level reasoning to explain why increasing the concentration of [HCl] in the reaction between HCl (aq) and $CaCO_3$ (s) will increase the rate of the chemical reaction.

Answer: Increasing the concentration of HCl results in more H^+ ions per volume of solution. These ions collide more frequently with the $CaCO_3$ particles more frequently increasing the rate of the chemical reaction.

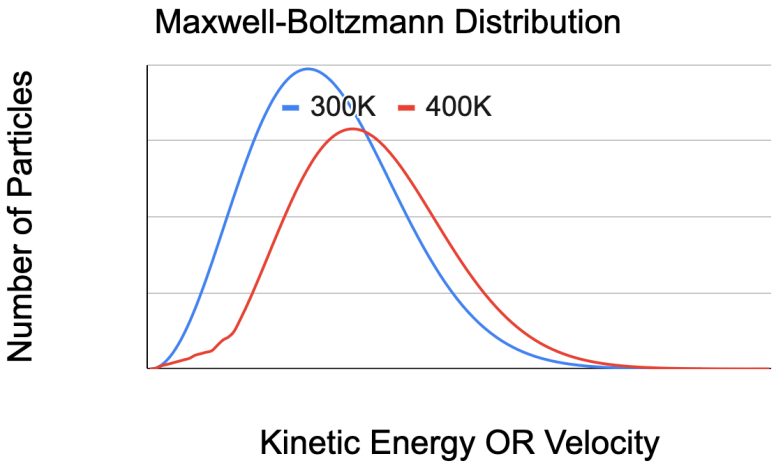
Hint: The explanation of why a strong acid like HCl dissociates into H^+ and Cl^- ions is in unit 8.

5.5.C: Re-draw a Maxwell Boltzmann Distribution after a temperature change has occurred.

1. The curve below represents a Boltzmann distribution at 300K, on the same graph sketch the distribution at 400K.

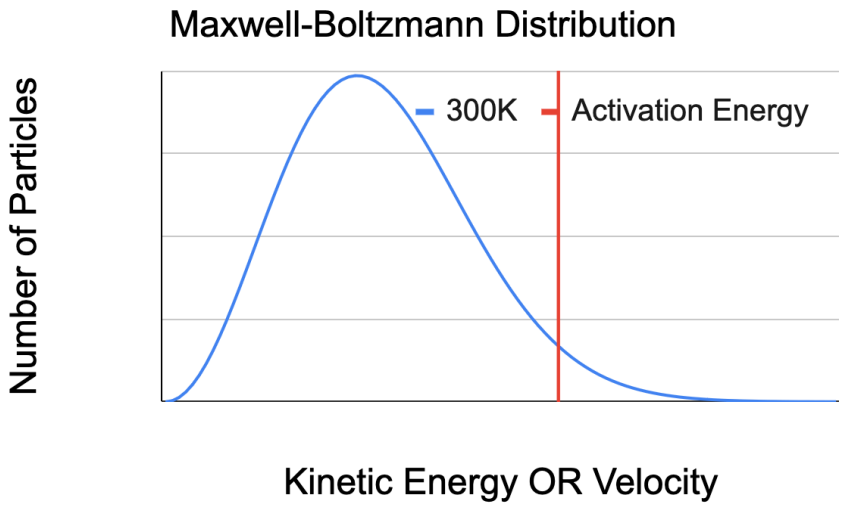


Answer: the distribution should be shifted to the right because the average kinetic energy is now greater and slightly compressed to attempt to maintain the same area under the curve.

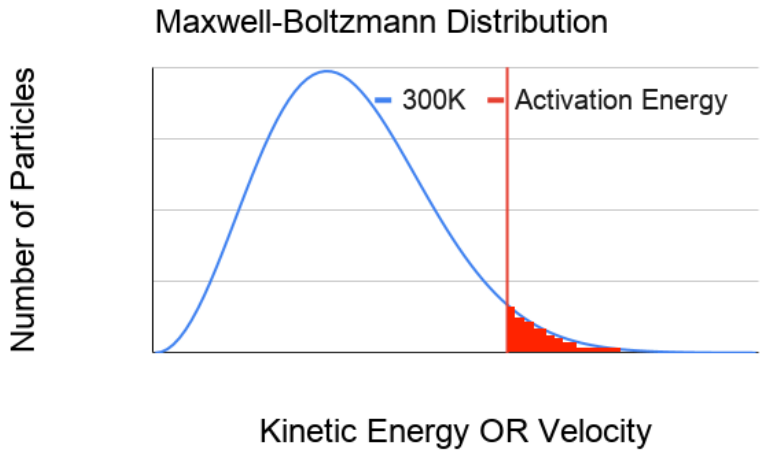


5.5.D: Apply knowledge of how Maxwell-Boltzmann distributions connect to activation energy and reaction rate

1. In the image below shade the region under the curve that corresponds to particles with sufficient kinetic energy to overcome the activation energy



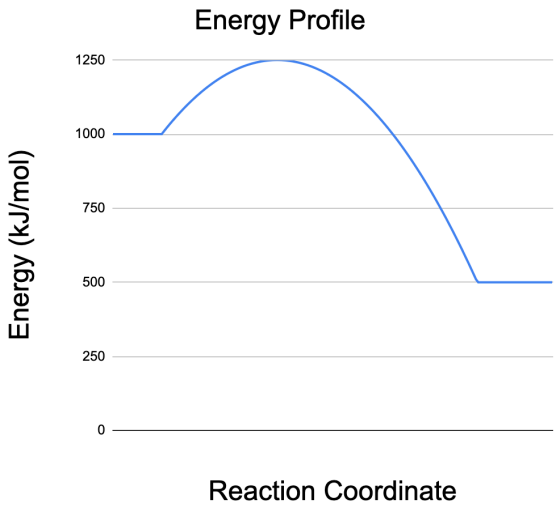
Answer: The area under the curve beyond the activation energy line represents the particles with sufficient kinetic energy for an efficient collision.



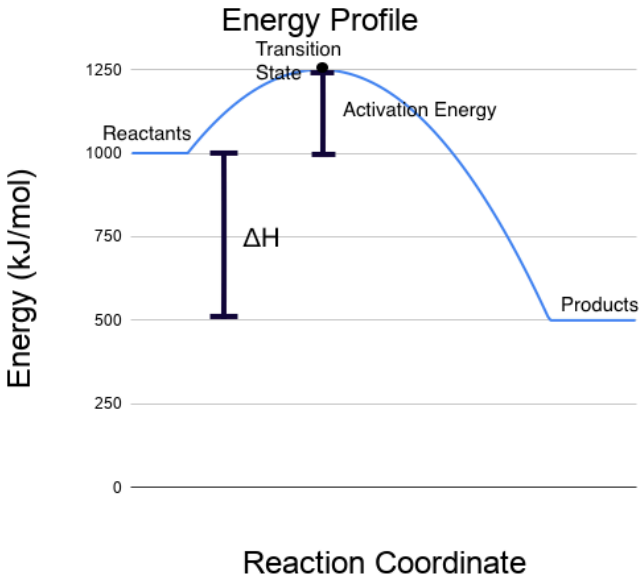
5.6 Reaction Energy Profile.

5.6.A: Label the areas on a reaction energy profile: reactants, transition state, products, activation energy, and change in enthalpy (ΔH).

1. Label the reactants, transition state, products, activation energy, and change in enthalpy (ΔH) on the energy profile below.

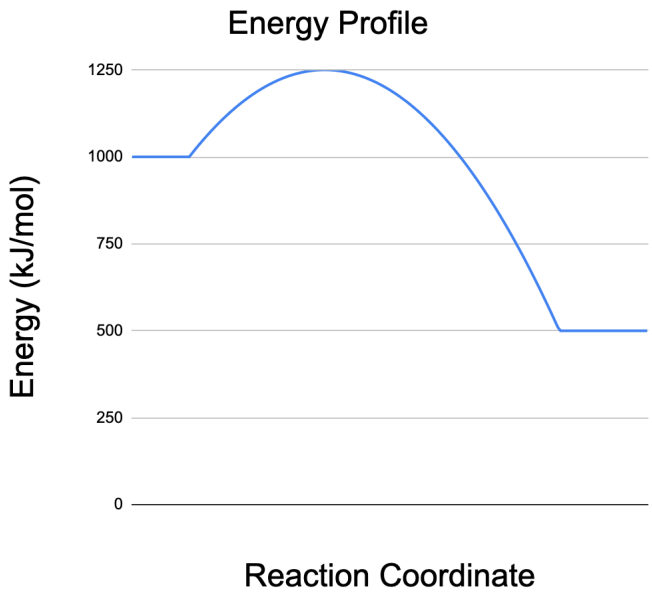


Answer:



5.6.B: Determine the values of activation energy and change in enthalpy (ΔH) for a reaction using its energy profile.

1. Determine the value of the activation energy and the change in enthalpy (ΔH) for the reaction depicted by the energy profile below.



Answer: The difference between the transition state and the reactants is the activation energy (1250 -1000= 250kJ/mol) and the difference between the product and reactants is the ΔH (500-1000= -500kJ/mol).

5**.6.C: Justify the relationship between temperature, activation energy, and rate of a reaction. (This relationship is explained with the Arrhenius equation but questions requiring calculating the formula are excluded from the exam.**

1. A student states: Chemical reactions have higher reaction rates at higher temperatures because increasing the temperature decreases the activation energy of the reaction. Do you agree or disagree with the student? Justify your answer.

Answer: I disagree with the student. Activation energy is not affected by temperature. Instead, as temperature increases, the average kinetic energy of the molecules increases, resulting in a greater fraction of molecules having enough energy to overcome the fixed activation energy. Therefore, the reaction rate increases.

5.7 Introduction to Reaction Mechanisms.

5.7.A: Identify the: reactants, products, intermediates, catalysts from a reaction mechanism.

1. Identify each chemical species in the reaction mechanism as either a reactant, product, intermediate, or catalyst.

Step	Speed
$NO + O_3 \rightarrow NO_2 + O_2$	slow
$O + NO_2 \rightarrow NO + O_2$	fast

Answer: NO is consumed then reproduced therefore is a catalyst
NO_2 is produced then consumed therefore is an intermediate
O_3 is consumed therefore is a reactant
O_2 is produced therefore is a product

5.8 Reaction Mechanism and Rate Law.

5.8.A: Use the slow step of a mechanism to write the rate law for the overall reaction.

1. Use the reaction mechanism below to determine the overall rate law of the reaction.

Step	Speed
$NO_2 + Cl_2 \rightarrow NO_2Cl + Cl$	slow
$Cl + NO_2 \rightarrow NO_2Cl$	fast

Answer: The overall rate law is the rate law for the slow step. Therefore, the overall rate law is: rate= $[NO_2][Cl_2]$

5.8.B: Justify if a provided reaction mechanism is valid by verifying the sum of the elementary steps and that the rate law matches the rate determining step.

1. The reaction: $O_3 + O \rightarrow 2O_2$ has an experimentally determined rate law: rate = $k[NO][O_3]$. Justify whether the proposed mechanism below is a valid mechanism.

Step	Speed
$NO_2 + Cl_2 \rightarrow NO_2Cl + Cl$	slow
$Cl + NO_2 \rightarrow NO_2Cl$	fast

Answer: when the intermediate Cl is removed the elementary steps sum to the overall chemical reaction and the rate law for the slow step: rate=$k[NO_2][Cl_2]$ matches the experimentally determined rate law. Therefore the mechanism is valid.

5.9 Pre-Equilibrium Approximation.

5.9.A: Write a rate law for the overall reaction when the slow step is not the first step by substituting species from the fast equilibrium step.

1. Write the overall rate law based on the reaction mechanism below.

Step	Speed
$A + 2C \leftrightharpoons AC_2$	Fast
$A + AC_2 \rightarrow 2AC$	Slow

Answer: the slow step typically produces the overall rate law, which would be rate=$k_2[A][AC_2]$.

However the overall rate law should not contain an intermediate. The first step contains an equilibrium so the rate laws for the forward and reverse reaction can be written as:

$Rate_{forward} = k_1[A][C]^2$ and $Rate_{reverse}=k_{-1}[AC_2]$.

The since they are at equilibrium:

$Rate_{forward}=Rate_{reverse}$ therefore $k_1[A][C]^2 = k_{-1}[AC_2]$

This can be solved for $[AC_2]$:

$$[AC_2] = \frac{k_1[A][C]^2}{k_{-1}}$$

Then substituted into the overall rate law for the intermediate $[AC_2]$:

$$Rate = k_2[A][AC_2] = \frac{k_2[A]k_1[A][C]^2}{k_{-1}} = \frac{k_2k_1[A]^2[C]^2}{k_{-1}} = k'[A]^2[C]^2$$

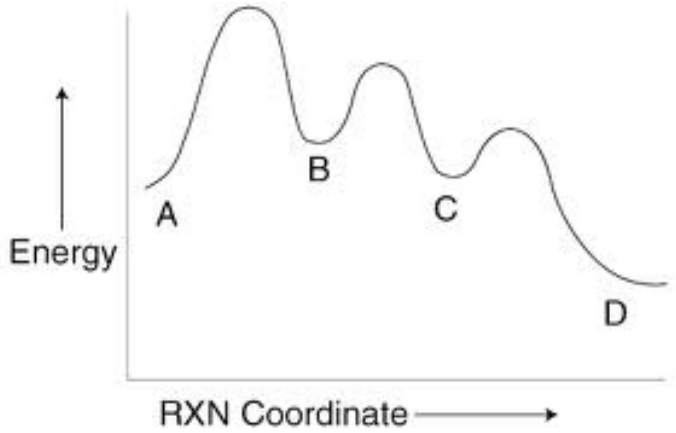
Overall rate law: Rate=$k'[A]^2[C]^2$ in this case k' is a rate constant made from k_1, k_{-1}, k_2

5.10 Multistep Reaction Energy Profile.

5.10.A: Draw conclusions about the relative rate of the elementary steps of a reaction mechanism by looking at the individual activation energies shown on a multistep energy profile.

1. Sketch an energy profile for a 3 step mechanism where the first step is the rate determining step.

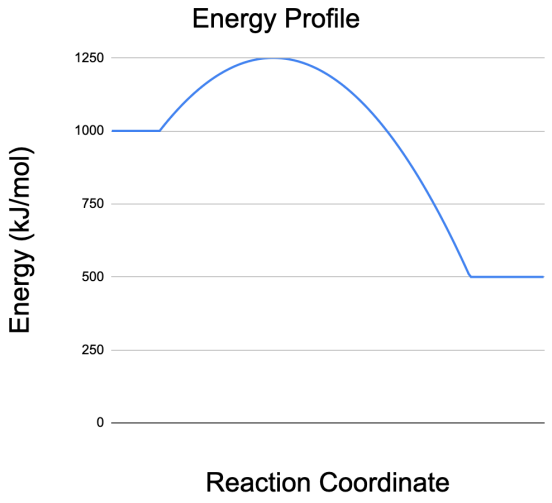
Answer: should have 3 peaks and the activation energy of the first step should be the greatest.



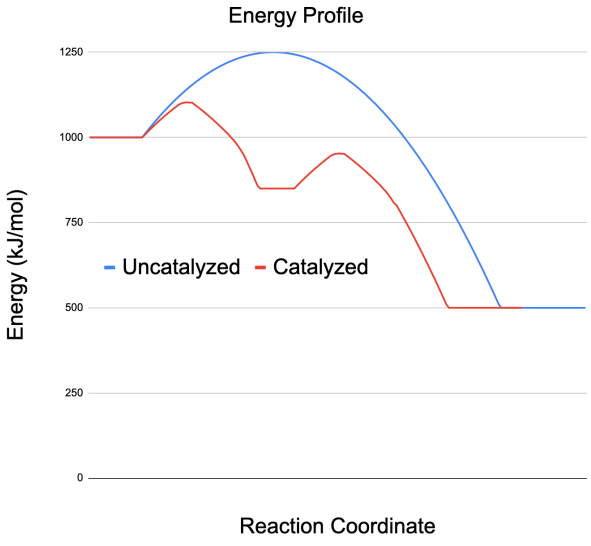
5.11 Catalysis.

5.11.A: Modify an energy profile to show the effect of a catalyst.

1. Sketch the energy profile for the reaction depicted below after a catalyst is added.



Answer: an energy profile with a smaller activation energy than the original plot. Since catalysts most often provide an alternative reaction mechanism a catalyzed energy profile will typically have a different number of steps than the uncatalyzed.



5.11.B: Explain how a catalyst increases reaction rate by either providing an alternative reaction mechanism where the rate determining step has a lower activation energy OR improving the probability of collisions being effective.

1. In the lungs the reaction of $CO_2 + H_2O \rightarrow H_2CO_3$ is catalysed by the enzyme carbonic anhydrase. Suggest what carbonic anhydrase does at the particle level that increases the rate of reaction.

Answer: carbonic anhydrase could bond with either the CO_2 or H_2O making a molecule which is able to react with the other reactant more favourably (with a lesser activation energy or better orientation).

The true mechanism involves carbonic anhydrase bonding with a H_2O which then causes the H_2O to deprotonate to OH^- which in turn allows it to bonds with CO_2.

H_2O + carbonic anhydrase $\rightarrow$ H_2O-carbonic anhydrase
H_2O-carbonic anhydrase + H_2O $\rightarrow$ ^-OH-carbonic anhydrase + H_3O^+
^-OH-carbonic anhydrase + CO_2 $\rightarrow$ HCO_3^- + carbonic anhydrase
HCO_3^- + H_3O^+ $\rightarrow$ $H_2CO_3 + H_2O$

Predicting the true mechanism would not be assessed on the AP exam. Insteading students would be assessed on being able to justify that the enzyme must have provided a lower energy reaction mechanism or improved orientation of reactants.