

This print-out should have 22 questions. Multiple-choice questions may continue on the next column or page – find all choices before answering.

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**001 10.0 points**

A and B react to form C according to the single step reaction



Which of the following is the correct rate equation for [B] and the correct units for the rate constant of this reaction?

1.  $\frac{\Delta[B]}{\Delta t} = -2k[A][B]; \quad 1/(M \cdot s)$

2.  $\frac{\Delta[B]}{\Delta t} = \frac{-2k[A][B]}{[C]}; \quad 1/(M \cdot s)$



3.  $\frac{\Delta[B]}{\Delta t} = -2k[A][B]^2; \quad 1/(M^2 \cdot s)$  **correct**

4.  $\frac{\Delta[B]}{\Delta t} = -k[A][B]^2; \quad 1/M^2$

5.  $\frac{\Delta[B]^2}{\Delta t} = -2k[A][B]^2; \quad 1/(M \cdot s)$

**Explanation:**

By definition,

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{1}{2} \frac{\Delta[B]}{\Delta t} = \frac{\Delta[C]}{\Delta t}$$

Since this is a simple-step reaction the rate law can be written from the balanced equation and is third order, where the units of  $k$  are  $M^{-2} \cdot s^{-1}$ .

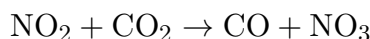
$$\text{Rate} = -\frac{1}{2} \frac{\Delta[B]}{\Delta t} = k[A][B]^2$$

$$\text{or } \frac{\Delta[B]}{\Delta t} = -2k[A][B]^2$$

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**002 10.0 points**

The reaction



has a rate law that is second order in  $NO_2$ . Which of these statements describes the mechanism that explains this unexpected rate law?

1. A multi-step reaction mechanism in which a first unimolecular decomposition of  $NO_2$  is the rate determining step.

2. A multi-step reaction mechanism in which a first bimolecular collision between  $NO_2$  molecules is the rate determining step. **correct**

3. A single-step reaction mechanism in which a bimolecular collision between  $NO_2$  and  $CO_2$  is the rate determining step.

4. A single-step reaction mechanism in which a first unimolecular decomposition of  $NO_2$  is the rate determining step.

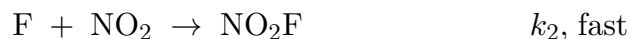
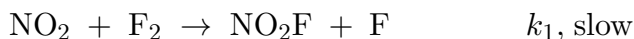
5. A single-step reaction mechanism in which a bimolecular collision between  $NO_2$  molecules is the rate determining step.

**Explanation:**

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**003 10.0 points**

Consider the mechanism



Which rate law would be proposed from this mechanism?

1. rate =  $k_1 [NO_2] [F_2]$  **correct**

2. rate =  $k_1 [NO_2F] [F]$

3. rate =  $k_2 [NO_2]^2$

4. rate =  $k_1 k_2 [NO_2]^2$

5. rate =  $k_2 [NO_2] [F]$

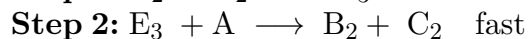
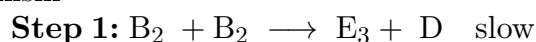
**Explanation:**

The first reaction is slow, which means it is the rate determining step, so the rate is mainly related to the concentration of  $NO_2$ .

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**004 10.0 points**

Determine the overall balanced equation for a reaction having the following proposed mechanism



and write an acceptable rate law.

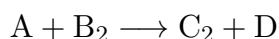
1.  $B_2 + B_2 \longrightarrow E_3 + D; R = k [B_2]^2$
2.  $A + B_2 \longrightarrow C_2 + D; R = k [A][B_2]$
3.  $E_3 + A \longrightarrow B_2 + C_2; R = k [E_3] [A]$
4.  $A + B_2 \longrightarrow C_2 + D; R = k [B_2]^2$  **correct**

**Explanation:**

Step 1:  $B_2 + B_2 \longrightarrow E_3 + D$  slow

Step 2:  $E_3 + A \longrightarrow B_2 + C_2$  fast

balanced equation, rate law = ?



(from the 2 molecules of  $B_2$  in the rate-determining step)

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**005 10.0 points**

A given reaction has an activation energy of 24.52 kJ/mol. At 25°C the half-life is 4 minutes. At what temperature will the half-life be reduced to 20 seconds?

1. 125°C **correct**
2. -1.19°C
3. 75.0°C
4.  $\geq 150^\circ\text{C}$
5. 115°C
6. 57.9°C
7. 25.5°C
8. -59.9°C
9. 100.°C

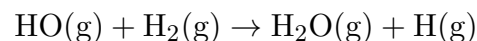
**Explanation:**

Use the Arrhenius equation. The 20 second reaction is running 12 times that of the 240 reaction. Put that ratio  $\left(\frac{240}{20} = 12\right)$  in for the  $\ln\left(\frac{k_a}{k_b}\right)$  term. Remember to use Kelvin for the temperatures.

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**006 10.0 points**

For the reaction



a plot of  $\ln k$  vs  $\frac{1}{T}$  gives a straight line with a slope equal to  $-5.1 \times 10^3$  K. What is the activation energy for the reaction?

1. 42 kJ/mol **correct**
2. 0.61 kJ/mol
3. 5.1 kJ/mol
4. 98 kJ/mol
5. 12 kJ/mol

**Explanation:**

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**007 10.0 points**

A certain reaction has an activation energy ( $E_a$ ) of 0.8314 kJ · mol<sup>-1</sup> and a rate constant ( $k$ ) of 2.718 s<sup>-1</sup> at -73 °C. At -173 °C, which expression for the rate constant is correct?

1.  $\ln k_2 = 0$
2.  $\ln k_2 = -0.5$
3.  $\ln k_2 = 1.5$
4.  $\ln k_2 = 1$
5.  $\ln k_2 = 0.5$  **correct**

**Explanation:**

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

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**008 10.0 points**

A food substance kept at 0°C becomes rotten (as determined by a good quantitative test) in 8.3 days. The same food rots in 10.6 hours at 30°C. Assuming the kinetics of the microorganisms enzymatic action is responsible

for the rate of decay, what is the activation energy for the decomposition process?

*Hint:* Rate varies INVERSELY with time; a faster rate produces a shorter decomposition time.

1. 23.4 kJ/mol
2. 0.45 kJ/mol
3. 2.34 kJ/mol
4.  $6.72 \times 10^1$  kJ/mol **correct**
5.  $8.2 \times 10^{-7}$  kJ/mol

**Explanation:**

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**009 10.0 points**

A catalyst

1. changes the reaction mechanism to insure that  $K$  is increased.
2. increases  $K$  to favor product formation.
3. speeds up the reaction but does not change  $K$ . **correct**
4. speeds up the reaction and increases  $K$  to favor product formation.

**Explanation:**

$K$  is a thermodynamic variable based on  $\Delta G^0$ . A catalyst lowers the activation energy of the reaction ( $E_a$ ), which speeds it up. It does **NOT** do anything to the equilibrium position of the system, however.

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**010 10.0 points**

The fraction of molecules that collide with a kinetic energy equal to the activation energy for a reaction decreases rapidly with an increase in temperature.

1. True
2. False **correct**

**Explanation:**

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**011 10.0 points**

All else being equal, a reaction with a higher activation energy compared to one with a lower activation energy will

1. not be any different.
2. be more endothermic.
3. proceed slower. **correct**
4. be more exothermic.
5. proceed faster.

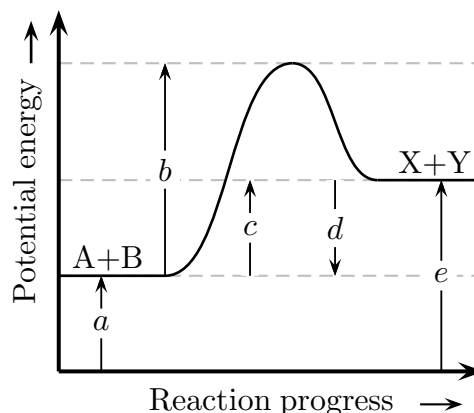
**Explanation:**

The larger the activation energy, the smaller the number of reactant particles that have the necessary energy and the slower the reaction.

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**012 10.0 points**

Consider the following potential energy diagram.



If a catalyst were added, which arrow would change, and how?

1. the length of arrow  $b$  would be smaller. **correct**
2. the length of arrow  $a$  would be smaller.
3. the length of arrow  $d$  would be larger.
4. the length of arrow  $a$  would be larger.
5. the length of arrow  $c$  would be larger.

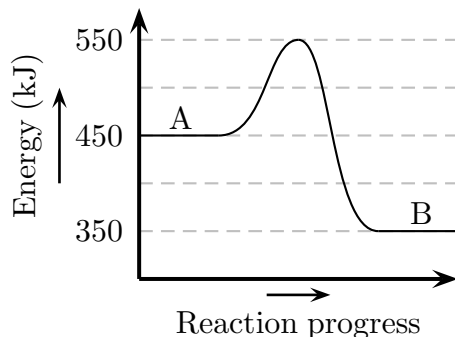
- the length of arrow  $b$  would be larger.
- the length of arrow  $e$  would be smaller.

**Explanation:**

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**013 (part 1 of 2) 10.0 points**

Consider potential energy diagram



What is the change in enthalpy ( $\Delta H$ ) for the reaction  $A \rightarrow B$ ?

- +350 kJ
- 50 kJ
- 350 kJ
- +100 kJ
- 100 kJ **correct**

**Explanation:**

$$\begin{aligned} H_i &= H_A = 450 \text{ kJ} \\ H_f &= H_B = 350 \text{ kJ} \\ \Delta H &= H_f - H_i = H_B - H_A \\ &= 350 \text{ kJ} - 450 \text{ kJ} \\ &= -100 \text{ kJ} \end{aligned}$$

Notice that  $\Delta H$  is negative; the reaction is exothermic.

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**014 (part 2 of 2) 10.0 points**

What is the activation energy  $E_a$  for the reaction in the previous question?

- +450 kJ
- +200 kJ
- +550 kJ

4. +350 kJ

5. +100 kJ **correct**

**Explanation:**

Activation energy  $E_a$  is the additional energy that must be absorbed by the reactants in their ground states to allow them to reach the transition state:

$$\begin{aligned} E_a &= E_{\text{transition state}} - E_{\text{reactant}} \\ &= 550 \text{ kJ} - 450 \text{ kJ} = 100 \text{ kJ} \end{aligned}$$

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**015 10.0 points**

A catalyst facilitates a reaction by

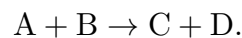
- decreasing the temperature at which the reaction will proceed spontaneously.
- lowering the activation energy of the reaction. **correct**
- shifting the position of the equilibrium of the reaction.
- making the reaction more exothermic.
- increasing the activation energy for the reverse reaction.

**Explanation:**

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**016 10.0 points**

Compound A reacts with compound B and forms products C and D according to the equation



This reaction is found to proceed very slowly at first, then to proceed very quickly until virtually all A and B have been consumed. Suggest an explanation for this.

- Compound B is really a very reactive metal ion.
- The reaction has a small activation energy.

3. Reaction rates increase as reactant concentrations decrease as a general rule.

4. The reaction is irreversible.

5. One of the products is a catalyst for the reaction. **correct**

**Explanation:**

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**017 10.0 points**

Which of the following does NOT affect the rate of a reaction?

1. the temperature of the reactants

2. the value of  $\Delta H$  **correct**

3. the value of  $E_a$

4. the presence of a catalyst

**Explanation:**

The presence of a catalyst increases reaction rate, as does increasing the temperature of the reactants. A large  $E_a$  slows down a reaction.

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**018 10.0 points**

Which of the following statements is true?

1. If the exponents in the rate-law match the coefficients in the balanced chemical equation, then we know that the reaction takes place in one step.

2. The exponents in the rate-law must match the coefficients in the balanced chemical equation for the reaction.

3. If the exponents in the rate-law do not match the coefficients in the balanced equation, then we know that the reaction does not take place in one step. **correct**

4. The rate-law for a reaction can be predicted from the balanced chemical equation.

**Explanation:**

Rate laws are written based on experimen-

tal data, not the balanced equation.

The coefficients in the balanced equation are used in writing the rate law only in the case where the reaction is known to take place in only one step.

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**019 10.0 points**

Reaction mechanisms usually involve only unimolecular and/or bimolecular elementary steps. Is this generally true or false and give a statement as to why?

1. False, because mechanisms can have any molecularity.

2. True, because collisions of higher molecularity are statistically very rare. **correct**

3. True, because the activation energy for collisions of higher molecularity would be too great.

4. False, because the rate-determining step for most reactions is termolecular.

**Explanation:**

It is statistically unlikely that any reaction requiring the simultaneous collision of 3 or more molecules will occur frequently enough to contribute to the rate of the reaction. Termolecular and higher molecularities would happen so infrequently that there would not be measurable rate of reaction.

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**020 10.0 points**

Which of the following is/are always true concerning collision and transition state theory?

- I) Transition states are short-lived;
- II) A balanced reaction shows which species must collide for the reaction to occur;
- III) Intermediates are short-lived.

1. I, III

2. I, II

3. I only **correct**

4. III only

5. II only

6. II, III

7. I, II, III

**Explanation:**

Transition states are relatively very high energy, unstable, ill-defined and thus short-lived species. The mechanism shows which species must collide. Intermediates are products or early steps in a mechanism that are consumed stoichiometrically in subsequent steps.

**021 10.0 points**

Consider the reaction mechanism

Step	Reaction
1	$\text{Cl}_2 + \text{Pt} \rightarrow 2 \text{Cl} + \text{Pt}$
2	$\text{Cl} + \text{CO} + \text{Pt} \rightarrow \text{ClCO} + \text{Pt}$
3	$\text{Cl} + \text{ClCO} \rightarrow \text{Cl}_2\text{CO}$
overall	$\text{Cl}_2 + \text{CO} \rightarrow \text{Cl}_2\text{CO}$

Which species is/are intermediates?

1. ClCO

2. Cl, ClCO **correct**

3. Pt, ClCO

4. Pt

5. Pt, Cl

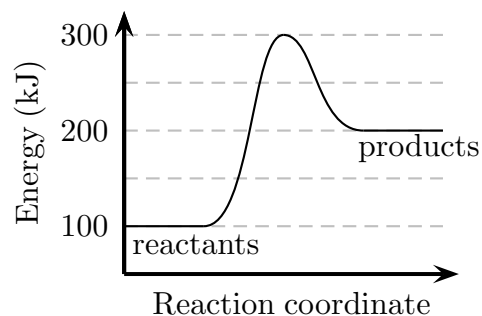
6. Cl

**Explanation:**

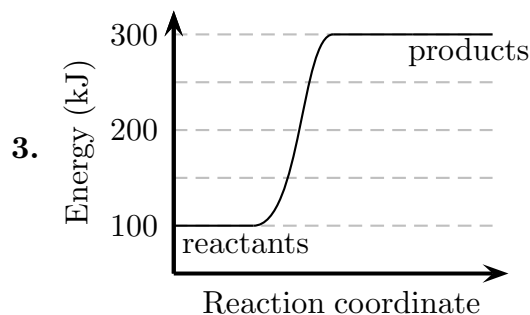
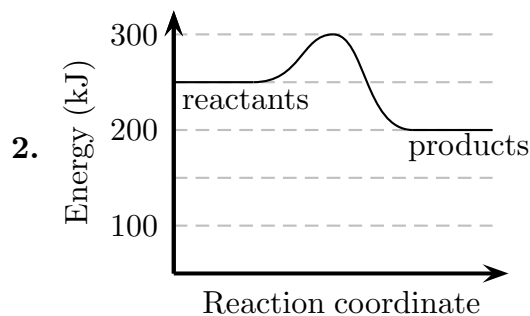
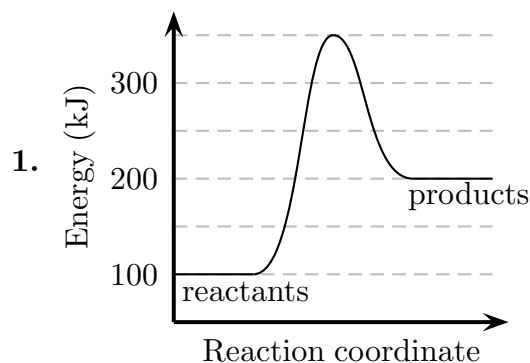
Both Cl and ClCO are produced in early steps and stoichiometrically consumed in subsequent steps; neither appears in the overall reaction.

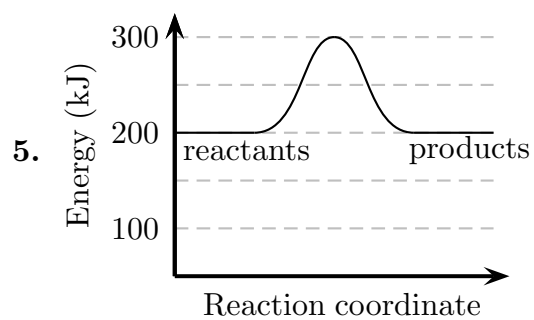
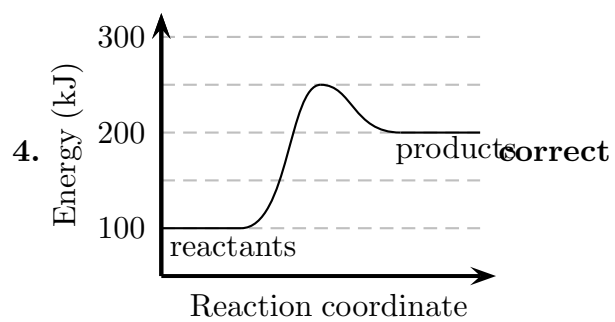
**022 10.0 points**

An enzyme is a biological catalyst. If the graph



refers to an uncatalyzed reaction, which graph would show the same reaction in the presence of a catalyst?





**Explanation:**