




Question No. 1 of 10

Instruction: (1) Read the problem statement and answer choices carefully (2) Work the problems on paper as needed (3) Pick the answer (4) Go back to review the core concept tutorial as needed.

 <p>Question</p>	<p>1. All of the following statements about collision theory are true EXCEPT:</p> <p>(A) Molecule collides to proceed reactions. (B) The reaction rate is equal to the collision frequency. (C) The collision must have enough energy to overcome reaction barrier. (D) Elementary steps show which molecules actually collide with which molecules. (E) An effective collision must have correct orientation.</p>
 <p>Feedback</p>	<p>A. Incorrect This is true. For bimolecular reaction, molecules must collide to start the first step of reactions.</p> <p>B. Correct This is false. The reaction rate is proportional to collision frequency. There are energy factor and steric factor need to be considered.</p> <p>C. Incorrect This is true. If the intermediates do not have enough energy, the molecules will separate again.</p> <p>D. Incorrect This is true. Elementary step illustrates two molecules collide to proceed reaction.</p> <p>E. Incorrect This is true. This is the steric requirement of collision theory.</p>
 <p>Solution</p>	<p>Correct Answer: B</p> <p>Collision theory proposes three conditions for a reaction to take place:</p> <ol style="list-style-type: none"> 1. There must a collision of two reactant molecules. 2. One molecule must collide with another molecule at the right orientation. 3. The total kinetic energy of two molecules combined must be high enough to overcome the reaction barrier.

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Instruction: (1) Read the problem statement and answer choices carefully (2) Work the problems on paper as needed (3) Pick the answer (4) Go back to review the core concept tutorial as needed.

**Question**

2. All of the following statements about reactions in solution are true EXCEPT:

- (A) Encounters between reactants in solution occur in a very different way from in gases.
- (B) The encounter frequency in solution is higher than in a gas since the molecules stay much closer to each other.
- (C) The determination of activation energy in solution is more difficult because of the cage effect.
- (D) Cage effect is the long lasting of one molecule near another molecule because of the hindering presence of solvent molecules.
- (E) The encountered pair of reactants may acquire enough energy to react even they do not have enough energy to do so when first formed.

**Feedback**

A. Incorrect

This is a true statement. Reactions in solution occur in a different manner because of the existence of the solvent molecules.

B. Correct

The encounter frequency is much less in solution since the reactant molecules need to jostle their way through the solvent.

C. Incorrect

This is a true statement. The determination of activation energy is difficult because of cage effect.

D. Incorrect

This is a true statement. The solvent molecules act as cage to limit the movement of reactant molecules

E. Incorrect

This is a true statement. This effect makes it much more difficult to evaluate the activation energy of reaction in solution.

Correct Answer: B

Reactions in the solution take place in a very different manner than in gases. Reactant molecules must jolt their way through the solvent to get nearby each other. Once they get closer, the solvent molecules will also "cage" them to stay with each other, which allow them to find the correct orientation of collision, and accumulate enough energy to overcome reaction barrier.

**Solution**

Question No. 3 of 10

Instruction: (1) Read the problem statement and answer choices carefully (2) Work the problems on paper as needed (3) Pick the answer (4) Go back to review the core concept tutorial as needed.

**Question**

3. Which of the following statement about Activated Complex Theory (ACT) is correct?

- (A) ACT assumes all reactions are endothermic since it needs to go through a reaction barrier.
- (B) Activated complex is a reaction intermediate, sometimes it will appear in a reaction mechanism which consists of elementary reactions only.
- (C) Once the activated is formed, the decay of activated complex is just like a unimolecular reaction.
- (D) Thermodynamic principles cannot be applied to activated complexes since they are unstable molecules and can never reach thermal equilibrium.
- (E) None of the above.

**Feedback**

A. Incorrect!
ACT has nothing to do with whether the reaction is exothermic or endothermic.

B. Incorrect!
The activated complex should never appear in an elementary reaction mechanism.

C. Correct!
Then the activated complex falls apart by unimolecular decay into products.

D. Incorrect!
The activated complexes still follow the principles of thermodynamics.

E. Incorrect!
One of the answers is correct.

**Solution**

Correct Answer: C

The activated complex theory is an attempt to identify the principal features governing the size of a rate constant in terms of the events that take place during the reaction.

The cluster of atoms corresponding to the region close to the maximum is the activated complex. Although some might revert to reactants, the activated complex will transform to products once it passes through the potential energy peak.

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Instruction: (1) Read the problem statement and answer choices carefully (2) Work the problems on paper as needed (3) Pick the answer (4) Go back to review the core concept tutorial as needed.

**Question**

4. Which of the following statement about Potential Energy Surface (PES) is correct?

- (A) Each reactant corresponds to a saddle point on the PES.
- (B) Each transition state corresponds to a local minimum point on the PES.
- (C) The actual path of atoms in the course encountered always follows the minimum path from the reactant to the product.
- (D) PES is used to illustrate the potential energy as a function of the relative positions of all atoms taking part in the reaction.
- (E) SO_3

**Feedback**

A. Incorrect!

Each reactant corresponds to a local minimum point on the PES.

B. Incorrect!

Each transition state corresponds to a saddle point on the PES.

C. Incorrect!

The actual path of atoms in the course of encounter depends on their total energy, i.e. the sum of their kinetic energies.

D. Correct!

A potential surface usually has potential energy as Z-axis, and reaction coordinates as X- and Y-axis.

E. Incorrect!

One of the answers is correct.

**Solution**

Correct Answer: D

Potential energy surface is illustrated to represent potential energy as a function of the relative positions of all the atoms taking apart in the reaction. It is a good tool to discover the orientation for an effective collision.

Question No. 5 of 10

Instruction: (1) Read the problem statement and answer choices carefully (2) Work the problems on paper as needed (3) Pick the answer (4) Go back to review the core concept tutorial as needed.

**Question**

5. Assume that the diffusion coefficient for a reactant in aqueous solution at 25°C is $4.0 \times 10^{-9} \text{ m}^2\text{s}^{-1}$. If the critical reaction distance is 0.65 nm, what is the rate constant for the second order diffusion-controlled reaction?

- (A) $3.0 \times 10^{20} \text{ L mol}^{-1} \text{ s}^{-1}$.
- (B) $5.5 \times 10^{15} \text{ L mol}^{-1} \text{ s}^{-1}$.
- (C) $3.9 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$.
- (D) $6.0 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$.
- (E) $8.0 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$.

**Feedback**

A. Incorrect!

Good try! Check your calculation. Use the rate constant equation for a diffusion-controlled reaction $K_d = 4\pi R^* D N_A$, where R is the distance between molecules at which they react and D is the sum of the diffusion coefficients of the two reactant species in the solution.

B. Incorrect!

Good try! Check your calculation. Use the rate constant equation for a diffusion-controlled reaction $K_d = 4\pi R^* D N_A$, where R is the distance between molecules at which they react and D is the sum of the diffusion coefficients of the two reactant species in the solution.

C. Correct!

Good job! Apply the rate constant equation for a diffusion-controlled reaction $K_d = 4\pi R^* D N_A$, where R is the distance between molecules at which they react and D is the sum of the diffusion coefficients of the two reactant species in the solution.

D. Incorrect!

Good try! Check your calculation. Use the rate constant equation for a diffusion-controlled reaction $K_d = 4\pi R^* D N_A$, where R is the distance between molecules at which they react and D is the sum of the diffusion coefficients of the two reactant species in the solution.

E. Incorrect!

Good try! Check your calculation. Use the rate constant equation for a diffusion-controlled reaction $K_d = 4\pi R^* D N_A$, where R is the distance between molecules at which they react and D is the sum of the diffusion coefficients of the two reactant species in the solution.

**Solution**

Correct Answer: C

The rate constant for a diffusion-controlled reaction is given as:

$$k_d = 4\pi R^* D N_A$$

$$\begin{aligned} k_d &= 4\pi(0.65 \times 10^{-9} \text{ m}) \times (2 \times 4.0 \times 10^{-9} \text{ m}^2\text{s}^{-1}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \\ &= 3.9 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ &= 3.9 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

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Instruction: (1) Read the problem statement and answer choices carefully (2) Work the problems on paper as needed (3) Pick the answer (4) Go back to review the core concept tutorial as needed.



Question

6. For a reaction $\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$, its steric factor is 1.7×10^{-6} with a collision cross section as 0.12 nm^2 and activation energy of 94.3 kJ mol^{-1} . What is the rate constant of this bimolecular reaction at 300°C ?

- (A) $3.09 \times 10^{-20} \text{ M}^{-1} \text{ s}^{-1}$
- (B) $5.57 \times 10^{-16} \text{ M}^{-1} \text{ s}^{-1}$
- (C) $3.91 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$
- (D) $8.64 \times 10^{-12} \text{ M}^{-1} \text{ s}^{-1}$
- (E) $2.24 \times 10^{-11} \text{ M}^{-1} \text{ s}^{-1}$



Feedback

A. Incorrect!

Good try! First calculate the reduced mass of spherical H_2 and C_2H_4 . Convert the reduced mass with atomic mass unit ($1.66 \times 10^{-27} \text{ kg/u}$). Apply the integrated rate constant equation to calculate the k at a given temperature.

B. Incorrect!

Good try! First calculate the reduced mass of spherical H_2 and C_2H_4 . Convert the reduced mass with atomic mass unit ($1.66 \times 10^{-27} \text{ kg/u}$). Apply the integrated rate constant equation to calculate the k at a given temperature.

C. Incorrect!

Good try! First calculate the reduced mass of spherical H_2 and C_2H_4 . Convert the reduced mass with atomic mass unit ($1.66 \times 10^{-27} \text{ kg/u}$). Apply the integrated rate constant equation to calculate the k at a given temperature.

D. Correct!

First calculate the reduced mass of spherical H_2 and C_2H_4 . Convert the reduced mass with atomic mass unit ($1.66 \times 10^{-27} \text{ kg/u}$). Use the integrated equation with the steric factor, activation energy and collision section.

E. Incorrect!

Good try! First calculate the reduced mass of spherical H_2 and C_2H_4 . Convert the reduced mass with atomic mass unit ($1.66 \times 10^{-27} \text{ kg/u}$). Apply the integrated rate constant equation to calculate the k at a given temperature.

Correct Answer: D

The reduced mass of two reactants $\mu(\text{H}_2 + \text{C}_2\text{H}_4) = 2 \times 28 / (2 + 28) = 1.87 \text{ u}$
 $\text{AMU} = 1.66 \times 10^{-27} \text{ kg/u}$

Apply the integrated rate constant equation for this bimolecular reaction:

$$k = P \sigma \left(\frac{8kT}{\pi \mu} \right)^{\frac{1}{2}} N_A e^{-\frac{E_a}{RT}}$$

$$= 1.7 \times 10^{-6} \left[0.12 \times (10^{-9} \text{ m})^2 \right] \times \left(\frac{8(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (300 \text{ K})}{\pi \times (1.87 \text{ u}) \times (1.66 \times 10^{-27} \text{ kg u}^{-1})} \right)^{\frac{1}{2}}$$

$$\times (6.022 \times 10^{23} \text{ mol}^{-1}) \times e^{-\frac{94.3 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times (300 \text{ K})}}$$

$$= 8.64 \times 10^{-15} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = 8.64 \times 10^{-12} \text{ L mol}^{-1} \text{ s}^{-1} = 8.64 \times 10^{-12} \text{ M}^{-1} \text{ s}^{-1}$$



Solution

Question No. 7 of 10

Instruction: (1) Read the problem statement and answer choices carefully (2) Work the problems on paper as needed (3) Pick the answer (4) Go back to review the core concept tutorial as needed.

**Question**

7. For a reaction to occur, there is a threshold energy to reach. There are only a fraction of molecular collisions with sufficient activation energy. What is the fraction of effective collisions when $E_a = 35 \text{ kJ mol}^{-1}$ at 298 K?

- (A) 0.001
- (B) 6.5×10^{-6}
- (C) 7.3×10^{-7}
- (D) 0.02
- (E) 0

**Feedback**

A. Incorrect!

Good try! Use the exponential formula of the activation energy and check the calculation carefully.

B. Incorrect!

Good try! Use the exponential formula of the activation energy and check the calculation carefully.

C. Correct.

Good job! Use the exponential formula of the activation energy to calculate the fraction of effective collisions, which is dimensionless.

D. Incorrect!

Good try! Use the exponential formula of the activation energy and check the calculation carefully.

E. Incorrect!

Good try! Use the exponential formula of the activation energy and check the calculation carefully.

**Solution**

Correct Answer: C

One reason that not every collision leads to a reaction is because that some collisions do not have enough energy to overcome the reaction barriers. There is only a fraction of molecular collision with high enough activation energy to trigger the reaction.

The fraction is given by $f = e^{-\frac{E_a}{RT}}$

$$f = e^{-\frac{E_a}{RT}} = e^{-\frac{35 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}} = 7.33 \times 10^{-7}$$

Question No. 8 of 10

Instruction: (1) Read the problem statement and answer choices carefully (2) Work the problems on paper as needed (3) Pick the answer (4) Go back to review the core concept tutorial as needed.



Question

8. Air contains 78.09% nitrogen, 20.95% oxygen, 0.93% argon, 0.039% carbon dioxide, and small amounts of other gases. The diameter of an O_2 molecule is about 2.96 \AA . Calculate the average collision frequency of O_2 in 1 atm atmosphere of 25°C .

- (A) $3.0 \times 10^{20} \text{ s}^{-1}$
- (B) $5.5 \times 10^{16} \text{ s}^{-1}$
- (C) $5.28 \times 10^{10} \text{ s}^{-1}$
- (D) $8.1 \times 10^9 \text{ s}^{-1}$
- (E) $1.20 \times 10^{10} \text{ s}^{-1}$



Feedback

A. Incorrect!

Good try! Check your calculation. First calculate the average molecular speed and then apply the collision frequency equation according to the Collision Theory. Be sure to convert the units with the end unit of s^{-1} .

B. Incorrect!

Good try! Check your calculation. First calculate the average molecular speed and then apply the collision frequency equation according to the Collision Theory. Be sure to convert the units with the end unit of s^{-1} .

C. Correct!

Good job! First calculate the average molecular speed and then apply the collision frequency equation according to the Collision Theory. Make the proper unit conversions and the ending unit is s^{-1} .

D. Incorrect.

Good try! Check your calculation. First calculate the average molecular speed and then apply the collision frequency equation according to the Collision Theory. Be sure to convert the units with the end unit of s^{-1} .

E. Incorrect!

Good try! Check your calculation. First calculate the average molecular speed and then apply the collision frequency equation according to the Collision Theory. Be sure to convert the units with the end unit of s^{-1} .



Solution

Correct Answer: C

Unit Conversions: $1 \text{ \AA} = 10^{-10} \text{ m}$; $\text{J} = \text{kg m}^2 \text{ s}^{-2}$; $\text{Pa} = \text{kg m}^{-1} \text{ s}^{-2}$

$$\bar{c} = \left(\frac{8RT}{\pi M} \right)^{\frac{1}{2}} = \left(\frac{8 \times 8.314 \text{ J K mol}^{-1} \times 298 \text{ K}}{3.142 \times 36 \times 10^{-3} \text{ kg mol}^{-1}} \right)^{\frac{1}{2}} = 418.6 \text{ ms}^{-1}$$

$$z = \sqrt{2} \sigma \bar{c} \left(\frac{p}{kT} \right) = \sqrt{2} \pi d^2 \bar{c} \left(\frac{p}{kT} \right)$$

$$= \sqrt{2} \times 3.142 \times (2.96 \times 10^{-10} \text{ m})^2 \times 418.6 \text{ ms}^{-1} \times \left(\frac{101.3 \times 10^3 \text{ Pa}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}} \right)$$

$$= 5.28 \times 10^{10} \text{ s}^{-1}$$

The average collision frequency of O_2 is $5.28 \times 10^{10} \text{ s}^{-1}$.

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Instruction: (1) Read the problem statement and answer choices carefully (2) Work the problems on paper as needed (3) Pick the answer (4) Go back to review the core concept tutorial as needed.



9. The diffusion rate constant can be related to the viscosity of the solution by a simple approximation. For a species in decylbenzene, the viscosity is 1.12cP. Estimate the magnitude of diffusion-controlled rate constant at 100°C.

- (A) $1.30 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$
- (B) $2.20 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
- (C) $4.31 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
- (D) $7.39 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
- (E) $1.29 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$



A. Incorrect!
Good try! Check your calculation and make the proper unit conversions. Apply the formula of the diffusion rate constant in terms of viscosity and temperature.

A. Incorrect!
Good try! Check your calculation and make the proper unit conversions. Apply the formula of the diffusion rate constant in terms of viscosity and temperature.

A. Incorrect!
Good try! Check your calculation and make the proper unit conversions. Apply the formula of the diffusion rate constant in terms of viscosity and temperature.

D. Correct.
Good job! Apply the formula of the diffusion rate constant in terms of viscosity and temperature.

E. Incorrect!
Good try! Check your calculation and make the proper unit conversions. Apply the formula of the diffusion rate constant in terms of viscosity and temperature.



Correct Answer: D

A correlation between viscosity and rate of diffusion may be related by the following formula: $k_d = 8RT/3\eta$.

Viscosity unit: centi-poise cP = $10^{-2}\text{P} = 10^{-2} \times 0.100 \text{ kg m}^{-1} \text{ s}^{-1} = 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$

Joule unit: J = $\text{kg m}^2 \text{ s}^{-2}$.

Volume unit: $\text{m}^3 = 1000 \text{ L}$

$$k_d = 8RT/3\eta = 8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (373.2 \text{ K}) / (3 \times 1.12 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) = 7.39 \times 10^6 \text{ J mol}^{-1} \text{ kg}^{-1} \text{ ms} = 7.39 \times 10^6 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ kg}^{-1} \text{ ms} = 7.39 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = 7.39 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1} = 7.39 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

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Instruction: (1) Read the problem statement and answer choices carefully (2) Work the problems on paper as needed (3) Pick the answer (4) Go back to review the core concept tutorial as needed.

**Question**

10. A solution reaction $A^- + B^+ \rightarrow P$ has an empirical rate constant as $k_2 = (1.020 \times 10^{12})e^{-(6004K)/T} \text{ L mol}^{-1} \text{ s}^{-1}$. What is the enthalpy of activation at 100°C?

- (A) 4.482 kJ mol⁻¹
- (B) 2.427 kJ mol⁻¹
- (C) 46.82 kJ mol⁻¹
- (D) 4.522 J mol⁻¹
- (E) 1.422 kJ mol⁻¹

**Feedback**

A. Incorrect!

Good try! Check your calculation. Obtain the activation energy from the empirical equation of rate constant. Use this formula: Enthalpy of activation = energy of activation - RT .

B. Incorrect!

Good try! Check your calculation. Obtain the activation energy from the empirical equation of rate constant. Use this formula: Enthalpy of activation = energy of activation - RT .

C. Correct!

Good job! Obtain the activation energy from the empirical equation of rate constant. Use this formula: Enthalpy of activation = energy of activation - RT .

D Incorrect!

Good try! Check your calculation. Obtain the activation energy from the empirical equation of rate constant. Use this formula: Enthalpy of activation = energy of activation - RT .

E. Incorrect!

Good try! Check your calculation. Obtain the activation energy from the empirical equation of rate constant. Use this formula: Enthalpy of activation = energy of activation - RT .

**Solution**

Correct Answer: C

From the rate constant empirical equation, we can obtain $-E_a/RT = -(6134K)/T$. Therefore, $E_a = (6134K)R$.

The enthalpy of activation can be calculated with its equation in solution phase:
 $\Delta^\ddagger H = E_a - RT = (6004K) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (373.2 \text{ K}) = 46817.3 \text{ J mol}^{-1} = 46.82 \text{ kJ mol}^{-1}$

The Enthalpy of Activation: $\Delta^\ddagger H = 46.82 \text{ kJ mol}^{-1}$