

Recitation Worksheet Four

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Textbook:

Chemistry & Chemical Reactivity

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Instructions:

- This recitation worksheet covers Ch. 14.5-14.7, 18.1-18.3
- Please enter your first and last name as it appears on the eLC roster (do not use a nickname that is not reflected in eLC).
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 - You must make sure the pages are in the correct order and have the same layout as the original worksheet when submitting to Gradescope regardless of your submission type.
 - Answers must be written in the corresponding answer boxes.
 - You must show your work when appropriate.
- This worksheet is due no later than **12:00 PM (noon) on the Saturday, September 21st.**
- A periodic table and formula sheet are attached to the end of this worksheet. Please keep these attached to your worksheet in the correct order when submitting to Gradescope.

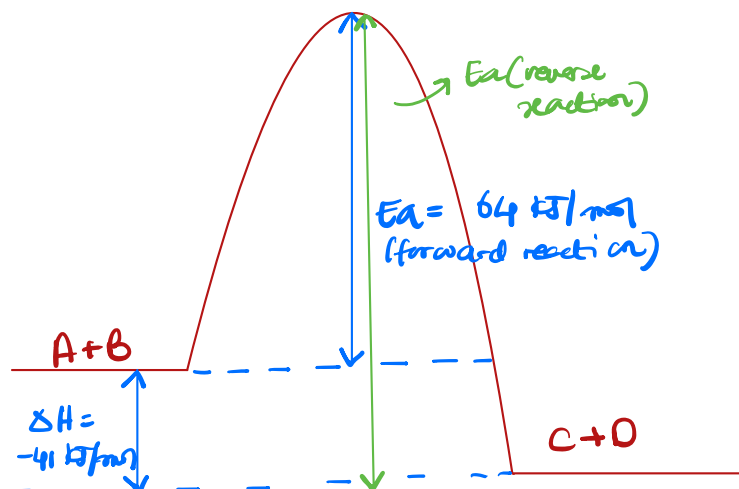
1. For a reversible reaction $A + B \rightleftharpoons C + D$, the enthalpy change of the forward reaction is -41 kJ/mol and the activation energy for the forward reaction is 64 kJ/mol. What is the activation energy in kJ/mol for the reverse reaction?

105

kJ/mol

$$\Delta H = E_a(\text{forward}) - E_a(\text{reverse})$$

$$\begin{aligned} E_a(\text{reverse}) &= E_a(\text{forward}) - \Delta H \\ &= 64 - (-41) \\ &= 105 \text{ kJ/mol} \end{aligned}$$



2. Which of the following statements about catalysts is **FALSE**:

D

- ~~A.~~ Catalysts do not appear in the balanced equation.
~~B.~~ Catalysts reduce the activation energy for a reaction.
~~C.~~ Biological catalysts are called enzymes.
 D. Catalysts do not alter the mechanism of the reaction and never appear in the rate law. *see B*
 E. Since catalysts are recycled, even a small amount of catalyst can accelerate a reaction. *True*

A) true - they are regenerated ∴ they do not appear in the balanced equation
B) True - by altering the mechanism of the reaction with a lower activation energy
C) true

3. The rate law for the reaction $2XY + Z_2 \rightarrow 2XYZ$ can be written as $\text{rate} = k[XY][Z_2]$. Which choice could possibly represent the mechanism for this reaction? ** Note: Rate law is based on the slow step*

B

- ~~A.~~ Step 1: $Z_2 \rightarrow Z + Z$ (slow)
 Step 2: $XY + Z \rightarrow XYZ$ (fast)
 Step 3: $XY + Z \rightarrow XYZ$ (fast)

Rate law = $k[Z_2]$
∴ incorrect

- B. Step 1: $XY + Z_2 \rightarrow XYZ + Z$ (slow) *Rate law = $k[XY][Z_2]$*
 Step 2: $XY + Z \rightarrow XYZ$ (fast) *∴ correct*

- ~~C.~~ Step 1: $2XY + Z_2 \rightarrow 2XYZ$ (slow)
 Step 2: $XYZ_2 \rightarrow XYZ + Z$ (fast)

Rate law = $[XY][Z_2]$

correct rate law but incorrect final equation

- ~~D.~~ Step 1: $2XY \rightleftharpoons X_2Y_2$ (fast)
 Step 2: $X_2Y_2 + Z_2 \rightarrow 2XYZ$ (slow)

- ~~E.~~ Not enough information is provided to predict the mechanism of this reaction.

② Step 2: $\xrightarrow{X_2Y_2}$
Rate = $k_2[X_2Y_2][Z_2]$
Rate = $k_3 \times \frac{k_1}{k_2} [XY]^2 [Z_2]$
is combined to k

to get the rate law for D is

*① Step 1: forward: $k_1[XY]^2$
 reverse: $k_2[X_2Y_2]$*

*rate of forward = rate of reverse
 $k_1[XY]^2 = k_2[X_2Y_2]$ *intermediate*
 $[X_2Y_2] = \frac{k_1}{k_2} [XY]^2$*

∴ Rate = $[XY]^2 [Z_2]$

$$t_{1/2} = \ln 2 / k$$

4. For the first-order reaction $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2 \text{NO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$. If $t_{1/2} = 22.5 \text{ h}$ at 20.0°C and 1.50 h at 40.0°C , calculate the activation energy in kJ/mol of this reaction.

103

kJ/mol

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

$$\textcircled{1} t_{1/2} = \frac{\ln 2}{k_1}$$

$$t_{1/2} = \frac{\ln 2}{k_2}$$

$$22.5 = \frac{\ln 2}{k_1}$$

$$1.50 = \frac{\ln 2}{k_2}$$

$$\therefore k_1 = \frac{\ln 2}{22.5}$$

$$k_2 = \frac{\ln 2}{1.50}$$

$$\textcircled{2} T_1 = 20.0^\circ \text{C} + 273.15 = 293.15 \text{ K}$$

$$T_2 = 40.0^\circ \text{C} + 273.15 = 313.15 \text{ K}$$

$$\textcircled{3} \ln \left(\frac{\ln 2 / 1.50}{\ln 2 / 22.5} \right) = -\frac{E_a}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{313.15} - \frac{1}{293.15} \right) \frac{1}{\text{K}}$$

$$2.708050201 = -E_a (-2.6205 \times 10^{-5})$$

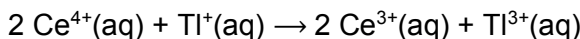
$$\therefore E_a = 1.033409731 \times 10^5 \frac{\text{J}}{\text{mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$= 1.03340973 \times 10^2 \text{ kJ/mol}$$

$$= 103.340973$$

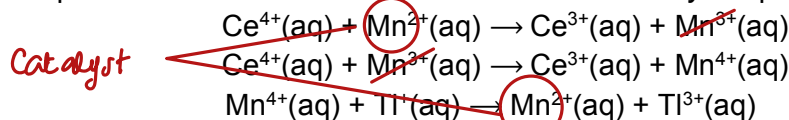
$$\approx 103 \text{ kJ/mol}$$

5. The uncatalyzed reaction between $\text{Ce}^{4+}(\text{aq})$ and $\text{Ti}^+(\text{aq})$ is very slow and occurs in a single elementary step given by



BC

Mn^{2+} can be utilized as a catalyst to increase the rate of this reaction. The *catalyzed* reaction is a three-step mechanism provided below. The overall rate law for the *catalyzed* process is $\text{rate} = k [\text{Ce}^{4+}][\text{Mn}^{2+}]$.



Which statements regarding the *uncatalyzed* and *catalyzed* reactions between $\text{Ce}^{4+}(\text{aq})$ and $\text{Ti}^+(\text{aq})$ are **TRUE**? Select all that apply.

- A. ☒ The rate law of the *uncatalyzed* reaction is $\text{rate} = k[\text{Ce}^{4+}][\text{Ti}^+]$.
 B. ☒ The *uncatalyzed* single elementary step reaction is slow because the probability of a three-particle collision is low.
 C. ☒ From the mechanism of the *catalyzed* process, Mn^{3+} is an intermediate.
 D. ☒ From the mechanism of the *catalyzed* process, the second step is the slow rate determining step.

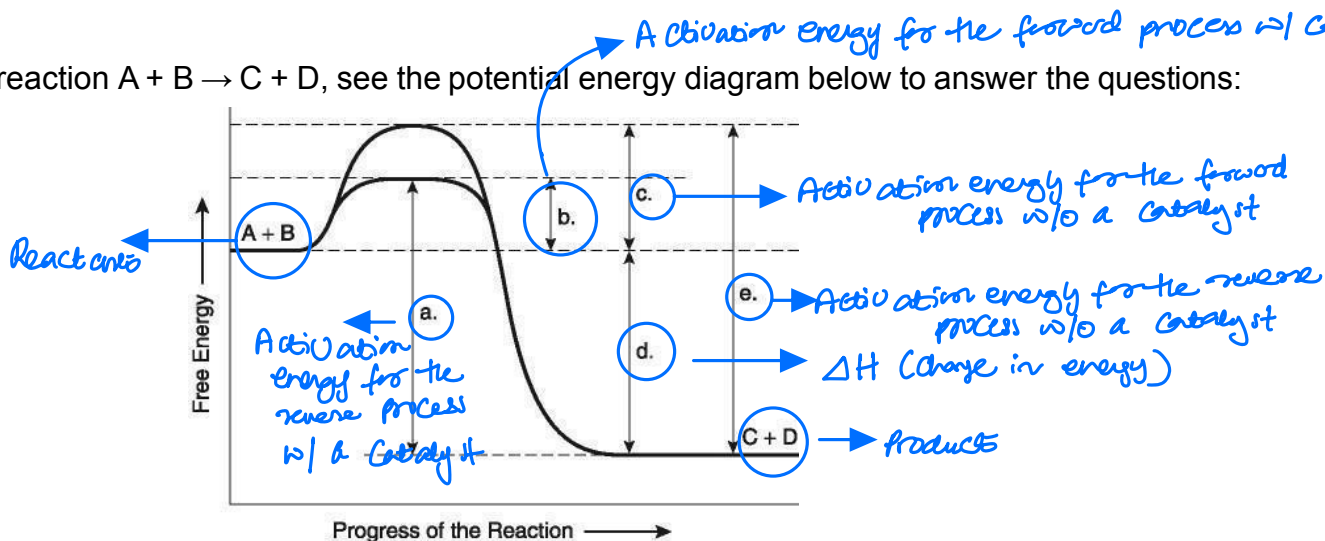
A) False - Rate law = $k [\text{Ce}^{4+}]^2 [\text{Ti}^+]$ from the elementary step

B) True - the probability of the collision of 3 particles in the correct orientation & enough kinetic energy equal to or higher than the activation energy is low

C) True - An intermediate is produced in one step in the mechanism & consumed in the following step

D) False - Does not match the rate law

6. For reaction $A + B \rightarrow C + D$, see the potential energy diagram below to answer the questions:



d

A. Which letter shows the change in energy for the overall reaction?

c

B. Which letter shows the activation energy without a catalyst? *implied for the forward reaction*

b

C. Which letter shows the activation energy with a catalyst? *implied for the forward reaction*

7. Determine the activation energy in kJ/mol for the reaction using the information in the table:

Temperature (°C)	Rate Constant (M ⁻¹ s ⁻¹)
330	0.98
550	1.60

9.2

kJ/mol

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

$$\ln \left(\frac{1.60}{0.98} \right) = -\frac{E_a}{8.314} \left(\frac{1}{823.15} - \frac{1}{603.15} \right)$$

$$0.490206336 = -E_a (-5.3298 \times 10^{-5})$$

$$\therefore E_a = 9.197462119 \times 10^3 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 9.2 \text{ kJ/mol}$$

$$\begin{aligned} T_1 &= 330 + 273.15 \\ &= 603.15 \text{ K} \\ T_2 &= 550 + 273.15 \\ &= 823.15 \text{ K} \\ k_1 &= 0.98 \\ k_2 &= 1.60 \\ R &= 8.314 \text{ J/mol} \cdot \text{K} \end{aligned}$$

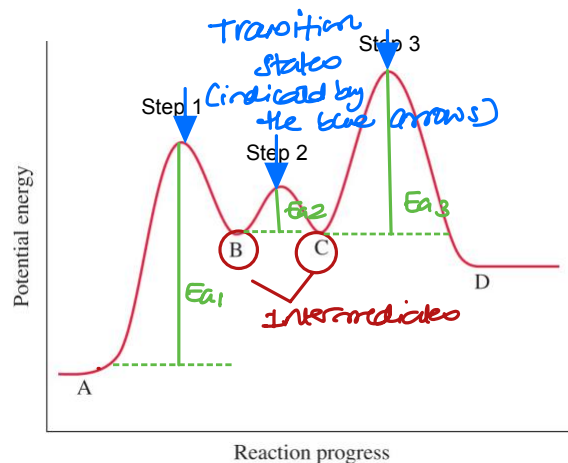
8. Using the potential energy diagram to the right, answer the following questions:

- A. What are the intermediates in the reaction? Insert letters without spaces in the answer box, example ABCD.

BC

- B. How many transition states are there? Insert a number, example 1, 2, 3, etc.

3



- C. Which step has the ^{lowest activation energy} largest rate constant? Insert a number, example 1, 2, 3, etc.

2

- D. Which step has the ^{highest activation energy} smallest rate constant? Insert a number, example 1, 2, 3, etc.

1

- E. Is step 1 of the reaction exothermic or endothermic?

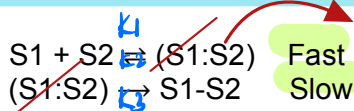
Endothermic

- F. Is the overall reaction exothermic or endothermic?

Endothermic

9. A mechanism has been proposed for the formation of a double helix DNA is given by:

ABD



intermediates are produced in a step in a mechanism & consumed in the following step

10. If S1 and S2 represent strand 1 and strand 2 respectively, which of the statements are **TRUE**? Select all that apply. Insert letters without spaces in the answer box, example **ABCD**.

- ☒ A. (S1:S2) represent the reaction intermediate in the mechanism.
☒ B. The rate for the formation of the DNA strand can be written as rate = $k [S1][S2]$.
☒ C. The rate for the formation of the DNA strand can be written as rate = $k [(S1+S2)]$.
☒ D. The second step in the mechanism is the rate determining step.
☒ E. The activation energy of the fast first step is higher and therefore it has a lower rate constant compared to the second slow step.

since the first step is a fast equilibrium step, the rate equation cannot be written based on the slow step because the rate equation will contain an intermediate

① For the fast step: Rate of forward = Rate of reverse

$$k_1 [S1][S2] = k_2 [(S1:S2)]$$

Rearrange in terms of intermediate

$$\therefore \frac{k_1}{k_2} [S1][S2] = [(S1:S2)]$$

② Rate of the slow step

$$\text{Rate} = k_3 [(S1:S2)]$$

Substitute

11. Which of the following statements regarding the rates of chemical reactions is **TRUE**?

C

- A. Reaction rates can be calculated only from collision frequency **False**
 B. The addition of a catalyst to a reaction can increase the rate of the reaction only if the temperature of the reaction increases **False**
 C. Reaction rates increase with temperature because a fraction of reactant molecules have higher kinetic energies compared to activation energy **True**
 D. $E_a < \Delta H < 0$ conditions can exist for a chemical reaction

A) $k = Ae^{-E_a/RT}$ depends on kinetic energy (RT) & activation energy of the reaction

B) False: a catalyst even at constant temperature can increase the rate of the reaction by altering the mechanism of the reaction

D) False: a reaction can be exothermic but cannot have a negative value for activation energy

12. In which of the following reactions will result in an increase in entropy? Select all that apply. Insert letters without spaces in the answer box, example **ABCD**.

DFG

- A. $\text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2\text{(s)}$ 1 mol of liquid changes to solid: $\Delta S < 0$
 B. $\text{Si(s)} + 2 \text{Cl}_2\text{(g)} \rightarrow \text{SiCl}_4\text{(g)}$ 2 mol gas produces 1 mol gas: $\Delta S < 0$
 C. $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O(s)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CuSO}_4 \cdot 5 \text{H}_2\text{O(s)}$ 2 mol gas to 0 mol gas: $\Delta S < 0$
 D. $\text{C}_6\text{H}_6\text{(l)} + \frac{15}{2} \text{O}_2\text{(g)} \rightarrow 6 \text{CO}_2\text{(g)} + 3 \text{H}_2\text{O(g)}$ 7.5 mol gas to 9 mol gas: $\Delta S > 0$
 E. $2 \text{H}_2\text{S(g)} + 3 \text{O}_2\text{(g)} \rightarrow 2 \text{H}_2\text{O(g)} + 2 \text{SO}_2\text{(g)}$ (not balanced) $\Delta S < 0$
 F. $\text{CCl}_4\text{(l)} \rightarrow \text{CCl}_4\text{(g)}$ $\Delta S > 0$
 G. $2 \text{HgO(s)} \rightarrow 2 \text{Hg(l)} + \text{O}_2\text{(g)}$ $\Delta S > 0$

Increase in no. of moles of gas from reactants to products: $\Delta S > 0$

F) $\Delta S > 0$ as liquid changes to gas

G) $\Delta S > 0$ when solid converts to liquid & gas

13. Calculate the entropy change in the surroundings that occur when 35.0 g of acetone (molar mass = 58.08 g/mol) condenses at its normal boiling point (56.1 °C). ΔH_{vap} of acetone is 29.1 kJ/mol.

53.3

J/K

obtaining a positive value for entropy confirms that when heat is released due to the condensation of acetone increases the entropy of the surroundings

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T} = -\frac{q_{\text{sys}}}{T}$$

$$= -\frac{(-\Delta H_{\text{cond}} \times \text{mol})}{T}$$

$$= -\frac{(-2.91 \times 10^4 \text{ J} \times 35.0 \text{ g acetone} \times \frac{1 \text{ mol acetone}}{58.08 \text{ g}})}{(56.1 + 273.15) \text{ K}}$$

$$= 53.260917 \text{ J/K}$$

$$\approx 53.3 \text{ J/K}$$

Condensation is an exothermic process
 $\therefore \Delta H_{\text{vap}} = -\Delta H_{\text{cond}}$
 Gas \rightleftharpoons liquid
 separation

14. Determine the boiling point for iron in °C from the given information: $\Delta H_{\text{vap}} = 349.6 \text{ kJ/mol}$ and $\Delta S_{\text{vap}} = 111.55 \text{ J/(mol}\cdot\text{K)}$.

2861

°C

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$$

$$111.55 \text{ J/mol}\cdot\text{K} = \frac{349.6 \text{ kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\therefore T = \frac{3134.020619 \text{ K}}{1.1155}$$

$$- 273.15$$

$$2861.020619 \text{ °C}$$

15. Which of the following has the substance with the greater entropy listed first? Select all that apply. Insert letters without spaces in the answer box, example ABCD.

AB

A. 1 mol $\text{Br}_2(\text{l})$ at 1 atm and 8 °C and 1 mol $\text{Br}_2(\text{s})$ at 1 atm and -8 °C

B. 10.0 mol of Na(s) at 1 atm and 5 °C and 100.0 g of Na(s) at 1 atm and 5 °C

C. MgS at 1 atm and 25 °C and KBr at 1 atm and 25 °C

D. 0.284 mol O_2 at 15.0 bar and 22.3 °C and 0.312 mol SO_2 at 0.110 bar and 32.5 °C

A) Entropy of liquids is greater than solids in addition the temperature of the liquid is higher

B) 10.0 mol Na are greater than a 100.0g Na (Entropy is an extensive property)

C) Entropy of KBr is greater than that of MgS (higher lattice energy)

D) Similar to C

16. Which of the following has the highest standard molar entropy?

A

A. $\text{N}_2\text{F}_4(\text{g})$

B. $\text{N}_2\text{H}_4(\text{g})$

C. $\text{NO}(\text{g})$

D. $\text{NH}_4\text{CO}_2\text{NH}_2(\text{s})$

E. $\text{NH}_4\text{OH}(\text{aq})$

States of matter in increasing order of entropy

Solids < liquids < gases

* D & E have lower entropy compared to A, B, C which are gases.

* A, B, & C are all gases but A & B have greater molecular complexity than C. F is heavier than N_2H_4 $\therefore \text{N}_2\text{F}_4$ has the highest standard molar entropy

17. Which of the following statements is **true** regarding the **second law of thermodynamics**? **Select all that apply**. Insert letters without spaces in the answer box, example **ABCD**.

AB

A. $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ for any spontaneous process *True*

B. $\Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$ for a reversible process *True for a reversible process*

C. The entropy of a perfect crystal at absolute zero (0 K) is zero

D. The energy of the universe is conserved in any process

E. All the above of the statements are true

c) False - third law

d) First law of thermodynamics ($\Delta E_{\text{univ}} = \Delta E_{\text{sys}} + \Delta E_{\text{surr}}$)

e) not true

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\therefore \Delta S_{\text{univ}} = 0$$

$$\therefore \Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$$

18. Which of the following **processes are spontaneous or non-spontaneous**? Insert (S) for spontaneous and (NS) for non-spontaneous.

NS

A. Splitting of water into hydrogen gas and oxygen gas

S

B. Dissolving table salt (NaCl) in water

S

C. Ripening of a banana

S

D. Vaporization of $\text{Br}_2(\text{l})$ at 60.0°C (boiling point of $\text{Br}_2(\text{l}) = 58.8^\circ\text{C}$)

S

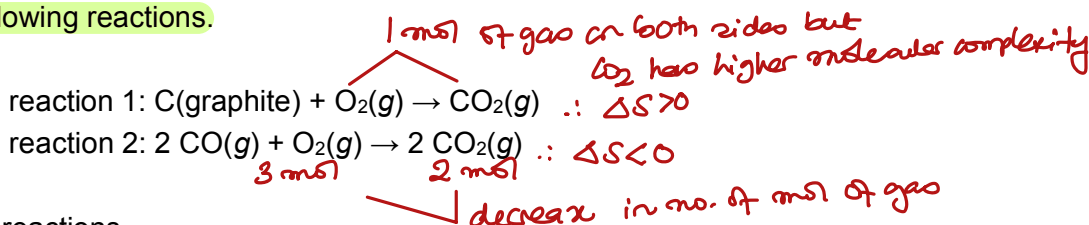
E. Combustion of natural gas (natural gas is a mixture of methane and ethane)

NS

F. Driving a car up the hill

19. Without doing any calculations, **determine whether the standard entropy change, ΔS° is positive or negative for each of the following reactions.**

B



A. ΔS° is positive for both reactions.

B. ΔS° is positive for reaction 1 but negative for reaction 2.

C. ΔS° is positive for reaction 2 but negative for reaction 1.

D. ΔS° is negative for both reactions.

Extra Practice Questions: these questions will not be graded

1. A factor that decreases the activation energy for a reaction:

- I) ~~decreases the rate constant~~ *Reaction is slow & False ↑*
- II) increases the rate constant *True ↑ K ↓ Ea*
- III) has no effect on the rate constant *False*
- IV) increases the product yield *NO relationship*
- V) might be a catalyst *True can change the activation energy of the reaction by changing the mechanism*

E

- A. I and IV
- B. II and IV
- C. I, IV, and V
- D. IV and III
- E. II and V

2. A catalyst:

- I) lowers activation energy *True by altering the mechanism of the reaction*
- II) provides an alternate reaction pathway *True see I*
- III) is consumed in the reaction and therefore does not appear in the chemical equation of each mechanism
- IV) speeds a reaction *False - repressed*
- V) is heterogeneous if it is in a different phase than the reactants *True*

E

- A. I, III, and IV
- B. I, IV, and V
- C. II, III, and IV
- D. II and IV
- E. I, II, IV, and V

3. Activation energy is:

E

- A. energy at the bottom of the reaction curve
- B. the heat energy in joules required to break the bonds in one reactant
- C. an energy that a catalyst brings to the system to activate one of the reactants
- D. the kinetic energy of solution stirring that brings the reaction to start
- E. minimum kinetic energy that molecules must bring to their collisions for a chemical reaction to occur

4. The entropy of gaseous _____ is the largest at 25 °C and 1 atm.

C

- A. C₂H₂
- B. H₂
- C. C₂H₆ *↪ highest molecular complexity*
- D. CH₄
- E. C₂H₂

5. For a process to be at equilibrium, it is necessary that

B

A. $\Delta S_{\text{sys}} = \Delta S_{\text{surr}}$.

B. $\Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$.

C. $\Delta S_{\text{sys}} = 0$.

D. $\Delta S_{\text{sys}} = 0$ and $\Delta S_{\text{surr}} = 0$.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

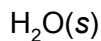
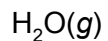
At equilibrium

$$\Delta S_{\text{univ}} = 0$$

$$\therefore \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

$$\therefore \Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$$

6. Place the following in order of **decreasing** standard molar entropy.



From smaller to larger entropy

A

A. $\text{H}_2\text{O}(g) > \text{H}_2\text{O}(l) > \text{H}_2\text{O}(s)$

B. $\text{H}_2\text{O}(s) > \text{H}_2\text{O}(l) > \text{H}_2\text{O}(g)$

C. $\text{H}_2\text{O}(g) > \text{H}_2\text{O}(s) > \text{H}_2\text{O}(l)$

D. $\text{H}_2\text{O}(l) > \text{H}_2\text{O}(s) > \text{H}_2\text{O}(g)$

E. $\text{H}_2\text{O}(s) > \text{H}_2\text{O}(g) > \text{H}_2\text{O}(l)$

solid, liquid, gas

Entropy increases