

CHEMISTRY GRADE 11 U-4 ANSWER WITHIN EXPLANATION

1) Rate determining step is the slowest step within a chemical reaction. The slowest step determines the rate of chemical reaction. The slowest step of a chemical reaction can be determined by setting up a reaction mechanisms. Answer :B

2

1. A possible mechanism for the reaction, $2A + B \rightarrow C + D$, is:

(I) $A + A \rightleftharpoons A_2$ fast, equilibrium
 (II) $A_2 + A \rightarrow A_3$ slow
 (III) $A_3 + B \rightarrow A + C + D$ fast

According to the mechanism, the rate law will be :

A) Rate = $k[A]$ C) Rate = $k[A]^2$
 B) Rate = $k[A]^2$ D) Rate = $k[A]^2[B]$

Wanted: To determine rate law for mechanisms with fast initial step.
 Given: Reaction mechanism
 Known: Step-1: set the forward rate law of the fast equilibrium is equal to the reversible fast equilibrium. $k_1[A]^2 = k_{-1}[A_2]$
 Step-2: the slow step's rate law is equivalent to the overall rate law. Recall that the rate determining step is the slowest step. Write the rate law for this step: $Rate = k_2[A_2][A]$
 Step-3: solve for the [intermediate] in terms of reactant in the overall.
 Step-4: substitute the expression for the [intermediate] into the rate law for the slow step to obtain the overall rate law.
 Solution: $Rate_f = Rate_r$
 $k_1[A]^2 = k_{-1}[A_2]$
 $Rate = k_2[A_2][A]$; this is the rate determining step (the slowest step)
 Solving for the intermediate; $[A_2]$, $[A_2] = \frac{k_1}{k_{-1}}[A]^2$;
 Substituting the value for the intermediate $[A_2]$ into the slow step;
 $Rate = \frac{k_1 k_2}{k_{-1}}[A]^2[A]$; since $\frac{k_1 k_2}{k_{-1}} = k$; the rate law for the overall is:
 $Rate = k[A]^3$
 Answer: C

3

What is the half-life of irreversible first order reaction, $A \rightarrow B$, if 75% of A is converted to B in 60 minutes?

A) 30minutes B) 20minutes C) 60minutes D) 80minutes

Wanted: $t_{1/2}$ of a first order reaction.
 Given: total time and % completed.
 Known: In a first order reaction, the concentration of reactant decreases by $\frac{1}{2}$ in each of a series of regularly spaced time intervals, namely $t_{1/2}$.
 Solution: $100\% \xrightarrow{t_{1/2}} 50\% \xrightarrow{t_{1/2}} 25\%$; (thus $50\% + 25\% = 75\%$ in two $t_{1/2}$)
 $t_{1/2} = \frac{\text{Total time elapsed}}{\text{The number of intervals}} = \frac{60 \text{ minutes}}{2 \text{ half times}} = 30 \text{ minutes}$
 Answer: A

4

Known: Reactants must collide with enough energy to react. At higher temperature collisions occur in a given time. Thus raising the temperature increases the reaction rate by increasing the number and the average kinetic energy of the collision.
 Answer: D

5

Wanted: the order of the reaction to give rate law.

Given: experimental data, initial rate and concentration change.

Known: the rate law is of the form: $\text{Rate} = k[A]^m[B]^n$, where m and n are orders with respect to the reactants.

Solution i) find m (order with respect A) using data from exp. 1 and 2 where [B] is constant

$$\frac{\text{Exp}_2}{\text{Exp}_1} = \frac{\text{rate}_2}{\text{rate}_1} = \frac{1.6 \times 10^{-4}}{4.0 \times 10^{-5}} = \frac{k[A]^m[B]^n}{k[A]^m[B]^n} = \frac{k[0.2]^m[0.1]^n}{k[0.1]^m[0.1]^n}$$

$$4 = \left(\frac{0.2}{0.1}\right)^m = 2^m$$

$2^2 = 2^m$ shows $m=2$ or second order in A

ii) find n (order with respect B) using data from exp. 1 and 3 where [A] is constant :

$$\frac{\text{Exp}_3}{\text{Exp}_1} = \frac{\text{rate}_3}{\text{rate}_1} = \frac{8.0 \times 10^{-5}}{4.0 \times 10^{-5}} = \frac{k[0.1]^m[0.2]^n}{k[0.1]^m[0.1]^n}$$

$$2 = 2^n \text{ shows } n = 1 \text{ or first order in B.}$$

Thus the rate law is : $\text{Rate} = k[A]^2[B]$; third overall.

Answer: B

6

Wanted: Factor that do not affect rate of zero order reaction

Known: For $A \rightarrow P$ zero order reaction; $\text{Rate} = k[A]^0 = k(1) = k$;

The change in temperature changes the value of k; thus temp. affects rate of zero order rxn. Increase in surface area increase surface contact, increase rate. Catalysts increase rate of any reaction by decreasing activation energy. Once the collision or contact is completed concentration change does not affect the rate of zero order reaction meaning rate is constant in terms of concentration of zero order reaction.

Answer: A

7

Wanted: unit for the rate of a chemical reaction.

Given: concentration in moles per liter and time in seconds

Known: reaction rate is the change in concentrations of reactants or products per unit time, in which reactant concentrations decrease while product concentrations increase.

$$\text{Rate of reaction} = - \frac{\text{Change in concentration of reactant}}{\text{Change in time}}$$

$$\text{Rate of reaction} = \frac{\text{Change in concentration of product}}{\text{Change in time}}$$

Solution: Substituting the units of concentration and time

$$\text{Rate of reaction} = \frac{\text{Moles per liter}}{\text{Seconds}} = \text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} = \text{M} \cdot \text{s}^{-1}$$

Answer: B

8

Wanted: expressing rate in terms of each component (reactant and product)

Given: $2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g)$

Known: for the hypothetical reaction : $aA + bB \rightarrow cC + dD$; where a, b, c, and d are coefficients of the balanced equation. In general, the rate is related to reactants or products concentration as follows:

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Note: negative for reactants show decrease in concentration with time, and positive for products increase in concentration with time.

$$\text{Solution: } \text{Rate} = -\frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t};$$

Since moles of $\text{NO}_2 = \text{NO}$; $-\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{NO}]}{\Delta t}$; the positive sign on the rate with

respect NO_2 makes it invalid (not valid). the valid relations are: $-\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{2\Delta[\text{O}_2]}{\Delta t}$;

$$\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t}; \quad \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t}$$

Answer: C

9

Wanted: $t_{1/2}$ of a first order reaction.

Given: total time and % completed.

Known: If in reaction, the concentration of reactant decreases by $\frac{1}{2}$ in each of a series of regularly spaced time intervals, namely $t_{1/2}$, is first order reaction. **Solution:**

$100\% \xrightarrow{t_{1/2}(2\text{hour})} 50\% \xrightarrow{t_{1/2}(2\text{hour})} 25\% \xrightarrow{t_{1/2}(2\text{hour})} \dots$; (thus $50\% + 25\% + 12.5\% = 87.5\%$) in 3 $t_{1/2}$ (3-half-lives) Three regularly spaced intervals take 6 hours showing $t_{1/2}$ is 2 hour. This equal time intervals show the reaction is first order. **Answer: B**

27. Suppose reactions $A \xrightarrow{k_f} B$ and $B \xrightarrow{k_r} A$ are both elementary processes with rate constant of $8 \times 10^2 \text{ s}^{-1}$ and $4 \times 10^4 \text{ s}^{-1}$ respectively. What is the value of the equilibrium constant for the equilibrium? $A \rightleftharpoons B$

- A) 2×10^{-2} B) 0.5×10^2 C) 4×10^2 D) 4×10^{-2}

Wanted: Equilibrium constant K_c for the reaction $A \rightleftharpoons B$

Given: $A \xrightarrow{k_f} B$; $k_{fd} = 8.0 \times 10^2 \text{ s}^{-1}$; $B \xrightarrow{k_r} A$; $k_{rv} = 4.0 \times 10^4 \text{ s}^{-1}$

Known: $\text{Rate}_{fd} = \text{Rate}_{rv}$

Solution:

$$\text{Rate}_{fd} = \text{Rate}_{rv}$$

$$k_{fd}[A] = k_{rv}[B]$$

$$K_c = \frac{[B]}{[A]} = \frac{k_{fd}}{k_{rv}} = \frac{8 \times 10^2 \text{ s}^{-1}}{4.0 \times 10^4 \text{ s}^{-1}} = 2.0 \times 10^{-2}$$

Answer: A

28. The reaction $A \rightleftharpoons B$ is at equilibrium.

10

Wanted: the rate expression

Given: experimental data, initial rate and concentration change.

Known: the rate law is of the form: $\text{Rate} = k[X]^m[Y]^n$ where m is order with respect X and n order with respect Y .

Solution: To find m , order in X and to find n , order in Y

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[X]^m[Y]^n}{k[X]^m[Y]^n}; \text{ and } \frac{\text{rate}_1}{\text{rate}_2} = \frac{k[X]^m[Y]^n}{k[X]^m[Y]^n}$$

$$\frac{0.45}{0.45} = \frac{k[3.0]^m[1.5]^n}{k[1.5]^m[1.5]^n}; \text{ and } \frac{1.8}{0.45} = \frac{k[3.0]^m[3.0]^n}{k[3.0]^m[1.5]^n}$$

$$1.0 = \left(\frac{3.0}{1.5}\right)^m \text{ and } 4 = \left(\frac{3.0}{1.5}\right)^n$$

$$1.0 = 2^m \text{ and } 2^2 = 2^n$$

$$m = 0; \text{zero order in } X \text{ and } n = 2; \text{second order in } Y$$

Thus the rate law expression is: $\text{Rate} = k[Y]^2$ **Answer: C**

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29. What is the half-life, $t_{1/2}$ for zero order reaction $A \xrightarrow{k} B$, (k is rate constant)?

- A) $\ln 2k$ B) $[A]_0/2k$ C) $\ln k[A]_0k$ D) $\ln 2[A]_0k$

Wanted: determining $t_{1/2}$, half life for the zero order reaction

Given: reaction $A \rightarrow B$ (k is rate constant)

Known: the rate law expression for zero order reaction is: $[A] = -kt + [A]_0$

In this case a plot of $[A]$ versus t gives a straight line of the slope $-k$

Solution: the integrated rate law by definition is: $[A] = -kt + [A]_0$

When $t = t_{1/2}$ by definition

$$[A] = \frac{[A]_0}{2} = -kt + [A]_0$$

$$[A] = \frac{[A]_0}{2}; \text{ at } t_{1/2} = [A]_0 \cdot \frac{[A]_0}{2} = \frac{[A]_0}{2}$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

Answer: B

12

Wanted: to predict by what factor the rate increases when conc. of a second order, $[\text{NO}]^2$ is doubled holding concentration of I_2 constant.

Given: $\text{Rate} = k[\text{NO}]^2[I_2]$ showing second order with respect NO and first order in I_2

Known: If the reaction is second order with respect a reactant, here NO when the conc. of that reactant is doubled the rate is increased by a factor of four (quadruple)

Solution:

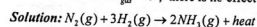
$$\begin{aligned} \text{Rate}_1 &= k[\text{NO}]^2[\text{I}_2] \\ \text{Rate}_2 &= k[2\text{NO}]^2[\text{I}_2] \\ \text{Rate}_2 &= 4k[\text{NO}]^2[\text{I}_2] \\ \text{Rate}_2 &= 4\text{Rate}_1 \end{aligned}$$

Answer: B

13)

Wanted: To describe the effect of change (disturbance) on position of equilibrium.
Known: According to Le Châtelier's Principle when disturbance occurs equilibrium shifts to reduce the disturbance until the system attains a new equilibrium.

- I) **The effect of change in concentration**
The equilibrium position shifts to the right if a reactant is added or a product is removed. The equilibrium position shifts to the left if a reactant is removed or product is added.
- II) **The Effect of a Change in Temperature:** a temperature increase favors the endothermic (heat-absorbing) direction and a temperature decrease favors the exothermic (heat-releasing) direction.
- III) **A change in volume (change in pressure)** increase or decrease conc. per unit area, and affects position of equilibrium as follows:
1. If the volume is lower (pressure is higher) which shift the reaction to ward the side with fewer moles of gas.
 2. If the volume is higher (pressure is lower), which shifts the reaction toward the side with large moles of gas.
 3. If $\Delta n_{\text{gas}} = 0$, there is no effect in the equilibrium position.



Increasing pressure: equilibrium shift to right to small number of moles. Adding more N_2 and H_2 : the equilibrium position shifts to the right if a reactant is added. Decreasing temperature favors the exothermic (heat-releasing) direction equilibrium position shifts to the right. Increasing the volume of the reaction container means decreasing pressure which shift the equilibrium to the left to small number of moles.

Answer: D

14)

Wanted: the rate law of mechanism with a **Slow Initial Step**.

Given: The mechanism of a reaction.

Known: All the elementary steps in a mechanism do not have the same rate. Usually one of the steps is much slower than the others, so limits how fast the overall reaction proceeds. This step is called the **rate-determining step** (or the **rate-limiting step**). Because the rate-

determining step limits the rate of the overall reaction, its rate law represents the rate law for the overall reaction.

Solution: The rate law for the rate-determining step (step-1) is slow compared with the second and the third steps. Thus the rate law for the slow initial step represents the rate law of the overall. That is: $\text{Rate} = k[\text{HOOH}][\text{I}^-]$

Answer: A

15)

Wanted: To describe dependence of rate on concentration.

Known: the Rate law is of the form: $\text{Rate} = k[\text{A}]^m[\text{B}]^n$; where the exponents m and n are reaction orders. The overall reaction order is the sum of the exponents $m + n$. If a reaction is first order (exponent is 1) rate is doubled by doubling the concentration of the reactant. If the rate is increased by a factor of four when the concentration is doubled, the reaction is second order with respect that reactant. Similarly the rate of third order reaction undergo eight fold increase when the concentration is doubled. **Solution:** $\text{Rate} = k[\text{A}]^m[\text{B}]^n$, the rate is doubled when the concentration of B is doubled, thus first order in B, i.e. $n = 1$; when both A and B doubled, the rate increases by a factor of eight thus showing the reaction is third overall.

$$\begin{aligned} m + n &= 3 \\ m + 1 &= 3 \\ m &= 3 - 1 = 2 \end{aligned}$$

The reaction is second order in A and first order in B and the rate law is: $\text{Rate} = k[\text{A}]^2[\text{B}]$

Answer: C

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