

1. Which of the following expressions would be equal to the rate of the reaction below?



1.  $-(\Delta[\text{KOH}] / 2 \cdot \Delta t)$
2.  $-(\Delta[\text{Na}_2\text{SO}_4] / \Delta t)$
3.  $(2 \cdot \Delta[\text{MnO}_2] / \Delta t)$
4.  $(\Delta[\text{H}_2\text{O}] / \Delta t)$
5.  $-(\Delta[\text{Na}_2\text{SO}_3] / 3 \cdot \Delta t)$  **Correct**
6.  $-(\Delta[\text{KMnO}_4] / \Delta t)$

Explanation: rate =  $-(\Delta[\text{KMnO}_4] / 2 \cdot \Delta t) = -(\Delta[\text{Na}_2\text{SO}_3] / 3 \cdot \Delta t) = -(\Delta[\text{H}_2\text{O}] / \Delta t) = (\Delta[\text{MnO}_2] / 2 \cdot \Delta t) = (\Delta[\text{Na}_2\text{SO}_4] / 3 \cdot \Delta t) = (\Delta[\text{KOH}] / 2 \cdot \Delta t)$

2. Consider the data below:

Experiment number	[A] M	[B] M	[C] M	[D] M	initial rate $\text{M} \cdot \text{s}^{-1}$
1	0.025	0.03	0.04	0.056	$1.04 \times 10^{-6}$
2	0.025	0.12	0.04	0.056	$4.16 \times 10^{-6}$
3	0.025	0.015	0.08	0.056	$5.2 \times 10^{-7}$
4	0.075	0.03	0.01	0.056	$9.36 \times 10^{-6}$
5	0.025	0.06	0.07	0.112	$1.04 \times 10^{-6}$

What is the overall order of this reaction?

1. 1
2. 2 **Correct**
3. 3
4. 4
5. 5
6. 6

Explanation:

The most obvious order to solve for first is the order B. This is because B is the only species for which two experiments were performed in which it was the only species whose concentration was changed. The order of B is 1, as shown below.

$$(\text{rate}_1 / \text{rate}_2) = ([\text{B}]_1 / [\text{B}]_2)^b$$

$$(1.04 \times 10^{-6} / 4.16 \times 10^{-6}) = (0.03 / 0.12)^b$$

$$(1/4) = (1/4)^b$$

$$b = 1$$

Comparing experiments 1 and 3, we can see that both B and C were varied, but fortunately, we've already solved for the order of B and so C is now accessible as well. We simply set up the solution as above and incorporate another term for the concentration of C.

$$(\text{rate}_1 / \text{rate}_3) = ([\text{B}]_1 / [\text{B}]_3)^b \times ([\text{C}]_1 / [\text{C}]_3)^c$$

$$(1.04 \times 10^{-6} / 5.2 \times 10^{-7}) = (0.03 / 0.015)^1 \times (0.04 / 0.08)^c$$

$$(2) = (2)^1 \times (1/2)^c$$

$$c = 0$$

Having determined that the order of C is zero, we can simply ignore it for the remainder of the solving this problem. Considering C as irrelevant, solving for the order of A is easy as it is the only unknown varied between experiments 1 and 4.

$$(\text{rate}_1 / \text{rate}_4) = ([\text{A}]_1 / [\text{A}]_4)^a$$

$$(1.04 \times 10^{-6} / 9.36 \times 10^{-6}) = (0.025 / 0.075)^a$$

$$(1/9) = (1/3)^a$$

$$a = 2$$

The concentration of D is only changed in experiment 5. Since we've determined all of the other orders, we can compare this to any other experiment and find the order of D. To simplify the math, comparing

to experiment 1 is best.

$$(\text{rate}_1 / \text{rate}_5) = ([B]_1 / [B]_5)^b \times ([D]_1 / [D]_5)^d$$

$$(1.04 \times 10^{-6} / 1.04 \times 10^{-6}) = (0.03 / 0.06)^1 \times (0.056 / 0.112)^d$$

$$(1) = (1/2)^1 \times (1/2)^d$$

$$d = -1$$

$$\text{rate} = k \cdot [A]^2 \cdot [B]^1 \cdot [D]^{-1}$$

The overall order is  $2 + 1 + -1 = 2$

3. What would be the units of the rate constant (k) for the rate law below?

$$\text{rate} = k \cdot [O_2] \cdot [CO]^{-1} \cdot [Cl_2]^1$$

1.  $s^{-1}$  **Correct**

2.  $M^{-2} \cdot s^{-1}$

3.  $M^{-1} \cdot s^{-1}$

4.  $M^1 \cdot s^{-1}$

Explanation:  $\text{rate} = k \cdot [O_2] \cdot [CO]^{-1} \cdot [Cl_2]^1$

The overall order is 1. The units on k are therefore  $s^{-1}$ .

4. Consider two hypothetical zero-order reactions. If reaction 1 is faster than reaction 2 at room temperature, but slower than reaction 2 at much higher temperatures, then reaction 1 must have the (larger/smaller) activation energy and must have the (larger/smaller) pre-exponential factor. (Hint: consider both the Arrhenius equation and combined Arrhenius equation.)

1. larger, smaller

2. larger, larger

3. smaller, smaller **Correct**

4. smaller, larger

Explanation: The fact that reaction 2 becomes faster than reaction 1 as the temperature is raised implies that it has a greater temperature dependence, in other words a smaller  $E_a$ . The fact that at room higher temperatures reaction 2 is faster means it has the larger pre-exponential term.

5. Consider the elementary reaction:



If  $k = 3.6 \times 10^2 s^{-1}$ , and there is initially 0.781 M  $H_2CO_3$ , what is the  $[H_2CO_3]$  after 1.2 ms have passed?

1. 0.507 M **Correct**

2. 0.349 M

3. 0.584 M

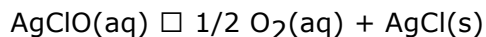
4. 1.203 M

Explanation:  $[H_2CO_3] = [H_2CO_3]_0 e^{-kt}$

$$= 0.781 e^{-(3.6 \times 10^2 s^{-1} \cdot 0.0012 s)}$$

$$= 0.507 M$$

6. Consider the reaction:



If an aqueous system initially has a  $[AgClO]$  of 112 mM and 3 minutes later has a  $[AgClO]$  of 7 mM, what is the half life of  $H_2O_2(aq)$ ?

1. 90 seconds

2. 180 seconds

3. 60 seconds

4. 45 seconds **Correct**

5. not enough information

Explanation  $112 \cdot 0.5^x = 7$

$x = 4$  half-lives

3 minutes = 180 seconds

$$t_{1/2} = 180/4 = 45 \text{ seconds}$$

7. To which of the following reactions would collision state theory not apply? (Note: consider the direction of the arrow in arriving at the correct answer).

1.  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$
2.  $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$
3.  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{O}(\text{g})$
4.  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  **Correct**

Explanation: A single reactant does not require a collision in order to achieve a transition state.

8. Consider the reaction mechanism below:

- step 1:  $2 \text{NO}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$   
step 2:  $\text{Br}_2(\text{g}) + \text{NO}(\text{g}) \rightleftharpoons \text{Br}_2\text{NO}(\text{g})$   
step 3:  $\text{Br}_2\text{NO}(\text{g}) + \text{NO}(\text{g}) \rightleftharpoons 2 \text{BrNO}(\text{g})$   
overall:  $\text{Br}_2(\text{g}) + 2 \text{NO}_2(\text{g}) \rightleftharpoons 2 \text{BrNO}(\text{g}) + \text{O}_2(\text{g})$

If step 3 is the slow step, addition of which of the species below would slow down the observed rate of the reaction?

1.  $\text{NO}(\text{g})$
2.  $\text{BrNO}(\text{g})$
3.  $\text{Br}_2(\text{g})$
4.  $\text{O}_2(\text{g})$  **Correct**
5.  $\text{Br}_2\text{NO}(\text{g})$

Explanation: A product produced before the rate-limiting step will inhibit the forward reaction in which it appear.