

MISCELLANEOUS EXAMPLES

Example – 18

Under certain conditions the reaction between sulphate (SO_4^{2-}) ions and hydrogen ions is first order in each of them, i.e., $\text{rate} = k[\text{SO}_4^{2-}][\text{H}^+]$. A student measured the initial rate of the reaction four times using the combinations of solutions shown in the following table. Write down the actual concentrations of *both* ions in each experiment and hence determine the value of the rate in terms of k .

Experiment	Solution of sulphate ions		Solution of hydrogen ions	
	Concentration /mol dm ⁻³	volume /cm ³	Concentration /mol dm ⁻³	volume /cm ³
A	0.5	125	0.05	125
B	0.5	250	0.05	250
C	0.5	500	0.05	500
D	0.5	500	0.05	125

Critical thinking

- (1) You will have to think carefully about the difference between concentration and volume.
- (2) In the rate law for a reaction, the concentration used are in terms of the number of moles of each reacting species w.r.t. the total concentration of the solution. Here the concentrations given are of the reactants before they have been brought together for reaction. We have been given the volume of each of the reactants' solution. When they are mixed, the total volume will change and hence, the concentration of the reacting species will change too. It is these new concentrations of the reacting species that should be put in the rate law to get the respective rate of reaction.

Solution: As pointed out the key thing to remember is that the rate will change if the *concentrations* of the reagents change.

In experiment A when the two solutions are mixed, the total volume becomes 250 cm³. This is twice the volume of each of the separate solutions, so their concentrations are halved just as they are brought together to react.

Hence, the concentration of SO_4^{2-} (0.5 m in a 125 cm³ solution) becomes $\frac{0.5 \text{ M}}{2}$ in a 250 cm³

solution. And the concentration of H^+ ions (0.05 M in a 125 cm³ solution) becomes $\frac{0.05}{2}$ in a 250 cm³ solution.

So, rate of the reaction in this case will be given by,

$$\text{rate} = k \left(\frac{0.5}{2} \right) \left(\frac{0.05}{2} \right) \text{ [substituting into the given rate law]}$$

$$\text{rate} = k \times 6.25 \times 10^{-3}$$

You are requested to provide the solution for experiments B, C and D yourself. The answers are given here:

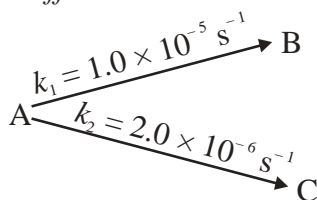
- (B) $\text{rate} = k \times 6.25 \times 10^{-3}$
 (C) $\text{rate} = k \times 6.25 \times 10^{-3}$
 (D) $\text{rate} = k \times 4.00 \times 10^{-2}$

Example – 19

A certain compound A, was found to undergo two parallel first order rearrangements, forming B and C respectively in the two arrangements. At 25° C, the first order rate constant for the formation of B was measured as $1.0 \times 10^{-5} \text{ s}^{-1}$ and for the formation of C as $2.0 \times 10^{-6} \text{ s}^{-1}$. What is the percentage distribution of the rearrangement products?

Critical thinking

What the question says is that the same compound A has tendency to form two different products by two different paths and both these different reactions can occur simultaneously:



Here, we can write the various rate laws as:

$$-\frac{d[A]}{dt} = k_1[A] + k_2[A] \quad \dots (i)$$

$$\frac{d[B]}{dt} = k_1[A] \quad \dots (ii)$$

$$\frac{d[C]}{dt} = k_2[A] \quad \dots (iii)$$

Dividing (ii) by (i), we get,

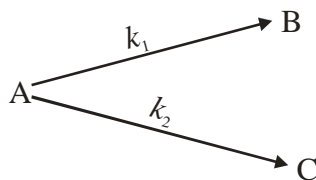
$$\frac{\frac{d[B]}{dt}}{-\frac{d[A]}{dt}} = \frac{k_1[A]}{k_1[A] + k_2[A]}$$

$$\Rightarrow \frac{d[B]}{-d[A]} = \frac{k_1 \cancel{[A]}}{(k_1 + k_2) \cancel{[A]}}$$

Hence LHS gives us the fraction of amount of B formed to amount of A reacted and this is equal to

$\frac{k_1}{k_1 + k_2}$. Can you see that you have all the information and analysis you need to get the answers for this question?

Solution:



$$\begin{aligned} \text{percentage of B formed can be obtained by} &= \left(\frac{k_1}{k_1 + k_2} \times 100 \right) \\ &= \left(\frac{1.0 \times 10^{-5}}{1.0 \times 10^{-5} + 2.0 \times 10^{-6}} \right) \times 100 \\ &= \left(\frac{1 \times 10^{-5}}{1.0 \times 10^{-5} + 0.2 \times 10^{-5}} \right) \times 100 \\ &= 83.33 \% \end{aligned}$$

$$\begin{aligned} \text{percentage of A formed can be obtained by} &= \left(\frac{k_2}{k_1 + k_2} \right) \times 100 \\ &= \left(\frac{2.0 \times 10^{-6}}{1.0 \times 10^{-5} + 2.0 \times 10^{-6}} \right) \times 100 \\ &= \left(\frac{0.2 \times 10^{-5}}{1.0 \times 10^{-5} + 0.2 \times 10^{-5}} \right) \times 100 \\ &= 16.67 \% . \end{aligned}$$

Example – 20

Two reactions (i) $A \rightarrow \text{products}$ and (ii) $B \rightarrow \text{products}$ follow first-order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half-life for the reaction at 310 K is 30 min. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300 K.

Critical thinking

The problem is actually very simple as all you have to do is certain calculations in a logical order. Arrange all the data in a diagram and it will be immediately clear to you so as to how you can solve this question.

In the solution to this problem, you will be provided with the rough draft of the data and then how it can be reorganised to see for yourself so as to how solution can be obtained.

It is expected of you that you make the rough draft and its reorganisation yourself first and then compare it with the one given here.

It is expected then that you provide the complete solution yourself. The answer is provided for cross-checking.

Solution: Rough Draft (data collection from Question)

$$2k_{A(300\text{K})} = k_{A(310\text{K})} \quad \dots \text{(i)}$$

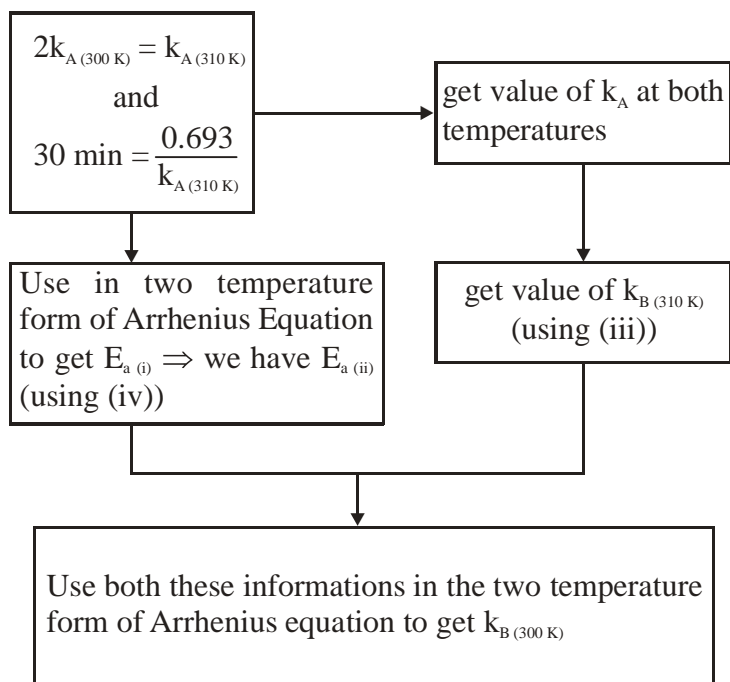
$$t_{\frac{1}{2}} \text{ (for (i) at 310 K)} = 30 \text{ min} \quad \dots \text{(ii)}$$

$$k_{B(310\text{K})} = 2 k_{A(310\text{K})} \quad \dots \text{(iii)}$$

$$E_{a(ii)} = \frac{1}{2} E_{a(i)} \quad \dots \text{(iv)}$$

$$k_{B(300\text{K})} = ? \quad \dots \text{(v)}$$

Reorganised draft



Answer $k_{B(300\text{K})} = \frac{1}{\sqrt{2}} k_{B(310\text{K})} = \frac{0.0462 \text{ min}^{-1}}{\sqrt{2}} = 0.0327 \text{ min}^{-1}$

EXERCISE

Rate of Reaction and Rate Law

- Q. 1** How will the rate of reaction $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$ change if the volume of the reaction vessel is diminished to one third of its initial value? (The rate law for this reaction involves all reactants and their respective orders are same as the stoichiometric coefficients.)
- Q. 2** One mole of gas A and two moles of gas B are introduced into one vessel, and two moles of gas A and one mole of gas B into a second vessel having the same capacity. The temperature is the same in both vessels. Will the rate of the reaction between gases A and B in these vessels differ if it is expressed by the equation (a) $\text{rate}_1 = k_1[\text{A}][\text{B}]$; (b) $\text{rate}_2 = k_2[\text{A}]^2[\text{B}]$?
- Q. 3** The reaction between substances A and B is expressed by the equation $\text{A} + 2\text{B} \rightarrow \text{C}$. The initial concentrations of the reactants are $[\text{A}]_0 = 0.03 \text{ mol/l}$ and $[\text{B}]_0 = 0.05 \text{ mol/l}$. The rate constant of the reaction is 0.4. Find the initial rate of the reaction and the rate after a certain time when the concentration of substance A diminishes by 0.01 mol/l . ($\text{rate} = k[\text{A}][\text{B}]^2$)
- Q. 4** How will the rate of the reaction $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ change if (a) the pressure in the system is increased three times; (b) the volume of the system is diminished to one-third of its initial value; and (c) the concentration of the NO is increased three times? ($\text{rate} = [\text{NO}]^2[\text{O}_2]$)
- Q. 5** Rate of a reaction $\text{A} + \text{B} \rightarrow \text{products}$, is given below as a function of different initial concentrations of A and B:

[A] (mol/l)	[B](mol/l)	Initial rate (mol/l/min)
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

Determine the order of the reaction with respect to A and with respect to B. What is the half-life of A in the reaction?

- Q. 6** For the given reaction, $\text{A} + \text{B} \rightarrow \text{products}$, following data were obtained.

	[A] (mol/l)	[B](mol/l)	Initial rate (mol/l/min)
	$[\text{A}]_0$	$[\text{B}]_0$	$R_0(\text{mol L}^{-1} \text{ s}^{-1})$
1.	0.1	0.2	0.05
2.	0.2	0.2	0.10
3.	0.1	0.1	0.05

- (a) Write the rate law expression (b) Find the rate constant

- Q. 7** The reaction, $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$ has a rate given by the rate law, $\text{Rate} = k[\text{H}_2][\text{Br}_2]^{1/2}$. (a) What are the units of the rate constant k ? (b) If the volume of the gas mixture is halved, by what factor is the rate changed?
- Q. 8** The reaction $v_1\text{A} + v_2\text{B} \rightarrow \text{products}$ is first-order with respect to A and zero-order with respect to B. If the reaction is started with $[\text{A}]_0$ and $[\text{B}]_0$, the integrated rate expression of this reaction would be

$$(a) \ln \frac{[\text{A}]_0}{[\text{A}]_0 - x} = k_1 t \quad (b) \ln \frac{[\text{A}]_0}{[\text{A}]_0 - v_1 x} = k_1 t \quad (c) \ln \frac{[\text{A}]_0}{[\text{A}]_0 - v_1 x} = v_1 k_1 t \quad (d) \ln \frac{[\text{A}]_0}{[\text{A}]_0 - v_1 x} = -v_1 k_1 t$$

Q. 9 Rate of a reaction, $A + B \rightarrow \text{products}$ is given as a function of different initial concentrations of A and B.

[A]/mol L ⁻¹	[B]/mol L ⁻¹	r ₀ /mol L ⁻¹ min ⁻¹
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

Determine the order of the reaction with respect to A and with respect to B. What is the half-life of A in the reaction?

Q. 10 For a first order reaction $A \rightarrow B$, the concentration of B at two instant is given: $[B]_{t=10 \text{ sec}} = 1.0 \text{ M}$ and $[B]_{t=25 \text{ sec}} = 4.0 \text{ M}$. Using this information can you calculate the instantaneous rate of the reaction at at least one instant in the interval from $t = 10 \text{ sec}$ to $t = 25 \text{ sec}$.

Q. 11 If the steady-state concentration of O_3 in a polluted atmosphere is $2.0 \times 10^{-8} \text{ mol/L}$, the rate of production of O_3 is $7.2 \times 10^{-13} \text{ M/hr}$, and O_3 is destroyed by the reaction, $2 O_3 \rightarrow 3 O_2$, what is the rate constant for the reaction, assuming a rate law, $\text{Rate} = - (1/2) \Delta [O_3] / \Delta t = k [O_3]^2$?

Q. 12 In the enzymatic fermentation of sugar, the sugar concentration decreased from 0.12 M to 0.06 M in 10 hours, and to 0.03 M in 20 hours. What is the order of the reaction? What is the rate constant k ?

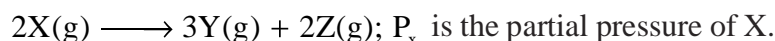
Q. 13 The rate law for the reaction, $Ce^{4+}(aq) + Fe^{2+}(aq) \rightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$, is: $\text{Rate} = (1.0 \times 10^3 \text{ M}^{-1}\text{s}^{-1}) [Ce^{4+}][Fe^{2+}]$. If 0.500 L of 0.0020 M $Ce(SO_4)_2$ is rapidly mixed with 0.500 L of 0.0020 M $FeSO_4$, how long does it take for $[Fe^{2+}]$ to decrease to $1.0 \times 10^{-4} \text{ M}$?

Integrated Rate Equation

Q. 14 The following statement(s) is (are) correct:

- A plot of $\log K_p$ versus $1/T$ is linear
- A plot of $\log [X]$ versus time is linear for a first order reaction, $X \rightarrow P$
- A plot of p versus $1/T$ is linear at constant volume
- A plot of p versus $1/V$ is linear at constant temperature

Q. 15 At constant temperature and volume, X decomposes as



Observation No.	Time (in minute)	P_x (in mm of Hg)
1	0	800
2	100	400
3	200	200

- What is the order of reaction with respect to X?
- Find the rate constant.
- Find the time for 75% completion of the reaction
- Find the total pressure when pressure of X is 700 mm of Hg.

- Q. 16** While studying the decomposition of gaseous N_2O_5 it is observed that a plot of logarithm of its partial pressure versus time is linear. What kinetic parameters can be obtained from this observation?
- Q. 17** The rate constant for the first-order decomposition of $\text{N}_2\text{O}_5(\text{g})$ to $\text{NO}_2(\text{g})$ and $\text{O}_2(\text{g})$ is $7.48 \times 10^{-3} \text{ s}^{-1}$ at a given temperature. (a) Determine the length of time required for the total pressure in a system containing N_2O_5 at an initial pressure of 0.1 atm to rise to 0.145 atm. (b) Find the total pressure after 100 s of the reaction.

The Arrhenius Equation.

- Q. 18** The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{ s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$ and $6.0 \times 10^{14} \text{ s}^{-1}$ respectively. The value of the rate constant as $T \rightarrow \infty$ is,
 (a) $2.0 \times 10^{18} \text{ s}^{-1}$ (b) $6.0 \times 10^{14} \text{ s}^{-1}$ (c) infinity (d) $3.6 \times 10^{30} \text{ s}^{-1}$
- Q. 19** At 380°C , the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1} . Calculate the time required for 75% decomposition at 450°C .
- Q. 20** The rate constant for the first order decomposition of a certain reaction is described by the equation $\log(k/\text{s}^{-1}) = 14.34 - (1.25 \times 10^4 \text{ K})/T$
 (i) What is the energy of activation of this reaction?
 (ii) At what temperature will its half-life be 256 minutes?
- Q. 21** The rate constant of a reaction is $1.5 \times 10^7 \text{ s}^{-1}$ at 50°C and $4.5 \times 10^7 \text{ s}^{-1}$ at 100°C . Evaluate the Arrhenius parameters A and E_a .
- Q. 22** A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol^{-1} .
- Q. 23** The activation energy of a certain reaction is 15 kJ/mol . The reaction is exothermic, yielding 19 kJ/mol . What is the activation energy of the reverse reaction?
- Q. 24** The activation energy of the reaction $\text{O}_3(\text{g}) + \text{NO}(\text{g}) \rightarrow \text{O}_2(\text{g}) + \text{NO}_2(\text{g})$ is 10 kJ/mol . How many times will the rate of the reaction change when the temperature is raised from 27 to 37°C ?
- Q. 25** The E_a of the reaction $\text{M} + \text{N} \rightarrow \text{O} + \text{P}$ is 80 kJ/mol . At 50°C , the products are formed at the rate of 0.15 mol/L/min . What will be rate of formation of products at 100°C ?
- Q. 26** The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre-exponential factor for the reaction is $3.56 \times 10^9 \text{ s}^{-1}$, calculate its rate constant at 318 K and also the energy of activation.
- Q. 27** A substance A was found to undergo two parallel first-order rearrangements $\text{A} \rightarrow \text{B}$ and $\text{A} \rightarrow \text{C}$ with rate constants $1.26 \times 10^{-4} \text{ s}^{-1}$ and $3.8 \times 10^{-5} \text{ s}^{-1}$, respectively. What were the percentage distribution of B and C?

TRY YOURSELF - III

1. (A), (D)
2. very high temperature (or) zero activation energy
3. (c)
4. (b), (c)
5. (c)
6. False
7. False
8. False (The rate of reaction increases with increasing temperature because the no. of molecules with E_a increases as the temperature increases. This has nothing to do with the reaction being exothermic/endothermic)
9. $\approx 311 \text{ K}$
10. $k_{27^\circ\text{C}} = 0.0231 \text{ min}^{-1}$
 $E_a = 43.85 \text{ kJ/mol}$
11. 227 kJ/mol
12. (a) Yes (b) No
13. No
14. reverse one
15. 5 times
16. 49.9 kJ/mol
17. 80.3 kJ/mol
18. (b), (d)
19. (b)
20. 283 K

EXERCISE

[ANSWERS KEY]

1. grow by 27 times.
2. (a) No, (b) Yes
3. 3×10^{-5} , 7.2×10^{-6}
4. (a) It will grow 27 times
(b) It will grow 27 times
(c) It will grow 9 times
5. 1, 0, 1.386 minutes
6. (a) $R_0 = k[A_0]$
(b) 0.5 sec^{-1}
7. (a) $(\text{mol/L})^{-1/2} \text{ s}^{-1}$
(b) 2.8
8. (c)
9. (a) one, zero
(b) 1.386 minutes
10. **Hint:** Use mean value theorem (differential calculus).
11. $0.25 \text{ M}^{-1} \text{ s}^{-1}$
12. (a) first order (b) $6.9 \times 10^{-2} \text{ hr}^{-1}$
13. 9 seconds
14. (A), (B), (D)
15. (i) 1
(ii) $6.93 \times 10^{-3} \text{ min}^{-1}$
(iii) 200 min
(iv) 950 mmHg
16. first order related
17. (a) 47.7 seconds
(b) 0.180 atm.
18. (b)
19. 20.4 minutes.
20. $E_a = 2.39 \text{ kJ/mol}$; $T = 669 \text{ K}$
21. $A = 5.45 \times 10^{10} \text{ s}^{-1}$; $E_a = 22012.7 \text{ J/mol}$
22. 100 kJ/mol
23. 34 kJ/mol.
24. 1.14 times

25. **Hint:** $(\text{rate})_{100^\circ \text{C}} = (\text{rate})_{50^\circ \text{C}} \left(\frac{k_{100^\circ \text{C}}}{k_{50^\circ \text{C}}} \right)$

26. **Hint**

$$\frac{2.303}{k_{298 \text{ K}}} \log \frac{100}{90} = t = \frac{2.303}{k_{308 \text{ K}}} \log \frac{100}{75} \xrightarrow{\text{gives}} \frac{k_{298 \text{ K}}}{k_{308 \text{ K}}} \xrightarrow{E_a = ?} \text{use in two temperature from of Arrhenius eqn to get } E_a$$

$$\downarrow k_{318 \text{ K}} = ?$$

$$\text{use } k = A \cdot e^{-E_a/RT}$$

(pre-exponential factor)

$$k_{318 \text{ K}} = 9.43 \times 10^{-4} \text{ s}^{-1}$$

$$E_a = 76.5 \text{ kJ/mol}$$

Q. 27 76.83% B and 23.17% C