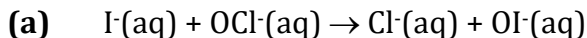


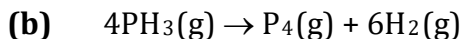
SOLUTIONS TO PRACTICE EXERCISE

KINETICS

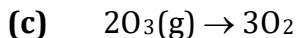
1. Write the rate expression for the reactions:



$$\text{Rate} = -\frac{\Delta[\text{I}^{-}]}{\Delta t} = -\frac{\Delta[\text{OCl}^{-}]}{\Delta t} = \frac{\Delta[\text{Cl}^{-}]}{\Delta t} = \frac{\Delta[\text{OI}^{-}]}{\Delta t}$$



$$\text{Rate} = -\frac{1}{4} \frac{\Delta[\text{PH}_3]}{\Delta t} = \frac{\Delta[\text{P}_4]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2]}{\Delta t}$$



$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t}$$

2. Consider the formation of molecular Hydrogen in reaction 1(b) which is 0.078 M/s .

(a) Calculate the rate at which $\text{P}_4(\text{g})$ is being formed.

$$\frac{\Delta[\text{P}_4]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{1}{6} (0.078 \text{ M/s}) = 0.013 \text{ M/s}$$

(b) At what rate is $\text{PH}_3(\text{g})$ reacting?

$$-\frac{1}{4} \frac{\Delta[\text{PH}_3]}{\Delta t} = \frac{\Delta[\text{P}_4]}{\Delta t} \quad \text{OR} \quad -\frac{1}{4} \frac{\Delta[\text{PH}_3]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2]}{\Delta t}$$

$$-\frac{\Delta[\text{PH}_3]}{\Delta t} = \frac{\Delta[\text{P}_4]}{\Delta t} \times 4 = 0.013 \text{ M/s} \times 4 = \mathbf{0.052 \text{ M/s}}$$

$$-\frac{\Delta[\text{PH}_3]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2]}{\Delta t} \times 4 = 0.078 \text{ M/s} \times \frac{4}{6} = \mathbf{0.052 \text{ M/s}}$$

3. Study the given data for the reaction between: $\text{F}_2(\text{g}) + 2\text{ClO}_2(\text{g}) \rightarrow 2\text{FCLO}_2(\text{g})$

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and answer all questions that following:

Table 1. Rate data for the reaction between

Exp	Reactant F ₂ (1)/M	Reactant (2)/M	Initial rate (M/s)
1	0.010	0.010	1.2×10^{-3}
2	0.010	0.040	4.8×10^{-3}
3	3.020	0.010	2.4×10^{-3}

- (a) By observation of the kinetics data (*in Table 1 above*) indicate if the rate is directly proportional to both reactants.

Looking at exp's 1 & 3: as [F₂] doubles, while holding [ClO₂] constant the reaction rate doubles. Thus the rate is directly proportional to [F₂] or rate \propto [F₂].

Similarly, the data in exp's 1 & 2 show that as the [ClO₂] is quadrupled at constant [F₂], the rate increases by 4 times. So the rate is also directly proportional to [ClO₂].

- (b) Write the rate law of the reaction.

$$\text{Rate} = k[\text{F}_2][\text{ClO}_2]$$

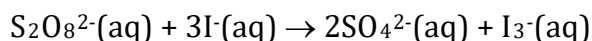
- (c) Calculate the rate constant of the reaction.

Using data from exp 1:

$$k = \frac{\text{rate}}{[\text{F}_2][\text{ClO}_2]} = \frac{1.2 \times 10^{-3}}{(0.10M)(0.010M)} = 1.2/M.s$$

Using data from exp 2 and 3 will also yield the same rate constant value.

4. The reaction between persulfate S₂O₈²⁻(aq) and iodide (I⁻(aq) is:



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Exp	S ₂ O ₈ ²⁻ (aq)/M	I ⁻ (aq) /M	Initial rate (M/s)
1	0.080	0.034	2.2 × 10 ⁻⁴
2	0.080	0.017	1.1 × 10 ⁻⁴
3	0.160	0.017	2.2 × 10 ⁻⁴

From the data given in Table 2 above:

- (a)** Determine the rate law

Exp 1 & 2 show that doubling the conc of [I⁻] while holding [S₂O₈²⁻] doubles the rate:

$$\frac{rate_1}{rate_2} = \frac{[2.2 \times 10^{-4}]}{[1.1 \times 10^{-4}]} = 2 = \frac{k(0.080M)^x(0.034M)^y}{k(0.080M)^x(0.017M)^y} = 2^y \quad y = 1$$

Exp 2 & 3 show that doubling the conc of [S₂O₈²⁻] while holding [I⁻] constant doubles the rate:

$$\frac{rate_3}{rate_2} = \frac{[2.2 \times 10^{-4}]}{[1.1 \times 10^{-4}]} = 2 = \frac{k(0.160M)^x(0.017M)^y}{k(0.080M)^x(0.017M)^y} = 2^x \quad (x) = 1$$

Therefore, rate = k[S₂O₈²⁻][I⁻]

- (b)** Give the order of the reaction with respect to the reactants and the overall order.

Rate is first-order wrt [S₂O₈²⁻]

Rate is first-order wrt [I⁻]

Overall order of the reaction = 1+1 =2 i.e a second order reaction

- (c)** Calculate the rate constant.

Using data from exp 1:

$$k = \frac{rate}{[S_2O_8^{2-}][I^-]} = \frac{2.2 \times 10^{-4}}{(0.080M)(0.034M)} = 0.08088/M.s$$

Using data from exp 2 and 3 will also yield the same rate constant value.

- (d)** Calculate the average rate of the reaction when the [S₂O₈²⁻] = 0.20 M and [I⁻] = 0.020 M

$$\begin{aligned} \text{Average rate of } [S_2O_8^{2-}] &= - \frac{[S_2O_8^{2-}]_{final} - [S_2O_8^{2-}]_{initial}}{\Delta t} \\ &= - \frac{[0.20M]_{final} - [0.080M]_{initial}}{\Delta t} \end{aligned}$$

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$$\begin{aligned}\text{Average rate of } [I^-] &= -\frac{[I^-]_{\text{final}} - [I^-]_{\text{initial}}}{\Delta t} \\ &= -\frac{[0.20M]_{\text{final}} - [0.017M]_{\text{initial}}}{\Delta t}\end{aligned}$$

5. The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of 1.45 yr^{-1} at 12°C . A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of $5.0 \times 10^{-7} \text{ g/cm}^3$.

Assume that the average temperature of the lake is 12°C .

For a First-order reaction: $\ln[A]_t - \ln[A]_o = -kt$ or $\ln([A]_t / [A]_o) = -kt$

- (a) What is the concentration of the insecticide on June 1 of the following year?

Substituting in the integrated equation for a first-order reaction

$$\ln[\text{insecticide}]_{t=1 \text{ yr}} = -(1.45 \text{ yr}^{-1})(1.00 \text{ yr}) + \ln(5.0 \times 10^{-7})$$

$$\ln[\text{insecticide}]_{t=1 \text{ yr}} = -1.45 + (-14.51) = -15.96$$

$$[\text{insecticide}]_{t=1 \text{ yr}} = e^{-15.96}$$

- (b) How long will it take for the concentration of the insecticide to drop to $3.0 \times 10^{-7} \text{ g/cm}^3$?

$$\ln(3.0 \times 10^{-7}) = -(1.45 \text{ yr}^{-1})(t) + \ln(5.0 \times 10^{-7})$$

Solving for t

$$\begin{aligned}T &= -[\ln(3.0 \times 10^{-7}) - \ln(5.0 \times 10^{-7})] / 1.45 \text{ yr}^{-1} \\ &= -(-15.02 + 14.51) / 1.45 \text{ yr}^{-1} \\ &= 0.35 \text{ yr}\end{aligned}$$

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6. The following data were obtained for the gas-phase decomposition of nitrogen dioxide at 300°C according to the reaction:



Consider the decomposition of NO_2 as shown in the equation above. The reaction is second order in NO_2 with $k = 0.543 \text{ M}^{-1}\text{s}^{-1}$. If the initial concentration of NO_2 in a closed vessel is 0.0500 M , what is the remaining concentration after 0.500 h?

Using the expression for a second-order reaction

$$\frac{1}{[\text{NO}_2]_t} = kt + \frac{1}{[\text{NO}_2]_{\text{initial}}}$$

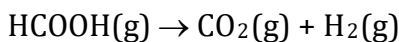
$$\frac{1}{[\text{NO}_2]_t} = (0.543 \text{ M}^{-1}\text{s}^{-1})(1800)\text{s} + \frac{1}{[0.0500\text{M}]_{\text{initial}}}$$

$$\frac{1}{[\text{NO}_2]_t} = (977.4 \text{ M}^{-1}) + 20 \text{ M}^{-1}$$

$$\frac{1}{[\text{NO}_2]_t} = 997.4 \text{ M}^{-1}$$

$$[\text{NO}_2] \text{ after } 0.50\text{h} = 1.003 \times 10^{-3}$$

7. Formic acid (HCOOH) decomposes in the gas phase at elevated temperatures as follows:



The decomposition reaction is determined to be first order. A graph of the partial pressure of HCOOH versus time for decomposition at 838 K is shown as the red curve in Figure 1 below. When a small amount of solid ZnO is added to the reaction chamber,

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the partial pressure of acid versus time varies as shown by the blue curve in Figure 1 shown below.

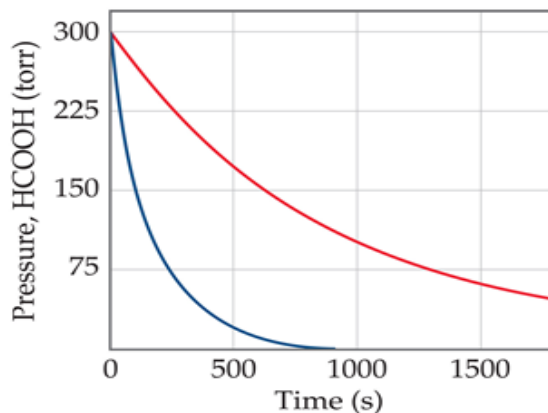


Figure 1. Variation in pressure of $\text{HCOOH}(g)$ as a function of time at 838 K. The red line corresponds to decomposition when only gaseous HCOOH is present. The blue line corresponds to decomposition in the presence of added $\text{ZnO}(s)$.

Reference: Chemistry, The Central Science, 10th edition, Theodore L. Brown; H. Eugene LeMay, Jr.; and Bruce E. Bursten

- (a)** Estimate the half-life and first-order rate constant for formic acid decomposition.

The initial pressure of HCOOH is 3.00×10^2 torr. On the graph we move to the level at which the partial pressure of HCOOH is 150 torr, half the initial value. This corresponds to a time of about 6.60×10^2 s, which is therefore the half-life.

The first-order rate constant is given by:

$$\text{Equation 14.15: } k = 0.693/t_{1/2} = 0.693/660 \text{ s} = 1.05 \times 10^{-3} \text{ s}^{-1}.$$

- (b)** What can you conclude from the effect of added ZnO on the decomposition of formic acid?

The reaction proceeds much more rapidly in the presence of solid ZnO , so the surface of the oxide must be acting as a catalyst for the decomposition of the acid. This is an example of heterogeneous catalysis.

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- (c) The progress of the reaction was followed by measuring the partial pressure of formic acid vapor at selected times. Suppose that, instead, a plot of the concentration of formic acid in units of mol/L was carried out.

What effect would this have had on the calculated value of k ?

If a plot of the concentration of formic acid in units of moles per litre was carried out the half-life for decomposition would still be determined as 660 seconds, and we would have computed the same value for k . Because the units for k are s^{-1} , the value for k is independent of the units used for concentration.

- (d) The pressure of formic acid vapor at the start of the reaction is 3.00×10^2 torr. Assuming constant temperature and ideal-gas behavior, what is the pressure in the system at the end of the reaction? If the volume of the reaction chamber is 436 cm^3 , how many moles of gas occupy the reaction chamber at the end of the reaction?

$$n = \frac{PV}{RT} = \frac{(600/760 \text{ atm})(0.436 \text{ L})}{(0.0821 \text{ L-atm/mol-K})(838 \text{ K})} = 5.00 \times 10^{-3} \text{ moles}$$

- (e) The standard heat of formation of formic acid vapor is $\Delta H_f^\circ = -378.6 \text{ kJ/mol}$. Calculate ΔH° for the overall reaction.

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{CO}_2(\text{g})) + \Delta H_f^\circ(\text{H}_2(\text{g})) - \Delta H_f^\circ(\text{HCOOH}(\text{g})) \\ &= -393.5 \text{ kJ/mol} + 0 - (-378.6 \text{ kJ/mol}) \\ &= -14.9 \text{ kJ/mol}\end{aligned}$$