Kinetics Problems

1) **Given the following data:**

[A] (M)	[B] (M)	Rate (M/s)
0.20	0.10	1.12×10^{-3}
0.20	0.20	4.48×10^{-3}
0.40	0.10	2.24×10^{-3}

Determine the:

(a) **rate expression for the reaction.**

(b) **rate constant.**

(c) **reaction rate when [A] = 0.12 M and [B] = 0.10 M.**

2) **Dinitrogen pentoxide decomposes as shown below.**

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

At 70° C, the value of the rate constant is 2.3×10^{-3}/s. If the initial concentration of N_2O_5 is 0.38 M, how much N_2O_5 remains after 2.5 minutes?

3) **Nitrosyl bromide decomposes as shown below.**

$$2NOBr(g) \rightarrow 2NO(g) + Br_2(g)$$

The activation energy for the reaction at 130° C is 78.6 kJ/mol. How many times greater is the rate constant when the temperature is increased to 160° C?

4) **Dinitrogen tetraoxide reacts with carbon dioxide as shown below.**

$$N_2O_4(g) + 2CO(g) \rightarrow 2CO_2(g) + 2NO(g)$$

(a) **What is the rate of reaction in terms of N_2O_4 ?**

(b) **How is the rate of N_2O_4 disappearance related to the appearance of NO?**

(c) **If N_2O_4 reacts at the rate of 11 M/s, what is the rate of NO formation?**

5) **Phosphine decomposes as shown below.**

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$$

This reaction takes place at 100° C and the rate constant is 0.372 M/min.

(a) **How long does it take for the phosphine to drop to one-fifth of its original concentration?**

(b) **What is k at 70° C if the activation energy is 73.2 kJ/mol?**

6) **Given the following data:**

[A] (M)	Rate (M/s)
0.10	0.010
0.20	0.042
0.30	0.097
0.40	0.158

Determine the reaction rate when [A] = 0.15 M.

Solutions

1) (a) $\text{Rate} = k[A]^m[B]^n$

$\text{Rate}_1 = k(0.20\text{ M})^m(0.10\text{ M})^n$

$\text{Rate}_2 = k(0.20\text{ M})^m(0.20\text{ M})^n$

$\text{Rate}_1/\text{ Rate}_2 = k(0.20\text{ M})^m(0.10\text{ M})^n/\ k(0.20\text{ M})^m(0.20\text{ M})^n$

$(1.12 \times 10^{-3}\ \cancel{\text{M/s}})/(4.48 \times 10^{-3}\ \cancel{\text{M/s}}) = \cancel{k(0.20\text{ M})^m}(0.10\ \cancel{\text{M}})^n/\ \cancel{k(0.20\text{ M})^m}(0.20\ \cancel{\text{M}})^n$

$0.25 = (0.10/0.20)^n$

$0.50^n = 0.25,\ n = 2$

$\text{Rate}_1 = k(0.20\text{ M})^m(0.10\text{ M})^2$

$\text{Rate}_3 = k(0.40\text{ M})^m(0.10\text{ M})^2$

$\text{Rate}_1/\text{ Rate}_3 = k(0.20\text{ M})^m(0.10\text{ M})^2/\ k(0.40\text{ M})^m(0.10\text{ M})^2$

$(1.12 \times 10^{-3}\ \cancel{\text{M/s}})/(2.24 \times 10^{-3}\ \cancel{\text{M/s}}) = \cancel{k}(0.20\ \cancel{\text{M}})^m(\cancel{0.10\text{ M}})^{\cancel{2}}/\ \cancel{k}(0.40\ \cancel{\text{M}})^m(\cancel{0.10\text{ M}})^{\cancel{2}}$

$0.50 = (0.20/0.40)^m$

$0.50^m = 0.50,\ m = 1$

$\text{Rate} = k[A][B]^2$

(b) $\text{Rate} = k[A][B]^2$

$1.12 \times 10^{-3}\text{ M/s} = k \times (0.20\text{ M}) \times (0.10\text{ M})^2$

$k = 0.56\ \text{M}^{-2}\text{s}^{-1}$

(c) $[A] = 0.12\text{ M}$ $[B] = 0.10\text{ M}$ $k = 0.56\ \text{M}^{-2}\text{s}^{-1}$

$\text{Rate} = k[A][B]^2 = 0.56\ \text{M}^{-2}\text{s}^{-1} \times 0.12\text{ M} \times (0.10\text{ M})^2$

$\text{Rate} = 6.7 \times 10^{-4}\text{ M/s}$

2) $T = 70° C$ $[N_2O_5]_0 = 0.38\ M$ $[N_2O_5]_t = ?$

$k = 2.3 \times 10^{-3}/s$ $t = 2.5\ min$

$\ln[N_2O_5]_t - \ln[N_2O_5]_0 = -k \times t$

$\ln[N_2O_5]_t = -k \times t + \ln[N_2O_5]_0$

$\ln[N_2O_5]_t = -2.3 \times 10^{-3}/s \times 2.5\ \cancel{min} \times 60\ s/1\ \cancel{min} + \ln(0.38)$

$\ln[N_2O_5]_t = -1.31$

$[N_2O_5]_t = e^{-1.31} = 0.27\ M$

3) $E_a = 78.6\ kJ/mol$ $T_1 = 130° C + 273 = 403\ K$

$R = 8.31\ J/mol{\cdot}K$ $T_2 = 160° C + 273 = 433\ K$

$\ln(k_2/k_1) = E_a/R \times (T_1^{-1} – T_2^{-1})$

$\ln(k_2/k_1) = 78.6\ \cancel{kJ}/\cancel{mol}/(8.31\ \cancel{J}/\cancel{mol{\cdot}K} \times 1\ \cancel{kJ}/10^3\ \cancel{J}) \times (403^{-1}\ \cancel{K} – 433^{-1}\ \cancel{K})$

$\ln(k_2/k_1) = 1.63$

$k_2/k_1 = e^{1.63} = 5.1$

$k_2 = 5.1\ k_1$

4) (a) Rate = $-\Delta[N_2O_4]/\Delta t$

(b) Rate = $-\Delta[N_2O_4]/\Delta t = \Delta[NO]/2\Delta t$

(c) Rate = $-\Delta[N_2O_4]/\Delta t = \Delta[NO]/2\Delta t$

$\Delta[NO]/\Delta t = 2 \times 11\ M/s = 22\ M/s$

5) $T = 100°\ C$ $k = 0.372\ M/min$

$[PH_3]_t = 1/5 \times [PH_3]_0$

(a) $\ln([PH_3]_t/[PH_3]_0) = -k \times t$

$\ln(0.20 \times \cancel{[PH_3]_0}/(\cancel{[PH_3]_0}) = -0.372\ M/min \times t$

$-1.61 = -0.372\ M/min \times t$

$t = 4.33\ min$

(b) $\ln(k_2/k_1) = E_a/R(1/T_1 - 1/T_2)$

$\ln(k_2/k_1) = 73.2\ \cancel{kJ}/\cancel{mol}/(8.31\ \cancel{J}/\cancel{mol}\cdot K \times 1\ \cancel{kJ}/10^3\ \cancel{J})(1/373\ \cancel{K} - 1/343\ \cancel{K})$

$\ln(k_2/k_1) = -2.07$

$k_2/k_1 = e^{-2.07} = 0.12$

$k_2 = 0.12 \times k_1 = 0.12 \times 0.372\ M/min =$ 0.045 M/min

6) $Rate_2 = k[A]^m$

$0.042\ M/s = k(0.20)^m$

$Rate_4 = k[A]^m$

$0.158\ M/s = k(0.40)^m$

$Rate_2/Rate_4 = k[A]^m/k[A]^m$

$0.042\ \cancel{M/s}/0.158\ \cancel{M/s} = \cancel{k}(0.20)^m/\cancel{k}(0.40)^m = (0.20/0.40)^m = 0.50^m$

$0.27 = 0.50^m$

$m = 2$

$Rate_2 = k[A]^m$

$0.042\ M/s = k(0.20\ M)^2$

$k = 0.042\ M/s/(0.20\ M)^2$

$k = 1.0\ M^{-1}s^{-1}$

$Rate = k[A]^2$

$Rate = 1.0\ M^{-1}s^{-1} \times (0.15\ M)^2 = 0.022\ M/s$