

Differential Rate Laws WS (Homework)

For each reaction, determine the following:

- a. order of each reactant
- b. rate law expression
- c. overall order of reaction
- d. value of rate constant with proper units

1. The reaction: $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{NOCl}(\text{g})$ was studied at 10°C . The following results were obtained.

$$\text{rate} = k [\text{NO}]^m [\text{Cl}_2]^n$$

Experiment	$[\text{NO}]_0$ (mol/L)	$[\text{Cl}_2]_0$ (mol/L)	Initial Rate (mol/L · min)
1	0.10	0.10	0.18
2	0.10	0.20	0.36
3	0.20	0.20	1.45

a)
$$\frac{\text{Exp 3}}{\text{Exp 2}}: \frac{1.45 \text{ M/min}}{0.36 \text{ M/min}} = \frac{k(0.20)^m(0.20)^n}{k(0.10)^m(0.20)^n}$$

$$4 = 2^m \quad \therefore \text{2nd order w/ respect to NO}$$

$$m = 2$$

$$\frac{\text{Exp 2}}{\text{Exp 1}}: \frac{0.36 \text{ M/min}}{0.18 \text{ M/min}} = \frac{k(0.10)^m(0.20)^n}{k(0.10)^m(0.10)^n}$$

$$2 = 2^n \quad \therefore \text{1st order w/ respect to Cl}_2$$

$$n = 1$$

b)
$$\text{rate} = k [\text{NO}]^2 [\text{Cl}_2]^1$$
 c) 3rd order overall d)
$$0.18 \text{ M/min} = k (0.10)^2 (0.10)^1$$

$$k = 180 \text{ } \frac{1}{\text{M}^2 \cdot \text{min}}$$

2. The reaction: $2\text{I}^-(\text{aq}) + \text{S}_2\text{O}_8^{2-}(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq})$ was studied at 24°C . The following results were obtained.

$$\text{rate} = k [\text{I}^-]^m [\text{S}_2\text{O}_8^{2-}]^n$$

Experiment	$[\text{I}^-]_0$ (mol/L)	$[\text{S}_2\text{O}_8^{2-}]_0$ (mol/L)	Initial Rate (mol/L · s)
1	0.080	0.040	12.5×10^{-6}
2	0.040	0.040	6.25×10^{-6}
3	0.080	0.020	6.25×10^{-6}
4	0.032	0.040	5.00×10^{-6}
5	0.060	0.030	7.00×10^{-6}

a)
$$\frac{\text{Exp 2}}{\text{Exp 1}}: \frac{6.25 \times 10^{-6} \text{ M/s}}{12.5 \times 10^{-6} \text{ M/s}} = \frac{k(0.040 \text{ M})^m (0.040 \text{ M})^n}{k(0.080 \text{ M})^m (0.040 \text{ M})^n}$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^m \quad \therefore \text{1st order w/ respect to I}^-$$

$$m = 1$$

$$\frac{\text{Exp 1}}{\text{Exp 3}}: \frac{12.5 \times 10^{-6} \text{ M/s}}{6.25 \times 10^{-6} \text{ M/s}} = \frac{k(0.080 \text{ M})^1 (0.040 \text{ M})^n}{k(0.080 \text{ M})^1 (0.020 \text{ M})^n}$$

$$2 = 2^n \quad \therefore \text{1st order w/ respect to S}_2\text{O}_8^{2-}$$

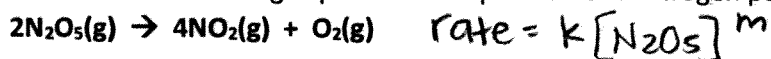
$$2b) \text{ rate} = k[\text{I}^-]^1 [\text{S}_2\text{O}_8^{2-}]^1$$

c) 2nd order overall

$$d) 12.5 \times 10^{-6} \text{ M/s} = k (0.080 \text{ M})^1 (0.040 \text{ M})^1$$

$$k = 3.9 \times 10^{-3} \frac{1}{\text{M} \cdot \text{s}}$$

3. The following data were obtained for the gas-phase decomposition of dinitrogen pentoxide.



Trial	$[\text{N}_2\text{O}_5]_0$ (mol/L)	Initial Rate (mol/L · s)
1	0.0750	8.90×10^{-4}
2	0.190	2.26×10^{-3}
3	0.275	3.26×10^{-3}
4	0.410	4.85×10^{-3}

a)
$$\frac{\text{EXP 2}}{\text{EXP 1}}: \frac{2.26 \times 10^{-3} \text{ M/s}}{8.90 \times 10^{-4} \text{ M/s}} = \frac{k(0.190 \text{ M})^m}{k(0.0750 \text{ M})^m}$$

$$2.5 = 2.5^m$$

$$m = 1$$

\therefore 1st order w/ respect to N_2O_5

b) $\text{rate} = k[\text{N}_2\text{O}_5]^1$

c) 1st order overall

d) $8.90 \times 10^{-4} \text{ M/s} = k(0.0750 \text{ M})^1$

$$k = 1.19 \times 10^{-2} \frac{1}{\text{s}}$$

4. The reaction $\text{I}^-(\text{aq}) + \text{OCl}^-(\text{aq}) \rightarrow \text{IO}^-(\text{aq}) + \text{Cl}^-(\text{aq})$ was studied, and the following data were obtained:



Experiment	$[\text{I}^-]_0$ (mol/L)	$[\text{OCl}^-]_0$ (mol/L)	Initial Rate (mol/L · s)
1	0.12	0.18	7.91×10^{-2}
2	0.060	0.18	3.96×10^{-2}
3	0.030	0.090	9.88×10^{-3}
4	0.24	0.090	7.91×10^{-2}

5. After determining the rate law and rate constant in Question #4, calculate the initial rate for an experiment where both I^- and OCl^- are initially present at 0.15 mol/L.

4a)
$$\frac{\text{EXP 1}}{\text{EXP 2}}: \frac{7.91 \times 10^{-2} \text{ M/s}}{3.96 \times 10^{-2} \text{ M/s}} = \frac{k(0.12 \text{ M})^m (0.18 \text{ M})^n}{k(0.060 \text{ M})^m (0.18 \text{ M})^n}$$

$$2 = 2^m$$

$$m = 1$$

\therefore 1st order w/ respect to I^-

$$\frac{\text{EXP 2}}{\text{EXP 3}}: \frac{3.96 \times 10^{-2} \text{ M/s}}{9.88 \times 10^{-3} \text{ M/s}} = \frac{k(0.06 \text{ M})^1 (0.18 \text{ M})^n}{k(0.03 \text{ M})^1 (0.09 \text{ M})^n}$$

$$4 = 2(2^n)$$

$$2 = 2^n$$

$$n = 1$$

\therefore 1st order w/ respect to OCl^-

$$4b) \text{ rate} = k[\text{I}^-]^1 [\text{OCl}^-]^1$$

c) 2nd order overall

$$d) 7.91 \times 10^{-2} \text{ M/s} = k(0.12 \text{ M})^1 (0.18 \text{ M})^1$$

$$k = 3.7 \frac{1}{\text{M}\cdot\text{s}}$$

$$5) \text{ rate} = k[\text{I}^-]^1 [\text{OCl}^-]^1$$

$$\text{rate} = \left(3.7 \frac{1}{\text{M}\cdot\text{s}}\right) (0.15 \text{ M})^1 (0.15 \text{ M})^1 = 0.083 \text{ M/s}$$