1) Suggest experimental means by which the following reactions can be monitored for rate.

a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

measure amount of CO_2 gas released. (P or V)

b) $2HCl(aq) + Na_2S_2O_3(aq) \longrightarrow S(s) + 2NaCl(aq) + H_2O(l)$

measure amount of $S_{(s)}$ formed.

c) $2HgCl_2(aq) + C_2O_4^{2-}(aq) \longrightarrow 2Cl^-(aq) + 2CO_2(g) + Hg_2Cl_2(s)$

gas formation solid formation

2) Iron (III) chloride is reduced by tin (II) chloride in the following reaction.

$2FeCl_3(aq) + SnCl_2(aq) \longrightarrow 2FeCl_2(aq) + SnCl_4(aq)$

The concentration of Fe^{3+} ion at the beginning of an experiment was 0.03586M and after 4.00 min it was 0.02715M. What is the average rate of reaction of $FeCl_3$ in this time? What is the rate of formation of tin (IV) chloride? (Ans: 0.00218M/min; 0.00109M/min))

$$\frac{(0.0356 - 0.02715)\,M}{(4-0)\,min} = \boxed{0.00218\,M/min}$$

$$\frac{1}{2}\,\frac{SnCl_4}{FeCl_3} \times 0.00218\,M/min = \boxed{0.00109\,M/min}$$

3) In the reaction below the rate of reaction is 0.258 M/s with respect to A. What is the rate of appearance of D? What is the rate of disappearance of B? (Ans: 0.561 M/s; 0.387 M/s)

$2A + 3B \longrightarrow C + 4D$

0.258M

appear. of D.

$$\frac{1}{2} \times 0.258M = \frac{1}{4}[D]$$

$$[D] = \frac{1}{2} \times 0.258M \times 4$$

$$= \boxed{+0.516M}$$

disap. of B.

$$\frac{1}{2} \times 0.258M = \frac{1}{3}[B]$$

$$\frac{1}{2} \times 0.258M \times 3 = [B]$$

$$= \boxed{-0.387M}$$

4) The rate of the following reaction is measured and the data obtained is listed in the table below. $2NO_2 + F_2 \longrightarrow 2NO_2F$

Exp		$[NO_2]$, M	$[F_2]$, M	Initial rate M/s
1		0.100	0.100	0.026
2		0.200	0.100	0.051
3		0.200	0.200	0.103
4		0.400	0.400	0.411

a) Show the calculations to find the rate law. What is the overall order of reaction? (Ans: 3) 2
b) What is the value of rate constant, k? (Ans: $6.1 \times 10^{-3}\ M^{-1}\ s^{-1}$)

a) F_2 exp $\frac{3}{2} = \frac{0.2}{0.1}$ $\frac{0.103}{0.051}$ 2 : 2 1st

NO_2 exp $\frac{2}{1}$ $\frac{0.2}{.1}$ $\frac{0.051}{0.026}$ 2 : 2 1st

} total 2 overall.

b). $Rate = k[NO_2][F_2]$

$$k = \frac{0.026\ M/s}{0.1\ M \times 0.1\ M} = 2.6\ M^{-1}s^{-1}$$

5) The rate of the following reaction in aqueous solution is monitored by measuring the rate of formation of I_3^-. Data obtained are listed in the table below.

$S_2O_8^{2-} + 3I^- \longrightarrow 2SO_4^{2-} + I_3^-$

Exp	$[S_2O_8^{2-}]$, M	$[I^-]$, M	Initial rate M/s
1	0.038	0.060	1.4×10^{-5}
2	0.076	0.060	2.8×10^{-5}
3	0.076	0.120	5.6×10^{-5}

a) Determine the order of the reaction with respect to $S_2O_8^{2-}$, and with respect to I^- and overall. (Ans: 1,1, 2)
b) What is the value of rate constant, k? (Ans: $6.1 \times 10^{-3}\ M^{-1}\ s^{-1}$)
c) What would be the initial rate of reaction if $[S_2O_8^{2-}] = 0.083$ M and $[I^-] = 0.115$ M? (Ans: 5.8×10^{-5} M/s)

a) $[S_2O_8^{2-}]$ $\frac{exp\ 2}{exp\ 1}$ $\frac{0.076}{0.038} = \frac{2.8 \times 10^{-5}}{1.4 \times 10^{-5}}$ 2 : 2 ≡ $\boxed{1^{st}\ order}$

$[I^-]$ exp $\frac{3}{2}$ $\frac{0.12}{0.06} = \frac{5.6 \times 10^{-5}}{2.8 \times 10^{-5}}$ 2 : 2 ≡ $\boxed{1^{st}\ order}$

$Rate = k[S_2O_8^{2-}][I^-]$ $\boxed{\text{overall } 2^{nd} \text{ order}}$

b) $$k = \frac{Rate}{[S_2O_8^{2-}][I^-]} = \frac{1.4 \times 10^{-5}\ M/s}{0.038\ M \times 0.06\ M} = \boxed{6.14 \times 10^{-3}/Ms}$$

c) $$Rate = 6.14 \times 10^{-3}/Ms \times 0.083\ M \times 0.115\ M = \boxed{5.86 \times 10^{-5}\ M/s}$$

6) The decomposition of ammonia on tungsten is zero order at 1100 °C with k of 3.40×10^{-6} M/s).
   a) Determine [NH_3] at t = 335 s, if initially [NH_3] is 0.0452 M.
   b) What is the half-life for the reaction in which [NH_3] = 0.0452 M
   (Ans: 0.0441 M; 1.85 hr)

a) $[A]_t = -kt + [A]_0$
$= (-3.40 \times 10^{-6} \times 335\,s) + 0.0452 = \boxed{0.0441M}$

b) $\frac{[A]_0}{2k} = t_{1/2}$; $t_{1/2} = 6647s \equiv \boxed{1.85hr}$

7) A first order A ⟶ products, has a rate constant k, of 0.0462 min^{-1}.
   a) What is the concentration of A at the time when the reaction is proceeding at a rate of 0.0150 M min^{-1}? (Ans: 0.325M)
   b) It takes 12 mins for the reaction to 12% completion and 48 min to 56% completion. Without doing detailed calculations, determine how long it should take the reaction to 78% completion? (*Hint*: what is the % remaining each time?) (Ans: 84 min)

a) Rate = k[A]
$[A] = \frac{Rate}{k}$
$= \frac{0.0150M/min}{0.0462/min}$
$= \boxed{0.325M}$

b) $[A]_0 \xrightarrow[T_1]{12min} [A]_1 \xrightarrow{T_2} [A]_2 \xrightarrow{T_3} [A]_3$
12% 56% 78%
48 min
88% remaining 44% remaining. 22% remaing
$A_1 \rightarrow A_2$ is 50% decrease in
$A_2 \rightarrow A_3$ 50% dec. [48 − 12 = 36 mins.
$T_1 + T_2 + T_3 = 12 + 36 + 36 = \boxed{84mins}$

8) The initial concentration of H_2O_2 is 0.2546 M and the rate constant is $9.32 \times 10^{-4}\ s^{-1}$. What will be the [$H_2O_2$] at t = 35s? (Ans: 0.246M)
1st order

$\ln \frac{[H_2O_2]_t}{[H_2O_2]_0} = -kt$

$\ln \frac{[H_2O_2]_t}{0.2546} = -9.32 \times 10^{-4}\,s^{-1} \times 35\,s$
$= 0.03262$

take inverse ln on both sides.

$\frac{[H_2O_2]_t}{0.2546} = 0.9679$

$[H_2O_2]_t = 0.9679 \times 0.2546$
$= \boxed{0.246M}$

9) A reaction that is second order in reactant A has $[A]_o$ = 0.200 M. The half life is 45.6 sec. What is [A] after 3.00 min? (Ans: 0.-0403 M)

det. k

$$t_{1/2} = \frac{1}{k[A]_0} ; \quad k = \frac{1}{t_{1/2}[A]_0} = \frac{1}{45.6s \times 0.2M} = 0.110 \ M^{-1}s^{-1}$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} ; \quad \frac{1}{[A]_t} = \left(0.110 M^{-1}s^{-1} \times (3 \times 60)s\right) + \frac{1}{0.2M}$$

$$= 24.8/M \quad \boxed{[A] = 0.0403M}$$

10)The thermal decomposition of phosphine (PH_3) into phosphorous and molecular hydrogen is a first order reaction.

$$4PH_3 \longrightarrow P_4 + 6H_2$$

The half-life of the reaction is 35.0 s at 680 °C. Calculate:

a) The first order rate constant for the reaction. (Ans: 0.0198/s)

b) The time required for 95 % of the phosphine to decompose. (Ans: 151s)

a) $$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{35 \ s} = \boxed{0.0198/s}$$

b). 5% phosphine left.

$$\frac{[A]_t}{[A]_0} = \frac{5\%}{100\%} = \frac{0.05}{1}$$

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{0.05}{1} = -0.0198 \times t$$

$$-2.996 = -0.0198t$$

$$t = \frac{-2.996}{-0.0198} = \boxed{151s}$$

11)The decomposition of ethylene oxide at 652 K is a first order reaction with k = 0.0120 min^{-1} and an activation energy of 218 kJ/mol.

$(CH_2)_2O\ (g) \longrightarrow CH_4\ (g) + CO\ (g)$

Calculate:

a) The rate constant of the reaction at 525 K, and

b) The temperature at which the rate constant k is 0.0100 min^{-1}.

(Ans: 7.14 x 10^{-7} min^{-1}; 649 K)

a) $\ln \frac{k_2}{k} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\ln \frac{0.0120}{k_1} = \frac{218 kJ/mol \times 1000}{8.3145 J/mol\,K} \times \left(\frac{1}{525} - \frac{1}{652}\right)$

$= 2.622 \times 10^4 \times 3.71 \times 10^{-4}$

$= 9.73$

anti ln both sides

$\frac{0.0120}{k_1} = 1.68 \times 10^4$; $k_1 = \frac{0.0120}{1.68 \times 10^4}$

$= \boxed{7.14 \times 10^{-7} /min}$

b) $\ln \frac{0.0120}{0.01} = \frac{218 kJ/mol \times 1000}{8.3145 J/mol\,K} \times \left(\frac{1}{T_1} - \frac{1}{652 K}\right)$

$6.954 \times 10^{-6} = \left(\frac{1}{T_1} - \frac{1}{652}\right) K^{-1}$

$\boxed{T_1 = 649 K}$

12)Given the same concentrations, the reaction at 250 °C, is 1.50 x 10^3 times faster than the same reaction at 150°C. Calculate the activation energy for this reaction. (Ans: 135KJ/mol)

$CO\ (g) + Cl_2\ (g) \longrightarrow COCl_2\ (g)$

$T_2 = 250 + 273 = 523 K$; $T_1 = 150 + 273 = 423 K$.

$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$.

$\ln 1.5 \times 10^3 = \frac{E_a}{8.314 J/mol\,K} \times \left(\frac{1}{423} - \frac{1}{523}\right) K^{-1}$

$7.31 = \frac{E_a}{8.314} \times 4.52 \times 10^{-4}$

$E_a = \frac{7.31 \times 8.314}{4.52 \times 10^{-4}} = 1.35 \times 10^5 J/mol$

$= \boxed{135 kJ/mol}$