EXAM 4

December 3, 2004

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a <u>brief justification or explanation</u>.
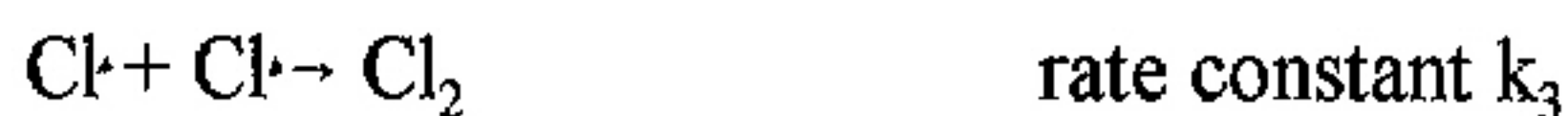<u>*Give units for all quantities*</u>*!*

YOUR NAME   <u>SOLUTIONS</u>

Some data: $R = 8.314$ J K^{-1} mol^{-1} 1 atm = 101325 Pa $N_A = 6.022 \times 10^{23}$ mol^{-1}

(1)   *34 points*

A possible mechanism for the formation of phosgene from carbon monoxide and chlorine, overall reaction $Cl_2 + CO \rightarrow COCl_2$, is as follows:

$$Cl_2 \rightarrow 2\ Cl\cdot \qquad \text{rate constant } k_1$$
$$Cl\cdot + CO \rightarrow ClCO\cdot \qquad \text{rate constant } k_2$$
$$Cl\cdot + Cl\cdot \rightarrow Cl_2 \qquad \text{rate constant } k_3$$
$$Cl_2 + ClCO\cdot \rightarrow Cl\cdot + COCl_2 \qquad \text{rate constant } k_4$$

Derive the rate law for this chain reaction, and deduce the overall order of reaction. Be sure to explain your work.

Assume steady-state for the radical intermediates

$$0 = \frac{d[Cl]}{dt} = 2k_1[Cl_2] - k_2[Cl][CO] - 2k_3[Cl]^2 + k_4[Cl_2][ClCO] \qquad (i)$$

$$0 = \frac{d[ClCO]}{dt} = k_2[Cl][CO] - k_4[Cl_2][ClCO] \qquad (ii)$$

Add (i) and (ii): $2k_1[Cl_2] - 2k_3[Cl]^2 = 0$

$$\therefore \quad [Cl] = \sqrt{\frac{k_1}{k_3}}\,[Cl_2]^{1/2}$$

rate $v = \dfrac{d[COCl_2]}{dt} = k_4[Cl_2][CClO]$

which by (ii) $= k_2[Cl][CO]$

$$= k_2\sqrt{\frac{k_1}{k_3}}\,[CO][Cl_2]^{1/2}$$

overall order $= 1 + \frac{1}{2} = \frac{3}{2}$.

(2) *33 points.*

A reaction is measured to have a rate constant of 20 s^{-1} at 298 K, and 100 s^{-1} at 350 K. Assuming Arrhenius behavior, derive the Arrhenius parameters and predict the rate constant at 400 K. What is the reaction order?

Arrhenius eqn. $k = A e^{-\frac{E_a}{RT}}$

so $\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$

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

$\therefore \ln \left(\frac{20}{100} \right) = \frac{E_a}{R} \left(\frac{1}{350} - \frac{1}{298} \right)$

$\therefore \underline{\underline{E_a = 26.84 \text{ kJ mol}^{-1}}}$

$20 \text{ s}^{-1} = A e^{-\frac{26840}{8.314 \times 298}}$

$\therefore \underline{\underline{A = 1.01 \times 10^6 \text{ s}^{-1}}}$,

$k_{400K} = 1.01 \times 10^6 \text{ s}^{-1} \times e^{-\frac{26840}{8.314 \times 400}}$

$= \underline{\underline{316 \text{ s}^{-1}}}$.

Units of s^{-1} indicate a <u>first-order</u> reaction.

(3)   *33 points*

The reaction $2A + 3B \rightarrow C + 2D$ is found to be 4th order in A and zero order in B.

a) Write out the rate law to show the reaction rate v in terms of concentrations (no work needed for this step).

b) Through consideration of d[A]/dt, integrate this rate law and find the half-life $t_{1/2}$ of A. You may assume that initially the concentration of A is $[A]_0$ and that of B is $[B]_0$.

a) $v = -\frac{1}{2} \frac{d[A]}{dt} \left(\text{or } -\frac{1}{3} \frac{d[B]}{dt} \text{ or } \frac{d[C]}{dt} \text{ or } \frac{1}{2} \frac{d[D]}{dt} \right).$

b) $v = k[A]^4 [B]^0 = k[A]^4$

$\therefore \frac{d[A]}{dt} = -2k[A]^4 \qquad \therefore \int [A]^{-4} d[A] = \int -2k \, dt$

$\therefore -\frac{1}{3}[A]^{-3} = -2kt + \text{const.}$

Substitute $t=0$: $\quad \text{const} = -\frac{1}{3}[A]_0^{-3}$

$\therefore \quad \frac{1}{3}[A]^{-3} = 2kt + \frac{1}{3}[A]_0^{-3}$,

$t_{1/2}$ is when $[A]$ has become $[A]_0/2$, so

$\frac{1}{3}\left(\frac{[A]_0}{2}\right)^{-3} = 2kt_{1/2} + \frac{1}{3}[A]_0^{-3}$

$\therefore t_{1/2} = \frac{1}{6k}\left\{ \frac{2^3}{[A]_0^3} - \frac{1}{[A]_0^3}\right\} = \frac{1}{6k} \cdot \frac{7}{[A]_0^3}$