

EXAM 4

November 20, 2015

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

YOUR NAME SOLUTIONS

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

$$dU = dq + dw \quad dS = dq_{\text{rev}}/T \quad \gamma = C_p/C_v \quad C_p - C_v = nR$$

$$dw = -p_{\text{ex}} dV \quad \text{Heat engine } \varepsilon = (T_h - T_c)/T_h \quad \text{adiabat: } pV^\gamma = \text{const}$$

$$H = U + pV \quad G = H - TS \quad A = U - TS$$

$$k = A \exp(-E_a/(RT)) \quad \text{mean K.E.} = 1.5 k_B T$$

$$d \ln K/d(1/T) = -\Delta H/R \quad \Delta_r G = \Delta G^\circ + RT \ln Q$$

(1) 30 points

Consider the reaction $A \rightarrow 3 B$ which has the rate law $v = k [A]^4$. Deduce the integrated rate law and hence determine the half-life of A. Show work.

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

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

When $t=0$, $[A] = [A]_0$ so the constant is $-\frac{1}{3}[A]_0^{-3}$

$$\therefore [A]^{-3} = +3kt + [A]_0^{-3}$$

When $t = t_{1/2}$, $[A] = [A]_0 / 2$

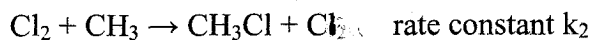
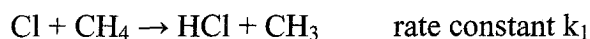
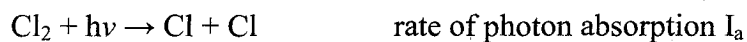
$$\therefore \left(\frac{[A]_0}{2}\right)^{-3} = +3k t_{1/2} + [A]_0^{-3}$$

$$\therefore \frac{8}{[A]_0^3} + \frac{1}{[A]_0^3} = 3k t_{1/2}$$

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

(2) 40 points

Consider the UV photochemical chlorination of methane with the proposed mechanism



The overall reaction is $\text{Cl}_2 + \text{CH}_4 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$. In terms of the concentrations of these four species, I_a and elementary rate constants, derive the rate law. You may assume that any chain carriers are in steady state.

If the absorption of 0.1 einstein of photons leads to formation of 3 mol of CH_3Cl , what is the quantum yield of this process?

$$0 = \frac{d[\text{Cl}]}{dt} = 2I_a - k_1[\text{Cl}][\text{CH}_4] + k_2[\text{Cl}_2][\text{CH}_3] - 2k_3[\text{Cl}]^2$$

$$0 = \frac{d[\text{CH}_3]}{dt} = k_1[\text{Cl}][\text{CH}_4] - k_2[\text{Cl}_2][\text{CH}_3]$$

add these equations: $2I_a = 2k_3[\text{Cl}]^2$

$$\therefore [\text{Cl}] = \sqrt{\frac{I_a}{k_3}}$$

$$v = \frac{d[\text{CH}_3\text{Cl}]}{dt} = k_1[\text{Cl}][\text{CH}_4] = k_1 \sqrt{\frac{I_a}{k_3}} [\text{CH}_4]$$

Quantum yield is $\frac{\text{amount product}}{\text{amount photons}} = \frac{3}{0.1} = 30$.

(3) 30 points

A proposed mechanism for the overall reaction $2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$ is



Treat this as a pre-equilibrium problem to deduce the rate law and the effective third-order rate constant k_{eff} in terms of k_1 , k_2 and k_3 . What are appropriate units for k_{eff} ?

Given that the activation energies for k_1 , k_2 and k_3 are 20, 35 and 12 kJ mol⁻¹, respectively, what is ΔH for the first step? What is the activation energy for k_{eff} ?

$$v = -\frac{d[\text{N}_2\text{O}_2]}{dt} = k_3 [\text{N}_2\text{O}_2][\text{O}_2]$$

$$\text{Pre-equilibrium } 2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \quad \text{has } K_{\text{eq}} = \frac{k_1}{k_2} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2}$$

$$\therefore [\text{N}_2\text{O}_2] = \frac{k_1}{k_2} [\text{NO}]^2 \quad \therefore v = \frac{k_1 k_3}{k_2} [\text{NO}]^2 [\text{O}_2]$$

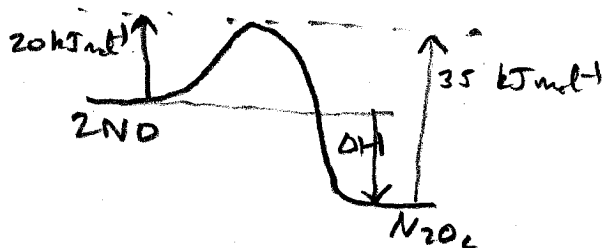
$$\text{and } k_{\text{eff}} = \frac{k_1 k_3}{k_2} \quad \text{Units are } \text{conc}^{-2} \text{ s}^{-1} \text{ such as } \text{M}^{-2} \text{ s}^{-1} \text{ or } \text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}.$$

$$k = A e^{-\frac{E_a}{RT}} \quad \therefore \ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \quad \text{so } E_a = -R \frac{d \ln k}{d(1/T)}$$

$$\ln k_{\text{eff}} = \ln k_1 + \ln k_3 - \ln k_2$$

$$\therefore \frac{d \ln k_{\text{eff}}}{d(1/T)} = \frac{d \ln k_1}{d(1/T)} + \frac{d \ln k_3}{d(1/T)} - \frac{d \ln k_2}{d(1/T)}$$

$$\therefore E_a = 20 + 12 - 35 = -3 \text{ kJ mol}^{-1}$$



$$\Delta H = 20 - 35 = -15 \text{ kJ mol}^{-1}$$