EXAM 4

29 November 2001

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 brief justification or explanation.

Give units for all quantities!   ***YOUR NAME*** SOLUTIONS

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

$C_p - C_V = nR$ $dU = dq + dw$ $dS = dq/T$ $H = U + pV$ $G = H - TS$ $A = U - TS$

Trouton's constant = $85\ J\ K^{-1}\ mol^{-1}$

(1) *34 points*

Consider the reaction $A \rightarrow B$ with a general rate law $v = k[A]^n$.

i) Assuming there is initially pure A with concentration $[A]_0$, find the concentration of A at a general time t in terms of $[A]_0$, k, n and t, i.e., obtain the integrated rate law.

iii) *Derive* an expression for the half life, $t_{1/2}$, in terms of k and $[A]_0$.

i) $v = -\frac{d[A]}{dt} = k[A]^n \quad \therefore \quad \int \frac{d[A]}{[A]^n} = \int -k\,dt$

$\therefore \frac{1}{1-n}[A]^{1-n} = -kt + c$, when $t=0$, $c = \frac{1}{1-n}[A]_0^{1-n}$

so $kt = \frac{1}{n-1}\left([A]^{1-n} - [A]_0^{1-n}\right)$.

ii) when $t = t_{1/2}$, $[A] = [A]_0/2$, so

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

$$= \frac{1}{n-1}[A]_0^{1-n}\left(2^{n-1} - 1\right).$$

(2) *33 points.*

A reaction has an activation energy of 40 kJ mol^{-1}. If the rate constant k is 20 M^{-2} s^{-1} at 298 K, use the above information to deduce

i) The reaction order.

ii) The rate constant at 308 K.

i) The units of k tell us it is a <u>3rd order</u> reaction.

rate $(M s^{-1}) = k (M^{-2} s^{-1}) \times$ concentration $(M)^3$

ii)

Arrhenius equation $k = Ae^{-E_a/RT}$

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

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

$T_1 = 308\ K$ $T_2 = 298\ K$ $k_2 = 20\ M^{-2} s^{-1}$

$\ln\left(\frac{k_1}{20}\right) = -\frac{40\,000}{8.314}\left(\frac{1}{308} - \frac{1}{298}\right) = 0.524$

$\frac{k_1}{20} = 1.69$ so $k_1 = 33.8\ M^{-2} s^{-1}$.

(3) *33 points*

Consider the overall reaction $A + 2B \rightarrow P$ with a proposed mechanism

$A + B \rightarrow C$ rate constant k_1

$C \rightarrow A + B$ rate constant k_{-1}

$B + C \rightarrow P$ rate constant k_2

Assume that the concentration of C is in a steady state.

i) What rate law is implied by this mechanism? HINT: consider the rate of formation of final product, P, and express your final answer in terms of elementary rate constants and the concentrations of A and B.

ii) What are the overall reaction orders predicted (a) when [B] is very large, and (b) when [B] is very small?

i) $$0 = \frac{d[C]}{dt} = k_1[A][B] - k_{-1}[C] - k_2[B][C]$$

$$\therefore \quad [C] = \frac{k_1[A][B]}{k_{-1} + k_2[B]}.$$

$$v = \frac{d[P]}{dt} = k_2[B][C] = \frac{k_1 k_2 [A][B]^2}{k_{-1} + k_2[B]}.$$

ii) a) $k_2[B] \gg k_{-1} \Rightarrow v \approx k_1[A][B]$

second order

b) $k_2[B] \ll k_{-1} \Rightarrow v \approx \frac{k_1 k_2}{k_{-1}}[A][B]^2$

third order