

**Assignment 4**  
**Chemical Kinetics**

1. A reaction is 50% complete in 10 minutes. It is allowed to proceed another 5 minutes. How much of the reaction would be complete at the end of these 15 minutes if the reaction follows zero order kinetics? *Exercise 19.4, page 590, Dogra and Dogra*

Answer:

Let  $[A]_0$  be  $1 \times 10^3 \text{ mol dm}^{-3}$ . Half of  $[A]_0$  is consumed in 10 minutes so  $k$  from equation is

$$k = ((1 - \frac{1}{2}) 10^3 \text{ mol dm}^{-3}) / 10 \text{ min} = 50 \text{ mol dm}^{-3}$$

Now in further 5 minutes i.e., after 15 minutes.

$$[A] = [1 \times 10^3 - 50 \times 15] \text{ mol dm}^{-3} = 250 \text{ mol dm}^{-3}$$

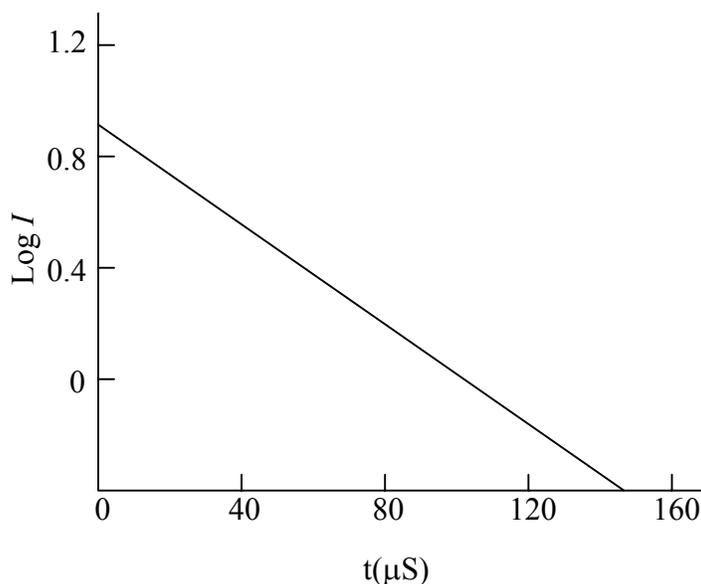
2. Phosphorescence emission of Acetone-d6 (0.05 M) in Acetonitrile at 20°C was measured at 450 nm. Calculate the rate constant for the emission and also calculate the average life-time of triplet state of acetone from the following data

$t(\mu \text{ sec})$	20	32	40	60	80	100	120	140
Intensity ( $I$ )	5.5	4.6	4.0	2.9	2.1	1.5	1.05	0.75
(Arbitrary units)								

Log $I$	0.74	0.66	0.60	0.46	0.33	0.18	0.025	0.12
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*Exercise 19.5, page 591, Dogra and Dogra*

Log  $I$  is plotted vs time in Figure below and slope obtained is  $- 0.72 \times 10^4 \text{ s}^{-1}$ .



Now  $k = -\text{slope} \times 2.303$   
 $= -(-0.72 \times 10^4 \text{ s}^{-1}) \times 2.303$   
 $= 1.66 \times 10^4 \text{ s}^{-1}$

Average life of triplet state =  $1/k$   
 $= 1/1.66 \times 10^4 \text{ s}^{-1} = 60 \mu\text{S}$

3. Half-life for disintegration of radium is 1590 years. Calculate the rate constant in  $\text{s}^{-1}$  and also how many years will be taken for the disintegration of 80% of the material?

*Exercise 19.11, page 597, Dogra and Dogra*

Answer:

$$t_{1/2} = 1590 \text{ years} = 5.014 \times 10^{10} \text{ S}$$

Using equation

$$t_{1/2} = 0.69/k$$

$$k = 0.69/(5.014 \times 10^{10} \text{ S}) = 1.376 \times 10^{-11} \text{ s}^{-1}$$

Now if  $[C]_0 = 100 \text{ mol dm}^{-3}$ ,  $[C] = 20 \text{ mol dm}^{-3}$

And using equation,

$$k = 1/t \ln [C]_0/[C]$$

$$t = ((2.303 \times 1590 \text{ years})/0.69) \log 100/20 = 3661.8 \text{ years}$$

4. The reaction  $2A + B \rightarrow C + D$  goes to completion and follows the following rate law

$$-d[A]/dt = k [A]^2[B]$$

Fill the gaps left in the following information

$10^6 \times [A]_0$ (mol dm <sup>-3</sup> )	$[B]_0 \times 10^6$ (mol dm <sup>-3</sup> )	half time (s)
300	40	62.6
300	60	-
5	300	625

*Exercise 19.12, page 597, Dogra and Dogra*

*In more than one reactant system, the half-life is the time for the half of the reactant present in small amount.*

In the first set, reactant  $B$  is in small amount, the half-life is for reactant  $B$ . Further the rate is first-order with respect to  $B$ , so the half-life is independent of initial concentration, i.e. missing data is 62.6s.

In the second set, the half-life is for reactant  $A$ , and rate is second order with respect to  $A$ , the equation

$$t_{1/2} = 2^{n-1} - 1 / (n-1) [C]_0^{n-1} k$$

Becomes

$$t_{1/2} = 1 / k [A]_0$$

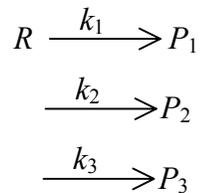
Now

$$(t_{1/2})_1 / (t_{1/2})_2 = 1 / k [A_1]_0 \times k [A_2]_0 / 1$$

Substituting the values

$$\begin{aligned} (t_{1/2})_2 &= (t_{1/2})_1 [A_1]_0 / [A_2]_0 \\ &= ((625\text{s})(5 \times 10^{-6} \text{ mol dm}^{-3}) / (10 \times 10^{-6} \text{ mol dm}^{-3})) \\ &= 312.5 \text{ s} \end{aligned}$$

5. A reactant  $R$  undergoes three first-order parallel reactions to give three products  $P_1$ ,  $P_2$  and  $P_3$  write the expression for the rate equation of each species.

*Exercise 19.19, page 605, Dogra and Dogra*

Rate of removal of  $R$  is

$$= d[R]/dt = k_1 [R] + k_2 [R] + k_3 [R]$$

$$= (k_1 + k_2 + k_3) [R]$$

And can be integrated to give

$$[R] = [R]_0 e^{-kt}$$

Where  $[R]_0$  is concentration of R at  $t = 0$  and  $k = k_1 + k_2 + k_3 =$  overall first order rate constant.

Similarly rate expressions for products are

$$d[P_1]/dt = -k_1/k d[R]/dt = k_1[R] = k_1 [R]_0 e^{-kt}$$

After integration with condition that at time  $t = 0$

$$[P_1] = [P_1]_0 \text{ we get}$$

$$[P_1] = [P_1]_0 + k_1/k (1 - e^{-kt}) [R]_0$$

Similarly

$$[P_2] = [P_2]_0 + k_2/k (1 - e^{-kt}) [R]_0$$

$$[P_3] = [P_3]_0 + k_3/k (1 - e^{-kt}) [R]_0$$

if  $[P_1]_0 = [P_2]_0 = [P_3]_0 = 0$ , the above equations reduced to

$$[P_1] = k_1/k (1 - e^{-kt}) [R]_0$$

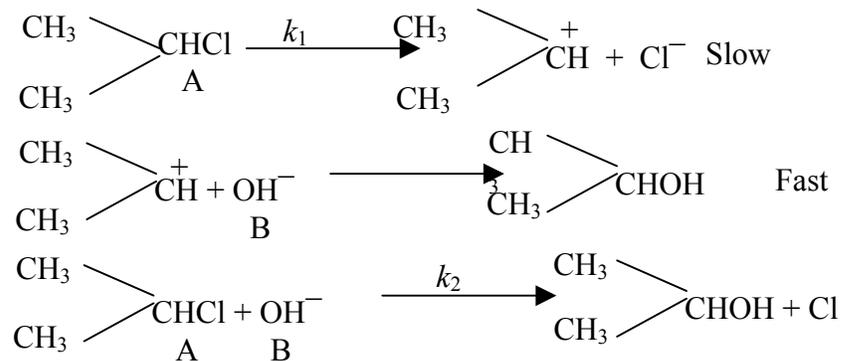
$$[P_2] = k_2/k (1 - e^{-kt}) [R]_0$$

$$[P_3] = k_3/k (1 - e^{-kt}) [R]_0$$

it is clear from equations that the products are formed in the ratios of these rate constants for respective reactions

$$[P_1]:[P_2]:[P_3]:: k_1 : k_2 : k_3$$

6. Isopropyl chloride undergoes hydrolysis in aqueous media by two reaction mechanisms. Write expression for calculating  $k_1$  and  $k_2$ .



*Exercise 19.20, page 607, Dogra and Dogra*

The rate determining step in scheme 1 is first one so the differential rate equation for the total removal of isopropyl chloride will be

$$-d[A]/dt = k_1 [A] + k_2 [A][B]$$

The simplest procedure is to write it as

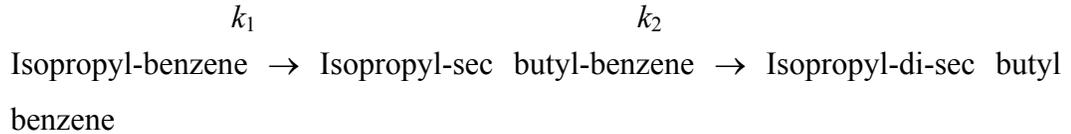
$$-1/[A] d[A]/dt = k_1 + k_2 [B]$$

Or

$$-d(\ln[A])/dt = k_1 + k_2 [B]$$

Plot of  $-d \ln [A]/dt$  vs  $[B]$  will be a straight line. Slope gives  $k_2$  and intercept gives  $k_1$ .

7. Isopropyl benzene is alkylated by n-butylamine in presence of hydrogen fluoride in a two step consecutive reaction as,



If the initial concentration of isopropyl is 100 mol and relative rate constants  $k_1 : k_2 :: 1:0.15$ , prepare a diagram showing the concentration of each species.

*Exercise 19.23 page 610, Dogra and Dogra*

Answer:

Let  $k_1 = 4.0 \times 10^{-2} \text{ min}^{-1}$ , so

$$k_2 = 0.15 \times 4 \times 10^{-2} = 0.6 \times 10^{-2} \text{ min}^{-1}$$

as a sample calculation give for  $t = 10 \text{ min}$

$$[R_1] = 100 e^{-4.0 \times 10^{-2}(10)} = 100 e^{-0.4} = 67$$

$$\begin{aligned} [R_2] &= ((100) (4 \times 10^{-2}) / (0.6 \times 10^{-2}) - (4.0 \times 10^{-2}) [e^{-4.0 \times 10^{-2}(10)} - e^{-0.60 \times 10^{-2}(10)}]) \\ &= -4 / (3.4 \times 10^{-2}) [e^{-4.0 \times 10^{-2}(10)} - e^{-0.60 \times 10^{-2}(10)}] = 31.76 \end{aligned}$$

$$R_3 = 100 - 67 - 31.76 = 1.24$$

Other data can be found out in a similar manner and tabulated as follows:

Time (min)	[A] (mol dm <sup>-3</sup> )	[B]	[C]	Time (min)	[A] (mol dm <sup>-3</sup> )	[B]	[C]
0	100	0	0	50	13.53	71.24	15.23
5	81.87	17.85	0.28	60	9.07	71.41	19.52
10	67.00	31.76	1.24	70	6.08	70.15	23.77
15	54.88	42.96	2.16	80	4.08	68.0	27.92
20	44.93	51.48	3.59	90	2.73	65.34	31.92
25	36.79	57.98	5.23	100	1.83	62.41	35.76
30	30.12	62.83	7.05	200	0.0033	35.05	64.95
40	20.19	68.79	11.02				

8. With the help of data given in question 8, calculate  $[B]_{\max}$  and  $t_{\max}$ , compare it with values obtained from the graph obtained.

*Exercise 19.24, page 611, Dogra and Dogra*

Substituting the respective values in equations

$$[R_2]_{\max} = [R_1]_0 (k_2/k_1)^{k_2/k_1-k_2}$$

and

$$t_{\max} = (\ln(k_2/k_1))/k_2/k_1$$

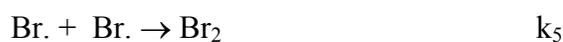
$$[B]_{\max} = (100\text{M}) ((0.15 \text{ min}^{-1})/(1.0 \text{ min}^{-1}))^{0.15/1-0.15}$$

$$= 71.55 \text{ M}$$

$$t_{\max} = ((\ln(1.0/0.15))/(1.0 - 0.15) \text{ min}^{-1}) = 55.80 \text{ min}$$

*The agreement with the Figure holds good.*

9. Thermal gas phase reaction between  $\text{H}_2$  and  $\text{Br}_2$  has the following mechanism,



Write the expression for  $d[\text{HBr}]/dt$ ,  $d[\text{H}]/dt$  and  $d[\text{Br}]/dt$

Assuming H. and Br. to be reactive intermediates, solve  $d[\text{HBr}]/dt$ , in terms of  $\text{H}_2$ ,  $\text{Br}_2$ , and HBr. What will be pseudo-order for the formation of HBr in the initial stage?

*Exercise 19.27, page 613, Dogra and Dogra*

The rate expression for three species are

$$d[\text{H}]/dt = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0$$

$$d[\text{Br}]/dt = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0$$

$$d[\text{HBr}]/dt = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}] - k_4[\text{H}][\text{HBr}]$$

solving the first equations,

$$[\text{Br}] = (k_1/k_5)^{1/2} [\text{Br}_2]^{1/2}$$

$$[\text{H}] = k_2(k_1/k_5)(([\text{Br}_2]^{1/2}[\text{H}_2])/(k_3[\text{Br}_2]+k_4[\text{HBr}])))$$

substituting [H] and [Br] in last equation gives

$$d[\text{HBr}]/dt = 2k_2 (k_1/k_5)^{1/2} (([\text{H}_2] [\text{Br}_2]^{3/2})/(k_3 [\text{Br}_2] + k_4 [\text{HBr}]$$

at initial states  $[\text{HBr}] = 0$ , above equation becomes

$$d[\text{HBr}]/dt = 2 (k_2/k_3) (k_1/k_5)^{1/2} [\text{H}_2] [\text{Br}_2]^{3/2} = k [\text{H}_2] [\text{Br}_2]^{3/2}$$

Pseudo-order is 3/2, 1 with respect of  $\text{H}_2$  and half with respect to  $\text{Br}_2$ .

The effective rate constant

$$k = 2 (k_2/k_3) (k_1/k_5)^{1/2}$$

10. If the activation energy of a reaction is  $80.9 \text{ kJ mol}^{-1}$ , calculate the fraction of molecules at  $400^\circ\text{C}$  which have enough energy to react to form products.

*Exercise 19.32, page 618, Dogra and Dogra*

Collisions will yield products if the energy possessed by the molecules is equal to or greater than activation energy. This is given as,

$$\Delta N/N_{\text{av}} = e^{-E_a/RT} = e^{-(80.9 \times 10^3 \text{ J mol}^{-1}) / ((8.314 \text{ K J}^{-1} \text{ mol}^{-1})(673 \text{ K}))}$$

$$= e^{-14.459} = 5.257 \times 10^{-7}$$

i.e. fraction of molecules which have enough energy to go for the formation of products is very small, i.e.  $5.257 \times 10^{-7}$ .

11. Consider the unimolecular reaction cyclopropane  $\rightarrow$  propylene. The value of  $\log A$  for high pressure limit is 15.17. Calculate the value of  $\Delta S^\ddagger$  for the reaction. Calculate the contribution of  $\Delta S_{\text{trans}}^\ddagger$  in the above reaction at 298 K.

*Exercise 19.35, page 620, Dogra and Dogra, Physical Chemistry Through Problems*

Answer:

According to equation

$$A = (k_b T/h) e^{1-\Delta n} e^{\Delta S^\ddagger/R}$$

$$\Delta n = 0$$

$$A = (k_b T_e/h) \exp(\Delta S^\ddagger/R)$$

Or

$$\Delta S^\ddagger/R = 2.303 \log A - 2.303 \log k_b T_e/h$$

$$e k_b T/h = ((1.38 \times 10^{-23} \text{ JK}^{-1}) (298\text{K})(2.718))/(6.62 \times 10^{-34} \text{ J s}) = 1.70 \times 10^{13}$$

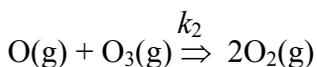
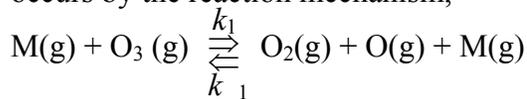
$$\Delta S^\ddagger/R = 2.303 \log A h/k_b T_e = 2.303 \log (1.479 \times 10^{15})/(1.70 \times 10^{13}) = 4.466$$

$$\Delta S^\ddagger = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (4.466) = 37.13 \text{ J K}^{-1} \text{ mol}^{-1}$$

Since the reactant and the product have the same mass  $\Delta S_{\text{trans}}^\ddagger = 0$ . The whole contribution is due to the internal degrees of freedom.

12. The decomposition of ozone,  $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$

occurs by the reaction mechanism,



where M is a molecule that can exchange energy with the reacting ozone molecule through a collision, but M itself does not react. Use this mechanism to derive the rate law for  $d[\text{O}_3]/dt$  assuming that the intermediate O(g) concentration can be treated by the steady-state approximation.

*Example 27-5, page 1104, McQuarrie and Simon, Physical Chemistry A Molecular Approach*

Answer:

The rate equations for  $O_3(g)$  and  $O(g)$  are

$$d[O_3]/dt = -k_1 [O_3][M] + k_{-1}[O_2][O][M] - k_2[O][O_3]$$

and

$$d[O]/dt = k_1[O_3][M] - k_{-1}[O_2][O][M] - k_2[O][O_3]$$

Invoking the steady-state approximation for the intermediate  $O(g)$  means that we set

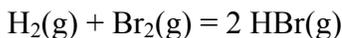
$d[O]/dt = 0$ . setting  $d[O]/dt = 0$  and solving the resulting expression for  $[O]$  gives us

$$[O] = \{k_1[O_3][M]\} / \{k_{-1}[O_2][M] + k_2[O_3]\}$$

Substituting this result into the rate equation for  $O_3$  then gives us

$$d[O_3]/dt = \{2k_1k_2[O_3]^2[M]\} / \{k_{-1}[O_2][M] + k_2[O_3]\}$$

13. In the initial states of the reaction described by



The observed rate law is

$$\frac{1}{2} d[HBr]/dt = k_{obs} [H_2][Br_2]^{1/2}$$

Show that this result is consistent with the rate law given in problem 10 and determine  $k_{obs}$  in terms of the rate constants of the mechanism.

*Example 27-7, page 1115, McQuarrie and Simon, Physical Chemistry A Molecular Approach*

In the initial stages of the reaction,  $[HBr] \ll [Br_2]$

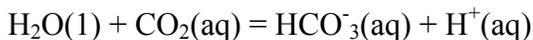
$$k_{-2}/k_3[HBr][Br_2]^{-1} \ll 1$$

This result allows us to simplify the denominator of the rate expression, obtaining the result,

$$\frac{1}{2} d[HBr]/dt = k_2K_{c,1}^{1/2} [H_2][Br_2]^{1/2}$$

The measured rate constant,  $k_{obs}$ , is equal to  $k_2K_{c,1}^{1/2}$

14. The enzyme carbonic anhydrase catalyses both the forward and the reverse reactions for the hydration of  $CO_2$  according to



Carbon dioxide is produced in tissue as one of the final products of respiration. It then diffuses into the blood system, where it is converted to the bicarbonate ion by carbonic anhydrase. The reverse reactions occur in the lungs, where  $\text{CO}_2(\text{g})$  is expelled. Carbonic anhydrase has a single active site, and its molecular mass is 30 000  $\text{g}\cdot\text{mol}^{-1}$ . If 8.0  $\mu\text{g}$  of carbonic anhydrase catalyse the hydration of 0.146 g of  $\text{CO}_2$  in 30 seconds at 37°C, what is the turnover number of the enzyme (in units of  $\text{s}^{-1}$ )?

*Example 27-9, page 1122, McQuarrie and Simon, Physical Chemistry A Molecular Approach*

Answer:

To calculate the turnover number, we need to determine the ratio of the number of moles of  $\text{CO}_2$  that react per second to the number of moles of enzyme present.

The number of moles of enzyme present is

$$\text{Number of moles of enzyme} = 8.0 \times 10^{-6} \text{ g} / 30\,000 \text{ g}\cdot\text{mol}^{-1} = 2.7 \times 10^{-10} \text{ mol}$$

The number of moles of  $\text{CO}_2$  reacted in 30 seconds is given by

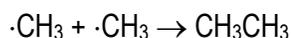
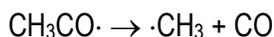
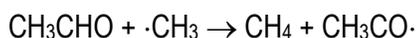
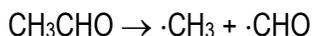
$$0.146 \text{ g} / 44 \text{ g}\cdot\text{mol}^{-1} = 3.3 \times 10^{-3} \text{ mol}$$

Or rate of  $1.1 \times 10^{-4} \text{ mol}\cdot\text{s}^{-1}$ . The turnover number is then

$$\text{Turnover number} = 1.1 \times 10^{-4} \text{ mol}\cdot\text{s}^{-1} / 2.7 \times 10^{-10} \text{ mol} = 4.1 \times 10^5 \text{ s}^{-1}$$

Thus, we see that each carbonic anhydrase molecule converts 410 000  $\text{CO}_2$  molecules to  $\text{HCO}_3^-(\text{aq})$  per second! It is one of the fastest working enzymes known.

15. Assuming that the following steps are involved in the thermal degradation of acetaldehyde, derive a rate expression for the formation of  $\text{CH}_4$ . (6 marks)



$$R = k_a [\text{CH}_3\text{CHO}]$$

$$R = k_b [\text{CH}_3\text{CHO}] [\cdot\text{CH}_3]$$

$$R = k_c [\text{CH}_3\text{CO}\cdot]$$

$$R = k_d [\cdot\text{CH}_3]^2$$

$$d[\cdot\text{CH}_3]/dt = k_a[\text{CH}_3\text{CHO}] - k_b[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] + k_c[\text{CH}_3\text{CO}\cdot] - 2k_d[\cdot\text{CH}_3]^2 = 0 \quad (1)$$

$$d[\text{CH}_3\text{CO}\cdot]/dt = k_b[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] - k_c[\text{CH}_3\text{CO}\cdot] = 0 \quad (2)$$

1 + 2,

$$k_a[\text{CH}_3\text{CHO}] - 2k_d[\cdot\text{CH}_3]^2 = 0$$

$$[\cdot\text{CH}_3] = (k_a/2k_d)^{1/2} [\text{CH}_3\text{CHO}]^{1/2}$$

$$d[\text{CH}_4]/dt = k_b[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] = k_b (k_a/2k_d)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

16. The value of  $\log A$  for an isomerisation reaction conducted at 298 K was found to be 15.17 in the high-pressure limit. Calculate the value of  $\Delta S^\ddagger$  for the reaction. (5 marks)

According to equation,

$$A = (k_b T/h) e^{-\Delta n} e^{\Delta S^\ddagger/R}$$

$$\Delta n = 0$$

$$A = (k_b T/h) \exp(\Delta S^\ddagger/R)$$

Or

$$\Delta S^\ddagger/R = 2.303 \log A - 2.303 \log k_b T/h$$

$$e k_b T/h = ((1.38 \times 10^{-23} \text{ JK}^{-1}) (298\text{K})(2.718))/(6.62 \times 10^{-34} \text{ J s}) = 1.70 \times 10^{13}$$

$$\Delta S^\ddagger/R = 2.303 \log A h/k_b T = 2.303 \log (1.479 \times 10^{15})/(1.70 \times 10^{13}) = 4.466$$

$$\Delta S^\ddagger = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (4.466) = 37.13 \text{ J K}^{-1} \text{ mol}^{-1}$$

17. Assume that the rate constant measured  $k_{\text{obs}} = k_1 k_2 / k_{-1}$ ,  $k_1$ ,  $k_2$  and  $k_{-1}$  are the rate constants of the elementary steps. The measured activation energy is negative. Derive an expression for the activation energy in terms of the activation energies of the elementary steps and explain how the overall activation energy is negative. (5 marks)

At high concentration,  $k_{\text{obs}} = k_1k_2/k_{-1}$ . Denoting the experimentally measured values of A and  $E_a$  by  $A_{\text{obs}}$  and  $E_{a,\text{obs}}$ , we have

$$k_{\text{obs}} = A_{\text{obs}}e^{-E_{a,\text{obs}}/RT}$$

if each step of the reaction mechanism shows Arrhenius behaviour, then each of the rate constants,  $k_1$ ,  $k_{-1}$  and  $k_2$  can be written in terms of an Arrhenius equation,

$$k_1 = A_1e^{-E_{a,1}/RT}$$

$$k_{-1} = A_{-1}e^{-E_{a,-1}/RT}$$

$$k_2 = A_2e^{-E_{a,2}/RT}$$

Substituting these equations into  $k_{\text{obs}} = k_1k_2/k_{-1}$  shows that

$$E_{a,\text{obs}} = E_{a,1} + E_{a,2} - E_{a,-1}$$

and

$$A_{\text{obs}} = A_1A_2/A_{-1}$$

Overall activation energy can be negative as  $E_{a,\text{obs}} = E_{a,1} + E_{a,2} - E_{a,-1}$