D. B. College (Jaynagar) Lect-27
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Ex.7 The optical rotations of sucrose in 0.5 N HCl at 35C at various time intervals are given below. Show that the reaction is of first order.

Time (minutes)	0	10	20	30	40	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	-11.1

Soln The inversion of sucrose will be first order reaction if the above data confirm to the equation, $k_1 = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$

where r_0, and r_∞ represent optical rotations initially, at the commencement of the reaction after t and at the completion of the reaction respectively.

In this case, $a_0 = r_0 - r_\infty = +32.4 - (-11.1) = 43.5$

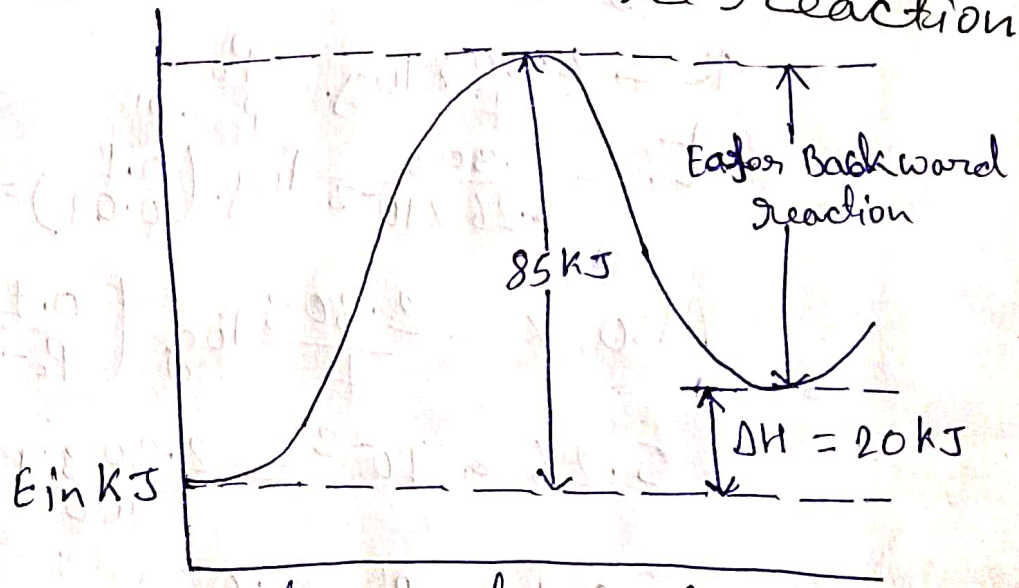
The value of k at different times is calculated as follows:

Time	α_t	$\alpha_t - \alpha_\infty$	k
10 min	+28.8	39.9	$\frac{2.303}{10}\log\frac{43.5}{39.9} = 0.008625\ min^{-1}$
20 min	+25.5	36.6	$\frac{2.303}{20}\log\frac{43.5}{36.6} = 0.008625\ min^{-1}$
30 min	+22.4	33.5	$\frac{2.303}{30}\log\frac{43.5}{33.5} = 0.008694\ min^{-1}$
40 min	+19.6	30.7	$\frac{2.303}{40}\log\frac{43.5}{30.7} = 0.008717\ min^{-1}$

The Constancy of k_1 indicates that the inversion of sucrose is a first order reaction.

Ex-8 For $A + B \rightarrow C + D$; $\Delta H = 20\ kJ\ mol^{-1}$; the activation energy of the forward reaction is 85 kJ/mol. Calculate activation energy of the reverse reaction.

Soln.



ΔH of forward reaction $= 20\ kJ\ mol^{-1}$

Energy of activation for forward reaction (E_a)

$= 85\ kJ\ mol^{-1}$

Energy of activation for backward reaction

$= E_a - \Delta H$

$= 85 - 20$

$= 65 \text{ kJ mol}^{-1}$

Ex.9 The reaction given below is observed to be first order with rate constant $2.56 \times 10^{-3} \text{ sec}^{-1}$. Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise 0.145 atm and also find the total pressure after 100 sec.

Soln. $2A(g) \rightarrow 4B(g) + C(g)$

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Initial	P_0	0	0
At time t	$P_0 - P'$	$2P'$	$P'/2$

$$P_{total} = P_0 - P' + 2P' + P'/2 = P_0 + \frac{3P'}{2}$$

$$P' = \frac{2}{3}(0.145 - 0.1) = 0.03 \text{ atm}$$

$$k = \frac{2.303}{t} \log \frac{P_0}{P_0 - P'}$$

$$t = \frac{2.303}{5.26 \times 10^{-3}} \log\left(\frac{0.1}{0.07}\right) = 67.82 \text{ sec}$$

$$\text{Also, } k = \frac{2.303}{t} \log\left(\frac{0.1}{P_0 - P'}\right)$$

$$5.26 \times 10^{-3} = \frac{2.303}{100} \log\left(\frac{0.1}{0.1 - P'}\right)$$

$$0.1 - P' = .059$$

$$P' = 0.041$$

$$P'_{total} = 0.1 + \frac{3}{2}(0.041) \simeq 0.162 \text{ atm}$$