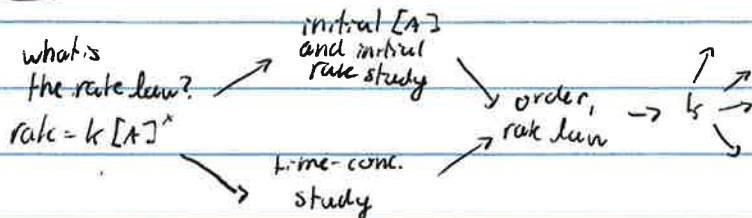


Today Jan 26: Sections 13.7-13.8 (end of new material)
 Monday 1/29 Finish ch. 13
 Wednesday 1/31 Celebration of knowledge



time	"trans" conc.	first order
0hr	1.00 mol/L	$rate = k [trans]^1$
40	0.66	time concentration expression: $\ln \frac{[A]_0}{[A]_t} = kt$
80	0.43	
120	0.28	
160	0.19	



$$\ln \left(\frac{1.00}{0.28} \right) = k(120)$$

$$k = 0.0106 \text{ hr}^{-1}$$

trans-dichloroethene → cis-dichloroethene

What is the rate if the conc. of "trans" = 1.24M

$$rate = k [trans]$$

$$rate = (0.0106 \text{ hr}^{-1})(1.24M)$$

$$rate = 0.0132 \frac{\text{mol}}{\text{L} \cdot \text{hr}}$$

half-life

1st order

$$t_{1/2} = \frac{0.693}{k}$$

$$t_{1/2} = \frac{0.693}{0.0106 \text{ hr}^{-1}}$$

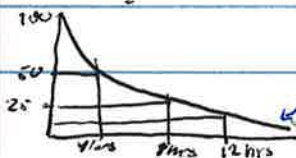
$$t_{1/2} = 65.4 \text{ hrs.}$$

zero order

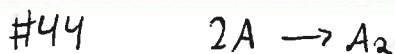
$$t_{1/2} = \frac{[A]_0}{2k}$$

2nd order

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



never completely goes away, just gets smaller

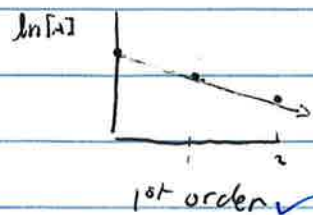
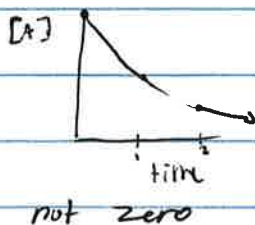


*when doing a picture problem turn it into a word problem

16 A 0 A ₂	8 A 4 A ₂	4 A 6 A ₂	2 A 7 A ₂
t=0	t=1min	t=2min	time = ?

What is the order?

time	[A]
0	16
1	8
2	4



rate = $k[A]^1$

time conc. expression:

$\ln \frac{[A]_0}{[A]_t} = kt$

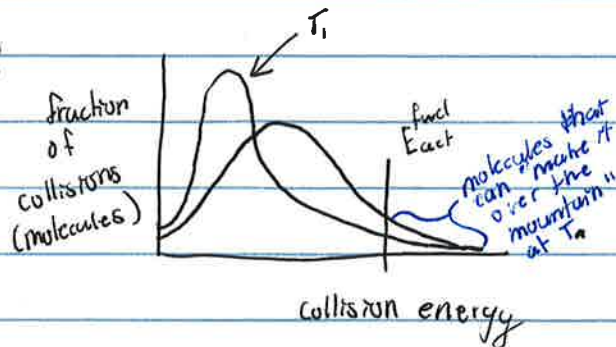
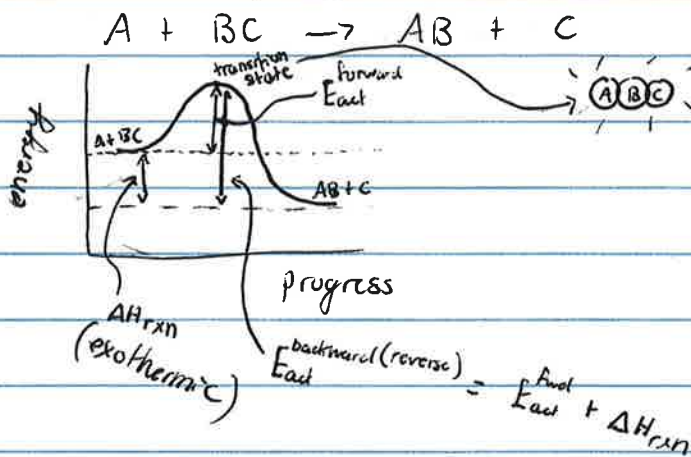
$\ln \left(\frac{16}{8}\right) = k(1)$
 $0.693 \text{ min}^{-1} = k$

how long until $[A] = 2$?

$\ln \left(\frac{16}{2}\right) = 0.693 t$

$t = 3 \text{ min}$

Reaction profiles



Energy diagram

fraction of molecules with enough energy to exceed E_{act}

$$f = e^{-E_{act}/RT} \quad R = 8.314 \text{ J/mol}\cdot\text{K}$$

example: $E_{act} = 60 \text{ kJ/mol}$

$$f = e^{-60000 \text{ J/mol} / (8.314 \text{ J/mol}\cdot\text{K})(300 + 298 \text{ K})}$$

$$f = 3.0 \times 10^{-11}$$



incorrect orientation

rate constant

$$k = \rho \cdot z \cdot f$$

\uparrow orientation \uparrow collision frequency \uparrow fraction

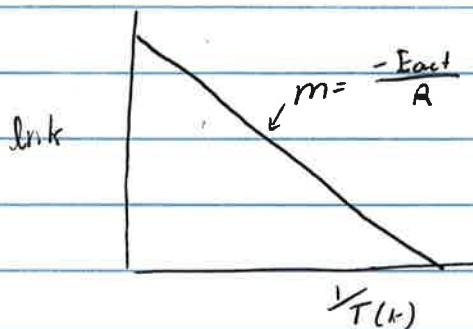
$$k = A e^{-E_{act}/RT}$$

$$\ln k = \ln(A) - E_{act}/RT$$

$$\ln(k) = \ln(A) - \frac{E_{act}}{R} \left(\frac{1}{T}\right)$$

$$y = B + mx$$

$$\ln(k) = \frac{-E_{act}}{R} \left(\frac{1}{T}\right) + \ln(A)$$



$$\ln(k_1) = \frac{-\Delta H_{act}}{R} \left(\frac{1}{T_1}\right) + \ln(A)$$

$$\ln(k_2) = \frac{-\Delta H_{act}}{R} \left(\frac{1}{T_2}\right) + \ln(A)$$

$$\ln(k_2) - \ln(k_1) = \frac{-\Delta H_{act}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-\Delta H_{act}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Organic chemists of old said "to double rate of reaction, raise temperature by 10 degrees"

$$\ln(2) = \frac{-\Delta H_{act}}{R} \left(\frac{1}{308} - \frac{1}{298}\right)$$

ΔH_{act} ~ 50ish kJ/mol