

## Worksheet 4 Solutions. Data Set 1 Solution:

First, determine the order of reaction; since a linear relationship is seen for  $\ln[C]$ , the reaction is first order. Therefore, the rate is  $k[C]$ .

### Data at 300K

Time(s)	[C]	1/[C]	ln[C]	[C]
1	0.12	8.333333	-2.1202	0.12
2	0.074	13.51351	-2.603	0.074
3	0.044	22.72727	-3.123	0.044
4	0.027	37.03704	-3.611	0.027
5	0.016	62.5	-4.135	0.016
6	0.009	111.1111	-4.710	0.009
8	0.0036	277.7778	-5.6268	0.0036
10	0.0013	769.2308	-6.6453	0.0013

### Data at 310 K

Time (s)	[C]	ln[C]	1/[C]	[C]
1	0.074	-2.6036	13.51351	0.074
2	0.027	-3.6119	37.03704	0.027
3	0.009	-4.7105	111.1111	0.009
4	0.0036	-5.6268	277.7778	0.0036
5	0.0013	-6.6453	769.2308	0.0013
6	0.0005	-7.6009	2000	0.0005
7	6.7E-05	-9.610	14925.37	6.7E-05
10	9E-06	-11.607	109890.1	9.1E-06

Solve for rate constant,  $k$ , and initial concentration,  $C_0$ , directly knowing the order, using integrated rate law:  $\ln [C] = -kt + \ln [C_0]$  so slope =  $-k$  and y intercept =  $\ln[C_0]$ .

At **300K** curve fit yields  $y = -0.5x - 1.6$ ;  $k = 0.5 \text{ sec}^{-1}$  and  $[C_0] = 0.2M$

At **310 K** curve fit yields  $y = -1.0x - 1.6$ ;  $k = 1.0 \text{ sec}^{-1}$  and  $[C_0] = 0.2M$

• Solve for half life,  $t_{1/2}$ , for second order reaction:  $t_{1/2} = 0.693/k$

At **300 K**,  $t_{1/2} = 0.693/0.5 \text{sec}^{-1} = 1.39 \text{ sec}$ . At **310K**,  $t_{1/2} = 0.693/1 \text{ sec}^{-1} = 0.693 \text{ sec}$

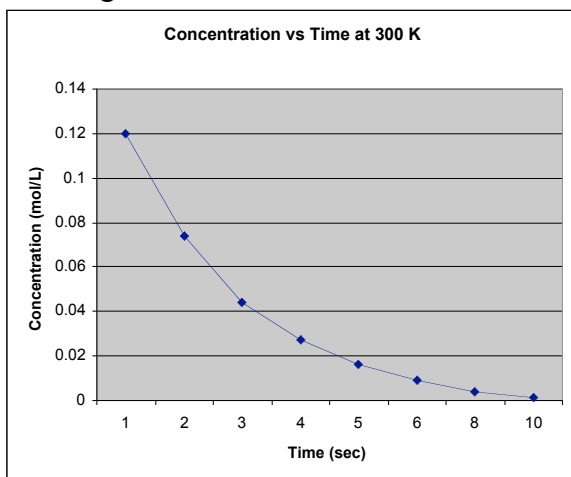
• Solve for activation energy,  $E_a$  using the combined Arrhenius equation :

$\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$  so  $\ln(1.0/0.5) = (E_a/8.3)(1/300 - 1/310)$

and substituting,  $E_a = 53,500 \text{ J}$  or **53.5 kJ**

• Solve for pre-exponential term,  $A$ :  $k = A \exp(-E_a/RT)$  so  $0.5 = A \exp(-53,500/8.3 \cdot 300)$

Rearrange and solve for  $A = 1.03 \times 10^9$



Plotting the concentration vs time and drawing a tangent line at  $x=2$  will yield a line with a slope that is equal to the instantaneous rate at 2 seconds.

## Data Set 2 Solution

### Data at 300 K

Time (s)	[C] Unk [C] <sub>0</sub>	1/[C]	ln[C]	[C]
0	[C] <sub>0</sub>			
1	0.182	5.494505	-1.7037	0.182
2	0.166	6.024096	-1.7957	0.166
3	0.153	6.535948	-1.8773	0.153
4	0.142	7.042254	-1.951	0.142
5	0.133	7.518797	-2.0174	0.133
6	0.125	8	-2.0794	0.125
8	0.111	9.009009	-2.1982	0.111
10	0.1	10	-2.3025	0.1

### Data at 313 K

Time (s)	[C] Unk [C] <sub>0</sub>	1/[C]	ln[C]	[C]
0	[C] <sub>0</sub>			
1	0.166	6.024096	-1.7957	0.166
2	0.142	7.042254	-1.9519	0.142
3	0.125	8	-2.0794	0.125
4	0.111	9.009009	-2.1982	0.111
5	0.1	10	-2.3025	0.1
6	0.09	11.11111	-2.407	0.09
8	0.076	13.15789	-2.577	0.076
10	0.066	15.15152	-2.71	0.066

Calculate **order** from method of initial rates (see handout on order of reaction) or from functional relationships of integrated rate law. Notice in this case that the 1/[C] result in the data table above is a straight line, indicating that this reaction is order  $x = 2$  in [C]. So rate =  $k[C]^2$ . Solve for rate constant, **k**, and initial concentration, **C<sub>0</sub>**, directly knowing the order, using integrated rate law:  $1/[C] = kt + 1/[C_0]$  so slope =  $k$  and y intercept =  $1/[C_0]$

At **300K** curve fit yields  $y = 0.5x + 5$

At **313 K** curve fit yields  $y = 1.0x + 5$

**k = 0.5 M<sup>-1</sup>sec<sup>-1</sup>** and  $1/[C_0] = 5$ , **[C<sub>0</sub>] = 0.2 M**

**k = 1.0 M<sup>-1</sup>sec<sup>-1</sup>** and  $1/[C_0] = 5$ , **[C<sub>0</sub>] = 0.2 M**

Solve for half life,  $t_{1/2}$ , for second order reaction:  $t_{1/2} = 1/k[A_0]$  and for 0.2 M

At **300 K**,  $t_{1/2} = 1/((0.5)(0.2)) = 10$  sec at **313K**,  $t_{1/2} = 1/((1.0)(0.2)) = 5$  sec

Solve for activation energy, **E<sub>a</sub>** using the combined Arrhenius equation :

$\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$  so  $\ln(1.0/0.5) = (E_a/8.3)(1/300 - 1/313)$

and substituting, **E<sub>a</sub> = 41,600 J or 41.6 kJ**

Solve for pre-exponential term, **A**:  $k = A \exp(-E_a/RT)$  so  $0.5 = A \exp(-41,600/8.3 \cdot 300)$

Rearrange and solve for **A = 8.7 x 10<sup>6</sup>**

## Data Set 3 Solution

### Data at 300 K

Time (s)	[C] Unk [C] <sub>0</sub>	1/[C]	ln[C]	[C]
0	[C] <sub>0</sub>			
0.05	0.1875	5.333333	-1.6739	0.1875
0.1	0.175	5.714286	-1.7429	0.175
0.15	0.1625	6.153846	-1.8170	0.1625
0.2	0.15	6.666667	-1.8971	0.15
0.25	0.1375	7.272727	-1.9841	0.1375
0.3	0.125	8	-2.0794	0.125
0.35	0.1125	8.888889	-2.1848	0.1125
0.4	0.1	10	-2.302	0.1

### Data at 305 K

Time (s)	[C] Unk [C] <sub>0</sub>	1/[C]	ln[C]	[C]
0	[C] <sub>0</sub>			
0.05	0.175	5.714286	-1.74297	0.175
0.1	0.15	6.666667	-1.8971	0.15
0.15	0.125	8	-2.0794	0.125
0.2	0.1	10	-2.3025	0.1
0.25	0.075	13.33333	-2.5902	0.075
0.3	0.05	20	-2.9957	0.05
0.35	0.025	40	-3.6888	0.025
0.4	0	N/A	N/A	0

Calculate **order** from method of initial rates (see handout on order of reaction) or from functional relationships of integrated rate law. Notice in this case that the [C] result in the data table above is already a straight line, indicating that this reaction is order  $x = 0$  in [C]. So rate =  $k$ . Solve for rate constant, **k**, and initial concentration, **C<sub>0</sub>**, directly knowing the order, using integrated rate law:  $C = -kt + C_0$  so slope =  $-k$  and y intercept =  $C_0$

At **300K** curve fit yields  $y = -0.25x - 2$

At **305 K** curve fit yields  $y = -0.5x - 2$

**k = 0.25 M<sup>-1</sup>sec<sup>-1</sup>** and **[C<sub>0</sub>] = 0.2 M**

**k = 0.5 M<sup>-1</sup>sec<sup>-1</sup>** and **[C<sub>0</sub>] = 0.2 M**

Solve for half life,  $t_{1/2}$ , for first order reaction:  $t_{1/2} = C_0/2k$

At **300 K**,  $t_{1/2} = 0.2/((0.25)(0.2)) = 0.4$  sec at **310K**,  $t_{1/2} = 0.2/((0.5)(0.2)) = 0.2$  sec

Solve for activation energy, **E<sub>a</sub>** using the combined Arrhenius equation :

$\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$  so  $\ln(.5/.25) = (E_a/8.3)(1/300 - 1/305)$

and substituting, **E<sub>a</sub> = 105,400 J or 105.4 kJ** Solve for pre-exponential term, **A**:  $k = A \exp(-E_a/RT)$  so  $0.5 = A \exp(-105,400/8.3 \cdot 300)$

Rearrange and solve for **A = 1.1 x 10<sup>9</sup>**

