Experiment-3

Study of a Non-Catalytic Gas-Solid Reaction by Thermo Gravimetric Technique

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Objectives

1. To determine conversion and reaction rate constant for the decomposition of sodium bicarbonate pellets
2. To calculate activation energy in the temperature range of 100 – 200 ^oC

Theory

Reaction under consideration:

$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

The unreacted core model is applied for the analysis of the above reaction. It has been seen to satisfy most of the non-catalytic gas-solid reactions. The reaction rate can be controlled by the resistance at the pellet surface, the diffusional resistance at the boundary layer formed and the resistance due to the product layer being formed. At low conversions, it can be concluded that both the diffusional resistances (gas film and ash film) can be neglected and reaction is mostly governed by the chemical resistance. Lievenspiel's equation is used to convert the weight lost at any instant to weight lost per unit area of interface by introducing a dimensionless factor f that represents fractional thickness of the reacted solid at any instance. The indication of reaction completion is when f attains the value of the ratio of length to diameter (a) of cylindrical pellet.

Rate equation: $R_0 d_0 f = kt$

Where,

R_0 = initial pellet radius (cm)

d_0 = density of reactant pellet (g/ cm^3)

t = reaction time (s)

k = modified rate constant

The relation between reaction conversion x and f is:

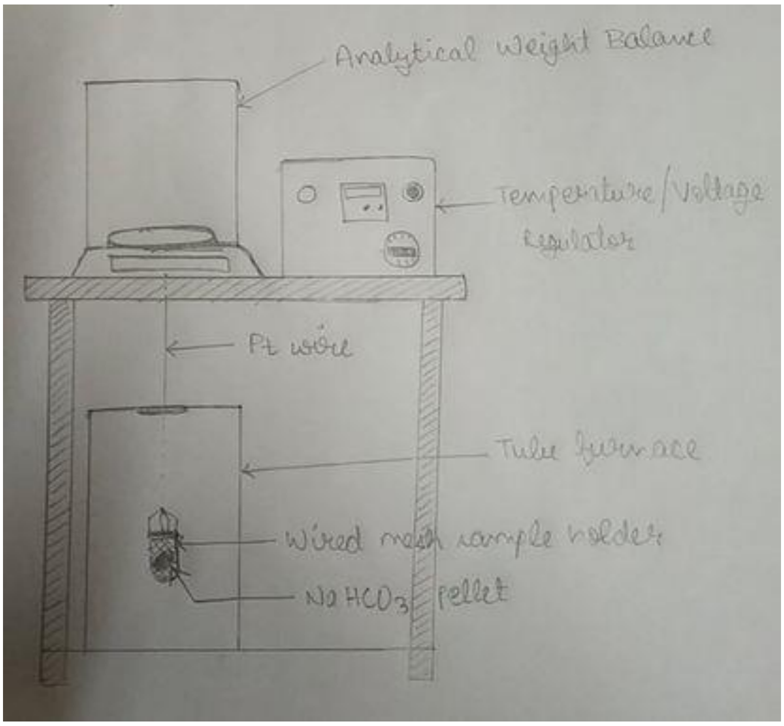
$$f = 1 - (1 - x)^{1/3}$$

For a cylindrical pellet with a given ratio of length/ diameter, reaction conversion is given by:

$$x = 1 - \frac{(a - f)(1 - f)^2}{a}$$

Therefore, for any x we can find f from the above equation and then calculate $R_0 d_0 f$ for each time instance t. $R_0 d_0 f$ vs t will give a straight line for chemical resistance control. At different temperatures we can plot different lines to get different values of k and then to find activation energy by plotting ln k vs 1/T.

Schematic



Observations and Calculations

Initial pellet radius = 0.9 cm (R_0)

Density of pellet = 2.2 g/ cm^3 (d_0)

1. **T = 120 ºC, a = 0.302995**

Time (min)	**Weight of pellet (gm)**	**ΔWeight (gm)**	**x**	**f**	**R_0d_0f (gm/ cm^2)**	**k (gm/ cm^2 min)**
0	2.284	0	0	0	0	0.0021
1	2.273	0.011	0.0012	0.000226472	0.0004	
2	2.213	0.071	0.0080	0.0015126	0.003	
3	2.139	0.145	0.0163	0.00308891	0.0061	
4	2.073	0.211	0.0237	0.00450036	0.0089	
5	2.007	0.277	0.0312	0.00593678	0.0118	
6	1.945	0.339	0.0381	0.00726358	0.0144	
7	1.881	0.403	0.0453	0.00865353	0.0171	
8	1.834	0.45	0.0506	0.00968029	0.0192	
9	1.779	0.505	0.0568	0.0108853	0.0216	
10	1.723	0.561	0.0631	0.0121141	0.024	
11	1.673	0.611	0.0687	0.0132101	0.0262	
12	1.623	0.661	0.0744	0.0143293	0.0284	
13	1.582	0.702	0.0790	0.0152352	0.0302	
14	1.542	0.742	0.0835	0.0161238	0.0319	
15	1.515	0.769	0.0865	0.0167174	0.0331	
16	1.486	0.798	0.0898	0.0173716	0.0344	
17	1.47	0.814	0.0916	0.017729	0.0351	
18	1.464	0.82	0.0922	0.0178482	0.0353	

2. **T = 140 ºC, a = 0.390**

Time (min)	Weight of pellet (gm)	ΔWeight (gm)	x	f	R_0d_0f (gm/ cm^2)	k (gm/ cm^2 min)
0	2.659	0	0	0	0	0.0031
1	2.649	0.01	0.00107	0.000234512	0.00046433	
2	2.585	0.074	0.00795	0.00174594	0.00345696	
3	2.46	0.199	0.02139	0.00471638	0.00933843	
4	2.38	0.279	0.02999	0.00662969	0.01312679	
5	2.287	0.372	0.03998	0.008866479	0.01755563	
6	2.197	0.462	0.04966	0.0110436	0.02186633	
7	2.118	0.541	0.05815	0.0129652	0.0256711	
8	2.049	0.61	0.06556	0.0146507	0.02900839	
9	1.973	0.686	0.07373	0.0165181	0.03270584	
10	1.92	0.739	0.07943	0.0178267	0.03529687	
11	1.864	0.795	0.08545	0.0192139	0.03804352	
12	1.813	0.846	0.09093	0.0204813	0.04055297	
13	1.775	0.884	0.09501	0.0214278	0.04242704	
14	1.738	0.921	0.09899	0.0223535	0.04425993	
15	1.72	0.939	0.10092	0.0228032	0.04515034	
16	1.712	0.947	0.10178	0.0230038	0.04554752	

3. T = 160 °C, a = 0.290

Time (min)	Weight of pellet (gm)	ΔWeight (gm)	x	f	R_0d_0f (gm/ cm^2)	k (gm/ cm^2 min)
0	2.196	0	0	0	0	0.0037
1	2.166	0.03	0.00434	0.000797504	0.001579058	
2	2.052	0.144	0.02083	0.00384462	0.007612348	
3	1.954	0.242	0.03501	0.0064867	0.012843666	
4	1.86	0.336	0.04860	0.00903818	0.017895596	
5	1.745	0.451	0.06524	0.0121886	0.024133428	
6	1.672	0.524	0.07580	0.0142032	0.028122336	

7	1.587	0.609	0.08809	0.0165632	0.032795136	
8	1.521	0.675	0.09764	0.0184085	0.03644883	
9	1.47	0.726	0.10502	0.0198415	0.03928617	
10	1.424	0.772	0.11167	0.021138	0.04185324	
11	1.399	0.797	0.11529	0.0218459	0.043254882	
12	1.394	0.802	0.11601	0.0219869	0.043534062	
13	1.391	0.805	0.11645	0.0220731	0.043704738	

Temperature T (K)	**1/T (K^{-1})**	**k (gm/ cm^2 min)**	**ln (k)**
393	0.002545	0.0021	-6.16582
413	0.002421	0.0031	-5.77635
423	0.002364	0.0037	-5.59942

Sample Calculation :-

$T = 120^\circ C$, $a = 0.302995$

initial pellet radius = 0.9 cm (R_0)

pellet density = 2.2 g/cm^3 (d_0)

At t = 0 min, weight = 2.284 gm

At t = 1 min, weight = 2.273 gm

Δweight = 2.284 − 2.273 = 0.011 gm

similarly, calculating the other Δweight values :

$\Sigma \Delta$weight = 8.89 gm

x at t = 1 min, $= \frac{0.011}{8.89} = 0.0012$

$$x = 1 - \frac{(a-f)(1-f)^2}{a}$$

$$\therefore 0.0012 = 1 - \frac{(0.302995-f)(1-f)^2}{0.302995}$$

solving this equation, f = 0.000226472

$R_0 d_0 f$ = 0.000226472 × 0.9 × 2.2 = 0.0004 g/cm^2

similarly, calculating $R_0 d_0 f$ for all t and plotting the curve, the slope comes out to be :

$k = 0.0021\ g/cm^2\ min$

$T\ (\text{in K}) = 120 + 273 = 393\ K$

$1/T = 0.002545\ K^{-1}$

$\ln k = \ln(0.0021) = -6.16582$

similarly, performing calculations for other temperatures, $\ln k$ vs $1/T$ is plotted.

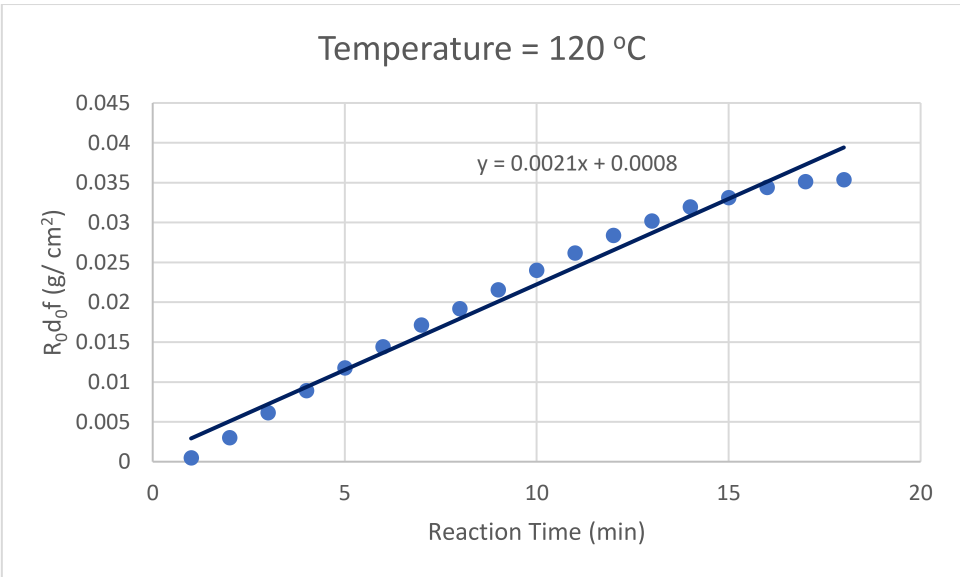
$\text{slope} = -\frac{E_A}{R} = -3131.2$

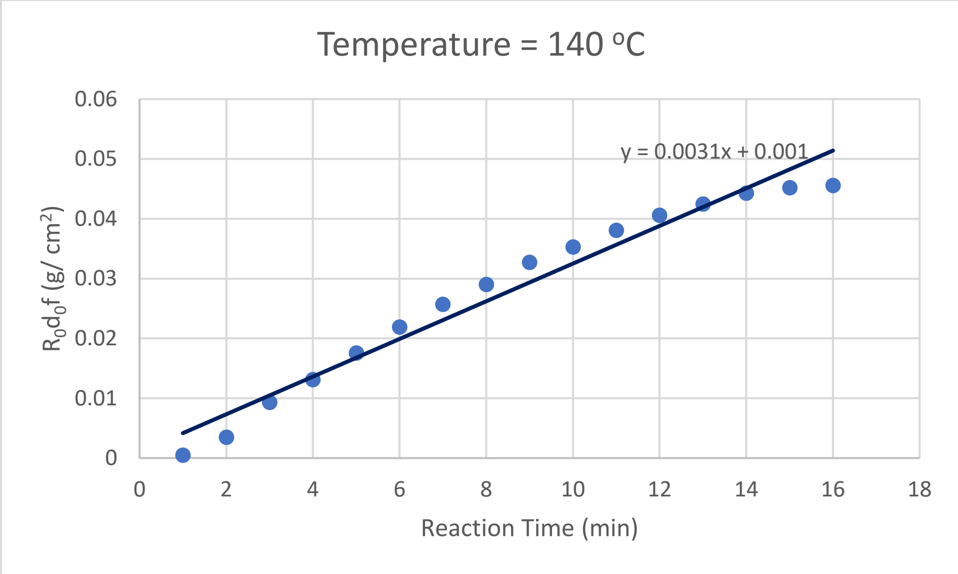
E_A: activation energy of reaction

R: universal gas constant.

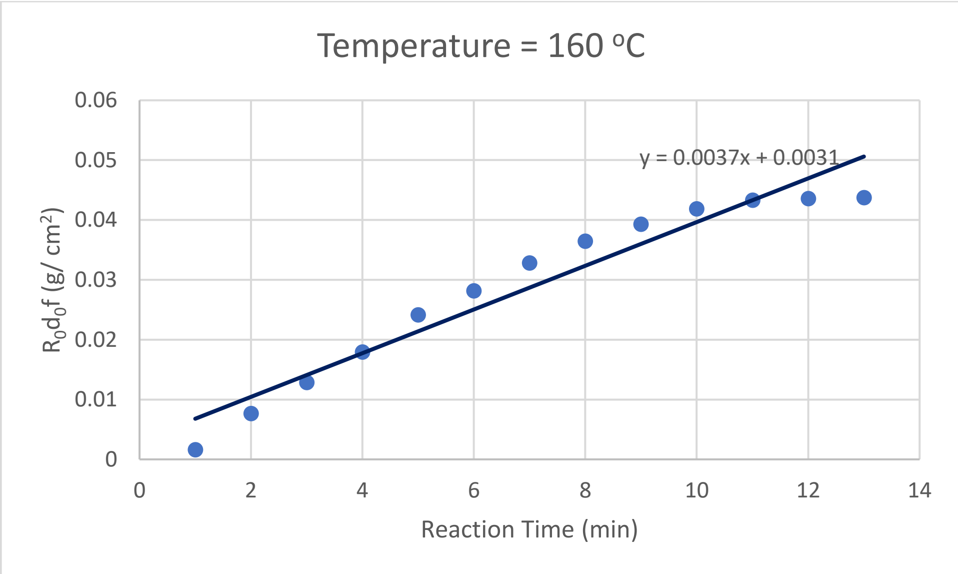
$\Rightarrow E_A = 3131.2 \times 8.314 = 26032.8\ J/mol.$

Plots

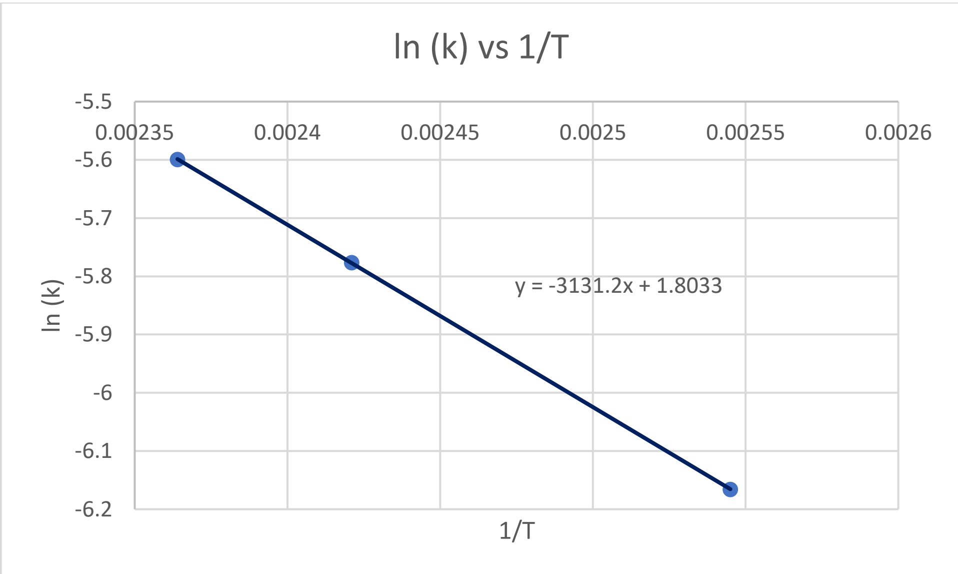




Temperature = 140 ºC
R_0d_0f (g/ cm²)
0.06
0.05
0.04
0.03
0.02
0.01
0
0 2 4 6 8 10 12 14 16 18
Reaction Time (min)
y = 0.0031x + 0.001



Temperature = 160 ºC
R_0d_0f (g/ cm²)
0.06
0.05
0.04
0.03
0.02
0.01
0
0 2 4 6 8 10 12 14
Reaction Time (min)
y = 0.0037x + 0.0031



ln (k) vs 1/T
ln (k)
-5.5
-5.6
-5.7
-5.8
-5.9
-6
-6.1
-6.2
0.00235 0.0024 0.00245 0.0025 0.00255 0.0026
1/T
y = -3131.2x + 1.8033

Results

The modified rate constant for various temperatures are as follows:

T = 120 ^oC: **0.0021 g/ cm^2 min**

T = 140 ^oC: **0.0031 g/ cm^2 min**

T = 160 ^oC: **0.0037 g/ cm^2 min**

The activation energy for the given reaction for temperature range 100 – 200 ^oC is calculated to be **26032.8 J/ mol = 26.033 kJ/ mol**.

Discussion

1. There are 2 methods to perform thermo-gravimetric technique: in inert atmosphere (nitrogen, helium, argon) or in presence of oxygen. Here, we are using air which is more inclined towards the technique in the presence of oxygen. Proper way is to use oxygen cylinders to heat it in presence of pure oxygen therefore, some deviations in readings were inevitable.
2. Usually, vernier callipers used have a zero error present in them, therefore, it is to be noted that the zero error is taken into consideration while measuring length and diameter of the pellet.
3. Since the pellet is composed of $NaHCO_3$, a powdered material, therefore, it is to be handled with care such that minimum particles are lost while using it. Some loss is unavoidable when we will be measuring its dimensions. During that the powder particles can break off from the pellet and result in very slight decrease in weight from the one intended.
4. The heat from the furnace is not entirely supplied to the pellet because there is also the platinum wire which can absorb some of the heat due to radiation effects. Therefore, it might take slightly less time to reach the desirable state than expected.
5. The purpose of the stainless-steel wired mesh basket is to probably absorb the heat from the furnace easily and distribute it evenly throughout the pellet medium.