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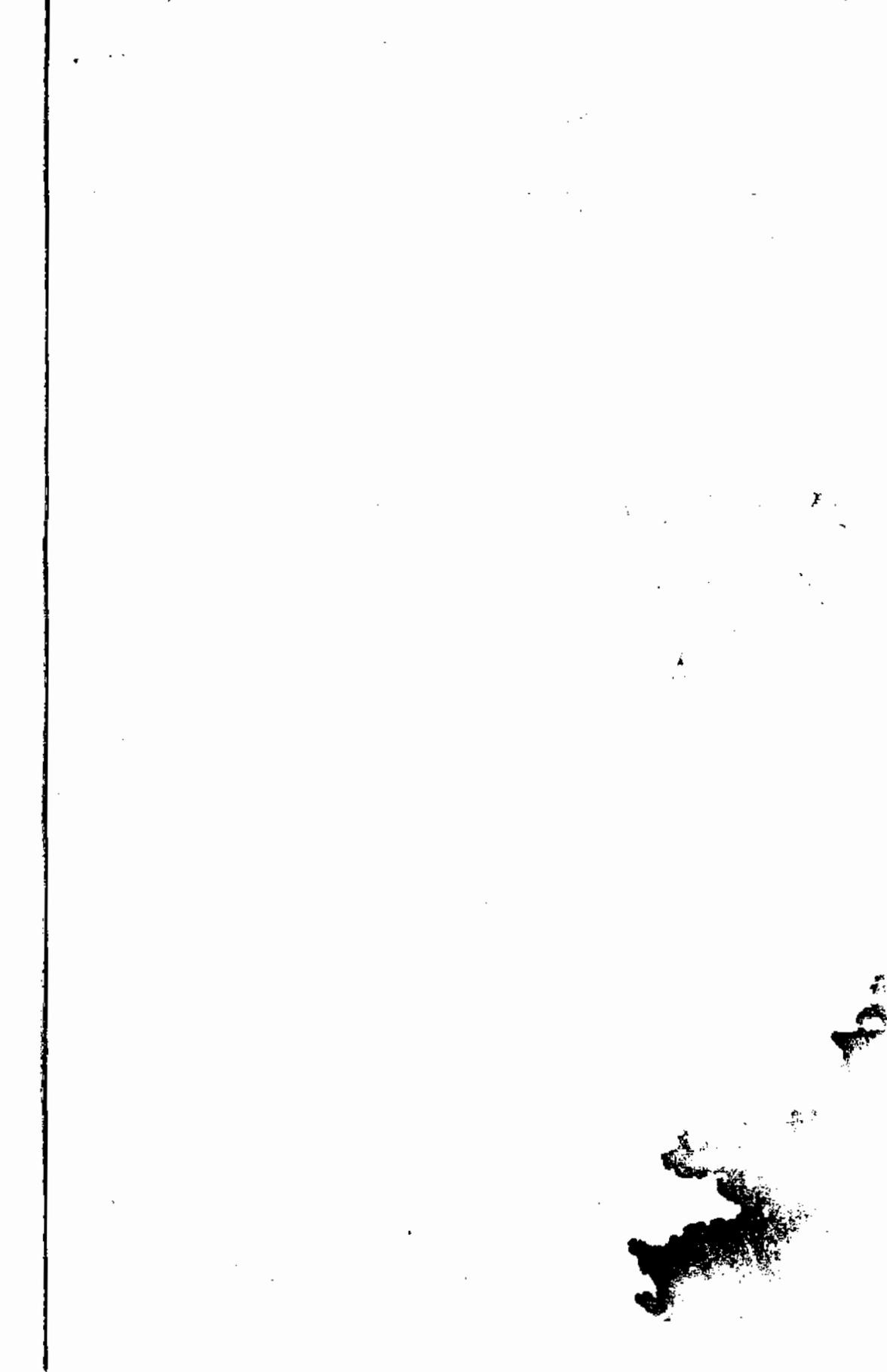
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CONTENTS

	Page
1. <i>Kinetics of Decomposition of some Calcium Salts,</i> By Kh. M. Abdel Salam, E.-Ezzo and S. Shafik	1
2. <i>The Role of Dietary Protein and Schistosomiasis Infection on the Growth Rates and Blood Serum Proteins in Mice,</i> By M. Ashry, J. Tawfic and N. Khalil	15
3. <i>Modern Aspects and Analytic Technique for Accurate Determination of Magnetic Susceptibility Using Dolginov Astatic Magnetometer,</i> By Abdel Hay H. El-Assar and Kamel A. El-Dehemy	23
4. <i>Standard Charts for Direct Determination of Magnetic Susceptibility Using the Principal Equation of Dolginov Astatic Magnetometer,</i> By Kamel A. El-Dehemy and Abdel Hay H. El-Assar	31
5. <i>On the Normal Impact on a Flexible Membrane,</i> By Ahmed Galal El-Sakka	43
6. <i>Strength Characteristics of Hostalen Gur,</i> By Ahmed Galal El-Sakka	49
7. <i>The Effect of some Dissolved Nutrients on the Distribution and Periodicity of Chlorophyceae and Cyanophyceae in El-Zomor and El-Mansoriya Canals, Giza, Egypt,</i> By W.S. Abou El-Kheir and A.A. El-Shimi	57
8. <i>Note on the Distribution of Algal Flora in El-Gemaih and ELKharg, EL-Riyadh, Saudi Arabia,</i> By W.S. Abou El-Kheir	69
9. <i>The Waste Land in the Making,</i> By Adel Salama	77
10. <i>Some Romantic Elements in Emily Bronte's Verse,</i> By Eva S. Saigh	101

	Page
11. <i>Un Programme de Grammaire Française,</i> Par Dr. Mahmoud Sami El Sibai	139
12. <i>The Protective Effect of Gelatin on the Storage Stability of Active Dry Yeast,</i> By Mohamed I. Mahmoud	201
13. <i>The Effect of the Water Activity of the Growth Medium on Protein Content and Polysaccharide Composition of the Sugar Tolerant Yeast Saccharomyces Mellis,</i> By Mohamed I. Mahmoud	207
14. <i>Tunnel Diode Supper-Regenerative Amplification,</i> By A.H. Abou El Ela, A.B. El-Baily and Th. Amh. ...	215
15. <i>Investigation of the Stability of the Solution of a Periodic System of Differential Equations,</i> By Mounir N. Bishai and Assma H. Abd-Alla	223
16. <i>Some Systematic Properties of Nuclei Far from the Stability Line,</i> By H. Abou-Leila, P.K. Gaorgy and S.M. Darwish ...	231
17. <i>Glyceride Structure and Phospholipid of some Chenopodiaceae Seeds,</i> By Seham Faid, Mahassen H. Abbassy & Fouad Osman	245
18. <i>Studies on the Chemical Constitution of Sheep Lipids,</i> By Y. El-Shattory, T. Z. Morad, M. A. Abbassy and Z. Shoeb	253

KINETICS OF DECOMPOSITION OF SOME CALCIUM SALTS

By

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ABSTRACT

The decomposition of calcium salts and its kinetics of dehydration were carried out by thermalgravimetric technique.

The effect of the water as a catalyst in the decomposition of the salts was studied. E_a for every salt was provided.

INTRODUCTION

In studying the thermal decomposition of Calcium salts, earlier work had been done on this decomposition. YAMAGATA (1) and others studied the decomposition of CaCO_3 and they showed that the decomposition initiates not only at the whole crystal surfaces but also along cracks formed in the interior by the mechanical stress of grinding.

MIKHAIL (2) and others studied the mechanism of the decomposition of $\text{Ca}(\text{OH})_2$. The mechanism is based on the assumption that the interface moves inward with a slowly diminishing velocity. This mechanism leads to an energy of activation of 14.3 K. Cal/mole.

TROKAM (3) and others studied the rate of decomposition of Calcium sulphate with additive compounds. They found acceleration of the reaction decomposition due to the appearance of centers of a liquid microphase Na_2SO_4 in the fused form should have ionic conduction as was demonstrated by electric conductivity measurements.

This work has been done on the decomposition of Calcium salts, the aim of this work is to define the effect of anions on the rate of decomp. Of the Ca cations.

EXPERIMENTAL

For tracing the effect of anions, sets of experiments had been done by using a system of conventional type as shown by ABDEL-SALAM (*). We used $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$ and CaCO_3 . Ea was calculated as mentioned by MAMPEL (5).

RESULTS

TABLE 1

Thermogravimetric Analysis of :

1. CaCO_3
2. $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$
3. $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$

Ca CO ₃			Ca (COO) ₂ · H ₂ O			Ca (NO ₃) ₂ · 3 H ₂ O		
Temp.	% de-comp	D.T.G.	Temp.	% de-comp.	D.T.G.	Temp.	% de-comp.	D.T.G.
68	0.48	0.01	48	0.2	0.023	49	0.44	0.026
110	0.88	0.014	65	0.6	0.036	75	1.12	0.032
145	1.28	0.022	87	1.4	0.057	71	2.24	0.044
190	2.28	0.056	101	2.2	0.042	155	4.24	0.233
215	2.68	0.0156	125	3.2	0.027	185	12.24	0.300
240	3.08	0.05	162	4.2	0.033	205	18.24	0.277
260	4.08	0.015	195	5.2	0.07	270	36.24	0.036
300	5.68	0.028	228	7.6	0.16	320	38.04	0.050
335	6.48	0.013	253	11.6	0.19	430	39.04	0.002
295	8.48	0.033	272	15.6	0.051	510	29.44	
			350	19.6	0.025			
			390	20.2	0.001			
			410	20.4	0.00058			
			445	20.6	0.01			
			465	20.8				

TABLE 2

Kinetics of Decomposition of Ca CO_3 in Air at different temp.

1 — 200 °C			2 — 250 °C		
Time (min)	1 — W/W_0	$(W/W_0)^{1/3}$	Time (min)	1 — W/W_0	$(W/W_0)^{1/3}$
8	0.0158	0.9947	6.75	0.0465	0.9842
13	0.0253	0.9915	10.5	0.0717	0.9754
15	0.0297	0.9900	12	0.0836	0.9714
18	0.0344	0.9883	13.5	0.0931	0.9681
23	0.0380	0.9868	16	0.0976	0.9663
33	0.0437	0.9851	25	0.0995	0.9656
48	0.0485	0.9835			
72	0.0503	0.9828			

3 — 300 °C			4 — 400 °C		
Time (min)	1 — W/W_0	$(W/W_0)^{1/3}$	Time (min)	1 — W/W_0	$(W/W_0)^{1/3}$
3	0.0465	0.9842	1	0.0604	0.9795
4.5	0.0674	0.9763	2	0.1070	0.9629
6	0.0931	0.9681	2.5	0.1256	0.9554
7.5	0.1116	0.9604	4.5	0.1302	0.9545
14	0.1288	0.9581	14.5	0.1328	0.9537
20	0.1218	0.9574			

TABLE 3

Kinetics of Decomposition of $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ In Air at diff. Temp.

1 — 150 °C			2 — 200 °C			3 — 225 °C		
Time (min)	$1 - W/W_0$	$(W/W_0)^{1/3}$	Time (min.)	$1 - W/W_0$	$(W/W_0)^{1/3}$	Time (min.)	$1 - W/W_0$	$(W/W_0)^{1/3}$
1.25	0.0074	0.9974	1.5	0.0264	0.9913	0.75	0.0183	0.9938
1.75	0.0151	0.9969	4.5	0.0838	0.9712	2	0.0525	0.9822
3.5	0.0282	0.9906	7.5	0.1360	0.9526	6	0.1569	0.9348
7	0.0622	0.9788	10.5	0.1883	0.9328	8	0.2093	0.9247
12	0.1016	0.9649	14	0.2146	0.9238	10.25	0.2618	0.9038
15	0.1278	0.9554	20	0.2193	0.9206	11.0	0.2878	0.8932
16	0.1356	0.9526	24	0.2216	0.9200	11.5	0.3130	0.8818
21	0.1435	0.9497				18	0.3402	0.8706
25	0.1487	0.9477				23	0.3455	0.8682
30	0.1514	0.9469						

4 — 250 °C			5 — 300 °C		
Time (min)	$1 - W/W_0$	$(W/W_0)^{1/3}$	Time (min)	$1 - W/W_0$	$(W/W_0)^{1/3}$
1.25	0.0525	0.9822	0.5	0.0264	0.9910
3.75	0.1092	0.9401	2.5	0.1693	0.9328
5.5	0.2407	0.9124	4.5	0.3192	0.8796
8.5	0.3455	0.8690	5.75	0.3977	0.8445
11	0.4370	0.8258	7.75	0.5024	0.7923
14	0.4449	0.8219	8.25	0.5285	0.7766
20	0.8471	0.8208	10	0.5417	0.7711
			13	0.5547	0.7637

TABLE 4

Kinetics of Decomposition of $\text{Ca}(\text{COO})_2$ in Air at different temp.

1.150 °C			2.200 °C		
Time (min)	$1 - W/W_0$	$(W/W_0)^{1/3}$	Time (min)	$1 - W/W_0$	$(W/W_0)^{1/3}$
3.5	0.0176	0.9940	3	0.0211	0.9951
9	0.0344	0.9883	7	0.0507	0.9828
11.5	0.0400	0.9870	9	0.0678	0.9768
12.25	0.0448	0.9869	10.25	0.0779	0.9744
14	0.0481	0.9847	11	0.0846	0.9729
17	0.0514	0.9826	16	0.1018	0.9649
25	0.0542	0.9815	17	0.1120	0.9590
40	0.0571	0.9811	19	0.1354	0.9528
			20	0.1489	0.9477
			22.25	0.1625	0.9419
			25	0.1727	0.9389
			29	0.1794	0.9385

3 - 225 °C			4 - 250 °C			5 - 300 °C		
Time (min)	$1 - W/W_0$	$(W/W_0)^{1/3}$	Time (min)	$1 - W/W_0$	$(W/W_0)^{1/3}$	Time (min)	$1 - W/W_0$	$(W/W_0)^{1/3}$
2	0.0169	0.9945	2	0.0339	0.9886	1	0.0451	0.9931
3	0.0304	0.990	4	0.0678	0.9768	3	0.1121	0.9711
4.25	0.0406	0.9963	5	0.0879	0.9699	5.5	0.1682	0.9401
5	0.0507	0.9828	7	0.1151	0.9601	9.55	0.2878	0.8932
6	0.0609	0.9792	11	0.1828	0.9350	13	0.3724	0.8563
7	0.0710	0.9757	165	0.2504	0.9093	14.75	0.4165	0.8358
8	0.0834	0.9717	18	0.2974	0.9016	20	0.4264	0.8510
8.5	0.0914	0.9685	20	0.8843	0.8945			
10	0.1048	0.9638	21	0.2878	0.8942			
11	0.1184	0.9590	0.8917					
13	0.1388	0.9515						
14.5	0.1580	0.9439						
18	0.1727	0.9389						
20	0.1896	0.9330						
23	0.2066	0.9266						
28	0.2274	0.9179						
30	0.2335	0.9152						
35	0.2368	0.9139						

TABLE 5

The rate constant and Activation Energy for the Decomp. of :

1. CaCO_3
2. $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$
3. $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in Air

Temp. (C)	K (min ⁻¹)	Log K	Ea (K cal/mol ⁻¹)
1— CaCO_3			
200	7.7×10^{-4}	$\bar{4}.8565$	
250	2.5×10^{-3}	$\bar{3}.3979$	
300	5×10^{-5}	$\bar{3}.6990$	10.4
400	1.75×10^{-2}	$\bar{2}.2340$	
2— $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$			
150	9.1×10^{-4}	$\bar{4}.9590$	
200	2.5×10^{-3}	$\bar{3}.3979$	
225	4×10^{-3}	$\bar{3}.6021$	8.75
250	5.7×10^{-3}	$\bar{3}.7559$	
300	1×10^{-2}	$\bar{2}.0000$	
3— $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$			
150	2.85×10^{-3}	$\bar{4}.4548$	
200	6.36×10^{-3}	$\bar{3}.8035$	
225	1×10^{-2}	$\bar{2}.0000$	7.83
250	1.57×10^{-2}	$\bar{2}.1959$	
300	2.75×10^{-2}	$\bar{2}.4393$	

DISCUSSION

The results of the thermo gravimetric analysis are given in table (1). It seems in the whole range of temperature that (1) CaCO_3 still decomposes with rising temperature and there is no sharp rise, (II) Calcium oxalate decomposes and gives sharp rise starting from about 200 to 300 C° where the solid nearly decomposes giving the oxide, (III) Calcium Nitrate starts decomposition very early than the Carbonate and Oxalate where the decomposition commences at about 150 to 230 C°. To illustrate the exact temperature at which the decomposition is very effective, results of differential thermogravimetric analysis is shown in Fig. (2). The Decomposition of $\text{Ca}(\text{NO}_3)_2$ occurs at 185°C, calcium Oxalate occurs at 253°C and Calcium carbonate has a broad peak, having a large range of temperature.

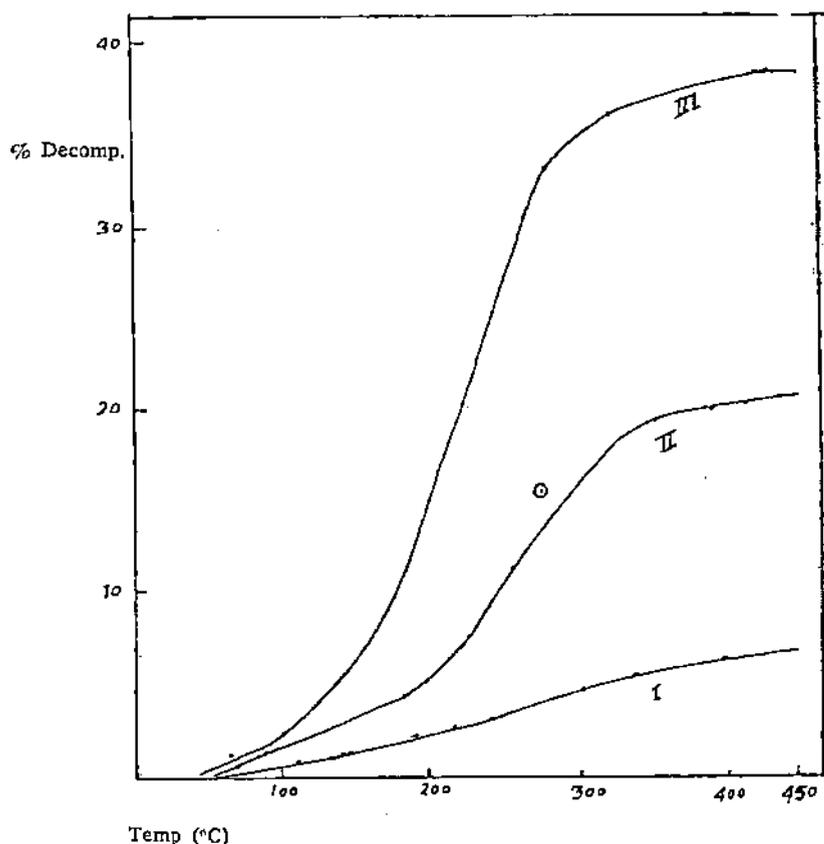


Fig. (1)

Thermogravimetric analysis of I. CaCO_3 . II $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$
 III $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$

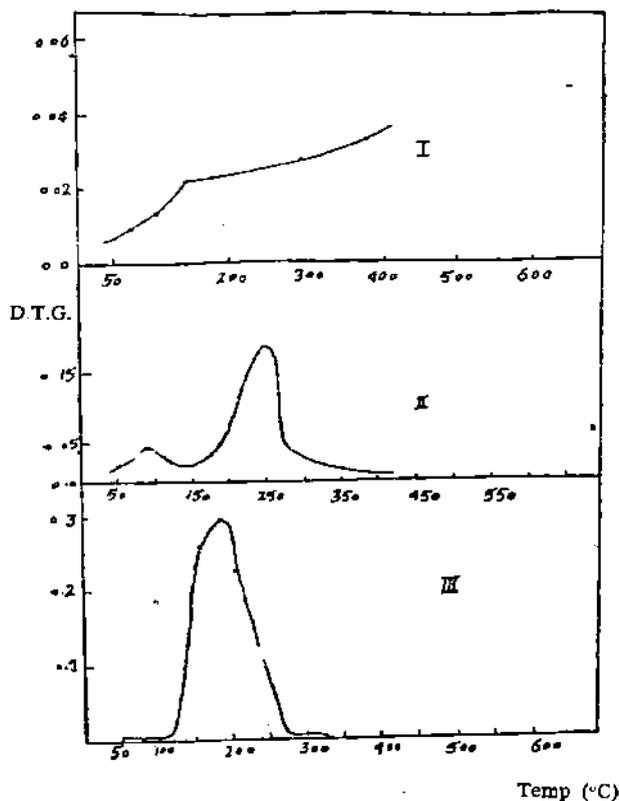


Fig. (2)

D.T.G. analysis of I. CaCO_3 II. $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$
 III $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$

The Kinetics of the isothermal decomposition of Calcium salts have been studied in air over an approximate range of temperature 150 - 400 °C. The results are presented in tables (2,3,4) and are graphically represented in Fig. (3, 4 and 5) as $(1-W/W_0)$ against time where w_0 is the weight of volatile products present in one gram of the sample before decomp. and $W = W_0 - \text{loss}$ in one gram of the sample after time t .

The early region of decomposition is convex to the time axis especially at higher temperature, it is difficult to ascribe this feature to the inevitable time lag in heating the solid or to acceleration in nuclei formation. Beyond this region the rate of decomposition is continuously decreased and gradually approaching zero value.

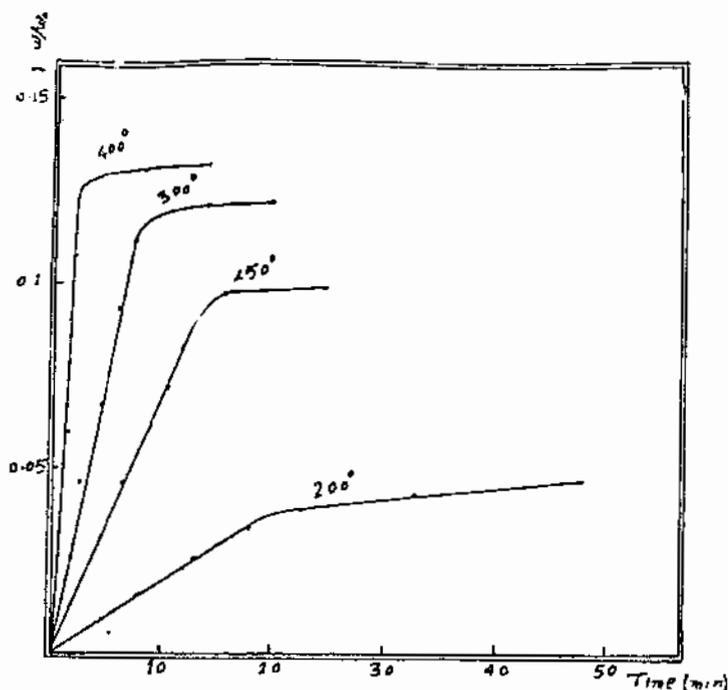


Fig. (3)

1 — (W/W_0) against t for CaCO_3 decomp.

The mechanism of decomposition obeys Mampelles theory (5). By plotting the relationship $(W/W_0)^{1/3}$ against time for the carbonate Oxalate and nitrate as shown in Fig. (6, 7, 8), we obtain straight lines with slope equal to the rate constant of the decomposition. According to Arrhenius equation, by plotting the value of $\log_{10}(K)$ against $1/T$ for the salts straight lines are obtained as in Fig. (9). The activation energy can be calculated from the slopes of obtained straight lines.

The Calculated activation energy are 7.83, 8.75 and 10.4 K Cal mole⁻¹ for Nitrate, Oxalate and Carbonate respectively.

It was found that E_a for nitrates Oxalates Carbonates. On studying the structure of these salts it is clear that the nitrates are resistant to decomposition than the Oxalate and the Carbonate, due to the unshared electron resonating between the bonds between Nitrogen and Oxygen in Nitrate group. It must be noted that the Calcium carbonate is easily decomposed than Oxalate and Nitrate, but experiments find the reverse direction. This may be due to the water of Crystallization which seems to play an important role in the decomposition. Dell and Weller(6) suggest that chemisorbed water catalyses the surface migration of ions.

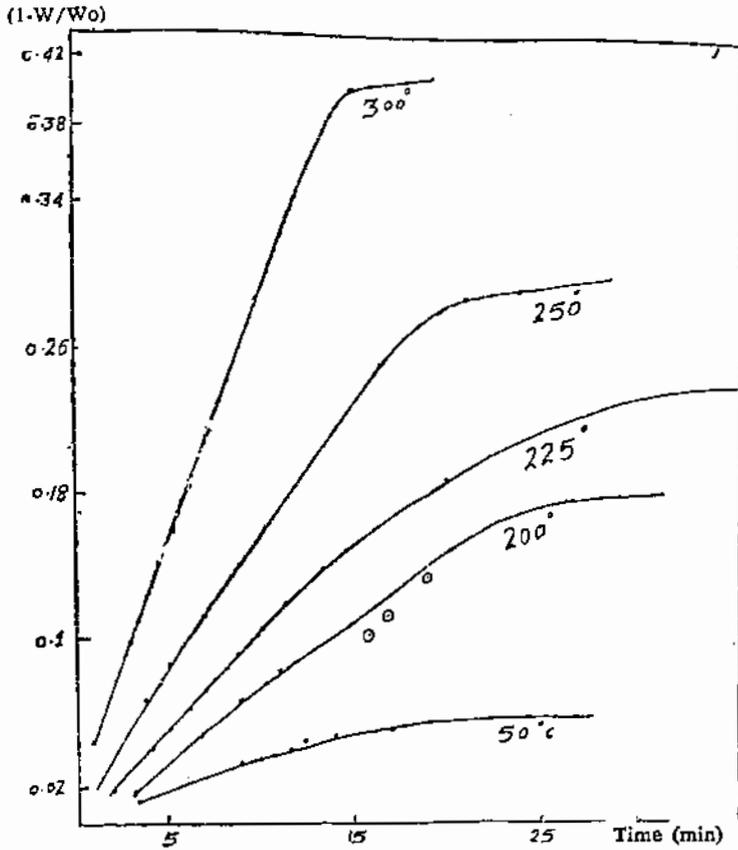


Fig. (4) $1 - (W/W_0)$ against t for $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$ decomp.

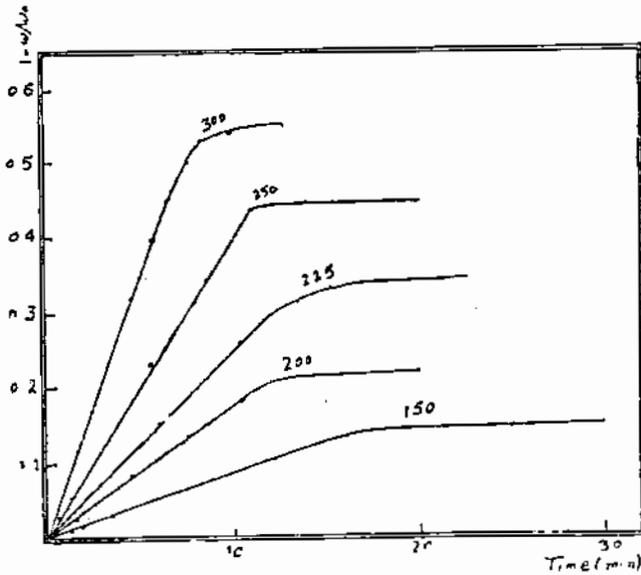


Fig. (5) $1 - W/W_0$ against t for $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ decomp.

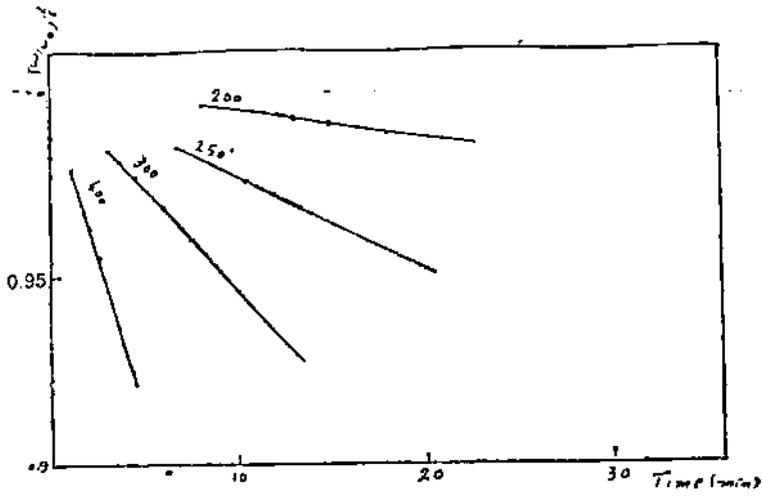


Fig. (6)
 $(W/W_0)^{1/3}$ against t for CaCO_3 decomp.

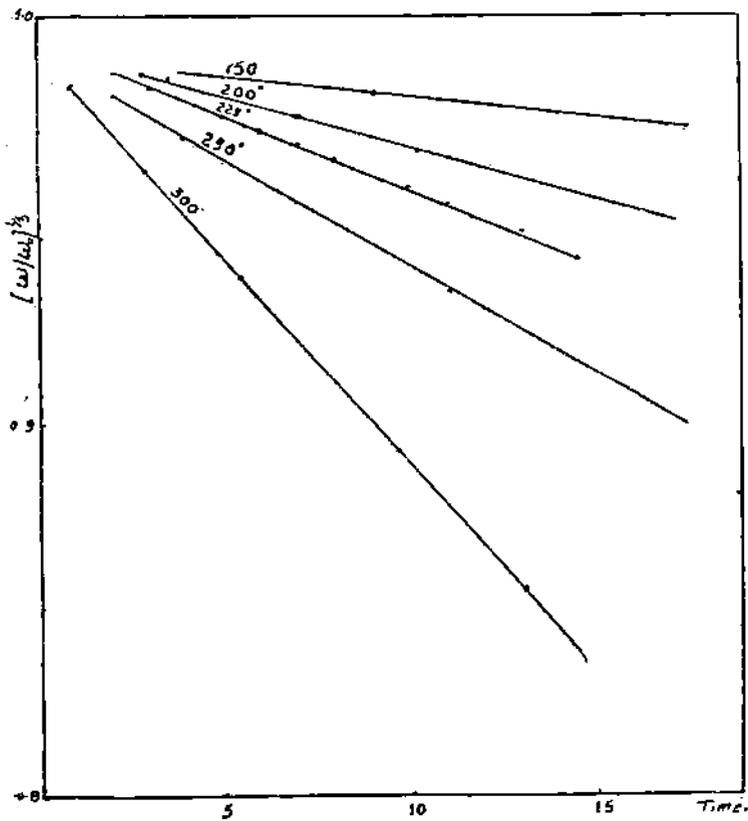


Fig. (7)
 $(W/W_0)^{1/3}$ against t for $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$ decomp.

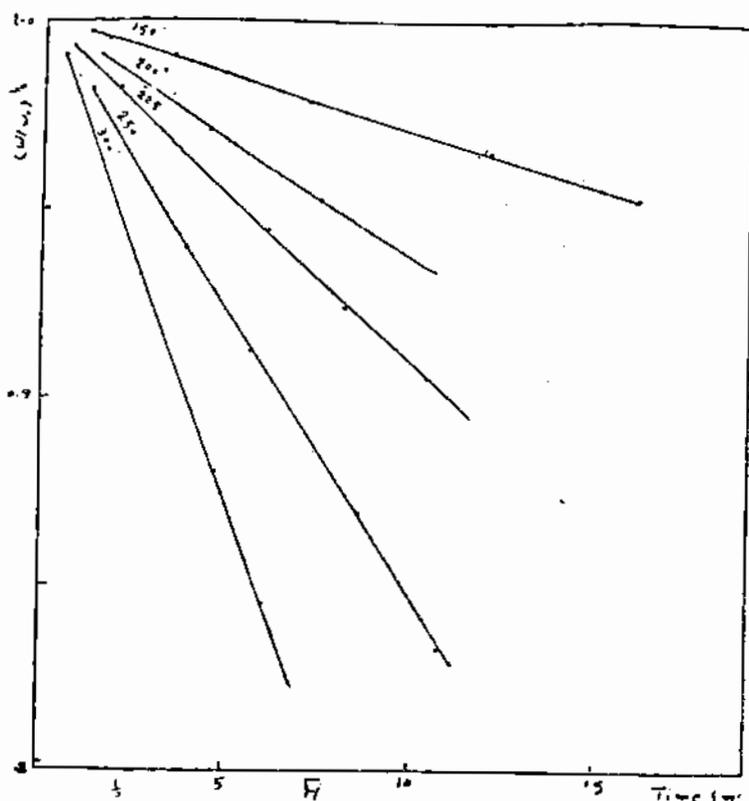


Fig. (8)

$(W/W_0)^{1/3}$ against t for $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ decomp.

The observed values of E_a may therefore be attributed to the fact nitrates contain $3\text{H}_2\text{O}$, the Oxalates contain H_2O and Carbonates have no mols of water.

The role of water as a catalyst involves the detachment of Calcium ions to form a Hydroxylated compound which is able to diffuse over the surface. When a suitable site for attachment is formed the Calcium compound is dehydrated and the water molecule can form a new mobile Calcium compound.

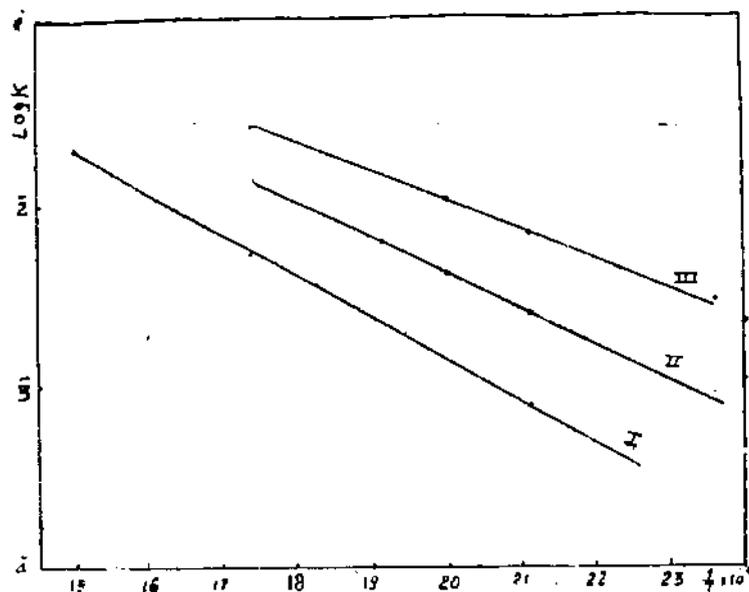


Fig. (9)

Arrhenius plot for the decomp. of I. CaCO_3 II. $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$
III. $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$

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