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Comparative Tharmal Energies of Manganese and Iron Soaps (Myristate and Stearate) By Thermogravimetric Analysis

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Abstract

Comparative studies of thermogravimetric analysis of manganese andiron soaps (myristate and stearate) have been usedto determine the rate of reaction kinetics of reaction and energy of activation by using the various equations Freeman Carroll's, Coat-Redern's and horowitz-Metzer's.

Thermogravimetric analysis of these soaps carried out by 780 series Stanton's Redford's (U.K) in the static air medium at constant heating 10° per minute and maintaining similar conditions throughout the investigations. The result shows that the decomposition reaction for manganese and iron transition metal soaps (myristate and stearate) are found to be kinetically zero order and the value for the energy of activation decomposition of manganese and iron soaps lies in the range 7.67 to 38.18 k.cal / mole activation energy increases with increasing the chain length.

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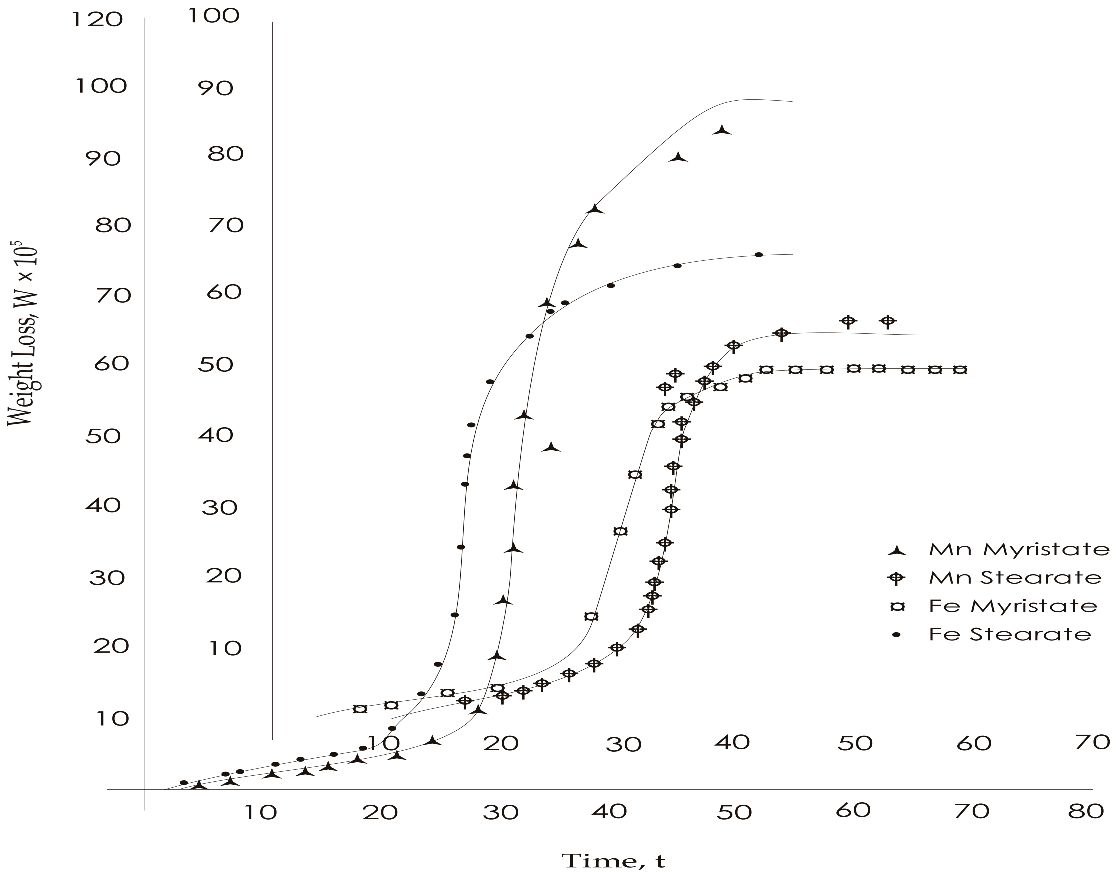
Keywords: TGA, isothermally, physical chemical, transition metals, decomposition, kinetically, activation energy, Myriston, stearon, chain length

Introduction

The study of transition metal soaps is becoming progressively useful in technical and as well as academic field. These transition metal soaps are insoluble in non polar solvent but it fairly soluble in organic (nonpolar) solvent or solvent mixture solution and have relatively high metal content which fand them useful in industries as well as is in academic field. The utility of metal soaps mainly depend on their physical state, stability, chemical reactivity and Solubility in various non-polar solvent or solvent mixtures. The physico-chemical characteristics and structure of metal soaps can be maintained up to an extent by the method and condition of their preparation. The heavy metal soaps have valuable application in technological and academic and other important Role in many diversified area like as driers, thickener, paints, catalysts, lubricants, wetting agent, plastic, cosmetics, ink, stabilizer etc. by several workers'*. TGA measure the amount of weight change of material i.e Manganese myristate and iron stearate either as a function of increasing temperature of isothermally or as a function of time by maintaining similar condition throughout the investigation and thermogram of manganese and iron soaps present in figure 1.

FIG 3.1 : Thermograms of Manganese and Iron Soaps



Method and Materials

All chemical were used of BDH /AR grade. Potassium myristate and stearate were prepared by refluxing Equivalent amount of corresponding fatty acids (myristate and stearate) and aqueous solution of potassium hydroxide for 6-8 Hours. Manganese and iron soaps were prepared by direct metathesis of corresponding potassium soap (myristate and stearate) with slight excess of Manganese chloride and ferric chloride respectively. The precipitated Soaps washed many times with acetone and distilled water. Theprepared soap dried in an air oven at 50°-60°. The final drying of precipitated soaps were carried out under the reduced pressure, finally the soaps were purified by recrystallization with Benzene methanol mixture. The purity of the soaps was confirmed by determining their melting point and absence of hydroxide group in the soaps were confirmed by studying their infrared absorption spectrum. Thethermogravimetric analysis of Manganese and iron soaps were carried out by 780 series-Stanton (U K) in static air medium at constant heating rate 10° per minute in nitrogen atmosphere and maintaining similar condition throughout the investigations.

Aim of study

The present work deals with comparative TGA measurement of the manganese and iron (myristate and stearate) soaps in solid state has been initiated with a view to obtain the value of energy of activation and order of the decomposition reaction of manganese and iron soaps.

Table – 1

THERMOGRAVIMETRIC ANALYSIS OF MANGANESE MYRISTATE

S. No.	Time, t (minute)	Temperature, T (A)	Weight of the soap decomposed, w × 10^3 (g)	dw/dt.10^6	w_r.10^3
1.	5.0	321	0.000	--	0.8874
2.	7.8	359	0.110	1.4102	0.8764
3.	9.8	364	0.0220	2.2449	0.8654
4.	11.7	390	0.0352	3.0085	0.8522
5.	13.2	415	0.0502	3.8030	0.8372
6.	15.4	427	0.0609	3.9545	0.8265
7.	17.6	450	0.0681	3.9261	0.8183

8.	21.4	480	0.0753	3.5189	0.8121
9.	25.2	525	0.0852	3.3809	0.8022
10.	27.2	540	0.1002	3.6838	0.7872
11.	28.9	555	0.1560	5.3979	0.7314
12.	29.5	568	0.2007	6.8034	0.6867
13.	30.2	575	0.2715	8.9900	0.6159
14.	30.9	582	0.3510	11.3592	0.5364
15.	31.6	589	0.4462	14.1202	0.4412
16.	32.3	596	0.5547	17.1734	0.3327
17.	33.4	605	0.6848	20.5029	0.2026
18.	34.8	620	0.7720	22.1839	0.1154
19.	39.3	650	0.8235	20.9542	0.0639
20.	42.9	710	0.8590	20.0233	0.0284
21.	45.1	735	0.8659	19.1995	0.0215
22.	48.4	760	0.8874	18.3347	0.0000

Table – 2

THERMOGRAVIMETRIC ANALYSIS OF MANGANESE STEARATE

S. No.	Time, t (minute)	Temperature, T (A)	Weight of the soap decomposed, $w \times 10^3$ (g)	$dw/dt.10^6$	$w_r.10^3$
1.	4	313	0.00	--	0.5580
2.	18.0	453	0.0237	1.3166	0.5343
3.	21.5	489	0.0320	1.4883	0.5260
4.	23.9	508	0.0418	1.7489	2.5162
5.	26.0	533	0.0523	2.0115	0.5057
6.	27.4	547	0.0680	2.4817	0.4900
7.	28.0	554	0.0825	2.9464	0.4755
8.	28.5	558	0.1048	2.6772	0.4532
9.	28.8	561	0.1274	4.4236	0.4306
10.	29.1	565	0.1502	5.0572	0.4078
11.	29.5	568	0.1670	5.6610	0.3910
12.	29.9	572	0.1950	6.5218	0.3630
13.	30.2	575	0.2241	7.4205	0.3339
14.	30.6	579	0.2580	8.4314	0.3000
15.	30.9	582	0.3072	9.9417	0.2508
16.	31.3	586	0.3282	10.4222	0.2318
17.	31.6	589	0.3685	11.6614	0.1895
18.	32.0	593	0.3945	12.3281	0.1635
19.	32.8	597	0.4270	13.0183	0.1310
20.	33.7	605	0.4510	13.3828	0.1070
21.	34.5	618	0.4710	13.6522	0.0870
22.	35.6	627	0.4755	13.3567	0.0825
23.	38.0	653	0.4838	12.7316	0.0742
24.	39.0	663	0.4980	12.7692	0.0600
25.	41.2	678	0.5150	12.5000	0.0430
26.	42.5	695	0.5166	12.1553	0.0414
27.	44.9	713	0.5290	11.7817	0.0290
28.	46.0	743	0.5436	11.8174	0.0144
29.	48.8	761	0.5528	11.3279	0.0052
30.	50.8	798	0.5580	10.9843	0.0000

Table – 3

THERMOGRAVIMETRIC ANALYSIS OF IRON (III) MYRISTATE

S. No.	Time, t (minute)	Temperature, T (A)	Weight of the soap decomposed, $w \times 10^3$ (g)	$dw/dt.10^6$	$w_r.10^3$
1.	4.0	323	0.0000	--	0.5221
2.	6.6	360	0.0134	2.0303	0.5087
3.	9.3	410	0.0220	2.3656	0.5001
4.	12.0	450	0.0344	2.8666	0.4877
5.	14.5	490	0.0454	3.1310	0.4767
6.	17.3	550	0.1478	8.5434	0.3743
7.	20.0	570	0.2840	14.2000	0.2381
8.	22.8	610	0.3550	15.5701	0.1671

9.	25.8	650	0.4558	17.6666	0.0663
10.	28.0	690	0.4730	16.8923	0.0491
11.	30.6	730	0.4795	15.6700	0.0426
12.	33.8	770	0.4920	14.5562	0.0301
13.	36.6	810	0.5050	14.3442	0.0171
14.	38.6	850	0.5058	13.1036	0.0141
15.	41.3	890	0.5090	12.3244	0.0131
16.	44.0	930	0.5120	11.6364	0.0101
17.	46.6	970	0.5175	11.1052	0.0046
18.	49.3	1010	0.5180	10.5071	0.0041
19.	52.8	1050	0.5190	9.8295	0.0031
20.	54.6	1090	0.5200	9.5238	0.0021
21.	57.5	1130	0.5221	9.0800	.00000

Table – 4

THERMOGRAVIMETRIC ANALYSIS OF IRON (III) STEARATE

S. No.	Time, t (minute)	Temperature, T (A)	Weight of the soap decomposed, w × 10^3 (g)	Dw/dt.10^6	$w_r.10^3$
1.	0.0	323	0.0000	--	0.7410
2.	4.0	339	0.0126	3.1500	0.7284
3.	8.8	361	0.0321	3.6477	0.7089
4.	9.5	378	0.0438	4.6105	0.6972
5.	13.2	415	0.0498	4.7720	0.6912
6.	16.3	432	0.0528	3.2392	0.6882
7.	18.5	460	0.0617	3.3351	0.6793
8.	20.4	470	0.0690	3.3823	0.6720
9.	21.2	485	0.0720	3.3962	0.6690
10.	23.1	510	0.0940	4.0392	0.6470
11.	25.8	538	0.1420	5.5038	0.5990
12.	27.3	548	0.1820	6.6666	0.5590
13.	27.7	550	0.2410	8.7003	0.5000
14.	28.0	555	0.3545	12.6607	0.3865
15.	28.4	558	0.4270	15.0352	0.3140
16.	29.0	565	0.4770	16.4482	0.2640
17.	29.4	567	0.5280	17.9591	0.2130
18.	30.5	578	0.5828	19.1081	0.1582
19.	31.5	589	0.6600	20.9523	0.0810
20.	32.8	602	0.6868	20.9390	0.0542
21.	33.6	609	0.6950	20.6845	0.0460
22.	36.5	640	0.7140	20.3013	0.0270
23.	42.5	690	0.7220	16.9880	0.0190
24.	51.0	785	0.7410	14.5294	0.0000

The weight of final Residue metal oxides are in agreement with theoretically calculated weight of manganese oxide and iron oxide from the molecular formula of the corresponding soaps. Thermal decomposition may be expressed as

$(RCOO)_2M \longrightarrow RCOR + MO \text{ or } M_2O_3 + CO_2$
Ketone Metal oxide Carbon Dioxide

Where R is $-C_{13}H_{27}$, and $-C_{17}H_{35}$ for myristate and stearate, respectively and M is manganese and iron metal.

The result of thermal decomposition of manganese and iron soaps have been explained in terms of various equations Freeman Carroll rate equation for thermal decomposition for various metal soaps may be expressed as

$$\frac{\Delta[\log(d\omega\omega/dt)}{\Delta\log\omega_r} = -\frac{E}{2.303R} \times \frac{\Delta[1/T]}{\Delta(\log\omega_r)} + n$$

Where,

T = Temperature on absolute scale;
n = order of decomposition reaction
E = Energy of activation;

ω_r = Difference between the total loss in weight and the loss in weight at time, t
i.e. $\omega_0 - \omega_t$; and
$(d\omega/dt)$ = Value of rate of weight loss obtained from the loss in weight vs time curves at appropriate time.

And the plots of $\frac{\Delta[\log d\omega\omega/dt}{\Delta[\log\omega_r]}$ vs. $\frac{\Delta(1/T)}{\Delta(\log\omega_r)}$ are shown in fig. 2.

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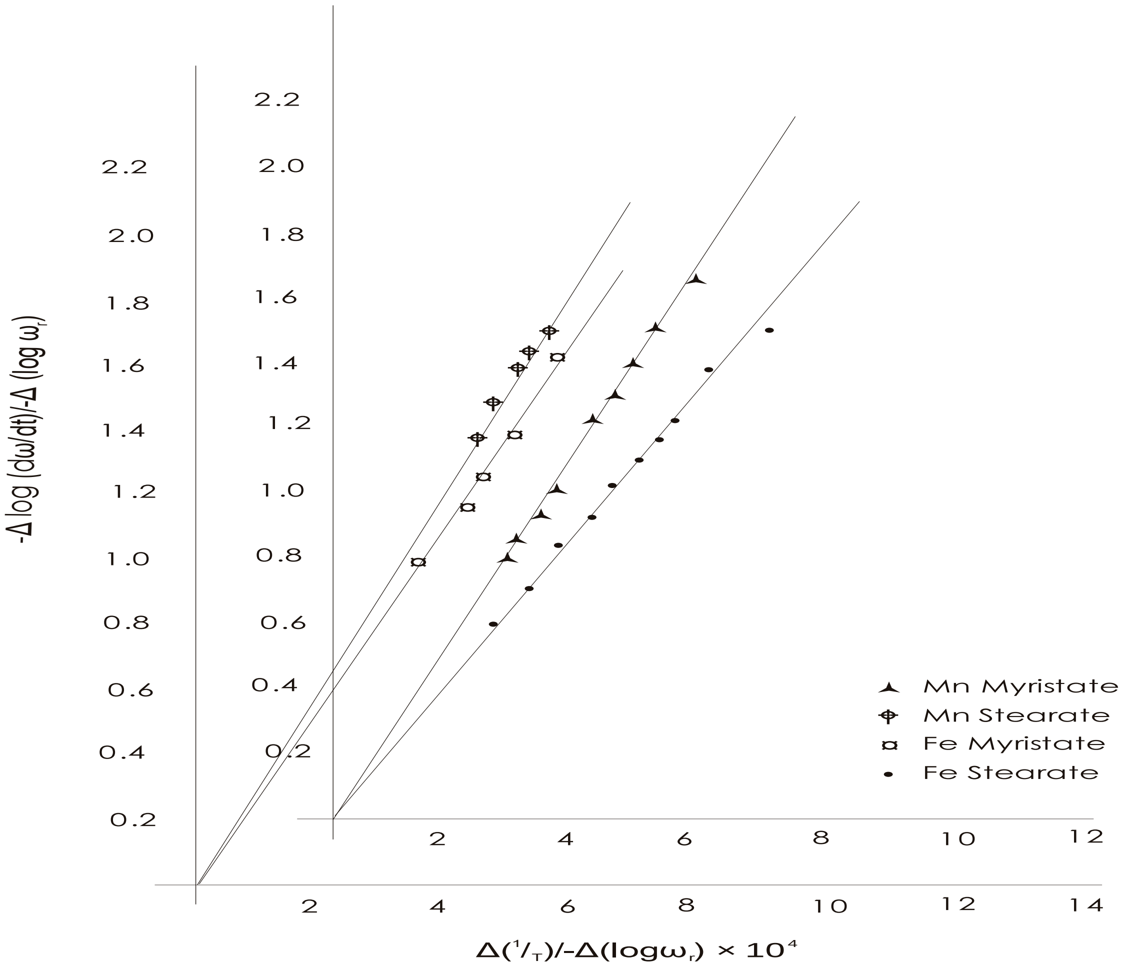
FIG 3.2 : Freeman -Carroll's type Plots



The result from Freeman Carroll's equation indicate that the thermal decomposition of these shops s ows Kinetically of zero order and the value of activation for the decomposition of manganese and iron soaps obtained from above plots lie in the range 15.1719.05 K.cal.per mole. Coats and Redfern's equation for the thermal decomposition of a compound can be expressed as:

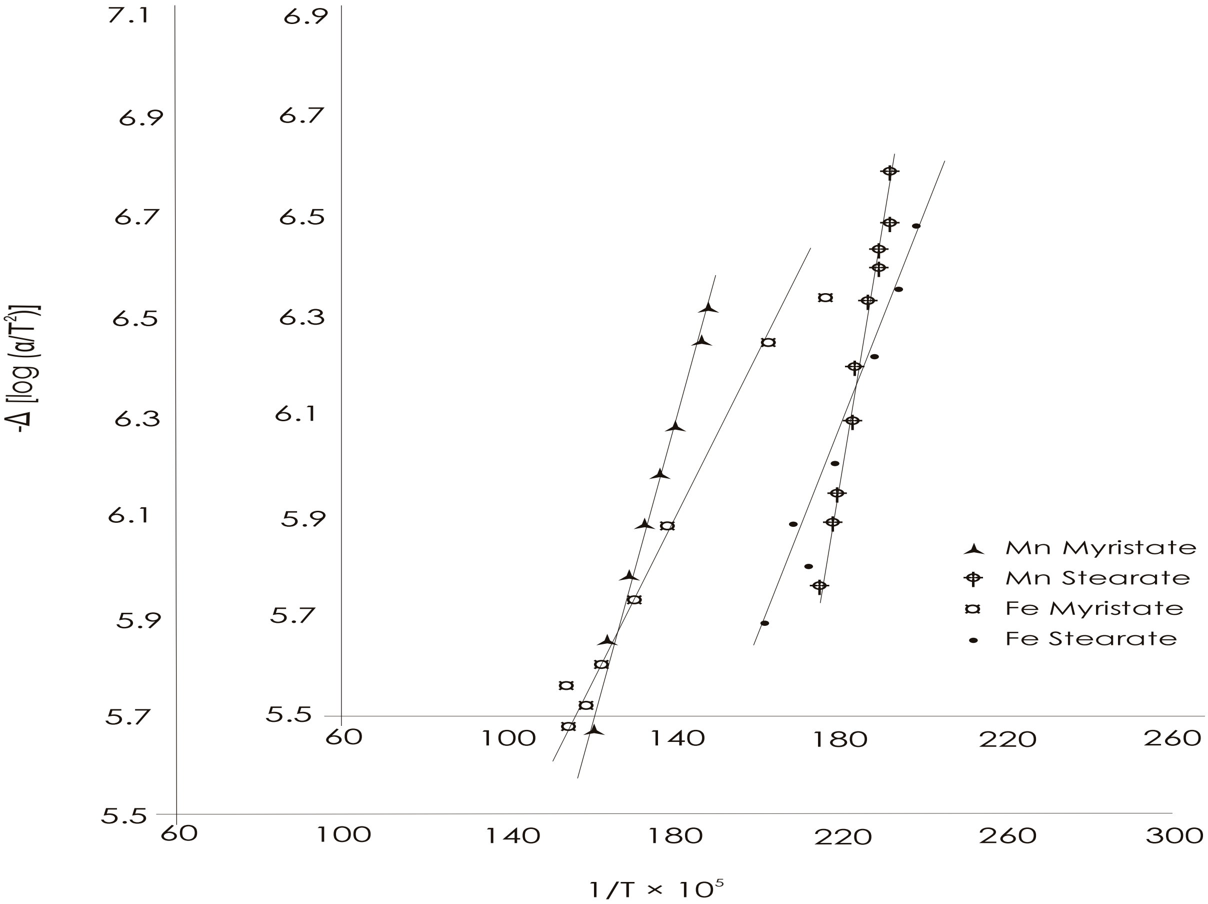
$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.303RT}$$

Where,
α = Fraction of the soap decomposed;
T = Temperature on absolute scale;
R = Gas constant;
A = Frequency factor;
a = Rate of heating in ^{O}C per minute;
E = Energy of activation; and
n = Order of reaction
The equation for zero order reaction can be written as:

$$\log\frac{\alpha}{T^2}=\log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.303RT}$$

It may be pointed out that the plots of log(a/T) against (1/T) should be a straight line with its slope equal to (-E/2.303R). The values of the energy of activation for manganese and iron soaps obtained from the plots (fig. 3) is found in the range of 17.84 7.67 K. cal. PermolIt may be pointed out that the plots of log(a/T') against (1/T) should be a straight line with its slope equal to (-E/2.303R). The values of the energy of activation for manganese and iron soaps obtained from the plots (fig. 3) is found in the range of 17.84 7.67 K. cal. mol.

FIG. 3.3. : Coats-Redfern's type plots



The value of energy of energy of activation for the thermal decomposition of manganese and Iron soaps of different fatty acids have also been calculated by using Horowitz and Metzger's equation and expressed as

$$\ln\left[\ln(1-\alpha)^{-1}\right]=\frac{E}{RT_S^2}.\theta$$

Where,

α = Fraction of the soap decomposed at time, t

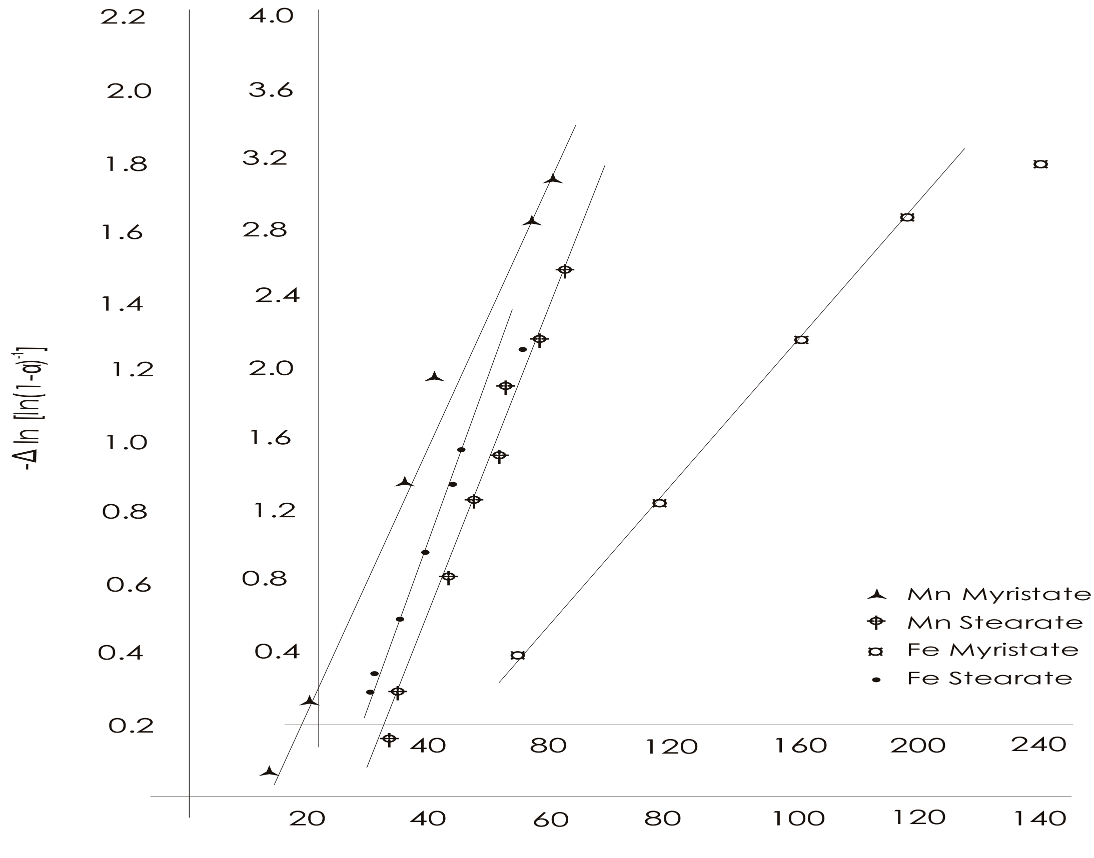
E = Energy of activation

T_S = Temperature on absolute scale at which the rate of decomposition is maximum, and

$\theta = T - T_s$

The plots of ln [ln (1 - α)$^{-1}$] against θ for manganese myristate, manganese stearate, iron myristate and iron stearate are shown in Fig. 3.4 and the value of energy of activation obtained from the slope of the curve lies in the range of 38.18 – 24.17 K. cal. Mol^{-1} (Table 5).

FIG 3.4 : Horowitz-Metzger type Plots



It is suggested that the surface of the soap molecules remain completely covered all the time by the molecules of gases product as the decomposition is fast and so the rate of the decomposition becomes constant and the process a kinetically of zero order and the comparative activation energy of manganese and iron soaps (myristate and stearate)for the process lies in the range of 38.18 7.67 K.calper mole.

Table – 5

ENERGY OF ACTIVATION (k cal. mol^{-1}) FOR THE DECOMPOSITION OF MANGANESE AND IRON SOAPS BY USING VARIOUS EQUATIONS.

S. No.	Name of the soap	Freeman and Carroll's Equation	Coats and Redfern's Equation	Horowitz and Metzger's Equation
1.	Manganese myristate	14.08	13.81	24.33
2.	Manganese stearate	15.17	17.84	25.48
3.	Iron myristate	13.05	7.67	24.17
4.	Iron stearate	10.05	9.80	38.18

Result and discussion

The value of decomposition process of metal soaps shows that initially decreases slowly because of removal or loss of water and carbon dioxide molecule and then fast due to the removal of ketone (carbonyl) and finally it is constant due to formation of oxide of manganese and iron as mention in Table 1-5.

Conclusion

it is concluded that the decomposition process of these metal soaps follows the zero order kinetic and activation energy lies in the range 38.18-7.67 k.cal per mol.

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