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Kinetics of Oxidation of Lead

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Abstract: The oxidation of lead at various temperatures has been studied by many scientists. At low temperature oxidation of lead is much faster. At lower temperature oxidation follows parabolic law and at higher temperature the linear law was found for low pressure. A reddish brown oxide is formed on the surface of metal. Three successive parabolic forms were observed during oxidation of liquid lead. Oxidation was studied for four different temperatures in range of 227^{0}C to 307°C.

Keywords: Oxidation, activation energy, parabola, anion vacancies, diffusion, intrinsic

I. INTRODUCTION

The oxidation of lead at high temperatures, especially in the molten form, has been studied widely. It has also been generally observed that at lower temperatures the oxidation is comparatively fast. Pilling and Bedworth [1] first performed a systematic study of the oxidation of lead wire (99.85 % pure) and found that at 300^{0}C the increase in mass followed a parabolic law. Smooth reddish brown oxide is found on surface of metal. Jenkins [2] with electron diffraction determined the structure of the oxide formed on molten lead. The oxide was found to be of the orthorhombic form of PbO known as Litharge. This observation was later confirmed by a more detailed study on the oxidation of molten lead between 500-700°C by Bircumshaw and Preston [3] they concluded that the early part of the process is consistent with the parabolic law, the constant in the equation being proportional to the first power of pressure. Gruhl[4] confirmed the validity of the parabolic law and farther observed that the oxide formed at low temperature (373°-480^{0}C) was tetragonal, while at comparatively high temperatures (570^0 - 600°C), the orthorhombic form was stable. At intermediate temperatures the presence of $Pb_3O_4$was suspected. During the oxidation of liquid lead three successive parabolic forms were observed by Weber and Baldwin [5] in contrast to a single one, throughout the oxidation of solid lead. The time of transition from one to the next becomes shorter with increasing temperature. The first parabola had a lower rate constant than the second, the constant of the third being slightly smaller than the first. The oxide was red or yellow PbO depending on whether the temperature was below or above 486°C, Their data on the oxidation of solid lead were in agreement with those of Pilling and Bedworth. Archbold and Grace [6] also found a parabolic law for oxidation of the liquid lead but comparatively an initial slow rate.The activation energy for temperature 473^0 C and 673°C was found to be 13 kcal/mole. Van Itterbeck's studies[7] on the oxidation of 300 to 4000^0 A sputtered Pb-films at low temperatures of -75^{0}C, -20^{0}C and 23^{0}C, revealed the curve to be parabolic up to 20 minutes and was followed by a linear change.

Anderson and Tare [8] studied the oxidation of thin evaporated lead films in the temperature range of -180^{0}C to 273^{0}C and at 10^{-2} to 10^{-5} mm Hg oxygen pressure. At the higher temperatures the linear law was found for low pressures and the oxide formed was the orthorhombic variety. At the lower temperature they found a direct logarithmic law. On the basis of the electrical conductivity and e.m.f. measurements, they concluded the presence of anion vacancies in lead oxide.

II. EXPERIMENTAL

The mass changes of the sample as a function of time were measured by Bradley [8] means vacuum balance. It is made up of silicon rod. At the two ends of balance beam two hooks were fused for suspending the specimen to be oxidised on one side and the counterpoise weight on the other with silica fibre. The evaporating filament was heated by passing current from transformer controlled by auto transformer. As a substrate plate for evaporated metal films thin microscope slide cover slips circular for lead were used. Evaporating assembly was replaced by B-50 ground glass joint having thermocouple well to measure the temperature of sample plate. The argon was then evacuated till a good vacuum was obtained. The temperature of sliding furnace was increased slowly to attain the required temperature within ±1^{0}C.The temperature was determined from e.m.f. of chromellalumel thermocouple which was cemented to the furnace as near as possible to the sample plate. Prior to oxidation studies, the actual sample temperature was calibrated as function of the thermocouple temperature with a thermocouple tip placed against the plate. Then thermocouple e.m.f. was measured and the sample temperature was obtained from the calibration curve. Table gives the detail of evaporation procedure.

S.No	Material	Sources	Evaporated from	Pre-treatment of filament before charging	Pre-treatment of charge and filament before evaporation	Manner of evaporation	Film thickness obtained ^{0}A
1	Lead	Atomic energy Estt. Mumbai, India	Wire conical basket	Flashed in 10-5 mm Hg vaccum	Kept molten in vaccum for 15-16 hours with external furnance	Heated in vaccum for ¾ hours then heated further till film of required thickness was obtained	2700 to 3000

Table 1

Table gives the details of oxidation procedure. Oxidation reaction was followed by noting the displacement of beam pointer.

S.No	Metal films	Temperature range ^{0}C	Pre-treatment of film before oxidation	Zero reading of the reaction in argonat mm Hg	Oxygen pressure mm Hg
1	Lead	227-309	Heated in vacuum at the experimental temp for 2 hours	30	30

Table 2

III.RESULTS

The oxidation kinetics were studied at four different temperature in range of 227^{0}C to 309^{0}C. figure 1 shows the oxygen uptake. In f figure 2 plots of log Δm vs log t are shown by using the general relation $(\Delta m)^n = Kt$, K is a constant and n is the index whose value has to be determined from experiments. It was observed from f figure 1that the fast uptake was followed by a slower uptake of oxygen by lead films. The values of n determined from the slope of these plots are listed in table 3, which also show the time when the slower uptake reaction starts.

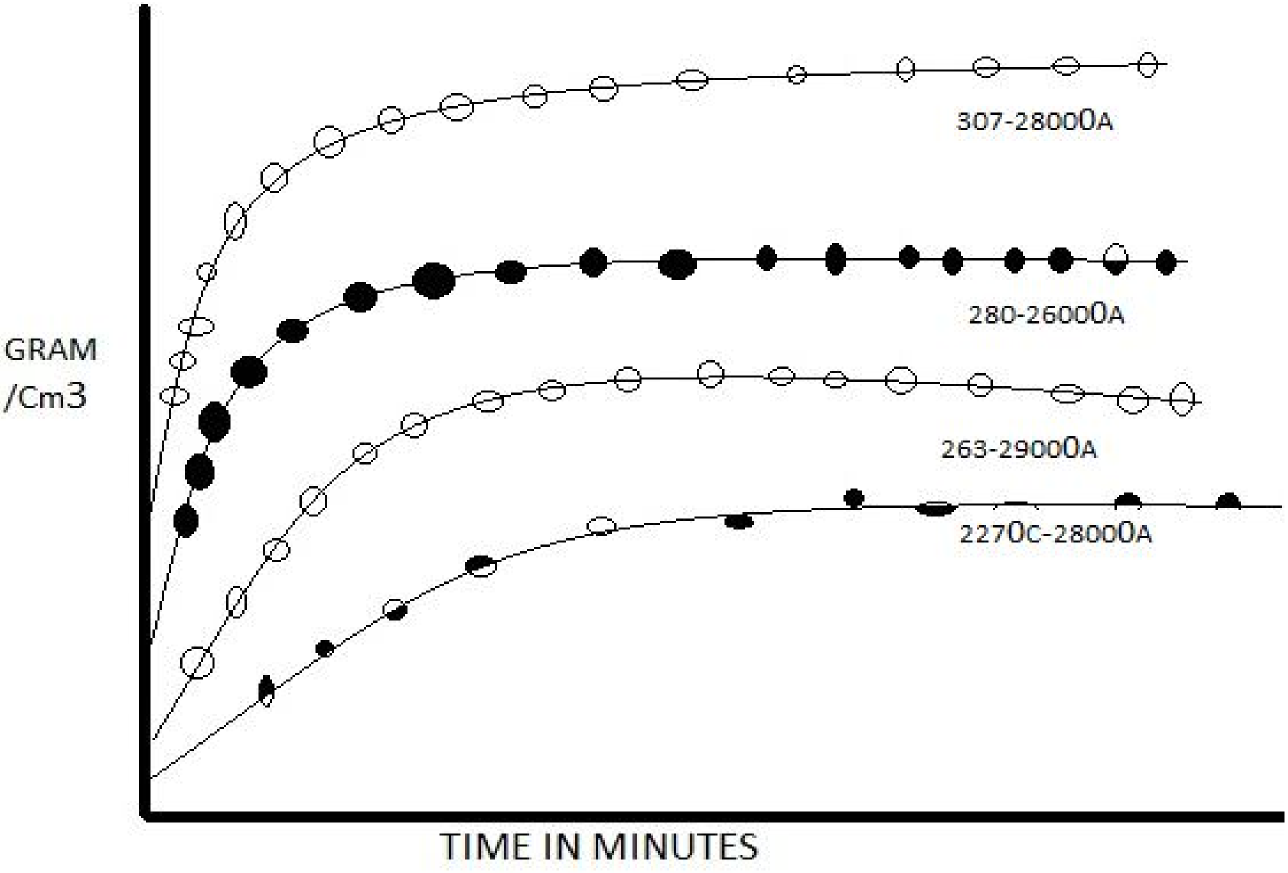

Fig- 1Kinetics of oxidation of Lead film under 30mm of Hg oxygen pressure at various temp

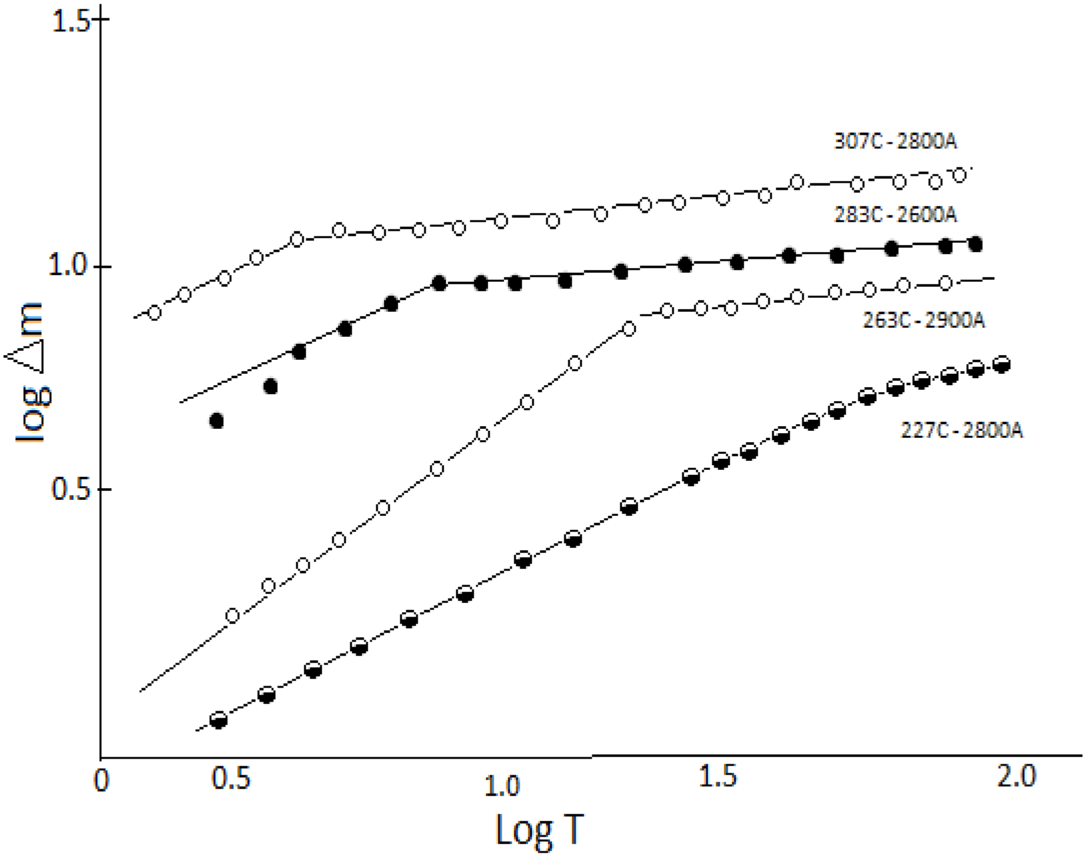

Fig-2 Kinetics of oxidation of Lead film under 30mm of Hg oxygen pressure at various temp

Temperature ^{0} C	n from slope of initial uptake	Break occurred at	
		µg/cm	T minutes
227	2	9.1	120.0
263	2	9.0	20.0
283	2	10.0	8.5
307	2	11.9	4.0

Table-3

The values of n for the initial oxygen uptake are 2.This indicates that the initial observations can be fitted in well with the parabolic growth law of oxidation. It is also observed from table-3 that the changeover from the fast to the slow uptake occurred earlier (although at slightly higher oxygen uptakes) at higher temperatures. Figure 3 shows the parabolic plots of the initial uptake at these temperatures. The reaction rates constant was determined from these plots and are given in table-4.

Using the values from table-4, the Arrhenius plot was made as shown in figure3. The adherence of all the points near the straight line indicates that the oxidation behaviour is the same throughout the temperature range studied. The activation energy obtained from the slope of the Arrhenius plot was found to be 23.96 Kilocalorie /mole.

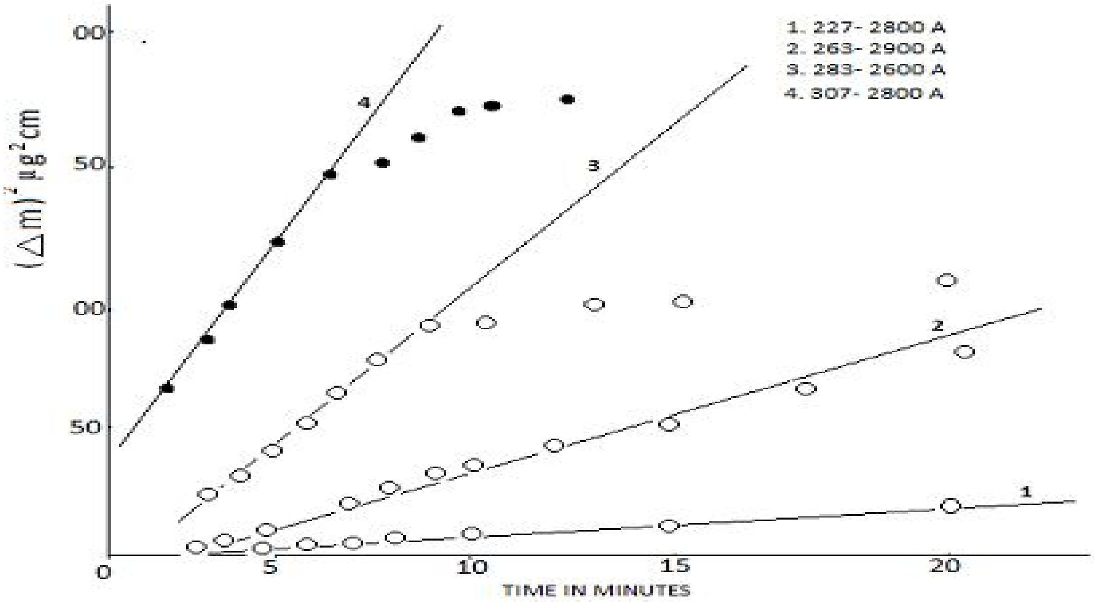

Fig-3oxidation of Lead film under 30mm of Hg oxygen pressure at various temp parabolic rate law

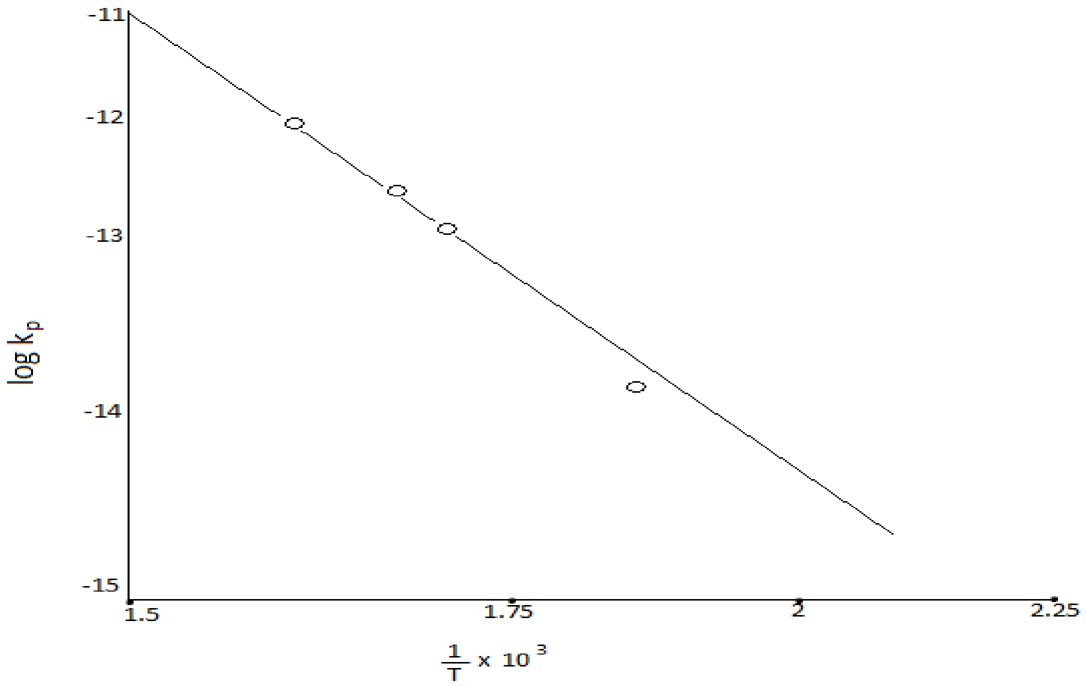

Fig-4 Temperature dependence of rate constant for oxidation of lead films by oxygen

Reaction rate constant from parabolic plots

Temperature^{0}C	Kp g^2cm^4/sec	Log kp	1/TX 10^3
227	1.38 X 10^{-14}	-13.8601	2.000
263	1.00 X 10^{-13}	-13.0000	1.866
283	2.20 X 10^{-13}	-12.6676	1.799
307	5.70 X 10^{-13}	-12.2441	1.724

Table-4

the value of 22.4 ca1/mole previously found for the activation energy of diffusion of oxygen In PbO, that for Pb in PbO is 66 kcal/mole [9] Some experiments with thinner lead films showed that the total oxygen uptake, when the lead film was completely oxidised, amounted to the formula PbO, the film being yellow in colour.

The parabolic rate constant Kp may be expressed as

Kp = 4.37 X 10^{-4} in the temperature range 227^0-307°C

The significant feature of the parabolic time dependence of the mass gain is indicative of a diffusion process being a rate controlling factor. The diffusion coefficients can be calculated from experimentally

Observed reaction rate constant by using the Mott-Gurneyequation

$Kp= 4D_1\rho^2\ \rho0^2$

Where D_1 is the diffusion coefficient for particles of type 1, ρ is the density of the oxide and ρ_0 is the mass

fraction of oxygen in the oxide. Anion diffusion wasassumed to predominate for calculations using this equation.

The calculated diffusion coefficients are shown in table5

Temperature ^{0}C	D_1cm^2/sec
227	9.37 X 10^{-15}
263	6.74 X 10^{-14}
283	1.48 X 10^{-13}
307	3.84 X 10^{-13}

Table- 5

These diffusion coefficients are plotted in figure 5 as a function of the reciprocal of the absolute temperature and expressed as

D = 3 ,2 X 10^{-4}exp (-22,960/T) cm ^{2} /sec

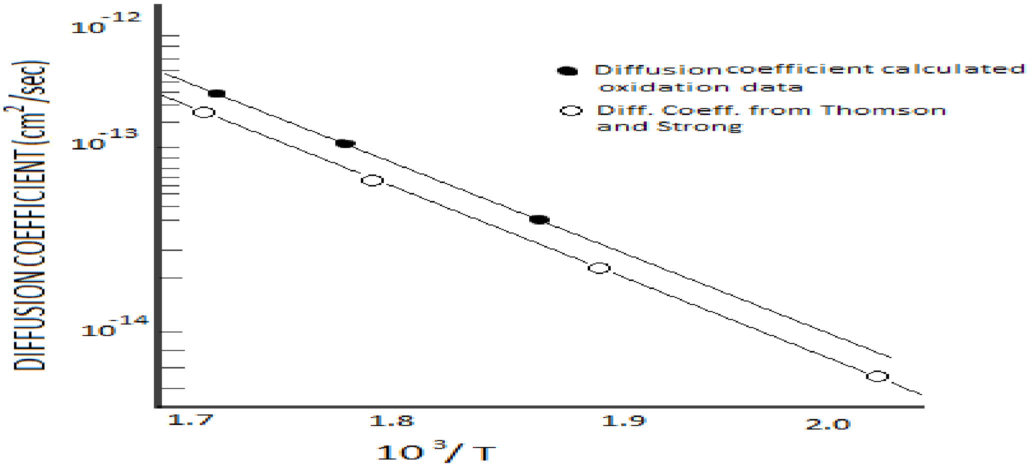

Fig-5 Diffusion coefficient calculated from oxidation state and Diffusion coefficient from Thomson and Strong

The lower carve in figure 5shows the oxygen ion diffusion coefficients obtained by extrapolating the data on the diffusion of oxygen in lead monoxide given by Thomson and Strong to lower temperature(i .e . 227^0-307°C), The temperature dependence of the diffusion coefficients is represented by

D = 5.39 X 10^{-5}exp (-22,400/RT) cm^2/sec

As observed from the above, the activation energies for the oxidation and oxygen ion diffusion are nearly the same and the values of the calculated and the experimentally found

diffusion coefficients come to

D (calculated) =9.886 x 10^{-15}/sec.

D (experimental)=8.121 X 10^{-15} cm^2/sec. at 227^C.

As mentioned, the fast uptake was followed by slower uptake of oxygen by lead films. After shifting the origin to the point where the slow oxygen uptake starts, the oxidation data again fitted well Inparabolic plots shown in figure 6 , The rate constants determined from the slope of the straight portion of (Δm vs t plots are listed in table-6)

Temprature^{0}C	Kp g^2/cm^4/sec
263	1.42 X 10^{-15}
283	3.92 X 10^{-15}
307	7.92 X 10^{-15}

Table-6

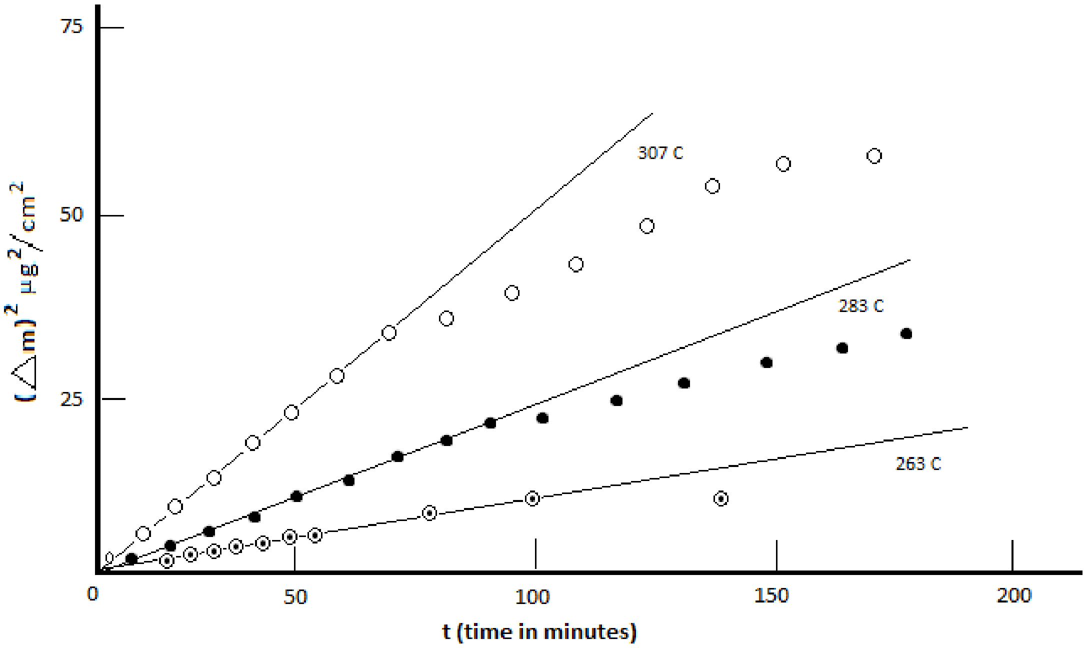

Fig-6 Parabolic plot for oxidation of lead film after first break second parabola

F ig .7 shows the Arrhenius plot, which gives the activation energy of 25.64 Kcal/mole which is again close to 22.4 Kcal/miole reported for the activation energy of diffusion of oxygen in lead monoxide as given above. And now the rate constant is
Kp = 3.73 X l^{-5}exp (-26,640/RT)

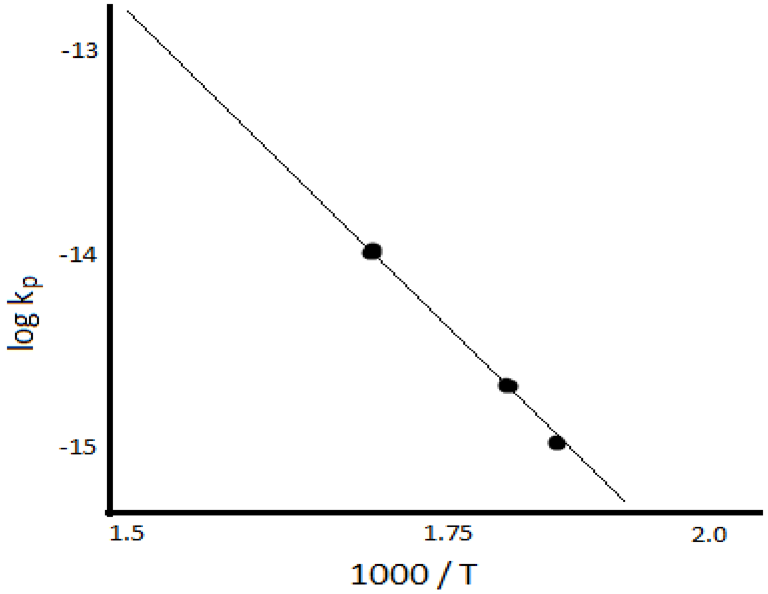

Fig- 7 Temperature dependence of rate constant for oxidation of Lead film

This has a lower frequency factor than that reported for the first parabola. It is noticed from figure 6 that again there are deviations from the parabolic law which have occurred as mentioned in table-7

Temperature ^{0} C	Deviation occurred from fig 6	
	T	M
283	80	4.19
307	76	6.09

Table-7

Again shifting to the point of break, the uptake again appear to be parabolic (figure8)

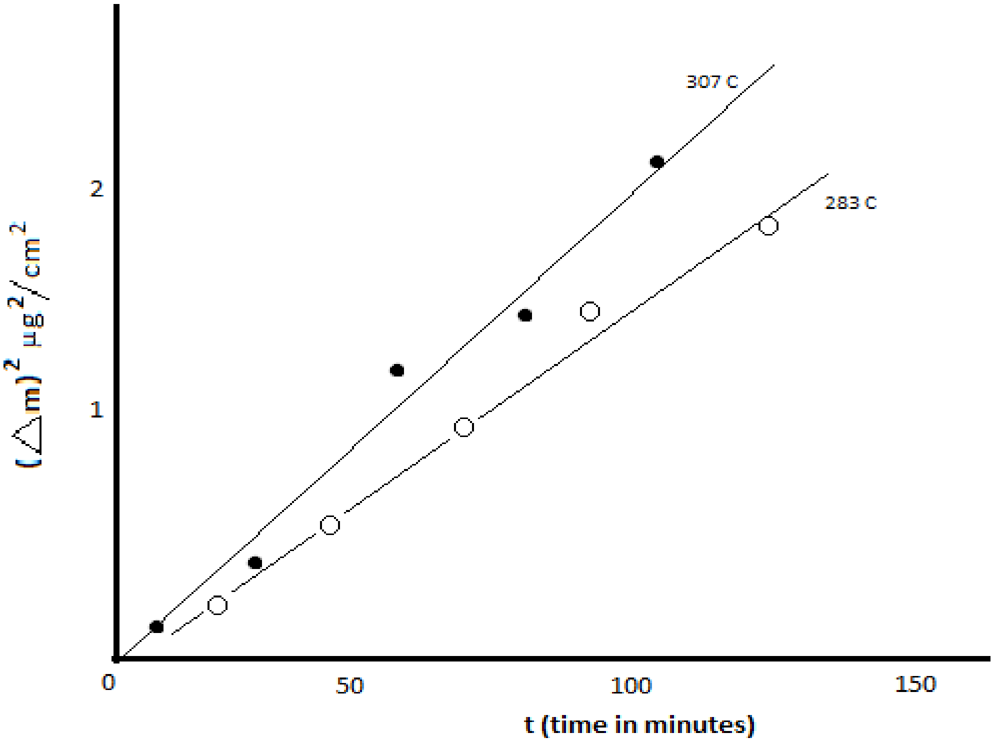

Fig-8 Parabolic plot for oxidation of Lead after second break third parabola

IV. DISCUSSION

Lead was found to oxidise according to the parabolic rate law in the temperature range (227^0-307°C), this is indicative of the process being controlled by the diffusion of ion or ion vacancies through the oxide as described by Wagnor [10]. We believe that the oxidation of lead films takes place by the diffusion of anion vacancies, which are generated at the metal-oxide interface and move towards the oxide-oxygen interface or due to the diffusion of oxygen ions towards metal-oxide interface. Of these we consider that the migration of anion vacancies to be more likely. This is mainly based on the data on the diffusion of Pb and 0 in PbO by Lindner and Terem[11]. The possibility of cations migration being the rate determining step in the oxidation of lead above 200°C has also been considered. It was concluded that as the rate of oxidation is about 1000 times that which could be accounted for by the rate of diffusion of lead in lead oxide, the diffusion of cations cannot be the rate controlling process. It is fairly unusual to observe anion diffusion in solid oxides occurring more rapidly than cation diffusion. However, it should be noted that in contrast to most of the oxides studied to date (i .e. Cu_2O, ZnOetc) , the ionic radii of the Pb^{+2} and 0^{-2} ions are identical (l.3 A) in contrast to the usual situation being a cation with a much smaller ionic radius. Therefore, the consideration of mass and size alone would indicate that the diffusion of oxygen could be faster than that of lead in lead oxide.

Thomson and Strong [9] determined the rate of diffusion of oxygen in lead monoxide in the temperature range 497^0-647^0. They calculated the rate constant of oxidation of lead at this temperature range assuming that the rate determining step is the diffusion of oxygen in lead monoxide. The agreement of the rate constant between the observed and calculated values confirmed this assumption. Hence, they concluded that at these temperatures oxidation occurs by oxygen diffusion. It seems reasonable to accept the conclusion valid at such lower temperature as used in the present investigation. By comparing the data for diffusion of Pb in PbO (Lindner and Terem) and 0 in PbO (Thomson and Strong), it could be said that only at very high temperatures i.e. above 727°C is the process likely to be dominated by the diffusion of cations. At temperatures below 727°C the diffusion of oxygen appears to be much faster than the diffusion of lead. Lindner and Terem's concluded that the cation diffusion cannot be the rate determining process, obviously suggests that even at lower temperatures the diffusion of oxygen could be faster than that of lead. Since the activation energies for anion and cation diffusion are quite different (2.4 Kcal. end 66 Kcal.

respectively) and the activation energy of 23.95 Kcal was found from experimental observations, the oxidation of lead does appear to be controlled by anion diffusion. Due to the formation of the first few monolayers by probably an entirely different mechanism, subsequent adsorption takes place on an oxide layer which is growing on the metal surface. The oxide formed is lead monoxide which, if stoichiometric, would contain an equal numer of lead and oxygen ions in a divalent state. It has been reported that orthorhombic lead monoxide is an n-type semiconductor, which suggests that the dominant mode of

non-stoichiometry is the presence of anion vacancies with the equilibrium.

PbO $\rightarrow O_2 + 2e + 0$ + Pb^{2+} □

Where 0 represents□ an anion vacancy.

The oxidation of lead film can be described as a diffusion controlled process, and the similarities in the activation energies for oxygen ion diffusion and oxidation suggests that the transport processes are related. The conductivity measurements on lead monoxide indicate that the non-stoichiometry corresponds to oxygen vacancies and it is expected that the oxidation process is also related to this type of defect. Oxygen ion diffusion in PbO takes place via a vacancy mechanism. The temperature dependence of intrinsic self-diffusion is determined by the sun of the energies required for vacancy formation and motion, Both the magnitude of the preexponential term and activation energy for oxygen ion diffusion were indicative of extrinsic behaviour, so that only the energy for mobility U should appear in the diffusion equation

D_O^{2-} = D°2- exp(-U/HT)

The vacancy concentration was fixed by impurities. The temperature dependence of the vacancy diffusion is determined only by the energy for mobility,

D_0□ = $D°_0$□xp(-U/HT)

From these relations, it is clear that the activation energies for oxygen ion diffusion in lead oxide and oxidation of lead should be the same, within the experimental error this is the case and it is concluded that both processes occur via oxygen vacancy diffusion. An estimate of the vacancy concentration or fraction of vacant lattice sites (0) , fixed by impurities in the PbO can be made by virtue of the relation between the oxygen12ion and oxygen vacancy diffusivities[12]

D_O^{2-} = (0□) D_0□

where the oxygen ion concentration (0^{2-}) is taken as unity. Assuming as before that the activation energies are equivalent, the vacancy concentration, or fraction, is given by

(0) = 5.39X10^{5}□3.20X10^{-4} = 1.69X10^{-1}

This is not an unreasonable value. The two sets of diffusion data plotted in figure 5 would differ by exactly this factor over the entire temperature interval if the activation energies were identical.

V. CONCLUSIONS

In conclusion, it may be stated that the oxidation of lead is controlled by anion diffusion. The low value of the activation energy and the comparison of the diffusion data indicates that diffusion proceeds by a vacancy mechanism rather than by motion of interstitial oxygen ions. It was found that the progress of oxidation of lead films with time at 263^0, 233^0 and 307^{0}C in 30 mm Hg oxygen pressure can be described by three different parabolic scaling constant, Weber and Baldwin[6] reported that the solid Pb obeys a single parabolic law, while liquid Pb undergoes three successive parabolic mass increase vs time laws, the first of which has a low constant relative to the later two parabolic constants. They assumed the predominant Pb304 formation at the beginning of the oxidation i.e. oxidelayers in the region where the first parabolic scaling constant is valid. In the region where the second parabolic scaling constant applies (below 540°C), yellow (above 486^{0}C) or red (below 486°C) PbO could be seen in addition to small quantities of Pb_3O_4which could be excluded from the region of third parabolic scaling constant. On the other hand, Gruhl assumes a predominant PbO formation followed by Pb_3O_4 formation, which is then held responsible for the decrease in the oxidation rate. As per observations, the initially fast oxidation rate is probably due to a predominant PbO formation The slow oxidation rate constant may indicate the formation of other type of oxide. But as observed in the case of thinner lead films the total oxygen uptake at long ages when the lead film completely oxidised amounted to the formula

PbO, the colour of the film being yellow in colour. Anderson and Tare reported that the oxidation of thin evaporated lead films in the temperature range (-182°C to 27 formed the orthorhombic lead monoxide (yellow PbO).

VI. ACKNOWLEDGMENT

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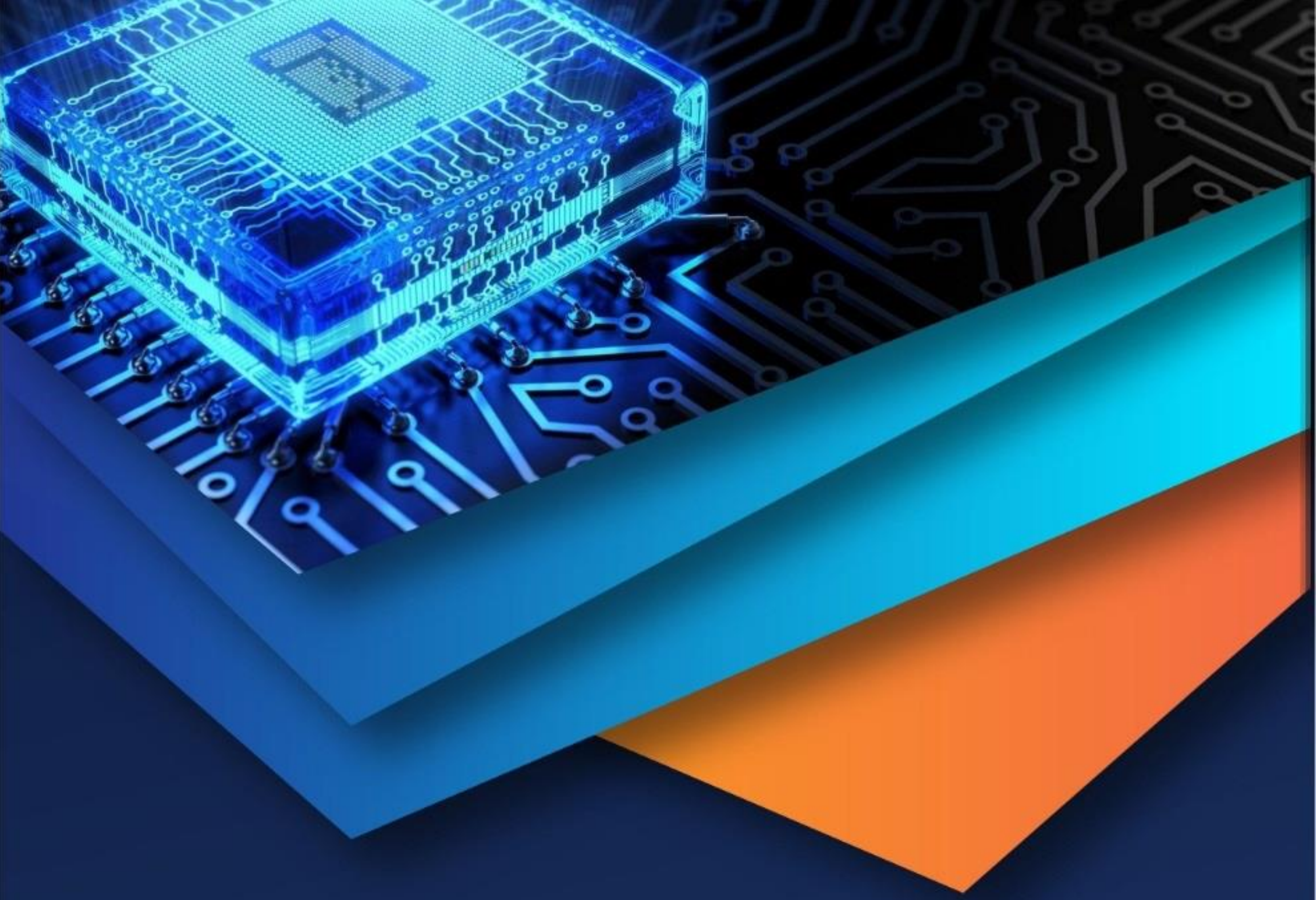

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