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Kinetics of Oxidation of Bismuth

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Abstract: Various oxide of Bismuth exist and out of these Bi_2O_3 is being studied in details. It exist in two crystalline form along with two cubical forms. Kinetics of oxidation was studied at different temperature. Kinetics measurement gives the value of activation energy 28Kcal/mol. The observed conductivity is a combinstion of electronic hole and ionic conductivities. The contribution due to the ions and electrons nsay be ascertained from an analysis of the transport number data.

Keywords: Oxidation, activation energy, specific conductivity, Transference Number, Rate Constant

I. INTRODUCTION

Existing X-ray and electron diffraction data leave many points about the oxidation of Bismuth compounds unexplained. The following have been mentioned in the literature: BiO, Bi_2O_3,Bi_2O_4,Bi_2O_5. Among these Bi_2O_3 has been studied in detail and there is little information on the structure of the others. Bi_2O_3 exists in several crystalline modifications, some of which can be prepared at room temperature only in presence of foreign ions. The following three forms have been reported α Bi_2O_3 monoclinic β Bi_2O_3 tetragonal and γ Bi_2O_3body centred cubic (a_o= 10.24A^o) The α form has been reported to be stable from room temperature to 700°C,after which the β form is stable.[1-4] No region of stability forγ Bi_2O_3 has been found from room temperature to its melting point. Thus β and γ forms are only metastable at room temperature.

Besides these, two cubic forms of bismuth oxide have been reported[5] in oxidised films of bismuth with a = 5.65 A^o and a = 7.02 A^o . The tetragonal (β form) was proposed as a super-structure of first cubic form.

Gat tow and Schuetze [6] obtained the β form of stoichiometric Bi_2O_3 by quenching the liquid bismuth oxide. On the other hand that condensed from the gas phase had an oxygen content as high as $Bi_2O_{3.5}$ X-ray and chemical evidence also indicated a continuous incorporation of 0 between the limit 3 to 3.5 . Oxygen is lost from $Bi_2O_{3.5}$ on heating, but under specified conditions a new phase γ $Bi_2O_{3.32}$ appears, which on annealing converts to α Bi_2O_3. Hund [7] reported that the pure β Bi_2O_3has an ideally occupied lattice and vacancies in the anion lattice.

A study of the yellowish bismuth oxide obtained by oxidation in air for 5 to 25 hours at 450 to 470°C of bismuth films vacuum deposited on NaCl crystals showed it to be oxygen deficient Bi_2O_{3-x} (x = 0.2 to 0.2) with a tetragonal structure with a simple relation to the cubic Bi_2O_3.

$$atet \approx acub/\sqrt{2}$$

$$ctet \approx 2\ acub$$

To elucidate the behaviour of oxidation of a metal, the nature of the defect structure of the oxide formed is most important which can be elucidated from the electrical conductivity measurements.

Mansfleld [9] studied the electrical conductivity and thermoelectric power dE/dT of bismuth oxide in pellet form over a temperature range of 160°C to 680°C end for variations of oxygen pressures from 10^{-4} cm Hg to 76 cm Hg, The results above 340°C and at atmospheric pressure are well represented by the formulae

$\sigma = A_1 \exp.(-\alpha/2T)$ and below 340°C by

$\sigma = A_2 \exp.(-\alpha/T)$ in which the values of the constants A_1, A_2 and α are very similar for two different specimens. The variation of σ with oxygen pressure at temperature above 500°C and for pressures down to 1 mm Hg obeyed the formulae, $\sigma = K(Po_2)^{3/4}$ He concluded that the current is mainly carried by holes,

Hauffe et al.[10] observed a transition from p-type -2 to n-type behaviour at oxygen pressure of about 10^{-2} mm Hg. In the region where the current carriers were electrons, the conductivity varied with 1/5 power of oxygen pressure. Fidryra [11] studied the nature of conductivity and the sign of the current carriers in Bi_2O_3 . Measurements of the Hall effect and Faraday effect showed that Bi_2O_3 is an electronic semiconductor, if the conductivity contains an ionic component, it is less than 0.2 % of the electronic component. The sign of the thermal EMF at temperatures below 230°C to 260°C corresponds to p type conductivity and at higher temperature to n type conductivity.

Konovalov et al. [12] measured the electrical conductivity of Bi_2O_3 between 200° and 700°C. The Bi_2O_3used was the orthorhombic modification only. For measurements in vascuo the following equation was found to apply

$$\log\sigma + 1.9076 = 4923/T$$

where σ is the specific conductivity and T the absolute temperature. This relation did not hold for measurements in air where for large values of 1/T the curve bends towards 1/T axis.

All these above conclusions were drawn from results obtained on polycrystalline pressed pellets. It is well known that the properties of thin films often differ appreciably from those in the bulk state. To correlate the oxidation behaviour with the defect structure of the oxide, it may be very useful to have data on the electrical properties of the thin films of oxides under more or less the same conditions as existing during studies on the oxidation kinetics.

On the oxidation kinetics of bismuth very few data are available in the literature, Voitovich [13] reported the oxidation of bismuth along with other metals in the 20° to 600°C temperature range. It was observed that the formation of thin layer of scale as a rule occurs in two stages and is described by logarithmic type equations.

Breuer [14] had studied the rate of oxidation of thin metallic vapour deposits and reported that the bismuth deposits, evaporated at room temperature, oxidised by a logarithmic law in the range 20° to 150°C in atmospheric air.

In what follows, we have studied the kinetics of oxidation of thin films of bismuth in oxygen (30 mm of Hg) and in the temperature range 175° to 250°C. The electrical conductivity of measurement of the oxide film and EMF of the metal-oxide cell were measured and the results were discussed to elucidate the nature of the defect structure of the oxide formed and the mechanism of the oxidation.

II. EXPERIMENTAL

A. Experimental Work Is Explained As

The evaporating filament was heated by passing current from a step-down transformer (230 V/10 V) controlled by a variable auto-transformer is a substrate plate for evaporated metal films thin microscope slide coverslips thickness 0.1 to 0.16 mm, circular (ca. 1.8 cm dia) for bismuth were used. This was an extremely delicate operation since the plates were extremely fragile and further they cracked easily due to sudden no uniform slight temperature variations. The temperature was deterrmined from the e.m.f. of ‘chromell alumel' thermo couple which was cemented to the furnace as near as possible to the sample plate. Prior to the oxidation studies, the actual sample temperature was calibrated as a function of the thermocouple temperature with a thermocouple tip placed against the plate. Thereafter the thermocouple e .n .f , was measured and the sample temperature vrs obtained from the calibration curve.

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	Bismuth	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	1200 to 2000

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	170-250	Heated in vacuum at the experimental temp for 2 hours	30	30

Table 2

B. Measurement of E.M.F. As a function of Temperature and Oxygen Pressure

For the determination of the transport number the following cell was set up :

$$\mathrm{Bi} \mid \mathrm{Bi_2O_3} \mid \mathrm{O_2(g)},\ \mathrm{Ag}$$

Attempts were made to measure the EMF of such cells by using thin Bi_2O_3films. However, the EMF observed was either zero or had very small value, presumably due to surface diffusion of oxygen or possibly due to the high porosity of Bi_2O_3 films.

Bi_2O_3 was therefore used in the pellet form prepared from finely ground Bi_2O_3powder by pressing in a die at 4000 lbs/(inch)^2 pressure. The pellets were then heated to 760°C in air for 16 hours and quenched. Density measurements indicated that it attained nearly 90-95 per cent of the theoretical (X-ray) density. It was polished into disks-shape, approximately 9.6 mm in diameter and 2-3 mm thick. One side of it was painted with silver paste and on the other bismuth film was deposited by vacuum evaporation. A pellet of Bi metal was similarly prepared from its powder. One face of this pellet was also polished.

The pellets of Bi and $Bi_2O_3$and silver foil with a spot welded silver leads were pressed together by means of a spring assembly. These precautions were considered sufficient to avoid gaseous diffusion of O_2 at Bi/ Bi_2O_3surface. The E.M.F. of the cell was measured with a Phillips vacuum tube voltmeter, having the measuring error less than 3% Prior to the measurements the whole system was evacuated to 10^{-6} mm Hg, and the temperature of the furnace increased to a selected value. The E.M.F. of the cell was measured at different temperatures end partial pressures of oxygen. Bi_2O_3pellets of different thicknesses also gave expected results within the limits of experimental error.

C. Conductivity. Measurements of Bi_2O_3 Films

For the resistance measurements, the Bi_2O_3films were prepared by evaporating the bismuth onto a transparent silica plate and oxidising it in a furnace in pure oxygen (ca. one atm. pressure) at 225^{0}C for several hours. It was observed that the black, lustrous film of bismuth became transparent yellowish in colour by oxidation. Two ends of the film were coated with aquadag and contact to aquadag was made by pressing with a screw assembly containing a silver foil, spot-welded to silver leads. The whole assembly was kept in a tube which could be either evacuated or in which desired gas pressure could be maintained, resistance of the sample was measured by means of R-I-E meter (Leads and Northrup, Cat. No. 5620) which could measure resistance from 1 Meg to 10^6 Meg with maximum error ±6%

Prior to the measurements the whole system was evacuated to 10^{-6} mm Hg. Then the temperature of the furnace was slowly raised to the selected temperature. After maintaining the required oxygen pressure, the resistance of the film was measured, resistance slowly changed till it acquired a constant value. Such equilibrium values were noted at different oxygen pressures and temperatures.

III.RESULTS

Kinetics of Oxidation: The kinetics of oxidation were studied at 30 mm.of oxygen pressure at 175^{0}C, 225°C, and 260°C. The oxygen uptake (Δm) by bismuth film vrs time t in minutes fig 1 The plots of $(\Delta m)^2$ vrs time fig 2 are straight lines which show that the oxidation of bismuth obeys parabolic law. After the formation of thicker oxide films, the previous straight line appears to bend down and the rate of oxidation becomes slower, apparently due to change in the mechanism. Further oxidation was not studied except for noting the total oxygen uptake after a period of several hours. The reaction constants, kp, at the different temperatures have been determined from the parabolic plots and represented in table 3

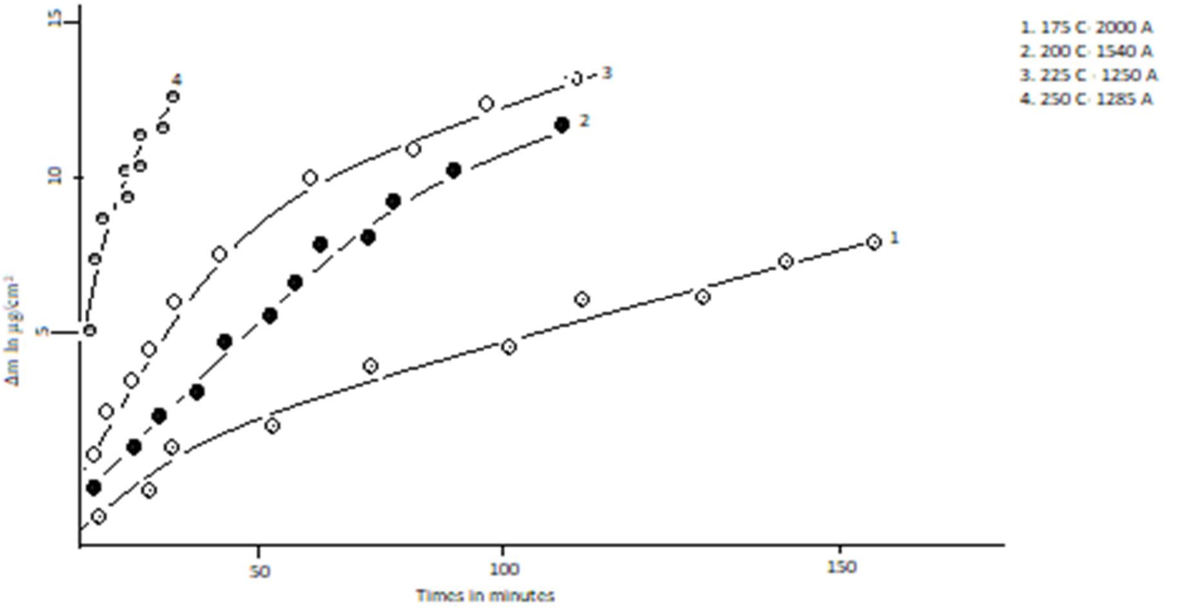

Fig-1Rate of Bismuth film oxidation in 76 mm of Hg oxygen pressure of cxygen over the temp. range 175^0- 250^{0}C

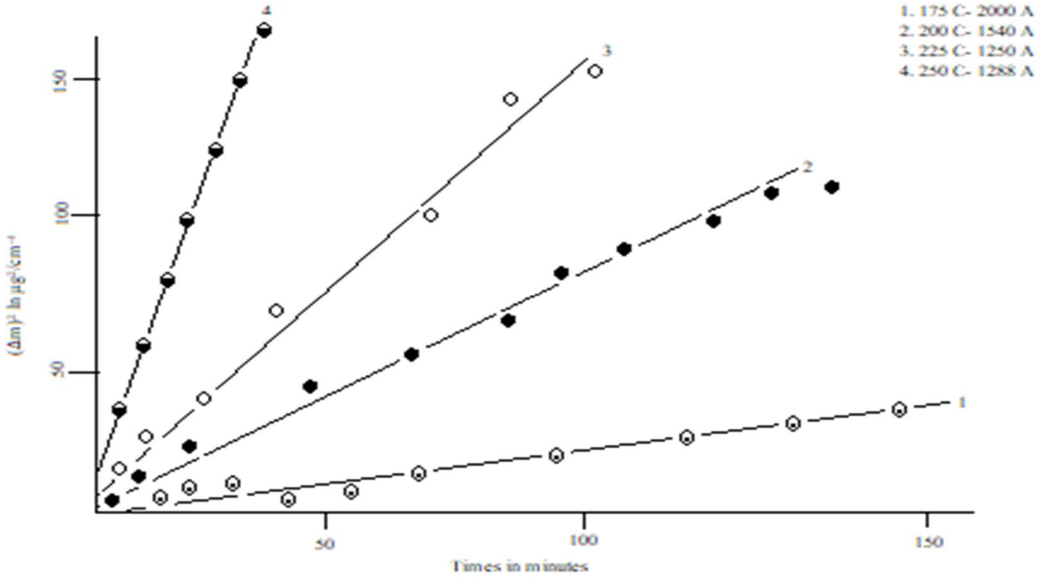

Fig-2 Oxidation of Lead of Bismuth film under 30 mm of Hg pressure in temp. range 175^0- 250^0C

Temperature ^{0}C	Kp g^2/cm^4/sec
175	1.90 X 10^{-15}
200	1.42 X 10^{-14}
225	2.33 X 10^{-14}
250	1.69 X 10^{-13}

Table-3

The activation energy ΔE for oxidation was calculated to be 28 Kcal/mole from the Arrhenius plot which is shown in f i g 2. The strict adherence to the Arrhenius relation: Kp= A exp (- ΔE/RT) throughout the temperature range studiedindicates the validity of the same mechanism throughout. From the Arrhenius plot we obtain equation for Kp

$$Kp = 8.51 \text{ X } 10^{-2} \exp^{-28000/RT}$$

A. Determination of Bi/O ratio

All the bismuth films studied weighing 300-500 μg were oxidised at 175°,200°,225° and 250°C at 30 mm Hg oxygen pressure for a prolonged period. The total amount of oxygen reacted with bismuth was calculated from the increase in mass of bismuth film attained at the final stage when no measurable change in mass was observed after more then six hours.

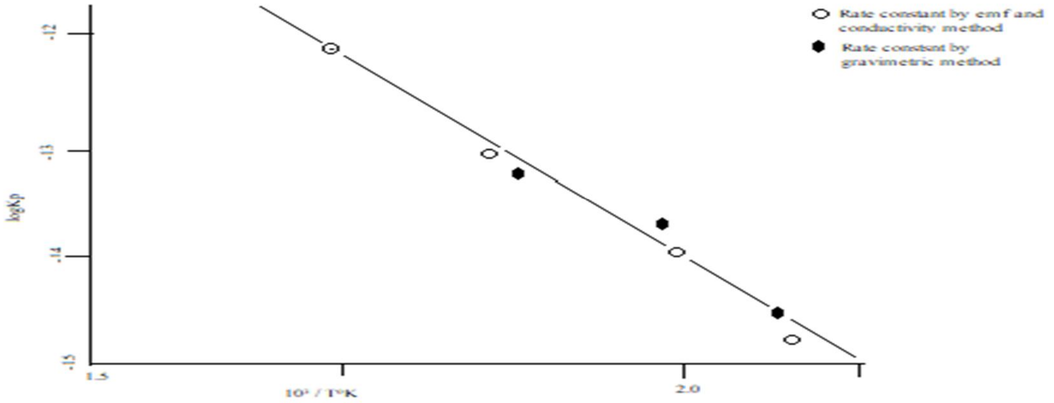

Fig-3 Temperature dependance of rate constants for oxidation of Bismuth film by oxygen

To roughly estimate the amount of oxidation of Bismuth that might have taken place during the deposition runs under the prevailing conditions, we carried out some parallel experiments with evaporated copper films. The latter was reduced with hydrogen and it was generally found that the mass loss due to this treatment corresponded to not more than 3 or 4 atomic layers of the oxides. Since the film thickness of the order of 1200-2000A^0,the corresponding correction for the value of the total oxygen uptake by the bismuth film would amount to about one per cent or less.The data are prevented in table 4. The fourth column gives the Bi/0 ratio. The average formula derived from these valutas was found to be $Bi_2O_{2.7-2.8}$ This is in agreement with the observation made by Zaryalova et al.[15] on such thin films. The changes in Bi/0 ratio with temperature and oxygen pressure were too small to be measured with the present experimental set up.

Oxygen uptake by Bismuth films at various temperature and Bi/O ratio

Temperature^{0}C	Mass of Bismuth film in µg	Total oxygen uptake in µg	Bi/O ratio	Oxide formula Bi_2O_x
175	498	51.6	0.7383	$Bi_2O_{2.70}$
	400	42.0	0.7299	$Bi_2O_{2.74}$
	374	38.7	0.7407	$Bi_2O_{2.70}$
200	425.5	46.0	0.7042	$Bi_2O_{2.34}$
	405	42.1	0.7353	$Bi_2O_{2.72}$
	383	41.1	0.7143	$Bi_2O_{2.30}$
225	337	34.4	0.7497	$Bi_2O_{2.67}$
	325	34.9	0.7133	$Bi_2O_{2.80}$
	312	33.5	0.7124	$Bi_2O_{2.80}$
250	320	33.5	0.7246	$Bi_2O_{2.76}$
	317.5	34.4	0.7143	$Bi_2O_{2.80}$

Table-4

Transference Number , Specific Conductivity and the reactlon rate Constants

The emf of the cell

$$\text{Bi} \mid \text{Bismuth Oxide} \mid 0_2\,(g)\,,\ \text{Ag}$$

was measured at various temperotures 175°,200°,225° and 250°C at 30 mm Hg oxygen pressure.The specific conductivity of the bismuth oxide pellet was also determined by measuring its resistance at these temperatures and pressure.

Considering the undergoing reaction to be $2Bi(s) + 3/2\ O_2(g) \rightarrow Bi_2O_3(s)$, the ionic transference number was calculated from the emf raeasuretnents according to the equation given by Wagner[16]

$$t_{ion} = -nEF/\Delta G$$

where F = 23,062 cal./volt, E = observed emf in volts and ΔG is the Gibba free energy change of the reaction. The value of ΔG was obtained from the standard Gibbs free energy change of the above reaction given by Coughlin[17].Since the reaction involves six equivalent of oxygen, 'n'is equal to 6.

The electron transference number te = 1- t_{ion} was also calculated for these temperatures and pressure.Ihe calculated transference numbers together with the measured emf and the specific conductivity values K are listed in table-6, ihe table 5 also shows ΔG^0 and ΔG values.

Temperature^{0}C	Emf observed in mV	Specific conductivity K(simen)	ΔG^0 Cal/mole	G^0 Cal/mole	ti_{on}	$T_e = 1- ti_{on}$
175	5 or <5	$5.90X10^{-9}$	-109000	-104700	0.009	0.99
200	25	$1.27X10^{-8}$	-107000	-102444	0.034	0.99
225	40	$2.38X10^{-8}$	-105800	-100005	0.055	0.94
250	60	$7.80X10^{-8}$	-104430	-99393	0.083	0.91

Table- 5

Calculate the reaction rate constants by using Uagner's equation

$$dn/dt = (\ ti_{on})teKAE_0 / 96500\ x$$

dn/dt is proportional to tht rate constant kp in the parabolic law of film growth, E_0 is the free energy decrease of the oxidation reaction in volts, the emf of the cell if we neglect polarization. The emf E_0 of the reection was calculated from the free energy equation $E_0 = RT/nF \ln Po_2 / Po_2'$

vrhere Po_2 is the oxygen pressure at which the oxidation reaction was carried out (30 mm Hg.) and Po_2' is the oxygen equilibrium pressure for coexistance of bismuth metal and bismuth oxide (dissociation pressure) given by

$$(Po_2')^{3/2} = e^{\Delta G/RT}$$

ΔG is the Gibbs free enrrgy of formation of Bi_2O_3, as shown in table-5

The values of Po_2' and Po are:

Temperature ^{0}C	Po_2'(atm)	Po (volts)
175	9.55×10^{-35}	0.483
200	2.88×10^{-22}	0.471
225	5.49×10^{-30}	0.459
250	1.99×10^{-28}	0.455

Table-6

dn/dt values were calculated by using the data presented in table-5 and table-6 and taking unit area and thickness of the film dn/dt and Kp are related by equation

$$dn/dt = Veg(z/M)^2\ Kp$$

where Veg is the volume of 1g equivalent of the oxide, (49.7/2 for Bi_2O_3), z is the valency of oxygen ion = 2 and M is atomic weight of oxygen = 16

The calculated dn/dt and Kp values are listed in table-7. The observed kp values from table-3 are also presented again in table-7, for comparison. The calculated Kp values from emf measurements are in good agreement with the values obtained by kinetic measurements. Taking into account that only average values of t_e and t_{ion} are taken to calculate the rate constant, the divergence between the experimentally observed and calculated value of Kp is not unexpected.

Calculated and observed Kp values

Temperature^{0}C	dn/dt	Kp(calculated) $g^2/cm^4/sec$	Kp(observed) $g^2/cm^4/sec$
175	2.651×10^{-16}	1.37×10^{-35}	1.90×10^{-35}
200	2.038×10^{-15}	1.05×10^{-14}	1.42×10^{-14}
225	2.913×10^{-35}	3.05×10^{-34}	2.33×10^{-34}
250	3.263×10^{-14}	1.68×10^{-13}	1.69×10^{-18}

Table-7

The emf of the cell was also measured in the 175^{0}C to 250^{0}C range and at 250 mtn and 760 mm Hg oxygen pressure.

The observed emf of the cell together with the transference number values are listed in table-8, Ihe ionic transference number t_{ion} are represented in fig.4 as t_{ion} vs T(^{0}C). It can be easily seen that the ionic transference number increases with temperature as well as oxygen pressure. It may be noted that the oxide layer is an overwhelming electronic conductor in the temperature and pressure range studied.

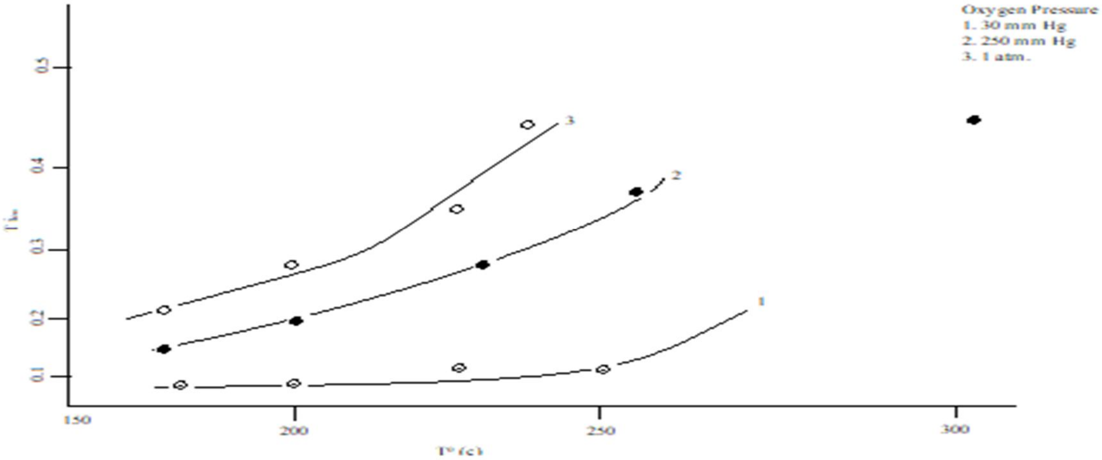

Fig-4 Temperature dependance of transference number t_{ion} 9n a growing Bi_2O_3 layer in oxygen at different oxygen level

EMF of the cell Bi| Bi_2O_3| O_2(g), Ag

Temperature^{0}C	Po_2 mm of Hg	Emf in mV	t_{ion}
175	30	5 or <5	0.009 or less
	250	30	0.039
	760	80	0.101
200	30	26	0.034
	250	70	0.091
	760	135	0.174
225	30	40	0.053
	250	125	0.166
	760	230	0.300
250	30	60	0.083
	250	200	0.269
	760	320	0.269

Table-8

Conductivity measurements: Conductivities of bismuth oxide films were measured four temperatures viz. 200^{0}C, 250°C, 280°C and 317°C and at various oxygen pressures ranging from 10^{-3} mm Hg to about 760 mm of Hg. The observed values are represented in table Nos. 9A, 9B, 9C and 9D

Conductivity measurements of Bi_2O_3 film as a function of oxygen pressure at 200^{0}C Oxide film thickness- 4000A^0 Area of the film- 0.3cm X 0.75cm

Po_2 mm of Hg	observed resistance ohms	Resistivity ohm.cm	Conductivity simon	Log σ	log Po_2
725	$3.95X10^9$	$3.95X10^5$	$2.53X10^{-6}$	-5.5966	2.8603
347	$3.90X10^9$	$3.90X10^5$	$2.56X10^{-6}$	-5.5918	2.5403
35	$3.58X10^9$	$3.58X10^5$	$2.80X10^{-6}$	-5.5533	1.5441
12	$3.50X10^9$	$3.50X10^5$	$2.86X10^{-6}$	-5.5441	1.0792
3	$3.28X10^9$	$3.28X10^5$	$3.05X10^{-6}$	-5.5153	1.0792
$5.0X10^{-1}$	$2.68X10^9$	$2.68X10^5$	$3.74X10^{-6}$	-5.4274	0.4771
$1.5X10^{-1}$	$2.20X10^9$	$2.20X10^5$	$4.54X10^{-6}$	-5.3424	-0.3010
$3.0X10^{-2}$	$1.70X10^9$	$1.70X10^5$	$5.88X10^{-6}$	-5.2305	-1.5259
$1.3X10^{-2}$	$1.61X10^9$	$1.61X10^5$	$6.21X10^{-6}$	-5.2068	-1.8861
$1.3X10^{-2}$	$1.60X10^9$	$1.60X10^5$	$6.25X10^{-6}$	-5.2041	-2.3979

Table-9A

Conductivity measurements of Bi_2O_3 film as a function of oxygen pressure at 250^0C Oxide film thickness- $4000A^0$
Area of the film- 0.3cm X 0.75cm

Po_2 mm of Hg	observed resistance ohms	Resistivity ohm.cm	Conductivity simon	Log σ	log Po_2
730	$1.90X10^{9}$	$1.90X10^{5}$	$5.26X10^{-6}$	-5.2788	2.8633
320	$1.75X10^{9}$	$1.75X10^{5}$	$5.71X10^{-6}$	-5.2431	2.5079
120	$1.80X10^{9}$	$1.80X10^{5}$	$5.56X10^{-6}$	-5.2552	2.0792
35	$1.75X10^{9}$	$1.75X10^{5}$	$5.71X10^{-6}$	-5.2432	1.5441
10	$1.60X10^{9}$	$1.60X10^{5}$	$6.25X10^{-6}$	-5.2442	1.0000
$6.5X10^{-1}$	$1.07X10^{9}$	$1.07X10^{5}$	$9.30X10^{-6}$	-5.0315	-0.1871
$7.0X10^{-2}$	$6.35X10^{8}$	$6.35X10^{4}$	$1.58X10^{-5}$	-5.8027	-1.1549
$1.25X10^{-2}$	$5.50X10^{8}$	$5.50X10^{4}$	$1.82X10^{-5}$	-5.7404	-1.9031
$4.0X10^{-3}$	$5.35X10^{8}$	$5.35X10^{4}$	$1.87X10^{-5}$	-4.7283	-2.3979

Table-9B

Conductivity measurements of Bi_2O_3 film as a function of oxygen pressure at 280^0C Oxide film thickness- $4000A^0$
Area of the film- 0.3cm X 0.75cm

Po_2 mm of Hg	observed resistance ohms	Resistivity ohm.cm	Conductivity simon	Log σ	log Po_2
730	$8.17X10^{8}$	$8.17X10^{4}$	$1.22X10^{-5}$	-4.9123	2.8633
320	$7.61X10^{8}$	$7.61X10^{4}$	$1.31X10^{-5}$	-4.8815	2.5079
120	$7.45X10^{8}$	$7.45X10^{4}$	$1.34X10^{-5}$	-4.8734	2.0792
35	$7.26X10^{8}$	$7.26X10^{4}$	$1.38X10^{-5}$	-4.8612	1.5441
10	$6.82X10^{8}$	$6.82X10^{4}$	$1.47X10^{-5}$	-4.8345	1.0000
$6.5X10^{-1}$	$4.02X10^{8}$	$4.02X10^{4}$	$2.49X10^{-5}$	-4.6045	-0.1871
$7.2X10^{-2}$	$2.48X10^{8}$	$2.48X10^{4}$	$4.026X10^{-5}$	-4.3951	-1.1427
$1.25X10^{-2}$	$2.09X10^{8}$	$2.09X10^{4}$	$4.78X10^{-5}$	-4.3225	-1.9031
$4.0X10^{-3}$	$2.05X10^{8}$	$2.05X10^{4}$	$4.89X10^{-5}$	-4.3107	-2.3979

Table-9C

Conductivity measurements of Bi_2O_3 film as a function of oxygen pressure at 317^0C Oxide film thickness- $4000A^0$
Area of the film- 0.3cm X 0.75cm

Po_2 mm of Hg	observed resistance ohms	Resistivity ohm.cm	Conductivity simon	Log σ	log Po_2
730	$4.60X10^{8}$	$4.60X10^{4}$	$2.17\ X10^{-5}$	-4.6749	2.8600
350	$4.05X10^{8}$	$4.05X10^{4}$	$2.47X10^{-5}$	-4.6075	2.5441
120	$3.80X10^{8}$	$3.80X10^{4}$	$2.63X10^{-5}$	-4.5797	2.0792
35	$3.55X10^{8}$	$3.55X10^{4}$	$2.81X10^{-5}$	-4.5508	1.5441
13	$3.42X10^{8}$	$3.42X10^{4}$	$2.92X10^{-5}$	-4.6346	1.1139
$7.50X10^{-1}$	$2.17X10^{8}$	$2.17X10^{4}$	$4.61X10^{-5}$	-4.3365	-0.1249
$8.65X10^{-2}$	$1.75X10^{8}$	$1.75X10^{4}$	$5.71X10^{-5}$	-4.2431	-1.063
$6.25X10^{-3}$	$1.30X10^{8}$	$1.30X10^{4}$	$7.69X10^{-5}$	-4.1140	-2.2041

Table-9D

A plot of log σ vs log Po_2 is shown In fig.5. A straight line relationship with a slope -1/σ in the pressure range $lO^{-2}$to 10^2 mm Hg indicate that σα $PO_2^{-1/\sigma}$ A deviation from this behaviour is observed at pressures above 10^2 mm Hg. An activation energy for conduction calculated from the Arrhenius plots which are shov;n in fig.6 was found to be 10.5 ±1 Kcal/mole. This value may be compared with 10.5 Kca1/mole reported by Mansfield[15] on bulk Bi_2O_3 and by Konovalov et al[16] between 300° to 700°C.

IV. DISCUSSION

The kinetics data fit in well with the parabolic law of Wagner [17]which is based on diffusion control mechanism.The calculated values of Kp on the basis of Wagner's mechanlsm are in good agreement with observed values of Kp. This also indicates that the diffusion is the rate determining process during the growth of oxide film.

Our kinetics measurements give the values of activation energy equal to 28 Kcal/mole, The diffusion of bismuth through Bi_2O_3 has been studied by Palkar et al.[18] and the activation energy was found to be 23 Kca1/mole.However, since the data on the diffusion of oxygen in Bi_2O_3 are not available in the literature, the role of oxygen diffusion in controlling the rate processes is difficult to check.

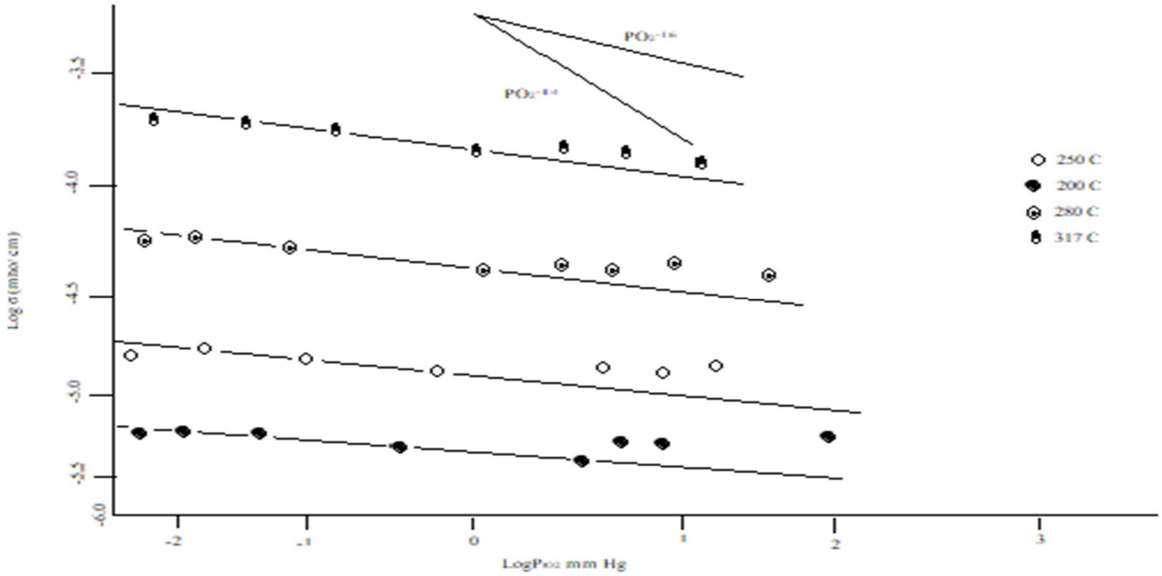

Fig -5 Oxygen Pressure dependence of conductivity of Bismuth oxide film at different temps

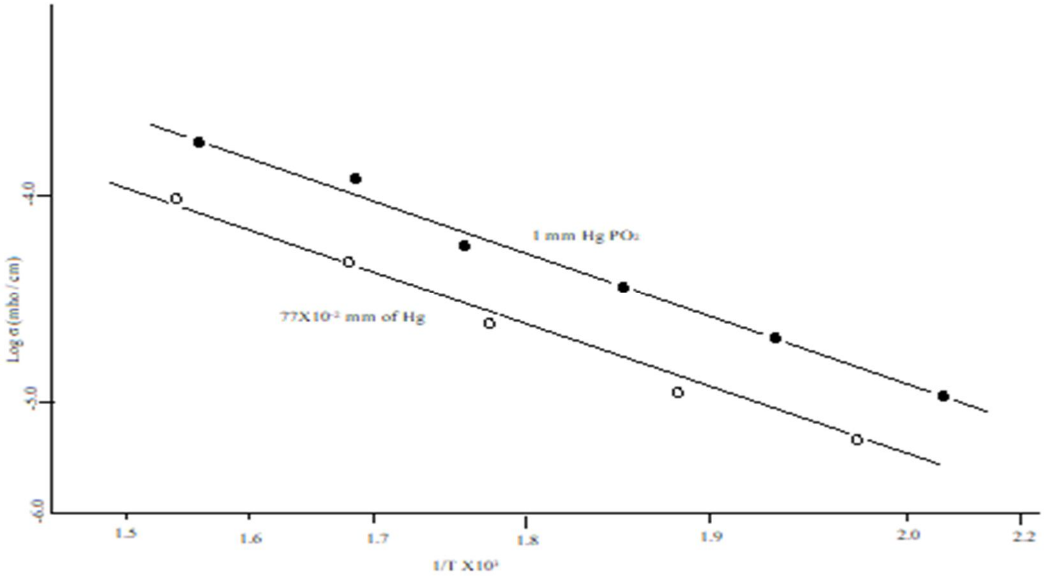

Fig- 6 Temperature dependance of the conductivity of Bismuth oxidde

The defect structure of the oxide formed on the metal during oxidation process is important to elucidate the reaction mechanlsin, Mansfield reported that Bi_2O_3 is a p-type oxide in bulk.

An electron diffraction pattern of the bismuth oxide film prepared under the conditions described above indicates that the compound is similar to the bulk Bi_2O_3 However, Bi/0 ratio (table-4) is found to be about 0.72 which is significantly greater than that calculated value of Bi_2O_3 which is 0.66.This shows that under the experimental condition a stable intemediate phase is formed, which is a gross defect structure of The defect may have arises either due to interstitial bismuth or due to oxygen vacancies. According to Zaryalova et al. bismuth oxide on prolonged heating, as we have done, stabilizes to a tetragonal phase with two molecules in a unit cell and vacancies (x = 0.2-0.3) at the oxygen lattice sites, Since B i/0 ratio estimated gravimetrically also points to nearly the same composition gives roughly two oxygen vacsncies per five unit cell on the average Kroger and Vink[19] have described a method by which the concentration of various imperfections can be calculated. The same method was used by Vest et al[20] in the case of zirconia, Following the seme, we have calculated the dependence of the concentration of electrons and holes on the oxygen pressure and compared with the observed conductivity behaviour as a function of oxygen pressure. It has been assumed that the mobility is not appreciably affected by the change of oxygen pressure and hence the conductivity is proportional to the concentration of electrons and holes.

The generation of electrons may be represented by one of the following equation

$$½ O_2 + O \square^{m} + me^{-} = O_{lattice}$$

$$3/2\ O_2 + 2Bi_1{}^{n} + 2n(e^{-}) = 3\ O_{lattice} + 2Bi_{lattice}$$

where $0 \square$ a denotes the oxygen vacancies and Bi_1 the interstitial bismuth,m and n represent the corresponding charges

Applying the law of mass action

$$(e^{-})^{m} = K.P_{O2}{}^{-1/2} / O \square^{m} \quad \text{---------} \quad (a)$$

$$(e^{-})^{2n} = K.P_{O2}{}^{-3/2} / (Bi_1)^{2n} \quad \text{---------} \quad (b)$$

When the compound deviates from the stoichiometry to a large extent then

$$O \square^{m} = 1/m\ e^{-} \quad \text{and} \quad Bi_1{}^{2n} = 1/2n\ e^{-}$$

In case of oxygen vacancies m may be either 0, 1 or 2 and n for bismuth Interstitials may be 0, 1, 2 or 3 Substituting the value for $O \square^{m}$ in equation (a) we obtain

$$(e^{-})\ \alpha\ P_{O2}{}^{-1/2(m+1)}$$

if m = 0, 1 or 2 we get (e^{-}) and hence the conductivity, proportional to -1/2, -1/4, -1/6 power of power of P_{O2}

Similarly substituting the value of $Bi_1{}^{2n}$ in eq (b) we get

$$(e^{-})\ \alpha\ P_{O2}{}^{-3/2(n+1)}$$

and for n = 0, 1 , 2 or 3 conductivity would be proportional to either - 1/0.66, -1/2, -1/3.3 or -1/4.66 power of pressure P_{O2}

Similarly conduction due to holes could be attributed either to bismuth vacancies or oxygen interstitials.On writing appropriate equations for the generation of holes and applying the law of mass action on similar lines as above we can easily obtain

1) In case of oxygen interstitials the conductivity is proportional to either t or ½, ¼ or 1/6 power of P_{O2}

2) in case of bismuth vacancies conductivity will be varying with 1 /0.66 , 1/2 , 1/3.3 or 1/4.66 power of P_{O2}

However, as observations indicate that Bi_2O_3 is deficient in oxygen at the pressures under consideration, conduction due to holes is regarded as negligible. Koreover, qualitative thermoelectric measurements shows that Bi_2O_3 films are n-type in these pressure and temperature ranges. The observed conductivity is a combinstion of electronic hole and ionic conductivities. The contribution due to the ions and electrons nsay be ascertained from an analysis of the transport number data. This relates to cation as well as anion mobilities. Since the concentration of Bi interstitials is very small compared to that of oxygen vacancies, diffusion of oxygen (anion) would always predominate over that of bismuth (cation). It can be seen from table-8 that an ionic contribution to the conductivity further increases as the pressure of oxygen is increased. This may partially explain the deviation from $P_{O2}{}^{-1/6}$ dependence of conductivity. Another possible reason for this deviation is that, as the pressure is increased the number of oxygen vacancies decreases and the conduction due to holes may start dominating with a 1/6 power of P_{O2} This would give rise to a bending of the curve at higher pressure. Finally, it may be noted that the results obtained are in disagreement with those of Hauffe et al. who found that n-type Bi_2O_3 changes to p-type et about 10^{-2} mm pressure of oxygen. However, Mansfield found no such change in the pressure range. This disagreement may have arisen due to the fact that the bismuth oxide used was studied in the form of thin film whereas they used the same in the bulk form.

In conclusion, the oxidation of bismuth film can be described as a diffusion controlled process. Ihe diffusion of oxygen are taking place via doubly charged oxygen vacancies, as being confirmed by conductivity measurements.

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