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CHAPTER I : INTRODUCTION

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## INTRODUCTION

The role of adsorption and desorption in the study of gas-solid reactions has long been recognised. Exhaustive, though not always illuminating, work has been carried out on adsorption and desorption of gases on oxide surfaces especially on oxides like ZnO, NiO, Cu<sub>2</sub>O, CoO etc., which are known to be good catalysts. These investigations showed that adsorption and desorption on solid surfaces are respectively the initial and final stages of any heterogeneous catalytic reaction. Interfaces between microcrystals in poly crystalline solids, pores and molecular voids in amorphous hydroxides and oxides may provide many possible sites for catalytic reactions<sup>1</sup>. In some cases the catalyst adsorbate reaction tend to produce bulk compounds, e.g. hydroxides and oxides<sup>2</sup>, so that the probability of diffusion of the adsorbed gas into the bulk (lattice incorporation)<sup>3-7, 14,25-27, 78</sup> has to be taken into account. In the case of semiconductors, however, the surface is usually assumed exclusively to take part and therefore the theory of heterogeneous catalysis on semiconductors inescapably starts from the theory of adsorption.

### 1.1 Adsorption:

Several theoretical<sup>8,9</sup> and experimental<sup>10-12</sup> studies carried out in thirties revealed the existence of two types of adsorption :-

(i) One taking part by the interplay of vanderwaal's force is termed physical adsorption. This is nonspecific, usually fast and have always a positive but low heat of adsorption around 2-10 Kcal/mole and (ii) One taking place by the interplay of exchange or coulomb type of forces known as chemisorption. This is specific, usually slow and have high heat of adsorption (10-100 Kcal/mole). However, physical adsorption with high heat of adsorption (if lattice rearrangement takes place) is not unknown whereas endothermic chemisorption<sup>13</sup> may also occur. Different authors have employed different criteria to distinguish between the two form of adsorption<sup>14,15,16,17</sup> and according to Boudart<sup>18</sup>, the difference between these two types is of degree than in kind.

Taylor<sup>19</sup>, from a study of adsorption of H<sub>2</sub> on MnO and MnO. Cr<sub>2</sub>O<sub>3</sub> suggested that certain activation energy might be associated with chemisorption, as in the case of chemical reactions. It has been suggested that rate of adsorption on a clean metal surface is independent of temperature requiring no activation energy<sup>20,21</sup> but there is some doubt regarding that conclusion<sup>21</sup>. Activation energy will be required if there is a potential barrier to cross, and may even arise in case of (so called) physical adsorption if repulsive forces act between the adsorbed molecules<sup>22</sup>. There might be difference of opinion as to the nature and reason of occurrence<sup>23</sup> of such a barrier, but its appearance in most cases of chemisorption is quite likely.

The observation of the regular decrease of heat of adsorption with coverage led Taylor<sup>24</sup> to suggest that a surface must consist of regions of varying degrees of unsaturation giving rise to the so called active centre. These "active centres" were thought of as specific points, edges or positions on the surface, which were capable of adsorption and initiating reaction both energetically and geometrically. The most active sites have high heat of adsorption (and consequently low activation energy). Gases are adsorbed first on those sites and then less active sites take part, and hence heat of adsorption decreases with increasing coverage. However, this can also be explained in terms of "induced heterogeneity"<sup>25</sup> or "repulsive interaction between adsorbed molecules"<sup>22,26,27</sup> or on the basis of electron distribution of permitted energy levels of the adsorbent<sup>28-29</sup>. The concept of active centres was apparently supported by the isotopic tracer studies of Roginsky<sup>30</sup> and of Emmett<sup>31</sup> and the experiments of Taylor and Liang<sup>32</sup>.

The notion of active centres without specifying their physical meaning is all that is required to construct a phenomenological theory of catalysis. A theory of adsorption and catalysis, proper, should explain the nature of active centres, reveal the elementary mechanism and should relate those characteristics to the electronic properties of the adsorbent<sup>33</sup>.

### 1.1.1 Theories of adsorption:

While the early contributions to the theories of adsorption were revealed in the works of Langmuir<sup>3</sup>, Polanyi<sup>34</sup> and Freundlich<sup>35</sup>, the modern theories of adsorption based on the application of quantum mechanics were developed by Tamm<sup>36</sup>, Lennard Jones<sup>9</sup> and others<sup>37-44</sup>. Because of the complex nature of the problems, the quantum chemical methods, so far have given very general ideas of the chemisorption bond, as for example the localisation of the bond<sup>41,42,46-48</sup>. A very simple molecular orbital picture of chemisorption has been given by Sutula<sup>49,50</sup> and recently Coulson and Blyholder<sup>51</sup> have applied simple Huckel L.C.A.O.M.O.<sup>45</sup> method of Goodwin<sup>42</sup> as developed by Grimley<sup>41</sup> and Coulson and Baldock<sup>43</sup>. Davison and Ho<sup>52</sup> have discussed the electron correlation effect in chemisorption using the spin polarised orbital method. These results though difficult to apply in concrete special cases, lead to interesting conclusions on the nature and the stability of bond being studied. Since in chemisorption it is important to know the quantitative properties of interacting partners, it is impossible to expect really interesting results until a semiquantitative theory based on the analogy with the quantum chemistry of organic compounds has been developed on a careful semiempirical approach to the solution. Therefore, the statistical theory of chemisorption on semiconductors<sup>14,15,53-55</sup> based on the theory of volume properties of semiconductors<sup>56-58</sup> is sometimes regarded as ahead of its time.<sup>44</sup>

However, they are simple and constructed in such a way as to permit qualitative correlation of adsorption and catalytic behaviours. The "Boundary layer theory of chemisorption" as developed by Hauffe and Weisz following Mott<sup>57</sup> (Metal semiconductor contact) takes into account adsorption only in ionic form. This model has various shortcomings in that it takes no account of such physicochemical aspects of adsorption as variations in the bond type and various physical refinements such as existence of the surface states and the problems associated with degeneracy are also beyond its scope. Volkenstein's 'electron theory of catalysis'<sup>14</sup> is more fundamental and rather wider in scope<sup>60</sup>. Excellent and authentic treatments of the Boundary layer theory<sup>15,61</sup> and Electron theory<sup>14,33</sup> of chemisorption are available. The role of electronic factor in the kinetics of chemisorption has also been discussed on these lines by several authors<sup>53,54,3,62-67</sup>.

Since these theories are based on the theory of semiconductors, a simple qualitative idea about semiconductors will be developed first.

### 1.1.2 Semiconductors:

Semiconductors are substances whose electrical conductivity is due to the motion of quasi free electrons and whose resistance at room temperature lies within the range from  $10^{-2}$  to  $10^9$  ohm-cm. Unlike metals the conductivity of semiconductors increases with the increase of temperature. The principal chemical constituent of a semiconductor phase is usually the

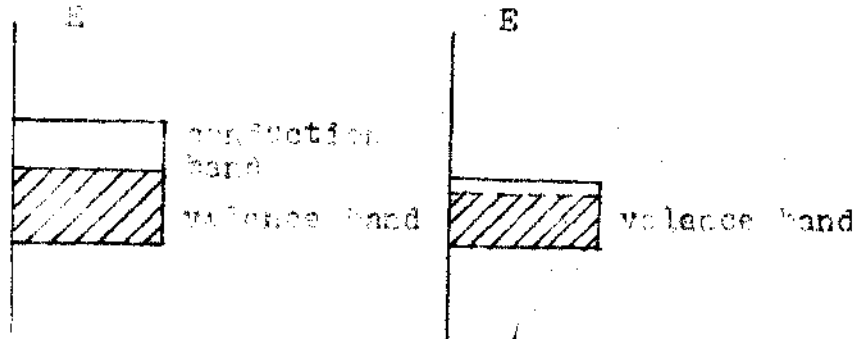
combination of at least two elements, most frequently a metal and oxygen. In terms of the band theory of solids, ideal ionic crystal of stoichiometric oxide has a filled valence band. In some cases, the distance between the valence band and the conduction band is small enough to make the electron transfer possible ( $\text{CuO}$ ,  $\text{Fe}_3\text{O}_4$ ) - the oxide then is reported as an intrinsic semiconductor. When the oxide possesses defects (due to the departure from stoichiometry or due to the presence of foreign ions), the local disturbances give rise, in the vicinity of one of the bands, to new energy levels accessible to electrons or containing them. When the levels created by the defects are normally occupied by electrons, the semiconductivity results from the passage of these electrons over to the conduction band: this is called normal or n-type semiconductor. When the levels are empty and are filled only as a result of an excitation, the semiconductivity is said to be abnormal or type p.

In case of conductors the Fermi energy of electrons is equal to the mean energy of electrons in the valence band (since it is half filled). In case of semiconductors the Fermi level will be exactly half way between the defect level and valence band or conduction band depending on whether it is p-type (pure) or n type (pure)<sup>68</sup>. In case of insulators or intrinsic semiconductors it will be located halfway between the conduction band and valence band. This is shown schematically in Fig.1.

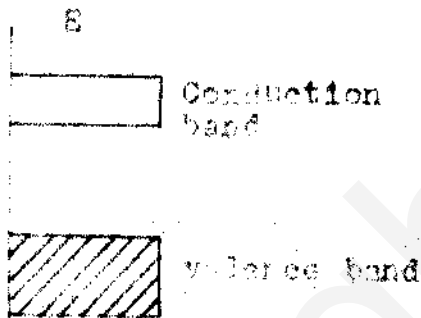
$\text{NiO}$  or  $\text{Cu}_2\text{O}$  as prepared, contains slight excess of oxygen. This can be explained only by the assumption that several

Fig.1

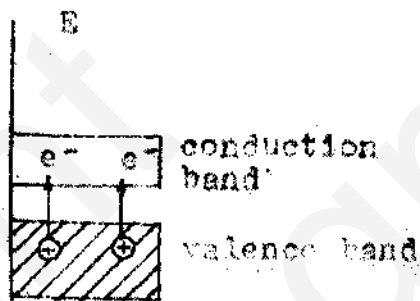
(i) Metals



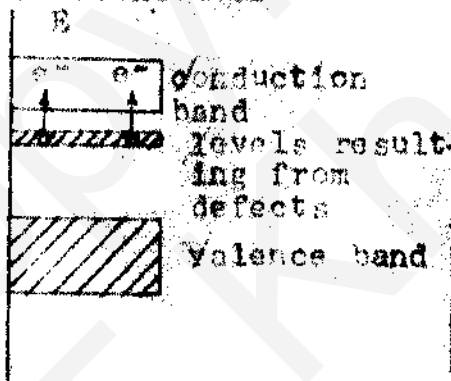
(ii) Insulator



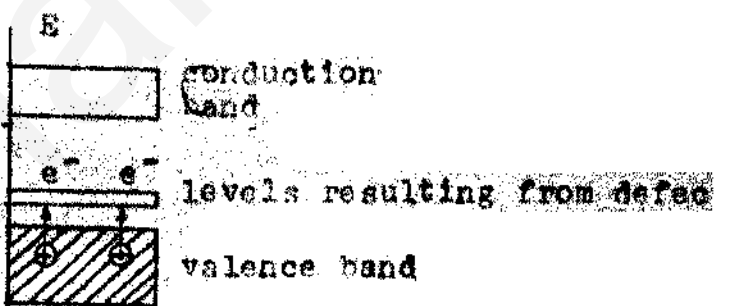
(iii) Intrinsic semiconductor



(iv) Type N semiconductor



(v) Type P semiconductor



Position of the energy bands responsible for electronic phenomena in solids.



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$\text{Ni}^{2+}$  or  $\text{Cu}^{+1}$  ions are missing which means that  $\text{Ni}^{3+}$  or  $\text{Cu}^{2+}$  are formed to preserve electrical neutrality. The normally and abnormally charged cations are not localized and an exchange of charge takes place giving rise to p-type semiconductivity. Similarly ZnO or CdO prepared, consists of zinc and cadmium atoms in the interstices (oxygen deficient) and charge exchange gives rise to n-type semiconductivity. On this basis oxygen adsorption (provided the character of the oxide remains the same in presence of oxygen) would increase the conductivity of p-type oxides and decrease that for n-type oxides. The reverse is true for hydrogen adsorption.

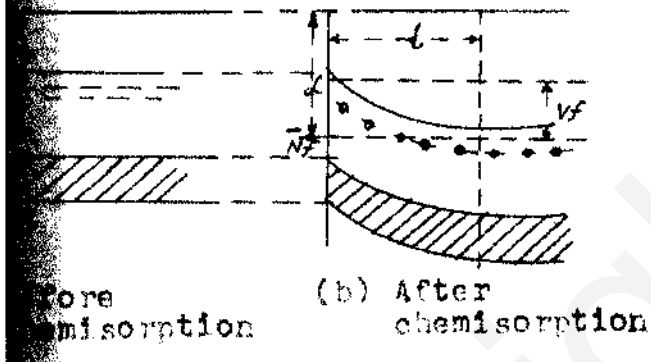
Semiconductivity can, therefore, be controlled by dissolving in the host lattice foreign ions of different valency or by irradiation. For example, introduction of  $\text{Li}_2\text{O}$  on NiO creates more of  $\text{Ni}^{3+}$  and introduction of  $\text{Al}_2\text{O}_3$  or  $\text{La}_2\text{O}_3$  in ZnO gives rise to more of zinc atoms. These defects may also be created during adsorption<sup>69,70</sup> (by this means insulators may also become semiconductors in situ<sup>69</sup> and acts as adsorbent). However, pure p-type or n-type semiconductors are rare. Under certain conditions one type of behaviour predominates. Cimino et al<sup>71</sup> noted surface p-type behaviour of ZnO during oxygen adsorption. The findings of Bhattacharyya and Chandrasekhar<sup>72</sup> may also be interpreted in terms of surface p-type behaviour<sup>132</sup> of ZnO. In NiO, presence of  $\text{Ni}^{+1}$  along with  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  is not unlikely; at least, it may be created during hydrogen adsorption<sup>73</sup>, and under certain conditions NiO may as well show surface n-type behaviour<sup>74</sup>.

### 1.1.3 Boundary layer theory & electron theory of chemisorption:

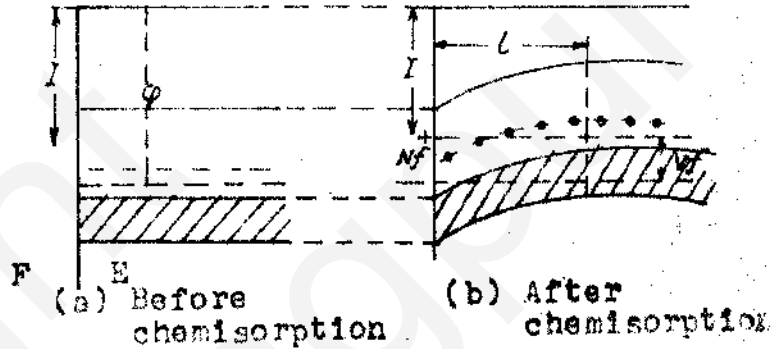
Chemisorption, as postulated by the boundary layer theory<sup>15,59,61</sup> takes place as a result of electron transfer between the gas and the semiconductor, and in any particular case the direction of the exothermic donation of electrons depends on the relative positions of two electron levels, i.e. Fermi level of the semiconductor and the ionisation potential or electron affinity of the chemisorbing gas. The flow of electrons causes a negative charge to accumulate in the acceptor system, where the energy of the electrons rises until it becomes equal to that of electrons in the donor system, after which electron flow ceases. This, however, affects the Fermi level of the semiconductor at the surface although that in the bulk remains unchanged. The positive or negative charge acquired by the semiconductor surface, in contrast to the metals, is not localized at the surface, but extends into finite distance (  $\ell$  ) into the semiconductor for obvious reasons<sup>61</sup>. The space charge so produced changes until equilibrium is attained<sup>59</sup>, and this greatly affects the conductivity of the system. The cases where a decrease in conductivity is noted are termed depletive chemisorption (anionic adsorption on n-type, cationic on p-type), whereas an increase in conductivity results in "cumulative chemisorption" (cationic in n-type, anionic in p-type). The cases of depletive chemisorption (exhaustion or Schottky barrier layer<sup>57,58</sup>) have been discussed exhaustively, whereas in the cases of cumulative chemisorption (inaundation boundary layer,  $O_2$  on NiO,  $H_2$  on ZnO ) it is normally assumed that the system

Fig. 2

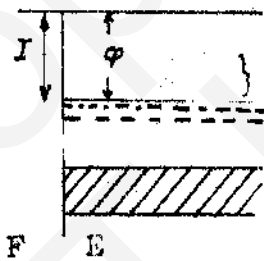
(i) Anionic chemisorption on a p-type semiconductor.



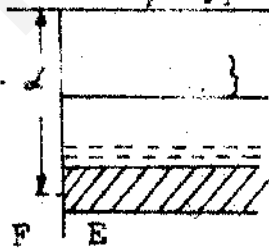
(ii) Cationic chemisorption on a p-type semiconductor.



(iii) Cationic chemisorption on a n-type semiconductor.



(iv) Anionic chemisorption on a n-type semiconductor.



Diagrammatic representation of depletive and cumulative chemisorption

E. Semiconductor ; F. Adsorbate

will be more metallic in character<sup>75</sup> and a double layer only will be formed at the surface<sup>15,25,59</sup>. Depletive chemisorption on n and p-type semiconductors<sup>59</sup> is shown schematically in Fig.2. In electron theory of chemisorption<sup>14</sup>, valencies freely wandering along the surface (i.e. free electrons and holes) and defects may play the role of active centres, and according to Volkenstein<sup>14</sup>, a weak non ionic chemisorption is the first stage in every chemisorption process which consequently passes to 'strong chemisorption' forming either a strong n-bond or strong p-bond depending on the condition of electron transfer.

✓ According to the above theoretical concepts, on lowering the Fermi level (by the introduction of lower valent ion to the lattice) the adsorption capacity with respect to acceptor molecules decreases while it increases with respect to donor molecules. The reverse is true for an increase in height of the Fermi level<sup>14,15</sup> (by introducing higher valent ion). Results of systematic reports are lacking, but various experiments have been carried out. However, Crane et al<sup>77</sup> observed a rise in the rate of oxygen recombination reaction (donor type) in Cr<sub>2</sub>O<sub>3</sub> doped ZnO (increasing n-typeness: rise in the height of Fermi level) with respect of ZnO, which is contrary to the prediction. Boundary layer theory predicts enrichment chemisorption where there is an increase in the number of charge carriers (O<sub>2</sub> on p-type Oxides)<sup>15</sup> - but the limited chemisorption of oxygen on NiO<sup>78-81</sup> argues for some modification of this simple boundary layer theory. According to van Houten<sup>82</sup>, strict applicability

of the band theory of solids to explain surface phenomena in transition metal oxides is an over simplification. The discrepancies can be explained<sup>77,78</sup> assuming chemisorption as a localized phenomenon. ✓

These theories predict a change in conductivity and work function of the semiconductor as a result of adsorption. The amount of conductivity change  $\Delta\sigma$  (also work function change  $\Delta\phi$ ) depends on the temperature and pressure, and on the nature of the semiconductor and gas. The kinetics of changes in  $\Delta\sigma$  following oxygen adsorption on thin layers of oxides have been examined in a series of papers<sup>88-90</sup>. It is through these studies on conductivity<sup>7,75,91</sup> and work function<sup>92-94</sup> changes as a result of adsorption that the existence of a weak form of chemisorption (requiring low activation barrier) has been demonstrated. These studies<sup>92</sup> revealed that in case of depletive chemisorption the work function varies linearly with coverage and in case of cumulative chemisorption it changes logarithmically with coverage, whereas the boundary layer theory postulates<sup>15</sup> in those cases a quadratic and a combined linear logarithmic dependence respectively.

According to the electron theory of catalysis, substances which charge the surface differently when adsorbed individually, should be adsorbed in mixtures more rapidly<sup>83</sup> and in larger quantities<sup>14</sup>. On the other hand, substances which produce charges of the same sign on the surface should interfere with one another. Recently, Roginskii et al<sup>84</sup> have obtained

results contrary to this prediction. It was concluded that the charging of the surface during the adsorption of one gas does not determine the magnitude of the adsorption of a second gas on the adsorption of the first<sup>85</sup>. The reason of these discrepancies are due to restrictions in the theory<sup>84</sup> which assumes uniformity of the surface and absence of interaction on the surface between adsorbed particles. The most serious drawback, however, is the underestimation of the chemistry of the process<sup>84,86</sup>. Each system should be considered in its own merits as a distinct chemical problem<sup>87</sup>.

It is obvious therefore, that these theories are by no means exact. For a clear understanding of chemisorption, it is necessary to possess a detailed appreciation of the environment of ions in the solid surfaces<sup>78,60,81</sup> and the overall chemistry<sup>86,87</sup> of the process. This is not taken into account in these approaches<sup>84,87</sup>. What is more, if the electron level in an atom or molecule adsorbing lies below the conduction edge, a localized surface state<sup>36,43</sup> can form irrespective of the Fermi level. This may very well be the mechanism by which common gases chemisorb<sup>87</sup> on metals and semiconductors. Surface states may also deny control over the Fermi level<sup>95</sup>. The cardinal virtue of these theories, however, is that they are capable of precise analysis and have succeeded so far in explaining the experimental findings in some way or other (i.e. with little modification on these lines). They are not at all complete<sup>7,14</sup>, and are still in a developing stage<sup>33</sup>.

#### 1.1.4 Nature of the bond formed in chemisorption, and other theories.

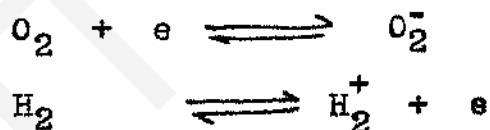
The doctrine of exchange or coulomb type of forces in chemisorption demands some rearrangement of charge cloud around a gas atom. The concept of one electron bond has been invoked by Pollard<sup>37</sup>, which according to Volkenstein<sup>14</sup> is definitely true for the case of "weak chemisorption". However, in strong chemisorption which gives rise to donor or acceptor bond, two electrons take part in the bond formation<sup>14</sup>. This, however, may also lead to ions:



According to boundary layer theory<sup>15</sup> which treats chemisorption as ionosorption, adsorption of gases may be represented as:



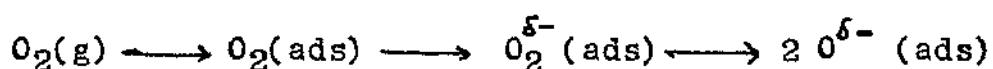
The formation of molecular ions is also not unlikely:



Which one will be formed is determined by energetic conditions. The representation of charged species as  $O_2^-$  etc is, of course, a crude simplification of the true state of affairs, partial sharing of electrons is quite likely<sup>96</sup>. Nevertheless symbols

such as  $O_2^-$ ,  $O^-$  etc are useful shorthand.

Following Czanderna<sup>97</sup> chemisorption of oxygen may be represented as :



The bonds formed may well be the charge transfer bonds of the Mulliken type. Matsen, Marcides and Hackerman<sup>98</sup> have applied this idea to study the relationships between the heats of adsorption and the ionisation potential of a number of substrate molecules. Recently, Lee and Mason<sup>99</sup> have developed a charge transfer theory of chemisorption and catalysis, in which the ground state wave function of the complex is described as a linear combination of a nobond state and a dative state.

It has been noticed that transition metals are most effective as catalysts and adsorbent<sup>100</sup> when their magnetic susceptibility is highest i.e. the number of unpaired electrons in the d-band is maximum. It has been concluded thus that on transition metals most of the gases form essentially covalent bonds with the partially filled d-band<sup>101</sup>. If the d-band is complete, such bands may be formed if d-s promotions are possible with sufficiently low energy as in the case of copper<sup>102</sup>. Detailed works on magnetic susceptibility confirms this view<sup>103</sup>. Basing on this idea, Bulgacov et al<sup>104</sup> have studied theoretically the various forms of hydrogen chemisorption on metals by the method of overlap integral. Such a possibility cannot be overruled in the case of semiconductors, at least in so far as to





increase the coordination number of specific sites<sup>105</sup> at the surface (with lower coordination than in the bulk) by the chemisorbed gas. This is just an extension of the Ligand field theory as encountered in coordination complexes<sup>106</sup>. This new advance treats the symmetry and extension of the corresponding surface orbitals using molecular orbital method (Ligand field theory)<sup>105</sup>.

The question of the nature of the bond formed in adsorption, however, is not yet clear. The type of bond formed may depend on temperature and pressure of the gas. Several types of bonds may be formed at the same time during the course of adsorption, i.e. the nature of the bond may change during the course of adsorption (more so in case of adsorption from mixtures<sup>84</sup>).

## 1.2 Kinetics and Mechanism of chemisorption:

In order to clarify the fundamental mechanism of chemisorption, it is important to investigate the kinetics of the process. The basic characteristic is the variation of the amount adsorbed  $q$  with time  $t$  at constant temperature: the kinetic isotherm  $q = f(t)$ . Most chemisorption processes are described by the Elovich equation<sup>107</sup>

$$\frac{d\theta}{dt} = a e^{-\alpha\theta} \quad \dots \quad (1)$$

where  $\theta$  is proportional to the amount adsorbed, and  $a$  and  $\alpha$  are constants ( $a > 0$ ,  $\alpha > 0$ ). If  $\theta = 0$  at  $t = 0$ , the

equation may be expressed (in integrated form) as

$$\theta = \frac{2.303}{\alpha} \log (t + t_0) - \frac{2.303}{\alpha} \log t_0 \quad \dots \quad (2)$$

$$\text{where } t_0 = 1/a\alpha \quad \dots \quad (3)$$

If, however,  $\theta = \theta_0$  at  $t = 0$  (some gas adsorbed at start), the equation takes the form:

$$\theta = \frac{2.303}{\alpha} \log (t + k) - \frac{2.303}{\alpha} \log t_0 \quad \dots \quad (4)$$

$$\text{where } k = t_0 e^{\alpha \theta_0} \quad \dots \quad (5)$$

If  $k \ll t$ , the equation can be expressed as :

$$\theta = \frac{2.303}{\alpha} \log a\alpha t \quad \dots \quad (6)$$

The method of evaluating the parameters  $a, \alpha, t_0$  and  $k$  have been given elsewhere<sup>108,109</sup>. If  $\theta = 0$  when  $t = 0$ ,

$$\left(\frac{d\theta}{dt}\right)_{t \rightarrow 0} = \frac{1}{\alpha t_0} = a \quad \dots \quad (7)$$

i.e. 'a' is the rate of initial massive adsorption. 'a' increases with temperature with an activation energy of about 10 Kcal/mole<sup>109,81</sup>. If, however some adsorption occurs at the start of the process ( $\theta_0$ ) then  $a^*$  defined by

$$a^* = \left(\frac{d\theta}{dt}\right)_{t \rightarrow 0} = \frac{1}{\alpha k} = a^* = a e^{-\alpha \theta_0} \quad \dots \quad (8)$$

gives the initial rate of adsorption<sup>110</sup> if the initial massive adsorption is without effect on the succeeding slow adsorption. Evidently  $\frac{2.303}{\alpha t}$  gives the rate of the overall process. According to Taylor and Thon<sup>110</sup>,  $\alpha$  is the characteristic of a

particular type of active centre and any discontinuity in the linear  $\theta$  vs  $\log(t + k)$  plot with a change of  $\alpha$  indicates a change over from one type of active site to another. Although there is difference of opinion as to the reason of occurrence of a break in  $\theta$  vs  $\log(t + k)$  plots (which may be due to lattice incorporation<sup>15,54</sup>, bulk and surface diffusion, reduction of the lattice by consumption of lattice ions<sup>15</sup>, all of which follow a logarithmic law), it may indicate the presence of multiple kinetic stages as suggested<sup>7,108,109</sup>. The rate at any time is given by  $r = \frac{d\theta}{dt} = \frac{2.303}{\alpha t}$ , and activation energy is usually determined by the use of Arrhenius equation

$r = A e^{-E/RT}$ , i.e.  $\frac{2.303}{\alpha t} = A e^{-E/RT}$  directly or by variations of this.

Several models have been proposed to account for Elovich kinetics. Three general assumptions are accepted in every model. They are :

- (i) The validity of the conventional kinetic formulation of the rate of reaction between a gas and a set of unoccupied sites.
- (ii) The rate of desorption is negligible
- (iii) The rate of reaction is

$$\frac{d\theta}{dt} = K P_n \quad \dots \quad (9)$$

where  $KP$  is proportional to the rate of collisions of gas molecules and  $n$  is the instantaneous number of unoccupied sites.

One type of models simply assume<sup>109,110,113,114</sup> that the expression

$$n = n_0 e^{-\alpha \theta} \quad \dots \quad (10)$$

is satisfied rather than the usual conservative relation  $n = n_0 - \theta$  where 'n<sub>0</sub>' is equal to the initial number of sites and is a constant. Hence at constant pressure equation (1) is obtained. Various mechanisms have been proposed to account for (10). According to Taylor and Thon<sup>109</sup> this reflects bimolecular site interaction at the stage of slow adsorption. They concluded that in the slow stage the kinetics are relatively insensitive to the mass action effect of the gas, and are determined principally by changes taking place in the adsorbent and introduced the idea of generation of active sites by the very act of adsorption  $C(g) + L = CV + (n - 1) V$  i.e.  $L = nV$  (theory of incorporating site generation<sup>109,115</sup>). In the opinion of Landsberg<sup>113</sup>, equation (10) can be explained by the assumption of steric hindrance (one molecule adsorbed affects more than one site<sup>114</sup>).

Another class of models<sup>15,61,116-119</sup> assume activation energy of adsorption to increase linearly with coverage, so that 'k' rather than 'n' in (9) is the exponential function of  $\theta$ . It is necessary, however, to restrict  $\theta$  to values much smaller than 'n<sub>0</sub>' in order that 'n' remains approximately constant. Several mechanisms have been proposed to account for a linear dependence of activation energy with coverage and two

of these have received considerable attention. The more satisfying of the two is based on the boundary layer theory. A kinetic expression similar to (1), however, is obtained only for cumulative and not for depletive chemisorption, except when the induced change<sup>25</sup> in the activation energy is considerably less than  $kT$ . The kinetic expression obtained for the depletive case was<sup>54</sup>

$$\frac{d\theta}{dt} = B \exp \left[ -\alpha (\theta + \theta^2/2an) \right] \quad \dots \quad (11)$$

where  $\alpha = \frac{4\pi e^2 a}{DkT} \quad \dots \quad (12)$

and for the cumulative case

$$\frac{d\theta}{dt} = a(\theta) e^{-\alpha \theta} \quad \dots \quad (13)$$

Even in the cumulative case, moreover, the similarity is rather forced, since the preexponential factor  $a(\theta)$  is proportional to  $\frac{1}{\theta^2}$  and it is necessary to neglect this substantial dependence on  $\theta$  in order to obtain equation (1). Reconsideration of this matter in the light of analogous barrier theory of rectification<sup>120</sup> gives for depletive chemisorption,

$$\frac{d\theta}{dt} = e \exp \left[ -b' (\theta_0 + \theta)^2 \right] \quad \dots \quad (14)$$

$$b' = \frac{2\pi e^2}{DkT} \quad \dots \quad (15)$$

where  $\theta_0$  is proportional to the amount adsorbed at the start.

However, recently Volkenstein and Peshev<sup>3,62</sup> have derived a kinetic expression similar to (1) free from the above objections. The second well-known mechanism requires the surface to be a priori heterogeneous<sup>118,119</sup> with respect to the activation energy of adsorption and the activation energy of adsorption and utilizes the concept of sites of varying potential<sup>121</sup>.

Several other empirical or derived equations have been proposed to account for chemisorption kinetics. Adsorption of O<sub>2</sub> on NiO, C<sub>3</sub>H<sub>7</sub>OH on ZnO, O<sub>2</sub> on ZnO containing Li<sub>2</sub>O and NH<sub>3</sub> on glass etc are found to obey a general equation of the type

$$\theta = k_1 t^{k_2} \quad \dots \quad (16)$$

This is an empirical equation usually known as Bangham-Burt equation and was also derived<sup>62,92</sup> theoretically. Eley<sup>113</sup> derived an equation

$$\frac{dq}{dt} = \alpha' (q_e - q) e^{-\gamma q/kT} \quad \dots \quad (17)$$

where 'q' is the amount of volume adsorbed at time t, (q<sub>e</sub>) at equilibrium and α' and γ are constants. Ghosh et al<sup>124</sup> proposed a power rate law :

$$\frac{dq}{dt} = kpq^{-n} \quad \dots \quad (18)$$

where q is the amount of gas adsorbed at a pressure P and n is a constant. Chemisorption of O<sub>2</sub> on TiO<sub>2</sub><sup>65</sup> is found to conform to

$$\frac{dq}{dt} = ae^{-\alpha q^2} \quad \dots \quad (19)$$

which had been put forward by Aigrain and Dugas<sup>53</sup> and Germain<sup>64</sup>.

Elovich equation, however, is obeyed in most cases of chemisorption and it is the only equation which allows one to find the kinetic parameters which can be given proper theoretical interpretations and whose variation with temperature, pressure and electronic structure of the solid can be studied. However, it is so frequently obeyed that mere linearity of trial plots is not a satisfactory criterion of its validity - temperature and pressure dependence of the parameters should be examined in terms of a given model<sup>61,125</sup>.  $\alpha$  is found sometimes to be inversely proportional to the pressure (particularly to the initial pressure in constant volume methods); no model except that of Freund<sup>126</sup> which uses Knudsen flow mechanism using diffusion as a rate limiting stage can account for this<sup>127</sup>, contrary to claims<sup>110,127</sup>. The models proposed to account for Elovich kinetics as evident, are self contradictory and a model free from all objections is yet lacking.

### 1.3 Adsorption studies on oxides and present state of knowledge on chemisorption.

Because of high reactivity and molecular simplicity, the adsorption studies of CO, H<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> on oxides holds a particularly important place in the understanding (and development of research) of chemisorption and heterogeneous catalysis. A vast amount of work has been done on oxides such as ZnO, NiO, Cu<sub>2</sub>O etc. and they have revealed a lot of information on various aspects of activated adsorption.

The first clear results to establish the existence of more than one type of chemisorption for reducing gases on oxides were that of Garner and Kingman<sup>12</sup>, who studied the adsorption of CO on ZnO·Cr<sub>2</sub>O<sub>3</sub>. Two types of chemisorption of H<sub>2</sub>, one between 0°C and 100°C and another at higher temperature was also reported for ZnO<sup>128</sup> and ZnO·Cr<sub>2</sub>O<sub>3</sub><sup>91</sup>. Keir and Roginskii<sup>129</sup> observed that above 100°C an appreciable fraction of the hydrogen is strongly adsorbed and can only be removed from the surface in the form of water by heating the specimen above 500°C. A weak adsorption of oxygen on ZnO at room temperature was also reported<sup>92,130</sup>. It has been pointed out that it is the high temperature adsorption of hydrogen which is responsible for the change of conductivity of ZnO and NiO<sup>88</sup> (although there is some doubt regarding the conclusion that the low temperature adsorption of H<sub>2</sub> on ZnO does not affect its conductivity<sup>132</sup>). Thus the concept of reversible chemisorption (gases desorbed unchanged) was introduced. However, according to Volkenstein<sup>133</sup>, the amount adsorbed which cannot be desorbed at the experimental temperature is irreversible adsorption. This may arise due to hindered desorption at the charged state (O<sub>2</sub> usually adsorbed as O<sup>-</sup>) and the occurrence of some secondary chemical reaction i.e.  $O_a^- + Zn_i^+ \rightarrow Zn^{2+} O^{2-}$  in case of O<sub>2</sub> on ZnO. Barry and Stone considered that predominant chemisorbed species in O<sub>2</sub> on ZnO adsorption is O<sup>-</sup> at room temperature and O<sup>2-</sup> above 300°C "stabilized by the diffusion of interstitial zinc towards the surface"<sup>134</sup>. These



studies along with others<sup>3,91-94</sup> clearly demonstrated the existence of 'weak' and 'strong' form of chemisorption. The ratio of these two forms is affected not only by temperature but also by the nature of the adsorbate and adsorbent<sup>135</sup>. Subsequent studies led to the recognition of at least five possible forms of chemisorbed oxygen:

- (i) weakly chemisorbed nonionic oxygen molecule ( $O_2$ )
- (ii) chemisorbed oxygen molecule ion ( $O_2^-$ )
- (iii) chemisorbed  $O^-$  ion
- (iv) chemisorbed  $O^{2-}$  ion ( $O^{2-}/\square_{s^-}$ )
- (v) lattice incorporation ( $O^{2-}/\Delta$ )

There is ample evidence to support the concept of chemical combination with lattice oxygen during chemisorption on oxides<sup>61</sup>. The main studies have been concerned with the chemisorption of CO, so extensively investigated by Garner<sup>136</sup>. This may lead to irreversible chemisorption, leaving, as a result the surface unsaturated with respect to oxygen. The ability to take up oxygen increased as a result of CO adsorption. Therefore, the postulate of surface carbonate ions was invoked, which was apparently supported by isotope exchange studies of Winter<sup>96a,60,137</sup>. However, the findings of Winter's experiments were nicely explained by Stone<sup>60</sup> considering the crystal structure of the oxides studied (environment). According to Stone, CO may also form complexes with adsorbed oxygen and the concentration and binding of excess oxygen may be the controlling factor in determining the type of kinetics to be

followed in oxidation over an oxide surface<sup>60,138</sup>.

It has been found that it is usually very difficult to make an oxide surface free of oxygen<sup>73,78,127</sup>, and probably this is one of the reasons for different adsorptive characteristics of the same substance prepared under different conditions<sup>139</sup>, (different conditions of preparation, moreover, may give rise to different defect structures).

Kinetics of chemisorption studied revealed the applicability of Elovich equation in most cases<sup>100,109</sup>. Valuable insight may be gained by careful kinetic studies. For instance, irregularity in the change of rate parameters has been frequently noted<sup>32,108,140,141</sup>. Low<sup>142</sup> has observed that the rate and extent of adsorption of  $H_2$  on  $ZnO$  increase in the temperature ranges  $0-80^\circ C$  and  $110 - 200^\circ C$  and decrease in the range  $80 - 110^\circ C$  — the change with temperature of the constant  $a$  and  $\alpha$  of the Elovich equation parallels changes in the amount adsorbed with temperature. A unique interpretation is out of reach, but these observations undoubtedly point to some changes in surface properties. Progressive reduction of the oxide by gases, i.e.  $NiO$  by  $CO$ , may be without effect on the kinetics<sup>127</sup> which may be explained in terms of diffusion of the defects to the bulk. Cotton and Fensham<sup>73</sup> explained the constancy in rate after some time in the adsorption of  $H_2$  on  $NiO$  assuming that  $H_2^+$  or  $H^+$  formed on the surface diffuse<sup>127</sup> to the bulk. Similarly  $OH^-$  formed by the attack of  $H_2$  on  $O^{2-}$  or  $O^-$  may diffuse to the bulk<sup>73,127</sup>. Czanderna<sup>97</sup> observed that above  $\theta = 0.65$  the rate

of adsorption of  $O_2$  on Ag decreased markedly with increasing temperature upto  $137^\circ C$  where as above  $\theta = 0.65$  the rate decreased slightly with decreasing temperature. Although opinions differ<sup>15</sup>, this may be taken to establish that the change in the nature of the active site<sup>109</sup> may take place after a certain coverage.

Multiple kinetic stages are of frequent occurrence. Interpretations for these phenomena that have been advanced include surface contamination, heterogeneity of the adsorbent surface<sup>108,142</sup> and the existence of multiple adsorbent adsorbate structures<sup>143</sup>. A great insight on the adsorbent - adsorbate structures can be obtained from spectral studies<sup>144-145</sup>.

Current thought on chemisorption emphasizes (a) the nature of the metal ion, regarding the chemisorbed species as in inorganic complex, (b) the electronic nature of the oxide, as indicated by its semiconducting properties, and (c) geometry of the lattice, as indicated by its crystal structure. As is shown, these ideas have been applied successfully to the adsorption of gases on n- and p-type semiconductor oxides, but the identification of the specific sites at which adsorption occurs is uncertain<sup>146</sup>. Valuable information on this aspect may be gained by adsorption studies on non-irradiated and irradiated (neutron or  $\gamma$ - irradiated) samples (preferably by E.S.R. method<sup>146,147</sup>). By this means it is possible to introduce calculated amount of defects (by varying dose rate, contact time and temperature) which affects the Fermi level of

the semiconductor. This can also be done in a gross way by doping and these provide very interesting experimental aspects of the theories of chemisorption. Exhaustive work has been done on this aspect, but very little effort<sup>84</sup> has been given on the adsorption of mixed gases which can as well be applied to prove, verify and extend the predictions of electron theory.

In short, experimental and theoretical work carried out so far has revealed various aspects of chemisorption, yet much more work is needed on single, doped and irradiated oxides with gases and mixture of gases for a fuller and better exposition of chemisorption.

### 1.3.1 Silver oxide (structure, electrical properties, as an adsorbent and catalyst)

Silver oxide is a basic oxide sparingly soluble in water. Normally black or dark grey in colour it is isomorphous with cuprous oxide and consists of a body centered lattice in oxygen and tetrahedral in Silver with  $\text{Ag} - \text{O} = 2.05 \text{ \AA}^\circ$  and  $\text{O} - \text{O} = 4.74 \text{ \AA}^\circ$ . This structure is unique in that it consists of two completely interpenetrating and identical frameworks which are not cross connected by any primary  $\text{Ag} - \text{O}$  bond. Each  $\text{Ag}^+$  ion has two near oxygen neighbours. This two fold coordination shown by  $d^{10}$  ions has been discussed by Dunitz and Orgel<sup>166</sup>. One view attributes it to a low d.s promotion energy and an ability of the n-d and (n + 1)s orbitals to hybridise and so

participate in the formation of linear bonds<sup>167</sup>.

It is diamagnetic in character, and its conductivity lies in the semiconduction range. Silver oxide decomposes at a comparatively low temperature and has been reported to be reduced by hydrogen at as low a temperature as  $40^{\circ}\text{C}$ <sup>148-150</sup>. Infrared<sup>151</sup> and decomposition<sup>152</sup> studies have indicated the presence of surface carbonate ion formed by adsorption of  $\text{CO}_2$  during its preparation. However, studies on progressive changes of surface area of the oxide as a result of evacuation indicated that a stabilized oxide can be produced by evacuation at  $173^{\circ}\text{C}$  for 250 hours (when the decomposition is less than 5%)<sup>152</sup>. The oxide can, moreover, be freed from surface carbonate ion by heating in vacuum at  $150^{\circ}\text{C}$  for 4 - 6 hours<sup>151,152</sup>.

Silver oxide has been used as an adsorbent and catalyst mainly in three forms<sup>153</sup>.

- (i) As an oxide layer formed on finely divided active Ag.
- (ii) As oxide precipitated under various conditions.
- (iii) As precipitated oxide annealed in oxygen at high pressures.

It has been demonstrated that surface silver oxide is thermodynamically more stable in comparison to the bulk<sup>154-155</sup>, i.e. heat of formation of surface silver oxide is  $-54 \pm 1$  Kcal/mole whereas that of the bulk is  $-7.3 \pm 1$  Kcal/mole<sup>154</sup>. However, heat of adsorption of oxygen on silver varies from as high a value as 130 Kcal/mole to 10 Kcal/mole at  $110^{\circ}\text{C}$  and from 116 Kcal/mole to 5 Kcal/mole at  $200^{\circ}\text{C}$  with increase in coverage (from

0 to 0.6 )<sup>156,157</sup>. The low heat of adsorption values reported by other workers<sup>158</sup> may be due to the fact that the studies were carried out with a silver surface containing adsorbed oxygen which is very difficult to remove<sup>6,156,159</sup>.

It has been suggested<sup>160</sup> that in the catalysis by silver, surface silver oxide is the active component. Although a vast amount of work has been done on silver, very little effort has been paid to precipitated silver oxide. Recently, Bhattacharyya and co-workers have shown that precipitated silver oxide (supported and unsupported) is a very good catalyst for the oxidation of ethylene to ethylene oxide and methanol to formaldehyde<sup>161-163</sup>.

Excess silver present in silver oxide may play the role of active centres in the adsorption of  $C_2H_4$  and ethylene oxide on  $Ag_2O$ <sup>164</sup> which obeys Elovich kinetics. However, it is not at all clear whether lattice  $O^{2-}$  or adsorbed  $O^-$  ion play any role in the adsorption of gases over silver oxide. Presence of strongly chemisorbed oxygen on silver oxide just as in silver<sup>159</sup> is not unlikely. This view is further supported by the fact that whereas  $Ag_2O$  is found to adsorb very little amount of oxygen<sup>153</sup>,  $Cu_2O$ , isomorphous with it, shows postmonolayer uptake of oxygen<sup>125,165</sup>. Excess oxygen present may be incorporated in the lattice through a  $Ag^{2+}$  transition state as in the case of  $Cu_2O$ <sup>167</sup>.

#### 1.4 Scope of the work

Silver oxide presents a number of special problems as an adsorbent arising from its decomposition characteristics, easy reducibility by  $H_2$  and CO and thermal instability relative to most other oxides. The studies on adsorption of  $O_2$ ,  $H_2$  and CO etc. over silver oxide would, therefore, be highly interesting. Literature survey revealed that apparently the only work on the adsorption of reducing gases on silver oxide is that of Allen<sup>168</sup> who studied the adsorption of hydrogen over  $Ag_2O$ . This work, however, does not throw any light either on the temperature of reduction by  $H_2$  or on the mechanism by which  $H_2$  is adsorbed over  $Ag_2O$ .

'It is now widely recognized that detailed studies of the effect of pressure and temperature on the adsorption of gases within a single chemical system provide one of the most valuable methods of investigating the general problem of gas solid interaction.<sup>125</sup> Studies on adsorption of hydrogen on  $Ag_2O$  has been performed with this aim in view to explain the mechanism of adsorption and the part played by the adsorbing gas and the solid surface.

To clarify the decomposition aspects, decomposition studies of  $Ag_2O$ , adsorption of CO and  $O_2$  over  $Ag_2O$  along with the above studies have been carried out.

Present day theories of catalysis envisage the Fermi level as a regulator of adsorption and catalytic activity. A change in the height of Fermi level will, therefore, affect the adsorption of gases on an oxide. It is well known that different methods of preparation and irradiation affects the Fermi level. Preliminary experiments on hydrogen adsorption over irradiated  $\text{Ag}_2\text{O}$  and  $\text{Ag}_2\text{O}$  prepared by two methods have been carried out to study these effects, and illustrate further clearly the proposed mechanism of hydrogen adsorption.

Studies on mixed gas adsorption in the literature are very few in number<sup>84</sup>. These studies provide a very valuable means for the confirmation of the predictions of the electron theory of chemisorption. The results of the mixed gas adsorption may be easily utilised to probe into the mechanism of single gas adsorption. Adsorption of  $\text{H}_2 + \text{O}_2$ ,  $\text{H}_2 + \text{CO}$  and  $\text{H}_2 + \text{He}$  mixtures, have been therefore, carried out over silver oxide.

It has been mentioned earlier that Bhattacharyya and coworkers<sup>161-163</sup> have shown that  $\text{Ag}_2\text{O}$  is a very good catalyst for the mild and controlled oxidation of a number of substances. However, the role played by the oxide surface is not much clear. Above studies and the studies on adsorption of  $\text{O}_2$ ,  $\text{CH}_3\text{OH}$  etc have been carried out to clarify certain aspects of the role of the  $\text{Ag}_2\text{O}$  surface.