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CATALYSIS AND THE INTERSTITIAL-ELECTRON MODEL FOR METALS

I. The Hydrogen-Electrode Reaction and the Kita Classification of Group IB and IIB Metals

By

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Abstract

A basis in metal structure is given for the classification by KITA of Cu, Ag and Au along with transition metals as "*d*-metals" and of Zn, Cd, Hg, Ga, In, Tl and Sn as "*sp*-metals". The structural basis is the known distortion of the metal ion cores (d^{10}-electron shells) of the latter group of metals which accompanies the observed lattice distortions and which leads to abnormally large screening of the ion cores by *d*-electrons in the direction perpendicular to the metal surface. Other properties of metals which show a difference in transition metals and "*sp*-metals" or a sharp discontinuity in properties between Group IB and IIB are chemisorption of xenon, gradations in M. P., B. P., and Heat of Atomization, work function, intermetallic distances, d^{10}-s promotion energy and gradation in internuclear distances of diatomic hydrides. Thus, the characterization of these Group IIB, IIIB and IVB metals as metals with weak positive fields perpendicular to the surface but strong positive fields in the lateral direction explains a large number of anomalous properties of these metals. This asymmetric positive field may also account for the electrochemical mechanism involving H_2^+ as an intermediate as proposed by HORIUTI for Group IIB, IIIB and IVB metals (*sp*-metals) rather than the H atom intermediate involved for Group IB and Transition Metals (*d*-metals). The different dependence of reaction rate on pH and other secondary factors for the two groups of metals is also discussed.

1. Introduction

The interstitial-electron model for the structure of metals[1] has emphasized that there are fundamental differences between metals with ion cores of 8-electron shells (rare gas shells, *e.g.* Na^+, Al^{3+}, Ti^{4+}) and metals with 18-electron shells (d^{10} shells, *e.g.* Cu^+, Zn^{2+}, Ga^{3+}). The difference lies in the much greater deformability and penetrability by electrons ($\bar{e}$) of the d^{10} shell as compared to the rare-gas shell[2,3]. It leads to a large effective positive field for the d^{10} ion cores, and the importance in chemical behavior is dis-

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cussed in text books. The transition metals with incomplete *d*-shells exhibit intermediate behavior, but they are distinctly different from the d^{10} metals. These differences in metals have been long recognized and in discussions of catalysis by metals[4,5], there is usually a division into transition metals or *d*-metals which are good hydrogenation catalysts and *sp*-metals (characterized as d^{10} metals above) which have little or no activity for hydrogenation reactions.

However, there appears to be a distictly different behavior of the Group IB metals and other group B metals in the hydrogen electrode reaction. A thorough study of both the hydrogen electrode reaction[6] and of electroreductions of hydrocarbons[7] led KITA to classify Cu, Ag and Au as "*d*-metals" along with transition metals and Zn, Cd, Hg, Ga, In, Tl and Sn as "*sp*-metals". This classification was further characterized[6] as involving an H atom intermediate for the "*d*-metals" and an H_2^+ intermediate[8] for the "*s*-*p*metals" with respect to the hydrogen electrode reaction.

This paper will be concerned with exploration of the basis for this experimentally well established classification with emphasis on the difference in Group IB and IIB metals. Although detailed descriptions of the metal surface on the basis of the interstitial-electron model will be necessary to discuss the hydrogen electrode reaction in detail, it has been shown by KITA[6] that bulk metal properties rather than details of electrode surface preparation are important in this reaction. The great simplicity of the hydrogen electrode reaction thus makes it appropriate for an initial use of the interstitial-electron model in interpretation of catalysis, and would not appear to require prior discussion of surface catalytic sites in detail.

2. Comparison of Group IB and IIB metals

A number of properties in which Group IIB metals differ strongly from IB metals will be discussed below. Differences will also be pointed out in the gradation of properties within B metals (*sp*-metals) from those within transition metals and metals with rare-gas ion cores. It will be shown that both these types of differences can be understood on the basis of two known properties of the ion cores. First, the d^{10} ion core is more deformable and more easily penetrated by electrons than the rare gas ion core[2,3]. Second, there is an ion core distortion in the case of IIB, IIIB and IVB metals which is not present in transition metals and Group IB metals. This ion core distortion was discussed in detail[1] in connection with metal structures and lattice distortion and was shown by the anisotropy of the diamagnetic susceptibility in the case of zinc and cadmium to be a distortion in the direction of the c-axis.

The strong positive field experienced by electrons in Cu, Ag and Au as compared to alkali metals provides an explanation for the large heats of atomization for the noble metals. A comparison of Group IIB metals with alkaline earth metals[9] shows the opposite effect for the d^{10} metals in this comparison. Further, the melting points and intermetallic distances as well as heat of atomization reflect a weaker positive field for the Zn ion core as compared to Ca (and also Cu). It is proposed that an ion core distortion for Zn^{2+} in the direction of the c-axis leads to greater screening of the nuclear charge in the direction perpendicular to the surface and that the properties in Table 1 are the result of the resultant weaker positive field for Zn^{2+}, Cd^{2+} and Hg^{2+} as compared to corresponding alkaline earth ion cores or Cu^{+}, Ag^{+} and Au^{+}.

TABLE 1. Comparison of melting points, heats of atomization and distances of closest approach for solid metals of Groups IIB and IB, and Groups IIA and IA

Zn	Cu		Ca	K	
420°	1083°	°C	850°	64°	°C
31	81	kcal/mole	42	21	kcal/mole
2.66	2.56	Å	3.94	4.63	Å
Cd	Ag		Sr	Rb	
321°	961°	°C	770°	39°	°C
27	68	kcal/mole	39	19	kcal/mole
2.98	2.89	Å	4.31	5.00	Å
Hg	Au		Ba	Cs	
−39°	1063°	°C	710°	30°	°C
15	87	kcal/mole	42	19	kcal/mole
3.01	2.88	Å	4.35	5.25	Å

NYHOLM[10] has discussed the difference in cohesion of alkaline earths and Group IIB metals in terms of valence state promotion energy. The d^{10} to $d^{9}s$ promotion energy is another illustration of the difference in Group IB and IIB metals. There are low values for Cu (2.7 ev), Ag (4.8) and Au (1.9) and high values for other Group B metals (Zn, 9.7; Cd, 10.0, Tl, 9.3; Hg, 5.3). The higher energy required to promote an electron from the d^{10} of Zn as compared to Cu is the combined effect of the more tightly bound *d*-electron and the more weakly bound *s*-electron in the case of Zn.

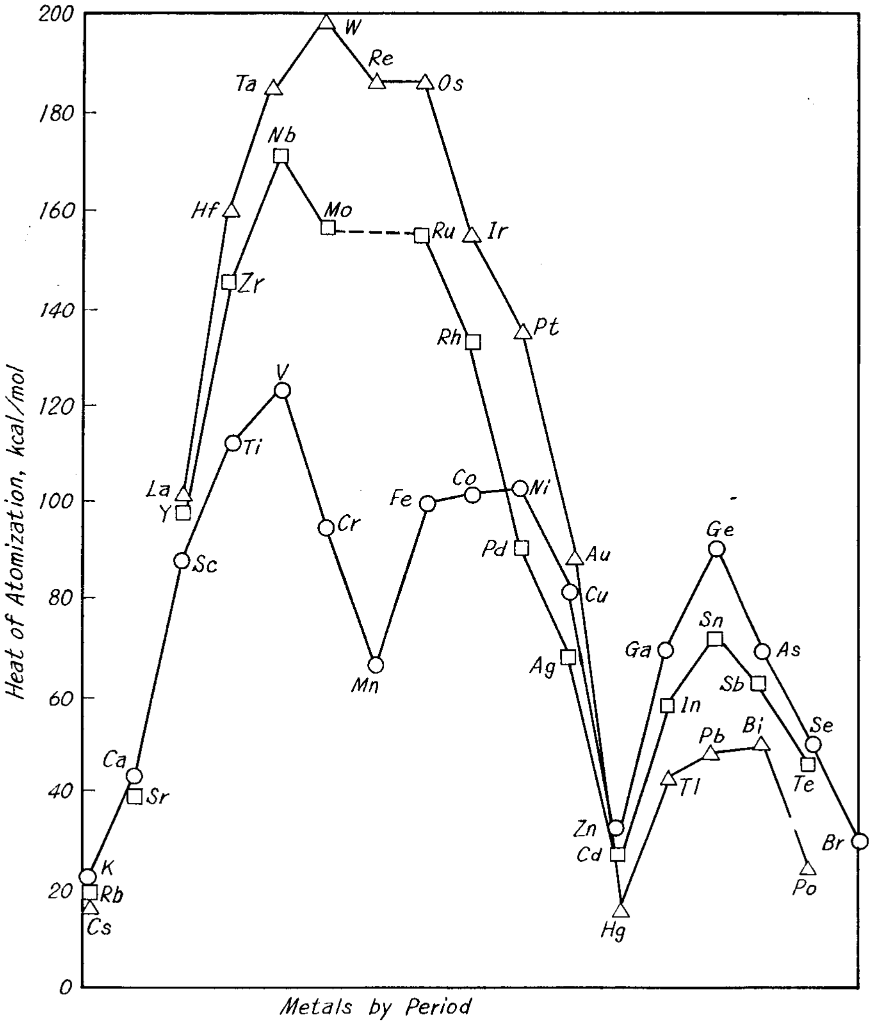

Fig. 1. Variation of Heat of Atomization of Metals for the Three Transition Series.

Figure 1 shows the gradations in heat of atomization for the 3 rows of transition metals and the corresponding group B metals. It is seen that there is an increase in ΔH in the order, 1st row<2nd row<3rd row for transition metals (*e.g.* V<Nb<Ta) while there is the opposite gradation for the d^{10} metals in Group B (Zn>Cd>Hg). There is an intermediate behavior for Group IB with the order Ag<Cu<Au (also, Pd<Ni<Pt). The transition metals show the expected increase in cohesion as atomic number increases.

The reversal in Group B metals can be understood when it is realized that the interpenetration of $\bar{e}$ plays an important role for these metals with highly deformable *d*-shells. The degree of distortion of ion cores will increase with polarizability of the d^{10} ion core which increases in the order Zn<Cd<Hg. The cohesive energy will be expected to have an inverse dependence on ion core distortion since distortion leads to more effective screening of the positive field. This accounts for the order Zn>Cd>Hg in heat of atomization. This property is complex since dissociation to atoms is involved. However, the gradations in M. P. and B. P.[11] show the same reversals, *i.e.* Ta>Nb>V but Zn>Cd>Hg. The effect of distortion in B metals provides an explanation for these trends in M. P. and B. P. as well.

KITA[6] has shown that a plot of log i_0 for the hydrogen electrode reaction against heat of atomization of the metals gives the familiar volcano type

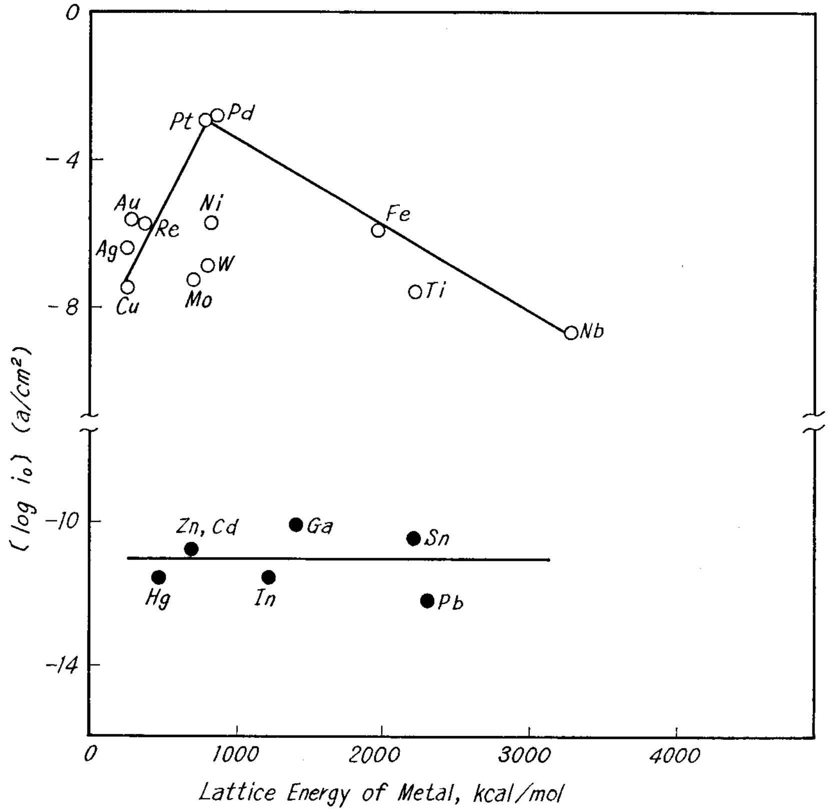

Fig. 2. Dependence of Activity for Hydrogen Electrode Reaction on Lattice Energy of Metal.

curve. It is of interest that a similar plot of log i_0 against lattice energy (see Part III, reference 1) as given in Fig. 2 shows a distinct difference in *sp*- and *d*-metals with little or no dependence on lattice energy for the *sp*-metals.

There is an unusual gradation in internuclear distances for the diatomic hydrides[12)] of B metals. Whereas the internuclear distances of hydrides with rare gas cations decrease with increasing core charge (*e.g.*, NaH>MgH>AlH>SiH) indicating an increase in binding strength, those for d^{10} metals increase in the order CuH<ZnH<GaH and then decrease to GeH. This is an indication that the effective positive fields of these ion cores in diatomic hydrides decrease in the order $Cu^+>Zn^{2+}>Ga^{3+}$. The highly polarizable hydride anion will have electrons which interpenetrate the ion cores as is the case for $\bar{e}$ in the corresponding metals. The greater penetration for Cu^+ which has the highest polarizability leads to the greatest binding strength for CuH (and greatest positive field for Cu^+).

Perhaps the most direct direct comparison of effective positive fields for Cu^+ as compared to Zn^{2+} on the metal surface is obtained from the measurements of surface potentials[13)] of adsorbed Xe. For Xenon the adsorption is predominantly due to polarization of the Xenon atom by metal ion positive cores on the surface, and upon adsorption of Xe there is a resultant decreases in work function of the metal. The change in work function are 0.66 ev for Cu and only 0.21 and 0.23 ev for Zn and Hg, respectively. This is a very clear indication for the considerably stronger positive field for the ion cores of Cu^+. For comparison it can be noted that the work function change ($\Delta\phi$) is larger for W (0.5 ev) (very strong + field) and is zero for Ca (very weak + field).

These data on surface potentials for Xe help to clarify the gradations in work functions for metals. There is an increase in work function in the order K (2.22 ev), Ca (2.76) and Sc (3.33) as expected from the increase in ion core charge from 1 to 3. However, for corresponding d^{10} metals there seems to be a slight decrease in work function[14)] in the order Cu (4.4 ev), Zn (4.24) and Ga (3.96). The smaller differences in this latter case as compared to that in Xe adsorption probably is due to influence of the less screened positive fields in the lateral directions from the ion cores. In any event the work functions of d^{10} metals also indicate a weak field for Zn^{2+} and Ga^{3+} since there is not the expected increase with core charge.

There have been numerous discussions of the properties of Cu and Zn which were directed to the valence of the ion core. These differ from the present discussion which takes the valence Zn^{2+} and Cu^+ as definite and ascribes the unusual behavior to distortion of electron shells. The discussions based on valence include those of Hume-Rothery15), Raynor16) and Plummer and Rhodin17). The discussion of the Engle-Brewer Correlation18) in a recent text19) clearly placed Cu with transition metals and Zn with other d^{10} metals as proposed by Kita. Engel20) considers that the d^{10} shell is not filled at Cu but is only filled between Cu and Zn (alloy data). In general these discussions point up the stronger + field (or higher valence) for Cu as compared to Zn. The ϕ values show that Zn, Ga and Sn do have strong $\bar{e}$ attraction; the terms weak and strong + field used in the paper are relative terms used for comparisons.

3. Metal Ion Cores in Group IIB. IIIB and Sn and Pb

The conclusion reached that in the metal surface the effective positive field of the ion core is weaker for Zn^{2+} than Cu^{+} may appear surprizing. However, the effects of deformed ion cores or "one-sided polarization" have been demonstrated for many compounds with d^{10} cations by Fajans21). The greater intermetallic distance (2.66 and 2.907 Å) for Zn compared to Cu (2.56) is a further indication of the difference in the two ion cores. The effect of an specially strong positive field of a d^{10} ion core3) which normally does not show a one-sided distortion is shown by the formation of auride ion in the intermetallic compound10) Cs^{+} Au^{-} where it is supposed that Au^{+} is completely interpenetrated by the 2 valence electrons.

It is the ion core distortion which is considered to be responsible for the discontinuity in behavior of Cu and Zn and the other members of Group IB and IIB, respectively. The trends in properties discussed above point to a continuation of the trend to Group IIIB and IVB, *i.e.* a still weaker field for Ga^{3+} than Zn^{2+} and possibly an even weaker positive field for Sn^{4+}. (Ge^{4+} is not included in this discussion since it is a semi-conductor).

Unusual properties of Group IIIB and IVB metals which substantiate

Table 2. Interatomic Distances (in Å) for Metals

Cu	Zn	Ga	Ge	As
2.55	2.66	2.70 (av.)	2.44	2.51
Ag	Cd	In	Sn	Sb
2.88	2.97	3.24	3.016	2.90
Au	Hg	Tl	Pb	Bi
2.88	3.00	3.40	3.40	3.10

the presence of deformed ion cores are presented in Table 2. The abnormally large interatomic distances for In, Tl and Pb, outlined in the Table, have been commented on in text-books[22)]. It has been suggested that these ion cores may have lone pairs of electrons, *e.g.*, $Tl^{3+}(\bar{e}_2)$, but it is felt that the picture of a distorted ion core is a more useful concept which is based on experimental evidence in the case of Zn and Cd. There is also evidence for distorted ion cores (the lattices are distorted from close packing) from anisotropy of diamagnetic susceptibility for all the outlined ion cores in Table 2 except for Pb. Pb forms a face centered cubic structure, and there is no evidence for ion core distortion. PbO, however, has a distorted lattice[21)].

Data on Surface Energies of Metals (see, *e.g.*, KITA[7)]) show a low surface energy for Zn, Cd, Hg, Tl, Pb and Sn as compared to Ag, Cu, Fe and Pt. This agrees with the conclusion that the first group of metals have weaker + fields of the ion cores at the metal surface.

4. Consequences of Asymmetric Screening of Ion Core in Group IIB and IIIB Metals

The positive field of the Cu^+ ion core at the metal surface is of such magnitude that Cu adsorbs H atoms (see Sect. 5) but does not dissociate H_2 molecules. It is suggested that because of the even weaker positive field of Zn^{2+} at the metal surface, Zn metal does not readily adsorb H stoms. The same would be true for the other Group IIB metals, Group IIB metals and Sn and Pb. There are calculated values for heats of chemisorption of hydrogen on these metals, but there are no experimental data. It follows, then, that in addition to the low hydrogenation activity expected for all d^{10} metals in reactions involving molecular H_2, Group IIB, IIIB and IVB metals will show little or no activity in reactions involving H atoms. Atomic hydrogen has been found to adsorb on finely divided Hg at liquid N_2 temperature[23]. However, all this hydrogen evolves on warming to room temperature.

The hydrogen electrode reaction observed on these latter group B metals has been postulated to proceed by a different mechanism[6,8)], the electrochemical mechanism involving H_2^+ as an intermediate in contrast to the H atom intermediate in the case of transition metals and Group IB metals.

In considering the details of the adsorption of H_2^+ and its subsequent release as H_2 it is necessary to speculate on the nature of the metal surface for the Group IIB–IVB metals. The distortion of the ion cores in the lattices of these metals is such that although the average positive field surrounding the ion cores increases with increasing positive charge from $Cu^+$to Zn^{2+} to Ga^{3+}, because of the distortion of the electron cloud, the actual positive field perpendicular to the surface (in the direction of the c-axis for Zn and Cd) diminishes from Cu^+ to Zn^{2+} to Ga^{3+}. This can be characterized as an asymmetric field, and the itinerant electrons of the surface layer experience a weaker positive field above the ion cores than in the regions between ion cores. This description is very close to the surface description suggested by KITA[24)].

5. Surface Model for the Hydrogen Electrode Reaction

The interstitial-electron formulation of Group IIB–IVB metals with non-homogeneous positive fields at the surface appears to conform to the general expectations of the behavior of these metals as catalysts for the hydrogen electrode reaction. It will now be shown that the model can also account for some of the secondary effects on the reactions such as the increase in activity of *sp*-metals with increase in pH, the opposite effect for *d*-metals, and the absence of an effect of solvent.

For transition metals the hydrogen electrode reaction involves the following two steps, the second of which is rate determining

$$H^+ + \bar{e} \rightarrow H(a) \qquad 2H(a) \rightarrow H_2 .$$

The proton can enter the reaction from H_2O or H_3O^+ in aqueous solution. It can be assumed that H adsorption on the electrode surface will occur by interaction of H atoms with the $\bar{e}$ of the metal surface and that strongest chemisorption will occur for metals with weakly bound electrons. The binding of H(a) to the electrode surface should be *inversely* proportional to the work function of the metal (ϕ). This view is supported by the inverse dependence of the hydrogen surface potential on ϕ of the metal and is discussed in detail in Paper IV of this series. It follows that the ease of detachment of H will be directly proportional to ϕ. The recombination of H atoms on the surface then also should be *directly* proportional to ϕ. The increase in activity for the hydrogen electrode reaction with increasing work function has been demonstrated experimentally for transition metals by KITA[6)] (see Fig. 3). By the same reasoning it is understandable that the activity increases with decreasing heats of chemisorption of hydrogen, as also shown by KITA[6)].

The surface of "*d*" metals can be pictured as having a relatively smooth layer of electrons above the layer of ion cores. Figure 4 shows a slightly larger spatial extension of the $\bar{e}$ layer in interstitial regions. This interstitial region is proposed to be the H atom adsorption site for close packed surfaces on the basis of the interstitial-electron model. The case for BCC metals

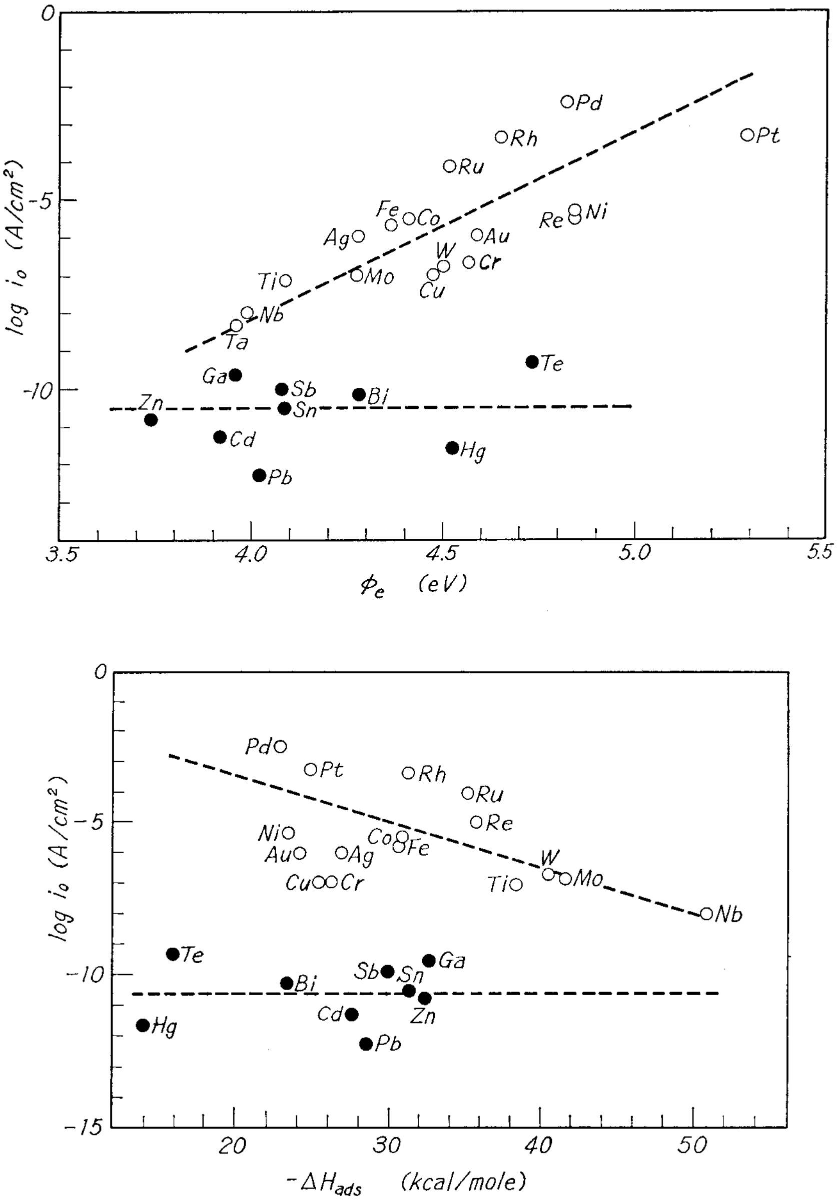

Fig. 3. Different Dependence of Rate of Hydrogen Electrode Reaction on Work Function and Heat of Chemisorption of Metals.

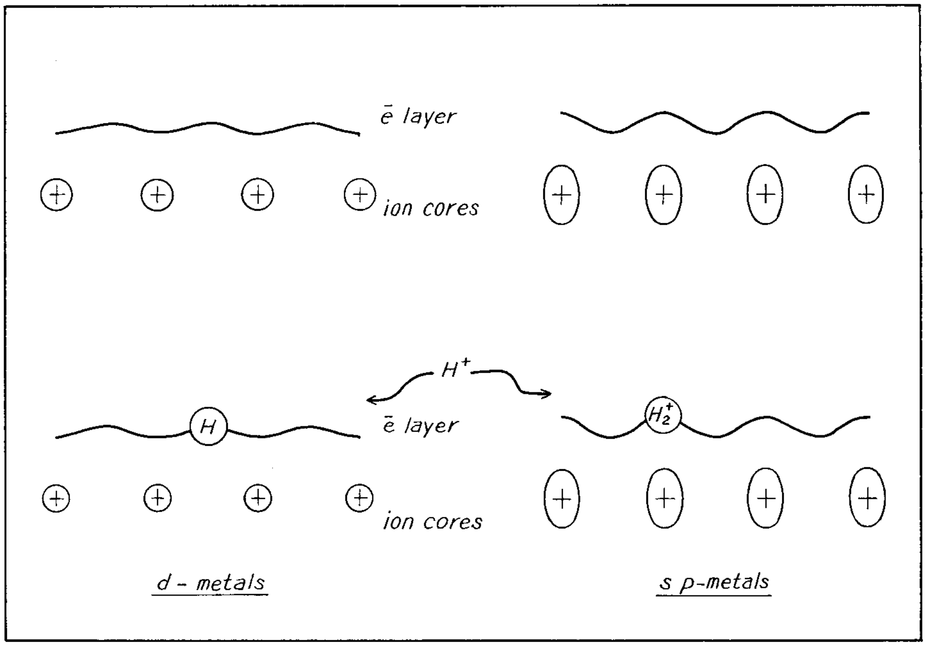

Fig. 4. Proposed extension of ē above surface layer of ion cores and adsorption sites of H_2^+ and H atoms.

and for non-close packed surfaces will be discussed in a complete characterization of the metal surface in Part II. By contrast the metal surface for "*sp*" metals is shown as having a definitely greater extension of ē density above the distorted ion cores. The region above the ion cores is considered to be the adsorption site of H_2^-. The model of Fig. 4 portrays the ease of removal of ē on the basis of screening of + fields of ion cores. It does not deal with complex questions of surface potential or actual electron densities.

In regard to secondary effects it is expected that any substance which strongly adsorbs on the positive ion cores will lead to a weakening of the binding of itinerant electrons which can result in a stronger chemisorption of H atoms. Thus, interaction of an anion such as OH^- with transition metals surfaces would be expected to lead to lowered activity for the hydrogen electrode reaction. The strong adsorption of OH^- accounts in this way for the lower activity of *d*-metals in alkaline solution. In would appear that in the case of Pb this effect of OH^- in allowing a stronger adsorption of H atoms actually leads to a shift in mechanism to the mechanism involving H atoms. It should be noted that no strong inhomogeneity of the Pb surface was indicated by its lattice structure.

The description of $H_2^+(a)$ on the surface of a d^{10} metal must be less detailed because there are no experimental data such as surface potentials to compare different metals. It is likely that H_2^+ is chemisorbed directly over the d^{10} metal ion core which is postulated to have the most easily movable electrons on the surface (greatest screening of ion core charge). The mechanism postulated[8)] for the hydrogen electrode over Group IIB–IVB metals also involves two steps, the second of which is rate determining

$$2H^+ + \bar{e} \rightarrow H_2^+(a) \qquad H_2^+(a) + \bar{e} \rightarrow H_2 .$$

Here the rate determining step involves one chemisorbed species and an electron also attached to the surface of the metal, and this combination is more complex than that involving recombination of two chemisorbed H atoms. The aysmmetry of the positive field of ion cores in Group IIB–IVB metals is such that with strong attachment of H_2^+ there will be an effect to increase the binding of a metal electron. This is the result of the shift of some of the screening *d*-electrons and itinerant electrons into the region between the ion core and the adsorbed H_2^+. This results in an over all greater binding of $\bar{e}$ to the surface. There are now effects on the reaction rate in opposite directions. Strong adsorption of H_2^+ would lead to higher concentration of H_2^+ on the surface and increased rate of reaction, while the accompanying greater binding of electrons would lead to lower reaction rate. This balancing of effects has been discussed in more detail by KITA[6)] although in slightly different terms. In any event the balancing of effects can account for the lack of dependence of rate of hydrogen electrode reaction for Group IIB–IVB metals on either work function or heat of chemisorption of hydrogen as shown in Fig. 3.

As already stated the characteristics of adsorbed H_2^+ are difficult to describe in detail, but it seems reasonable that H_3O^+ would compete with H_2^+ for adsorption sites on the metal surface. Attachment of OH^- would not be expected at a site proposed to have high electron density. This secondary effect of H_3O^+ would explain the decrease in activity of Group IIB–IVB metals in acid solution. For both types of metal solvents are not expected to have any secondary influence.

The shift in mechanism for Pt to the electrochemical mechanism at low overvoltages is of considerable interest. It suggests that there is little energy difference for the two mechanisms, and that with a lowered availability of electrons, Pt prefers to release an electron to form $H_2^+(a)$ rather than 2 $\bar{e}$ to form $2H(a)$.

6. Predictions of Secondary Effects based on Interstitial-Electron Model

In this preliminary consideration of the hydrogen electrode reaction it has been assumed that secondary effects (*e.g.* solution effects, the crystal plane of metal involved) would be small. However, the explanation of the difference between Group IB and other Group B metals is in terms which allow consideration of such secondary effects. The effect of pH was already discussed. The effect of surface active agents would depend on the groups involved at the surface. The anionic adsorbents with amine groups would be expected to adsorb away from ion cores of Group IIB–IVB metals and lead to an increase in activity by facilitating adsorption of H_2^+. Cationic adsorbents would interfere with H_2^+ adsorption and lower the activity. This is in agreement with the observed lowering of hydrogen overvoltage on Hg by an anionic surfactant and the raising of overvoltage by a cationic surfactant[24)]. The more general effect of a lowering in activity by both anionic and cationic surfactants as observed on transition metals and Cu is probably that due to interference in H atom recombination by the presence of a surfactant on the surface (adsorbed above M^{n+}).

The characterization of adsorption sites and availability of $\bar{e}$ on different lattice planes of metals will be treated in Part III and the chemisorption of H_2, CO, N_2 and O_2 will be discussed in Part IV of this series of papers. Secondary effects on the hydrogen electrode reaction due to lattice planes can then be discussed in detail.

Some speculation can be given here on the effects of the lattice distortion observed in HCP structures for Be, Sc, Ti, Zr, Y, La, Tl and the heavy rare earths. This is a distortion with c/a less than 1.633, an opposite and smaller distortion than that of Zn and Cd. Here, there is stronger binding in the direction of the c-axis so there will be a strong positive field of the ion core perpendicular to the surface but a weakened positive field in the lateral direction. This is expected to lead to a stronger adsorption of H atoms (in the region of itinerant electrons) but a lowered tendency to adsorb H_2^+ over the ion core. For Ti this is expected to lower its activity in the hydrogen electrode reaction as compared to a normal HCP structure. The effect for Tl would be a lowered tendency to adsorb H_2^+ and an increased tendency to chemisorb H atoms; this could possibly lead to a shift in mechanism for Tl under certain conditions as was observed for Pb. The above speculation is based on the assumption that the surface plane which predominates for polycrystalline material is the layer perpendicular to the c-axis. A plane through the c-axis would give a different prediction. For this reason a more careful consideration of the properties of the metal surface in general is desirable.

Of interest as electrodes would be alloy materials such as ε-phases which have been formulated by the interstitial-electron model as having an inhomogeneous distribution of electrons. $CuZn_3$ is a typical example. The γ-phases (Cu_5Zn_8) are more extreme examples of inhomogeneous structures.

7. Discussion

In discussions of catalysis it is appropriate to divide metals into the following three classes: (1) Metals with rare gas ion cores (8-electron shell), (2) Transition metals with incomplete *d*-shells, and (3) Metals with non-rare gas shells (d^{10} electron shells). The designations of *sp*-metals and *d*-metals used by DOWDEN[4)] and BOND[5)], and the different *sp*- and *d*-metal classification of KITA[6)] are essentially based on a valence-bond theory of metal structures. The author prefers to use the descriptive terms listed above and to emphasize the unusual nature of the experimental findings for the hydrogen electrode reaction by KITA[6)] as being exceptions to a more general behavior. It will be of great interest to see whether this behavior of Group IB metals in the hydrogen electrode reaction is shown in general in reactions over these metals involving H atoms. They certainly persist in electrode reductions of organic molecules.

The surface structure of transition metals and Group IB is described by the interstitial-electron model as homogeneous as compared to the more heterogeneous surface of metals of Groups IIB–IVB. This description will be elaborated on in Papers II and III of this series and differences for different crystal planes will be characterized. It did not appear necessary to use a more detailed description for treatment of the hydrogen electrode reaction. The inhomogeneity of the metal surface for Zn, Cd, Ga, etc. can also be described in terms of a greater localization of electrons for these metals. It will also be of interest to explore further consequences of this difference in type of metal surface for catalysis.

There has been extensive speculation about ion cores and electrons in this paper, but the *experimental facts* of the *lattice distortion* and *anisotropy of diamagnetic susceptibility* strongly support the concept of asymmetry of the positive field of the ion cores at the surface for Groups IIB–IVB metals. The general agreement of these ideas with those of KITA[6)] from a different point of view is quite striking.

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