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CATALYSIS AND THE INTERSTITIAL-ELECTRON MODEL FOR METALS

IV. Chemisorption on Metals

By

O. JOHNSON*

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Abstract

A description of chemisorption on a metal surface is given in terms of an interstitial-electron model for metals. The specific location of adsorption sites on different lattice planes, their relationship to itinerant electron density (ē), the degree of localization of itinerant electrons in a binding region for adsorption, and the interaction of *d*-electrons localized on the metal ion cores are all part of the description. The pattern of localization of ē in the interior of the metal leads to a similar kind of surface ē localization (surface state) which quite naturally provides a basis for "surface compounds" in chemisorption. Chemisorption is closely related to ordinary chemical binding in metal complexes and metal cluster compounds; participation by itinerant electrons provides the unique characteristics of chemisorption such as surface mobility and variable heat of chemisorption. A high degree of ē localization is associated with adsorptives which give a high heat of chemisorption and form immobile adatoms, and a low degree of ē localization is associated with low heats of chemisorption and mobile adatoms.

Adsorption of a molecule or atom on a metal surface takes place either (1) with transfer of ē from the adsorptive to the metal or (2) with transfer of ē to the adsorptive from the metal. The first predominates for physical adsorption (*e.g.*, Xe) and for chemisorption where the adsorptive is a low work function metal atom (*e.g.*, Cs) or a highly polarizable atom (*e.g.*, I). The second predominates for adsorptives with appreciable electron affinity (*e.g.*, O, H, CO). These characterizations are related to the *r*-state and *s*-state derived by TOYA from quantum-mechanical considerations although the predicted changes in metal properties are connected in this treatment to the specific electronic interactions rather than to the states themselves.

From observed work function changes on chemisorption of H, O, CO, halogens, Cs and Xe on the 3 major lattice planes of tungsten it is possible to demonstrate a linear dependence of the change in work function ($\Delta\phi$) on ϕ. This leads to the relation $\Delta\phi = \phi_M - \phi_A$ where $\Delta\phi$ is now the difference between the metal work function and ϕ_A, an apparent work function for adsorptive. This relation states explicitly the often expressed relation of metal work function and "electronegativity" of adsorptive. It also predicts the

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same terminal ϕ value upon chemisorption of a given adsorptive except where large entropy effects occur.

I. Introduction

Discussions of chemisorption over the past several years have moved from the use of valence-bond concepts to the use of the broader concepts of Molecular Orbital Theory. There is current interest in the concept of some kind of "surface compound"[1,2], in descriptions of the involvement of *d*-electrons in terms of ligand field theory[3], in wave mechanical calculations which include the (MA) ground and excited states as well as (M^+A^-) and (M^-A^+) states[4,5,6] and in interrelations between donor-acceptor complexes[7] or organometallic complexes[8] and chemisorbed species. The Interstitial-Electron Model[9] for the electronic structure of metals provides a framework for all of these concepts and provides some perspective for their respective roles in chemisorption. The "spatial arrangement of electrons" can be looked on as a common basis for the above viewpoints.

The chemisorption of H_2, CO, N_2, halogens, and O_2 will be considered in this paper. The interaction of these adsorptives with the metal surface will be discussed in terms of the electron distribution postulated for the metal surface in the previous paper[10]. A molecular orbital approach will be used in which interaction of metal ion cores, positive nuclei of chemisorbed molecules and electrons associated with both will be considered rather than localized (*e.g.* electron-pair) bonding between a metal atom and a chemisorbed molecule (or atom). Along with the chemisorption of the above molecules, the simpler cases of adsorption of an alkali metal atom and of xenon will be taken as examples of adsorption where (1) complete electron transfer to the metal occurs and (2) where there is only a polarization of electrons of the adsorbate, respectively.

A metal surface can be treated as an array of + ion cores whose + field is not completely screened by the layer of itinerant electrons above it. Such a surface will attract the electron cloud of many atoms or molecules. At the equilibrium position for a chemisorbed species, the interaction of the + nuclei of the chemisorbed species with metal electrons (both itinerant electrons and *d*-electrons localized on ion cores) must also be considered. This latter interaction which involves both the properties of itinerant electrons in the metal surface and the electrons of the adsorptive will be discussed below in terms of a "surface binding region". An attempt will be made in this paper to emphasize the factors of importance for all of these complex electronic interactions.

II. Model for Chemisorption on a Metal Surface

II-1. General Characteristics of Model

There are a wide variety of experimental observations on chemisorbed species. These include heats and entropy of chemisorption, ratios of chemisorbed species to metal atoms in surface, mobility of chemisorbed species, infra-red spectra, effect of chemisorption on work function, electrical resistance and magnetic properties, Accomodation Coefficients, Ion Neutralization Spectroscopy, extensive studies by LEED and FEM, flash desorption. There has been no unified interpretation of all of this data. The interstitial-electron model leads to certain clear expectations for chemisorption, but additional postulates must be made to describe the chemical binding in more detail. Such postulates are given below and are based on a broad consideration of principles of chemical binding and the special features of chemical binding in metals. These postulates are in part conclusions reached by others in various treatments of chemisorption and in part consequences of the interstitial-electron model.

Postulate 1. Chemisorption involves formation of a surface compound.

The kind of binding on a metal surface apprears to be very similar to that in transition metal complexes *e.g.* of H or CO. It involves movement of electrons either from metal or adsorptive into a binding region. This is the unique feature of chemisorption on a metal surface. There is rapid movement in and out of the surface binding region for moderate localization. A very high degree of $\bar{e}$ localization leads to immobility of adatoms. Such localization of $\bar{e}$ varies with metal, with adsorbate, with coverage and with temperature. These "binding regions" are pictured as having the same kind of dynamic movement of $\bar{e}$ as in the interior lattice of the metal. There can be various degrees of "homogeneity of binding regions" depending on the adsorptive in the same way as there was considered to be variations in "homogeneity of interstices" in intermetallic phases[9]. This will be considered further for each adsorbed gas.

As described by Molecular Orbital Theory there is rearrangement of electrons to place more electrons into a "binding region". In this paper the Interstitial-Electron Model will be used as the M. O. description of a metal, and the concept of $\bar{e}$ in binding regions, as used by FAJANS and BERLIN[11] and BADER[12], *e.g.*, will be used as the M. O. description of adatoms. Alternate descriptions appear more difficult for qualitative use, and the one chosen offers clear concepts of location of $\bar{e}$ density before and during chemisorption.

Postulate 2. Chemisorption on a metal surface continues until the attraction of electrons by adsorptive (ϕ_A) equals the attraction of ē by the metal surface (ϕ_M).

This states explicitly the often expressed relation between change in work function upon chemisorption ($\Delta\phi$) and "electronegativity" of adsorptive. It also implies a constant terminal work function for a given adsorptive on any metal, a relation which has been noted in the literature for some adsorptives.

Postulate 3. The site for chemisorption depends on both properties of the metal surface and properties of adsorptive.

The work function of metal, location and density of itinerant electrons above the surface and spatial extension of ion-core *d*-electrons characterize areas of high + field and high ē density on the metal surface.

The size, electron affinity and polarizability of adsorptive are important in determining its interaction with the metal surface. For $\phi_A \ll \phi_M$ chemisorption is expected at metal interstitial positions of high ē density. For $\phi_M \gg \phi_A$ chemisorption over M^{n+} or bridging 2 M^{n+} (regions of low ē density) is expected.

This model for chemisorption is a combination of localized binding and collective metal binding which appears to be a requirement for a realistic model. Perhaps the greatest difference of this model from the usual descriptions of chemisorption is the de-emphasis on *d*-orbitals or "holes-in-*d*-band". It should be emphasized that the chemical binding envisaged for the adsorbed atoms on a surface involves (1) an attraction by the positive ion core along with (2) an interaction of the adsorbate with itinerant electrons. Since both (1) and (2) depends on ϕ which changes with coverage, the optimum adsorption site may change with coverage. Likewise the direction of movement of electrons into the surface binding region or into the metal interior can change with coverage.

The model can indicate adsorption sites of strong + field and adsorption sites of high ē availability and thus suggest most appropriate adsorption sites for molecules of different ē affinity and different polarizability.

II-2. Surface Sites for Chemisorption

The sites for chemisorption are the same as those given by other treatments in that they provide for chemisorption over M^{n+}, for bridging of 2 M^{n+} and for interstitial adsorption. However, the interstitial-electron model adds to this picture of ion cores the likely positions of localized ē density at interstitial positions above the surface.

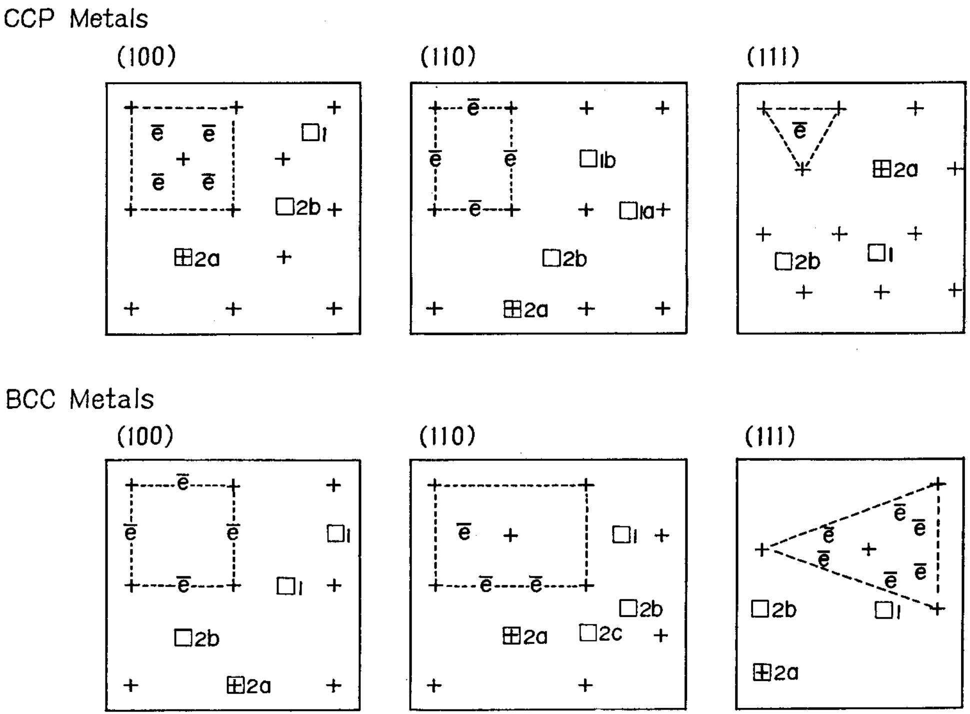

Fig. 1. Adsorption Sites on Different Crystal Planes of Metal Lattices. (Dotted line regions show interstitial location of ē above surface, $\square_1$ = sites for adsorptives which attract ē, $\square_2$ = sites in which M^{n+} attracts ē of adsorptive.)

Fig. 1 shows the location of adsorption sites for adsorptives like H, N, O, and CO on the different lattice planes of CCP, HCP and BCC metals. These adsorption sites are numbered to indicate (1) sites for interaction of adsorptive and ē and (2) sites for M^{n+} attraction of electrons of adsorptive. The location of adsorption sites is similar to those used in other treatments of chemisorption and which are usually based on distance to metal ion cores. However, the use of ē availability is closely related to M^{n+} distance as shown in Paper II. The sites designated as $\square_1$ (interstitial sites) are the most probable chemisorption sites for adsorbates of high electron affinity, and those designated as $\square_2$ (sites above M^{n+} or bridging sites) more likely for adsorbates of low electron affinity. Adsorption over ion cores is expected for Xe. Table 1 shows the direction of occupied *d*-orbitals in transition metals. This is discussed in Section II–4.

TABLE 1. Relation of occupied *d*-orbitals to adsorption sites

BCC Metals	100	110	111
Cr	d^2 to $\square_{2b}$	d^2 to $\square_{2a}$	None
Mo, W	d^2 to $\square_{2b}$	d^2 to $\square_{2b}$	d^2 to M^+
Fe	d^1 to $\square_{2a}$	d^2 to $\square_{2c}$	None
CCP Metals			
Ni	d^2 to $\square_{2b}$	d^2 to $\square_{1b}$	d^2 to $\square_1$
Pd, Pt	None	d^2 to $\square_{2a}$	d^2 to M^+
Rh	None	None	d^2 to M^+
Cu	d^2 to $\square_1$	d^2 to $\square_{1b}$	d^2 to $\square_1$
Ir	None	d^2 to $\square_{2a}$	d^2 to M^+
Ag, Au	d^2 to $\square_{2b}$	d^2 to $\square_{1a}$, $\square_{1b}$	None
HCP Metals	Close-packed layer		
Co	d^1 or d^2 to $\square_1$		
Re	d^2 to $\square_1$		
Ru	d^2 to $\square_1$		
Os	d^2 to $\square_1$		

II-3. Location of Chemisorbed Species in Surface Sites

Since there is no direct experimental data to show the exact location of adsorbed atoms on a metal surface and very little indirect indication, a surface model for chemisorption will depend heavily on the point of view of chemical binding. In this paper a very fundamental basis of chemical binding is used *i.e.* that of electrons in binding regions between positive nuclei. The unique characteristics of chemisorption on a metal surface must take into account the binding by itinerant electrons, and this is one of the major postulates in the present treatment. The experimental support for taking the interaction of adsorptive and itinerant electrons (or more generally, the combined M^{n+} ion core-itinerant electron system) as the major factor in chemisorption will now be outlined.

In hydrogen adsorption on Ni the linear decline in magnetic moment observed by SELWOOD[13)] indicates not only the same kind of binding at all coverages but an adsorption in which H atoms interact with itinerant electrons, since the ferromagnetic moment for Ni is itinerant. This interaction would occur, according to our model, for adsorption in interstitial positions. It was shown earlier[9] how the model accounted for the itinerant moment on Ni (and Co). The experiments of Geus[14] on Fe show a sharp decline in magnetic moment upon oxygen adsorption but no effect in H adsorption. Since the magnetic moment for Fe is on *d*-electrons on the $|Fe^{8+}(d^4)|$ ion core, this is further evidence that H adsorption is interstitial also on Fe. However, oxygen adsorption on Fe does show interaction with its *d*-electrons (pairing occurs), and oxygen adsorption over the ion core is possible. However, it is only on the 100 plane of BCC Fe that *d*-orbitals with unpaired electrons extend ⊥ to the surface; on the 110 plane, unpaired electrons extend along and above the edges. It is not possible to determine the behavior of polycrystallic iron since the exposure of 100 planes is not known.

Thus, although there is experimental support for interstitial adsorption of hydrogen for Ni, Co and Fe and calculations[4] which show it to be possible for other metals, the selection of adsorption sites for metals in general is largely guided by the model and the concepts of binding on the surface mentioned above (including electron affinity and ionization potential of adsorptive). Ion core adsorptive distances, discussed in the appendix, also support interstitial adsorption.

II-4. Influence of *d*-electrons

The interstitial-electron model has emphasized the availability of $\bar{e}$ at interstitial positions and the likelihood of adsorption of atoms or molecules which are electron acceptors in these positions. The possibility of adsorption directly above a metal ion core in cases where *d*-electrons are localized in this position was also pointed out. Since the relative availability of *d*-electrons as compared to itinerant electrons is fundamental to any quantitative treatment of binding on the surface the available information will be considered here.

Concerning the availability of *d*-electrons at the metal surface, the model predicts that since these are localized on M^{n+} rather than itinerant they are more strongly bound. This is indicated experimentally by FEM studies[15] which show that the transmission coefficient for *d*-electrons is 1 or 2 orders of magnitude less than that of itinerant electrons. This indicates that localized itinerant electrons on the surface are the regions of greatest electron availability. The possible exceptions of Group II–IV B metals was discussed in Part I.

A model for chemisorption on the metal surface has been presented in considerable detail. The decision as to which adsorption sites are occupied is implemented in Sect. IV. The test as to the usefulness of such a model will be both in its ability to predict trends in chemisorption and in its ability to interpret the complex behavior observed in experimental studies of chemisorption. In the following sections this is done for a variety of chemisorbed gases.

III. Interaction between a Metal Surface and Cs and Xe

This interaction of alkali metal atoms with metal surfaces has been extensively studied, and the electronic interactions have been given quantitative treatment. For the present purposes the major conclusion is that for each atom chemisorbed there is transfer of 1 electron to the metal lattice, and that this is accompanied by a large decrease in work function of the metal (approx -7.0 ev. for Cs on W when data are extrapolated to zero coverage). The interstitial-electron model considers that the resulting Cs^+ would be at the normal lattice position for M^{n+} of the metal and that the decrease in ϕ is due to the weaker binding of the greater total number of electrons per metal interstice. (The model[9] has given the interstitial-electron structure of W as $|W^{6+}(d^2), 2\bar{e}|_{BCC}$, which has 1/3 occupancy of interstices by electrons or on the average 1/3 $\bar{e}$/interstice.)

Adsorption of xenon occurs by polarization of the electron cloud of Xe by the positive field of M^{n+} with adsorption directly over the ion core. As expected from this description this is accompanied by a decrease in ϕ of the metal since $\bar{e}$ density is brought into the surface binding region, and there is considerable screening of M^{n+}. The $\Delta\phi$ values for complete surface coverage vary from -1.38 ev. for Xe on W to -0.87 ev. for A and -0.15 for Ne as expected for the decreasing polarizability from Xe to Ne. Compared to Cs adsorption, the adsorption of Xe on W and the resultant screening of the W^{4+} ion core is equivalent to bringing 0.2 $\bar{e}$ into the metal lattice per adsorbed Xe.

Since there is a linear dependence of $\Delta\phi$ on polarizability for rare gases these data on Xe and other rare gases can be used to estimate $\Delta\phi$ effects due to polarization in chemisorptions where more complex interactions occur. Data on rare gases will also be used for comparisons in dicussing heats of chemisorption and surface mobility in a subsequent publication.

For most metals it is correct to assume adsorption of rare gases directly over ion cores. However, in some transition metals occupied *d*-orbitals extend in this direction and not in the interstitial direction, *e.g.*, for Pt_{110}, Pd_{110}. In these special cases interstitial adsorption can occur since the

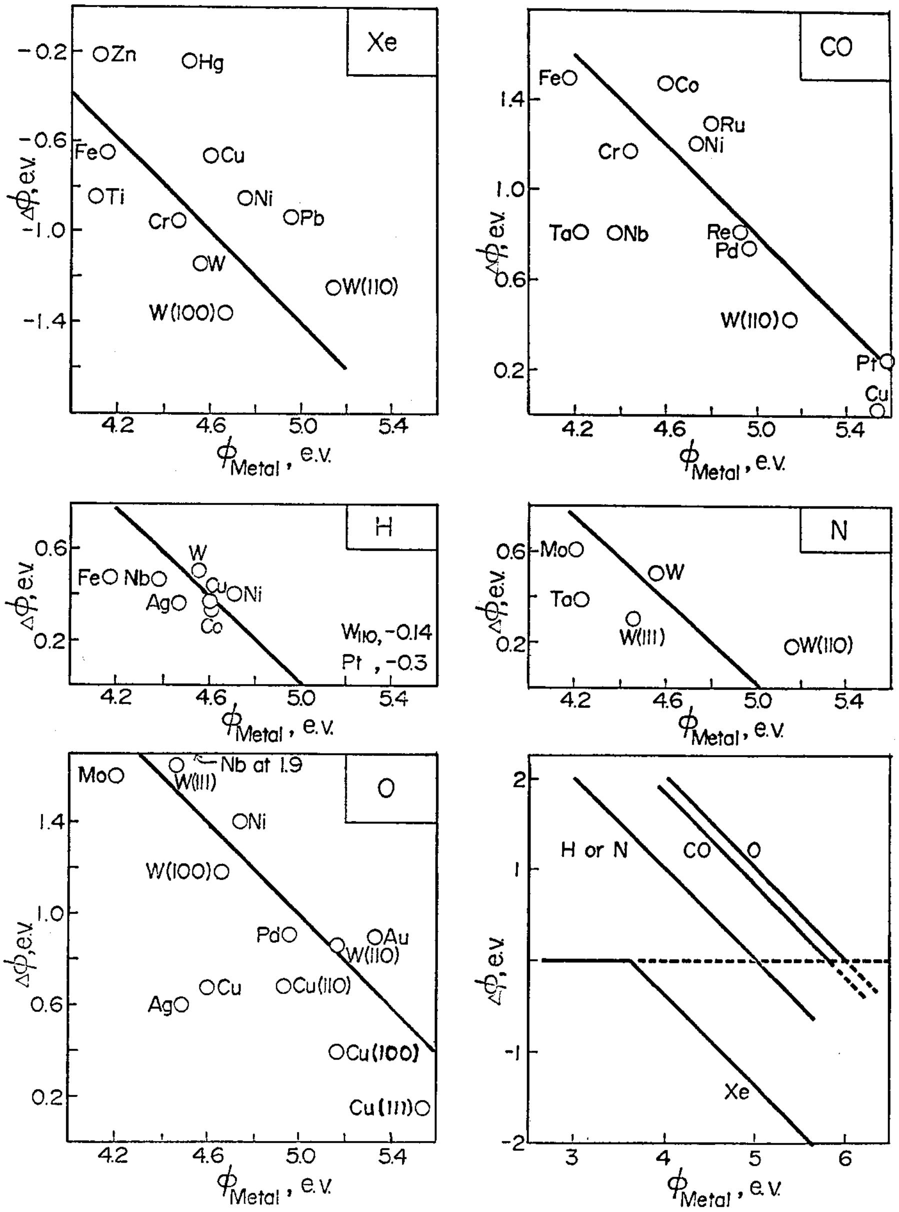

Fig. 2. Effect of Chemisorbed Gases on Work Function of Metals.

strongest positive field of ion cores is in this direction. There are no experimental data to check this.

The plot of $\Delta\phi$ for Xenon adsorption for several metals is shown in Fig. 2a. As expected there is a increase in $\Delta\phi$ with increasing positive field of metal ion cores (increasing ϕ). $\Delta\phi$ is negative for Xe adsorption (see sect. IV–1).

IV. Change of Metal Work Function upon Chemisorption of Various Gases

IV–1. Work Function Changes for Chemisorption on Different Lattice Planes of Tungsten

The change in ϕ upon chemisorption is a very important property since it directly reflects electronic changes in the metal. It has already been useful in understanding adsorption of rare gases and alkali metal atoms. In anticipation of the great complexity of electronic interactions in chemisorption for a variety of metals, the general trends as shown by measurements on different lattice planes of one metal will be reviewed first.

There is now sufficient accurate data available on the change in work function for different lattice planes of tungsten metal upon adsorption of several gases to make it possible to demonstrate a linear relation between $\Delta\phi$ and ϕ. Data taken for the most part from the compilation of SARGOOD, JOWETT and HOPKINS[16)] are given in Table 2 and are plotted in Fig. 3 for Cs, Ba, U, Xe, Argon, I, H, CO, O, OH. It is seen that there is a linear decrease in $\Delta\phi$ for increasing work function for all these adsorptives. On the basis of the model presented in Section II and the discussion of Section III this is explained as follows. For Cs, Ba, U the transfer of an electron to the metal lattice is expected to lead to a change in ϕ directly proportional to the difference in ϕ of the adsorptive and the metal surface. The absolute values of $\Delta\phi$ reflect such a difference. For the gases adsorbed by polarization the $\Delta\phi$ is expected to increase with increasing positive field of M^{n+} *i.e.*, with increase in ϕ. A positive $\Delta\phi$ is used for an increase in ϕ upon chemisorption and a negative $\Delta\phi$ for a decrease in ϕ.

For the majority of the adsorptives where $\bar{e}$ transfer from metal to adsorptive occurs the change in ϕ, now of opposite sign, is expected to be *inversely* proportional to ϕ of the metal, and it is observed that more positive $\Delta\phi$ occur for the lowest work function planes of tungsten. This relationship will be considered to hold for simple metals, and deviations will be examined to see what additional factors they indicate about metal binding. As an example, N_2, which will be discussed later appears to have

TABLE 2. Change in metal work function, ϕ, upon chemisorption[a].

Metal	ϕ_M, ev.	$-\Delta\phi$, Xe		$\Delta\phi$, H		$\Delta\phi$, CO		$\Delta\phi$, O		$\Delta\phi$, N	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
W (110)	5.15	(1.24)[b]	1.55	−0.14	−0.15	0.42	0.65	0.85	0.85	0.18	−0.15
W (100)	4.65	(1.36)[b]	1.05	0.54	0.35	0.55	1.15	1.18	1.35	−0.1	0.35
W (111)	4.45		0.85	0.30	0.55	0.85 (113)	1.35	1.65	1.55	0.3	0.55
W (poly)	4.55	1.14	0.95	0.5	0.45	0.86	1.25	1.6	1.45	0.50 (0.9)	0.45
Cu (111)	5.54		1.94			0.01	0.26	0.13	0.46		
Cu (100)	5.15		1.55		−0.15	0.11	0.65	0.39	0.85		
Cu (110)	4.92		1.32			0.02	0.88	0.68	1.08		
Cu (poly)	4.60	0.66	1.0	0.36	0.4			0.68	1.4	−0.45 (N_2)	0.4
Ca	2.75	0	0								
Ti	4.1	0.84	0.5								
Nb	4.37		0.77	>0.4	0.63	0.8[c]	1.43	1.9	1.63	−0.14 (N_2)	0.6
Ta	4.22		0.62	0.44	0.78	0.8[c]	1.58		1.78	0.38	0.78
Cr	4.44	0.95	0.84		0.56	1.15	1.36				
Mo	4.21		0.61	0.2	0.8			1.6	1.8	0.6	0.8
Mn	4.08		0.48		0.9						
Re	4.93		1.33		1.1	0.8	0.87				
Fe	4.16	0.66	0.56	0.47	0.84	1.5	1.64		1.84		
Ru	4.80		1.2		0.2	1.3	1.0				
Co	4.60		1.0	0.33	0.4	1.48	1.2		1.4		
Rh	4.7		1.1	0.4	0.3		1.1		1.3		
Ni	4.73	0.85	1.13	0.4	0.27	1.2	1.07	1.4	1.27		
Pd	4.95	0.94	1.35		0.05	0.74	0.85	0.9	1.05		
Pt	5.63		2.0	0.14 (−0.3)[d]	−0.63	0.23	0.17	1.2 (0.9)[e]	0.37		
Ag	4.44		0.84	0.34	0.56	0	1.36	0.6	1.56		
Au	5.32		1.72	0.18	−0.32			0.9	0.68		
Zn	4.11	0.21	0.51	0.08	0.89				1.89		
Hg	4.5	0.23	0.9		0.5				1.5		

a) Calculated ϕ based on equation $\Delta\phi=\phi_M-\phi_A$ where $\phi_A=3.6$ ev. for Xe, 5.0 ev. for H, 5.8 ev. for CO, 6.0 ev. for O and 5.0 ev. for N. b) Calculated from data in C. W. JOWETT and B. J. HOPKINS, Surf. Scie., **22**, 392 (1970). c) low values due to decomposition. d) at 295°K. e) Pt (100) est. from H_2O on Pt (110), C. W. JOWETT, P. J. DOBSON, B. J. Hopkins, Surf. Scie.,. **17**, 474 (1969).

a complex type of chemisorption.

The linear relation of $\Delta\phi$ and ϕ does not appear to have been illustrated previously. SARGOOD, JOWETT and HOPKINS[16] emphasized electronegativity relations. TOMKINS[17] stated there was no relation of ϕ and $\Delta\phi$ and suggested a dependence of $\Delta\phi$ on the 1st Ionization Potential of the metal. As

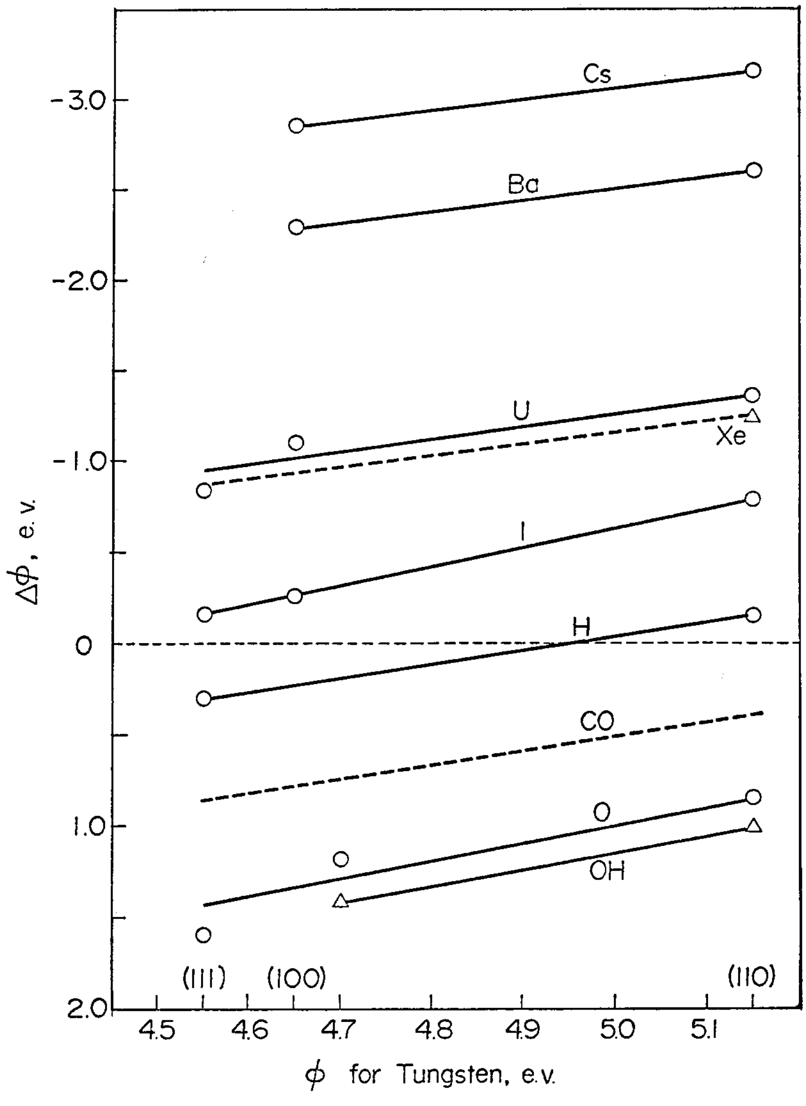

Fig. 3. Changes in Work Function for Single Crystal Planes of Tungsten Due to Chemisorption of Various Adsorptives.

will be seen below the $\Delta\phi$ vs. ϕ relation for polycrystalline metals has many deviations, and data on single crystal planes was needed to clearly demonstrate the relation. Such deviations for metals in general are not unexpected in view of the polycrystalline nature of the films used for measurement, the different coverages, and the combination of opposing effects on $\Delta\phi$. The relation $\phi_M - \phi_A = \Delta\phi$ implied by the linear relation of ϕ and $\Delta\phi$ will be discussed in Section V–5 after considering data for other metals.

It is surprizing that the increase in ϕ produced by CO and O are of the same order of magnitude as the decrease produced by Xe. However, if one views the addition of ē to the metal-electron system by adsorption of Cs or the screening of M^{n+} by polarization of Xe as equivalent to a repulsive effect on metal itinerant electrons, it is reasonable that this would have a larger effect (exponential dependence) per ē than the increase in ē attraction caused by removal of the same amount of ē charge by adsorptives such as CO or O.

For the purpose of making an estimate of such ē density transfer it can be assumed that in adsorption of O_2 there is formation of 2 O^- on the metal surface. This appears reasonable in view of the electron affinity of an O atom for 1 ē (1.465 ev.) and the tendency for many metals to incorporate oxygen as O^{2-} at higher temperatures. Adsorption of oxygen on W_{100} produces an increase in ϕ of 1.2 ev., and this will be taken as the $\Delta\phi$ for transfer of 1 ē from the itinerant electron density of the metal to the adsorbate. Then for CO on W_{100} there is transfer of 0.5 ē ($\Delta\phi = 0.6$) and for H on W_{100} there is transfer of 0.4 ē ($\Delta\phi = 0.5$) into a surface binding region.

The anomolous results for nitrogen on W can now be put on the basis of ē transfer. For W_{100} there is observed a decrease in ϕ of 0.1 ev. By comparison to data for Cs this indicates a transfer of 0.02 ē from N to metal. There is an increase in ϕ for W_{111} and W_{110} (weak adsorption) of 0.2 ev., corresponding to a transfer of 0.16 ē. Viewed on the basis of transfer of ē densities the differences for N_2 on different planes of W are not very great. Since the N atom has no ē affinity the above results are reasonable. The very weak adsorption on W_{110} is probably the most unusual aspect of the data. An increase in ϕ would not be expected on this high work function plane. Details of adsorption sites on the different planes, however, do provide a plausible explanation as shown in section IV–4.

IV–2. Chemisorption of Hydrogen on Tungsten

The data available on chemisorption of hydrogen on single lattice planes of tungsten offers an opportunity to see whether the interstitial-electron model can interpret the details of chemisorption.

On the 100 plane of tungsten TAMM and SCHMIDT[18)] concluded that there is a molecular β_1 adsorption with a heat of desorption of 26.3 kcal/mol and an atomic β_2 adsorption with a heat of desorption of 32.3 kcal/mol. The strongly bound "molecular H_2" shows 1st order kinetics of desorption and H_2–D_2 exchange (not expected for adsorbed H_2) and there is a β_1/β_2 ratio of 2/1. TOYA[19)] has shown the β_1 state also to be atomic, explaining the 1st order kinetics by a different desorption mechanism. The edges of unit cell are the expected adsorption site for the β_2-H adsorption where H in a bridge position is in the region of tetrahedral interstitial electrons. The interaction of H with $\bar{e}$ leads to localization of $\bar{e}$ around H and an increase in ϕ as observed. Due to screening of M^{n+} positive field by H adsorption, adjacent edges are not expected to be occupied by H which is in keeping with the c (2×2) structure observed by LEED. This corresponds to 1 H/2 W. When this coverage is reached ϕ has increased to about 4.8 ev. (about the same as on the bare 110 plane). This makes H adsorption more difficult since metal $\bar{e}$ are more strongly bound. The increase in ϕ also makes the energies of localized *d*-electrons on W nearer to itinerant electron energy. Subsequent chemisorption of H atoms can then proceed by interaction with *d*-electrons. Since they are directed at 45° above the centers of a unit cell this would lead to additional H adsorption of 1 H/W. The chemisorption of a total of 1.5 H/W is in agreement with the observed coverage.

Chemisorption on 110 tungsten is unusual in that after an initial small increase in ϕ there is a decrease in ϕ of 0.17 ev. Equal amounts of adsorption of H atoms in β_1 (27.0 kcal/mol) and β_2 states (32.7 kcal/mol) have been reported[18)]. On this lattice plane with the highest ϕ for tungsten, $M^+ - \bar{e}$ interaction is not expected to be important, so H will adsorb either over W or bridging 2 close neighbouring W. The latter is chosen as the more likely, and as with the 100 plane alternate sites are occupied as β_2 adsorption. At this point, adsorption sites (an equal number) with only 1 neighbor with H attached can be occupied. For both sites some screening of M^{n+} occurs, and this accounts for the small decrease in ϕ.

On the 111 plane of W there is an increase in ϕ of 0.30 ev. upon H adsorption. Desorption studies show there to be 4 types of atomic H and 1 molecular H_2 state. Chemisorption is expected in areas of interstitial electrons which are 3 center sites on the 111 plane. The interstitial model shows 4 adsorption sites/W. It is suggested that successive occupancy with increasing number of neighboring adsorbed H leads to the adsorption species of 14.1, 20.7, 30.4 and 36.6 kcal/mol, respectively. The γ adsorption state is molecular hydrogen.

IV-3. Chemisorption of CO on Tungsten and Nickel

The information on chemisorbed CO is not as complete as for hydrogen. On W_{100} there is an increase in ϕ[20) of about 0.5 ev. upon CO adsorption. There is one CO/W which is reduced to 1 CO/2 W at 1000°K to give a C (2 × 2) structure[21). The interstitial model predicts adsorption of CO where there can be $\bar{e}$ transfer to CO. This can occur in a bridging position on the unit cell edge where the CO molecule is attracted by $2\,M^+$, and $\bar{e}$ in tet positions are available for increased binding of the CO. It is also possible in bonding directly over M^+ with interaction with tet $\bar{e}$ on 4 sides. The latter are probably the most strongly bound CO. As with H, adjacent M^+ would not be expected to adsorb as strongly and a c (2 × 2) pattern would be expected. On the 110 plane there is a decrease in ϕ of about 0.1 ev. followed by an increase in ϕ of 0.3 ev. Desorption studies[21) show a β state (60 kcal/mol) and a state of lower activation energy. REDHEAD[22) has characterized the former as a bridged structure and the latter as linear. According to the interstitial-electron model, adsorption can be expected on the region of itinerant electrons (a 3 center position for the 110 plane) or over M^+. Since this is the high ϕ plane, $\bar{e}$ are strongly bound and smaller back transfer of electrons is expected. If chemisorption occurs first (α state) in the trigonal position the CO screens the positive field of $3\,M^+$ and there is a decrease in ϕ. This makes the possibility of back transfer of $\bar{e}$ possible and subsequent chemisorption (β state) over M^+ with an increase in ϕ.

There is also some data on 110 and 100 Ni. There is adsorption of CO on 100 Ni to form a 2 × 2 unit mesh, removed at 500°C, and a more weakly bound CO on 110 Ni. YATES and MADEY[23) have presented evidence for 5 kinds of chemisorbed CO on polycrystalline Ni. The expected adsorption of CO on 100 Ni would be bridging 2 close neighbors or directly over Ni. Either would form a 2 × 2 mesh and there would be tet $\bar{e}$ to contribute to the binding force. Adsorption on Ni_{110} is expected to be weaker since only $\bar{e}$ in the surface plane are available for back transfer. Chemisorption over Ni is most likely since this allows some interaction with $\bar{e}$ in *d*-orbitals of Ni. Bonding is expected to be weaker due to lack of $\bar{e}$ for transfer to CO.

IV-4. Chemisorption of Nitrogen on Tungsten

Nitrogen does not follow the pattern of chemisorption of H, O and CO either in the $\Delta\phi$ for individual lattice planes of W or in the gradation with coverage. The unusual behavior clearly lies with the 100 plane with the initial decrease in ϕ followed by an increase at higher coverage. The initial decrease in ϕ is associated with the β_2 state which shows a desorption energy of 75–80 kcal/mol. It has also been associated with a c (2×2) LEED Pattern.

The nitrogen atom is reported to have a negative electron affinity. Thus, the interaction with the system of itinerant electrons, shown to be important for O, halogen, H and CO, is not significant for nitrogen. One must look to a polarization of the N atom in the strong field of the tungsten ion cores. On this basis the 100 plane has the unusual feature of a large area between ion cores with no $\bar{e}$ in interstitial positions. (See Fig. 1) There are 4 adjacent $\bar{e}$ positions above the lattice plane. On the basis of the model, a N atom can become attached to the center of a 100 face of the unit cell; the 3 unpaired electrons of the nitrogen ($N^{5+}\ 1s^2\, 2p^{1,1,1}$) can become associated with the $\bar{e}$ in interstitial positions (these are 2/3 occupied in tungsten, $|W^{6+}(d^2), 4\,\bar{e}|$. This not only places more $\bar{e}$ in a binding region between N and 4 W but more $\bar{e}$ density in an interstitial position. The first has the effect of giving strong binding strength and the second of decreasing the metal work function. It is reasonable with such a substantial modification of the electron distribution that adjacent sites would not chemisorb N in the same way. The data indicate that after the strong chemisorption is complete, molecular adsorption of N_2 occurs on alternate sites. This normally gives rise to a decrease in ϕ but adsorption in alternate sites can influence the attachment of the 1st adsorbate to give a reversal of the initial effect. Also, there is further adsorption of N_2 at high pressures in a tightly bound state. The above picture fits the independent adsorption of CO in presence of either N_2 or H_2.

The chemisorption of N on W_{110} and W_{111} produces an increase in ϕ, and $\Delta\phi$ shows little change with coverage on W_{110} and an increase for W_{111}. Chemisorption on W_{110} is probably over M^+, and there must be some $\bar{e}$ attraction by a polarized N to account for the small increase in ϕ. The more complex surface of W_{111} may involve some N bridge chemisorption.

The adsorption site for N on the 100 plane of W can also be an adsorption site for Xe, and the strong binding by $4\,M^+$ can account for the larger $\Delta\phi$ for xenon adsorption on W_{100} (-1.36 ev.) as compared to that for W_{110} (-1.24 ev.). Alternatively, Xe–Xe repulsions on the close-packed W_{110} can account for a lowered $\Delta\phi$.

IV-5. Chemisorption of Oxygen and Halogens on Tungsten

There is a large increase in ϕ upon chemisorption of oxygen on all of the major crystal plane of W. In Fig. 3 the line for oxygen is drawn parallel to the halogens and indicates an unusually small increase for W_{100}. This is another manifestation of the unusual behavior of the W_{100} plane. The increase in ϕ upon oxygen chemisorption represents itinerant electron attraction by oxygen probably to form O^- in bridging positions.

A similar bridging adsorption is expected for the halogens. However, the data shows a decrease in ϕ upon chemisorption of Cl, Br and I on W_{110}. This must mean that although on W_{100} and W_{111} the halogen atoms can attract $\bar{e}$ to counteract their screening effect on M^+, on the high ϕ plane W_{110} the *screening effect* of the polarizable halogen predominates. The adsorption site expected on W_{110} is a 3 center site.

The gradations of $\Delta\phi$ on tungsten are of interest especially for halogens and oxygen. These are tabulated below for W_{100} and W_{110}.

Chemisorbed Atom	$\Delta\phi$ upon chemisorption, ev.	
	W_{100}	W_{110}
O	+1.2	+0.85
H	+0.54	−0.15
Cl	+0.6	−0.25
Br	+0.4	−0.31
I	−0.2	−0.78

For W_{110} the data follow the greater *screening effect* in the order I>Br>Cl>H. Oxygen has a polarizability between H and Cl, but its high electron affinity leads to the increase in ϕ. For W_{100} the halogens show the expected greatest effect in attracting electrons by Cl whose electron affinity is greatest and polarizability (and thus screening) is smallest. H shows the effect of lower screening than by halogens.

V. Chemisorption on Polycrystalline Metals

The complex situation for chemisorption in the case of single crystal planes of W makes any detailed interpretation of $\Delta\phi$ data for polycrystalline metal almost impossible. One way of handling the data is to assume the presence of predominantly high density planes, *i.e.* 111 for CCP and 110 for BCC, and in addition to consider effects only in cases of large changes in ϕ. The $\Delta\phi$ for H chemisorption of 0.5 reported for polycrystalline W is closer to the W_{111} value than that of W_{110} which has a $\Delta\phi$ of opposite sign. Recent data or single crystal planes give ϕ for $Cu_{111}=5.54$, $Cu_{100}=5.15$ and $Cu_{100}=4.92$ all higher than the best polycrystalline value of 4.60. The authors suggest that high index planes (of low ϕ) are present in polycrystalline films of Cu. In view of these large variations in $\Delta\phi$ for individual planes only broad trends will be considered significant in discussing $\Delta\phi$ data for polycrystalline metals. The tendency for any crystal plane to give the same terminal work function for a given adsorbate makes work function data at complete coverage best for comparisons.

V-1. Chemisorption of Hydrogen

Dissociative chemisorption of H_2 takes place for transition metals, and chemisorption of H atoms take place for Cu, Ag, Au, Hg as well as for Al, B, Ge and Si[24].

For the majority of metals under most conditions hydrogen chemisorption leads to an increase in work function (ϕ) and also in electrical resistance. This is the opposite behavior to both Xe and Cs and can be taken as an indication that metal electrons are attracted by the + nucleus of the chemisorbed hydrogen. The general features of the adsorption can be taken to include interaction of the H^+ core of the H atom with interstitial $\bar{e}$ on the metal surface along with the attraction of the chemisorbed H by the M^{n+}. This redistribution of electrons into a binding region between M^{n+} ion cores and the H^+ core would lead to stronger binding of remaining surface $\bar{e}$ in the region of the H atom and to a higher ϕ for the metal. The greatest interaction is expected for metals of low work function where $\bar{e}$ is least strongly bound by M^{n+}. This is illustrated by the decline in $\Delta\phi$ upon H adsorption with increasing ϕ of the metal in Fig. 2.

If a straight line is drawn through the $\Delta\phi$ data for H on tungsten as is done in Fig. 3 with the same slope as for other gases, the value[16] for $\Delta\phi$ on W_{100} is below the line. In Fig. 2 the values for Au (+0.18) and Pt (at 250°K) are considerably above the line. These latter 2 metals have high ϕ and possible lattice spacing change at the surface. W_{100} has the unusual chemisorption of a "molecular" H_2 species; the proposed interaction of H atoms with *d*-electrons can explain the high value for $\Delta\phi$. The exceptional behavior of Pt in giving a decrease in ϕ for adsorption at 295°K respresents an effect of screening of the field of ion cores. The $|Pt^{10+}(d^8)|$ attracts electrons of the H atom more than the H^+ of the H atom attracts $\bar{e}$ of metal. However, this behavior of Pt is in the expected direction of the trend of $\Delta\phi$ for Hydrogen as shown in Fig. 2.

After the initial chemisorption of H atoms on metals, further adsorption sometimes leads to decrease in work function. This has been considered due to adsorption of H_2 molecules over the layer of H atoms. However, careful studies indicate that this is also atomic hydrogen in the case of Ni and Cu[25], even though it gives the opposite effect on ϕ from the first half of the chemisorption of H. The first chemisorption is expected to occupy a network of widely spaced interstitial sites on Ni or Cu as $H^{\delta-}$ and gives an increase in ϕ of 0.3–0.4 volts. As ϕ of the metal is increased the interaction between H and $\bar{e}$ diminishes and polarization of H increases. The final chemisorption in positions between the original $H^{\delta-}$ gives predominately a screening interaction and although still $H^{\delta-}$ leads to a decrease in ϕ of 0.03 to 0.18 volts. The decrease in $\Delta\phi$ with ϕ of the metal can be a useful relation for estimating electron transfer in chemisorption of various gases. It is anticipated that when data become available for single crystals of more metals, effects of *d*-orbital occupancy will be apparent.

V-2. Chemisorption of CO

The chemisorption of CO is of special interest because it chemisorbs as a molecule, and the interaction with the metal surface will involve both polarization of the CO molecule and transfer of electrons to a surface binding region. The binding of a CO molecule is expected to be similar to that in the related transition metal complexes which have been extensively discussed using M. O. Theory.

The data for several metals indicate a linear increase in $\Delta\phi$ with decrease in ϕ from about a $\Delta\phi$ of zero for Pt to 1.6 ev. for Fe (Fig. 3). In the case of CO the data for polycrystalline tungsten is in agreement with the single crystal data. For Pt the small $+\Delta\phi$ is in keeping with the strong positive field of the Pt ion core *i.e.* there can be strong attraction of CO and resultant screening of Pt, but $\bar{e}$ transfer to orbitals of CO is probably the least for Pt of all the metals in Fig. 2. Very recent data[26] for CO chemisorption on single crystal planes of Cu indicate that earlier reported decreases of ϕ upon CO chemisorption on Cu were incorrect. The $\Delta\phi$ is 0.01 on Cu_{111}, 0.11 on Cu_{100} and 0.02 on Cu_{110}. The $\Delta\phi$ has been given as zero for Ag[27]. It is probable that the large decrease in ϕ (-0.8) for chemisorption of CO on Au is correct, and represents the effect of screening of the very strong positive field[28] of Au^+, (Au^{25+} $5d^{10}$, $4f^{14}$), an effect already shown to a lesser extent by Pt.

V-4. Chemisorption of oxygen, halogens and organic molecules

The data on oxygen chemisorption is limited because many metals react with oxygen to incorporate O^{2-} into the lattice. The data in Fig. 2 show the expected relation of ϕ and $\Delta\phi$ and the fair correspondence of data for single crystal planes of Cu and W with polycrystalline data for W, Mo, Cu, Ag, Ni, Hg and Pt.

There are a few data for organic molecules, and the expected decrease in metal work function due to screening of ion cores is observed. Typical data[29] are CH_4 on Hg ($\Delta\phi=-0.16$), C_2H_6 on Hg ($\Delta\phi=-0.23$), C_2H_4 on Hg (-0.27), C_2H_2 on Hg (-0.21), C_2H_6 on Ni (-0.77), C_2H_4 on Ni (-0.83),

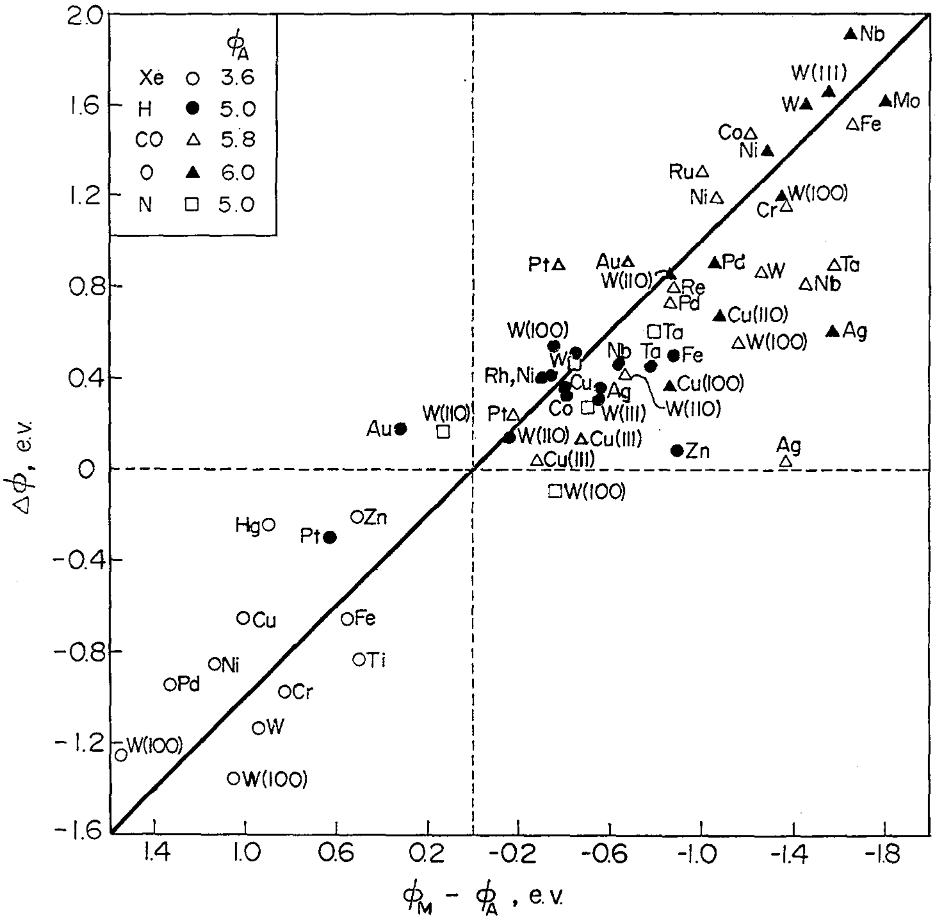

Fig. 4. Experimental Work Functions in Chemisorption compared to the Change in Work Function Calculated from $\phi_M - \phi_A$.

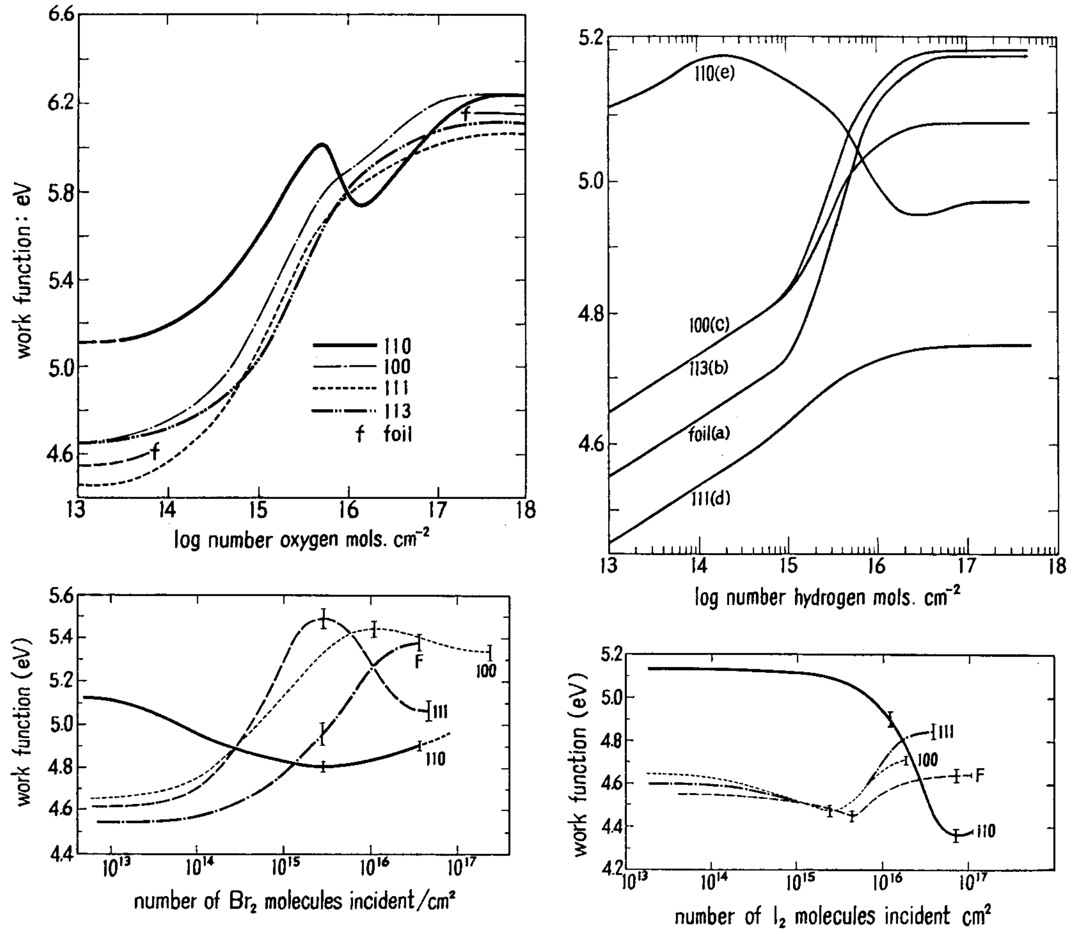

Fig. 5. Change in Work Function with Coverage for Tungsten. Data shows Variation in Terminal ϕ Values.

C_6H_6 on Ni (-1.3), CH_4 on Cu (-0.14), C_2H_6 on Cu (-0.69) an C_2H_4 on Cu (-1.23). There is an increase in $\Delta\phi$ with polarizability of the adsorbed molecule.

V-5. The linear ϕ vs. $\Delta\phi$ relation and terminal ϕ values

The plots of $\Delta\phi$ vs. ϕ in Fig. 2 and 3 show that upon chemisorption $\Delta\phi$ decreases linearly with ϕ of the metal. This makes it possible to define a terminal ϕ value for (Metal+adsorptive) which can be taken as ϕ_A, an apparent work function of adsorbate. This is considered to be a more useful number in discussing chemisorption than electronegativity which is commonly used[16] but which is not a clearly defined number. Calculated values of $\Delta\phi$ which are equal to $\phi_M-\phi_A$, where ϕ_A=the terminal ϕ value on chemisorption, are given in Table 2. The plot of $\Delta\phi_{obs.}$ vs. $\phi_M-\phi_A$ $(=\Delta\phi_{calc.})$ in Fig. 4 shows that this relation holds reasonably well for most metals. Some of the major deviations have already been discussed. The above equivalence of a terminal ϕ and electronegativity was pointed out by ELEY and SHOOTER[30] who suggested $\phi_A=5.9$ for H chemisorption was equivalent to an electronegativity of 2.1. The degree to which a constant terminal ϕ is shown is illustrated for several planes of W in Fig. 5. Figure 5 also shows the complex changes with coverage discussed above. There is the same terminal ϕ for all planes of W for oxygen chemisorption and also for halogens when effects of molecular adsorption are eliminated[16]. The rather wide variation of ϕ_H on W is believed to be due to entropy effects which are expected to influence ϕ_A at maximum coverage.

It is encouraging for application to catalysis that the $\Delta\phi$ vs. ϕ relation seems to hold quite well for polycrystalline metals. The opposing effects on ϕ of a metal of hydrocarbon molecules and of reacting species (H, O, CO, N, halogens) can provide a basis for predicting favorable electron transfer.

VI. Discussion

The interstitial-electron model has led to consistent explanations of the major phenomena in chemisorption in terms of 2 kinds of electronic interactions. The first is an attraction of the electron shells of adsorbate by M^{n+}. This effect produces a screening of the positive field of M^{n+} and leads to a decrease in ϕ. It is expected to give adsorption over the M^{n+} layer in areas of greatest positive field (*i.e.* in regions of low electron density). Although dependent on size and polarizability of the adsorbate, adsorption usually occurs directly over M^{n+} due to this kind of interaction. It is the only interaction present in adsorption of Xe. For alkali metals, *e.g.* Cs, such interaction leads to transfer of one ē to the metal lattice and incorporation of Cs^+ above the surface in a + ion core position.

The second type of electronic interaction in chemisorption is the attraction of metal electrons by adsorptive. This is expected for adsorbates with appreciable electron affinity such as H, O, and halogens and for polarized adsorbates such as CO and N which ordinarily have no electron affinity. For strong interaction of adsorptive with metal electrons this leads to chemisorption in an interstitial position above the surface. The model specifies for each metal surface when there is greatest ē localization above 2 neighboring M^{n+} and when above a triangle of 3 M^{n+}, and bridging or interstitial chemisorption is expected accordingly. This effect, which is a net attraction of itinerant electrons, gives an increase in ϕ.

d-Electrons localized on M^{n+} were shown to have influence in some cases. For effect (1) *d*-electrons perpendicular to the ion core would favor bridging or interstitial adsorption. For effect (2) such *d*-electrons would make adsorption over M^{n+} more favorable. It was shown that the major factors determining the actual position of adsorption as far as the metal surface was concerned were strength of M^{n+} positive field as indicated by ϕ of the metal, position of itinerant electron localization, spatial extension of occupied *d*-orbitals and location of other chemisorbed species already on the surface. In terms of the adsorptive, the electron affinity, ionization potential and polarizability all had a role in the optimum position for chemisorption on the metal surface.

The metal surface is thus characterized by the model as having regions of strong positive field of ion cores, regions of itinerant electron localization and regions occupied by *d*-electrons localized on the ion cores. Chemisorption in all cases involved electron redistribution into a binding region between metal ion cores in the surface and the adsorptive. The involvement of itinerant electrons in the binding is in keeping with the mobility of most chemisorbed species. Especially high localization of itinerant electrons in a surface binding region is connected with immobile chemisorbed species.

It is of interest to compare these conclusions to those of TOYA[4] who has formulated the only other model which has dealt with the complex metal electron interactions. The lattice plane model of HORIUTI and TOYA[4] is based on quantum mechanical calculations for hydrogen chemisorption on Ni, Cu, Pt and W. This model is presented in terms of positions of chemisorption, an *r*-type chemisorption over M^{n+} and an *s*-type chemisorption which is interstitial. On the basis of energies, *r*-type adsorption is postulated for W, *s*-type for Pt with some *r*-type, and both *r* and *s* types for Ni. An increase in ϕ and electrical resistance is associated with *r*-chemisorption and a decrease in ϕ with *s*-type chemisorption.

The interstitial-electron model also clearly distinguishes adsorption directly over M^{n+} as predominantly due to one effect and interstitial adsorption to another. The differences in the 2 models reflect the emphasis on spatial location of $\bar{e}$ in the interstitial model and electron energies in the lattice plane model of TOYA. As an example, the screening effect which is expected for polarizable molecules and can be associated with *r*-type chemisorption does not explain the usual increase in ϕ in the case of H chemisorption. However, a decrease in ϕ is observed for W_{110}. On this high ϕ plane of W, chemisorption is postulated in a bridging position of 2 W where there is no localization of $\bar{e}$ (alternatively, adsorption directly over W). It is believed that H atom attraction of $\bar{e}$ is sufficient to counteract the screening effect in all but high ϕ metals, and thus H chemisorption normally leads to an increase in ϕ.

The very unusual strong adsorption of a second type of hydrogen on W_{100} after partial coverage by H atoms may be of importance in regard to possible intermediate states on hydrogenation catalysts. This strongly adsorbed H may involve interaction with *d*-electrons localized on W. This provides a narrower energy range than that of itinerant electrons. It will be of interest to look for further cases of such chemisorption.

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References

1) T. B. GRIMLEY, in *Molecular Processes on Solid Surfaces*, Ed. E. DRAUGLIS, R. O. GRETZ and R. J. JAFFE, McGraw-Hill Book Co., N. Y., 1969, p. 249.
2) W. M. H. SACHTLER and P. Van Der PLANK, Surface Science, **18**, 62 (1969).
3) G. C. BOND, Disc. Faraday Soc., **41**, 200 (1966).
4) T. TOYA, This Journal., 209 (1961); J. HORIUTI and T. TOYA, Chap. 1 in *Solid State Surface Science*, Ed. M. GREEN, Marcel Dekker, N. Y., 1969.
5) L. JANSEN, *Molecular Processes on Solid Surfaces*, Ed. E. DRAUGLIS, R. B. CRETZ, R. J. JAFFE, McGraw-Hill Book Co., N. Y., 1969, p. 49.
6) A. Van der AVOIRD, Surface Science, **18**, 159 (1969).
7) K. TAMARU, Adv. in Catalysis, **20**, 327 (1969).
8) J. HALPERN, Proc. 3rd Int. Cong. on Catalysis, Amsterdam, N. Holland. Pub. Co.,

Amsterdam, 1965.

9) O. JOHNSON, Series of Pasers on Interstitial-Electron Model, Bull. Japan Chem, Soc., **45**, 1599, 1607 (1972).

10) O. JOHNSON, This Journal., **20**, 95 (1972).

11) K. FAJANS and T. BERLIN, J. Chem. Phys., **10**, 691 (1942).

12) R. F. W. BADER, Canadian J. Chem., **39**, 1253 (1961); J. Am. Chem. Soc., **86**, 5070 (1964).

13) P. W. SELWOOD, *Adsorption and Collective Paramagntism*, Acad. Press., N. Y., 1962, P. 104ff.

14) J. N. GEUS, Chap. 5, in *Chemisorption and Reactions of Metallic Films*, Ed. J. R. ANDERSON, Acad. Press., N. Y., 1971.

15) B. A. POLITZER and P. H. COLTER, Surface Science, **20**, 277 (1970).

16) A. S. SARGOOD, C. W. JOWETT and B. J. HOPKINS, Surface Science, **22**, 343 (1970).

17) F. C. TOMPKINS, Ch. 25 in *The Solid-Gas Interface*, Ed. E. A. Flood, Marcel-Dekker, Inc., N. Y., 1967.

18) P. W. TAMM and L. D. SCHMIDT, J. Chem. Phys., **54**, 4774 (1971).

19) T. TOYA, to be published in J. Vacuum Research, 1972.

20) R. R. FORD, *Adv. in Catalysis*, **21**, Acad. Press., N. Y., 1970, p. 92.

21) T. E. MADEY and J. T. YATES, Jr., Nuovo Cimento, Suppl., **5**, 483 (1967).

22) P. A. REDHEAD, Nuovo Cimento, Suppl., **5**, 586 (1967).

23) J. T. YATES, Jr. and T. E. MADEY, J. Chem. Phys., **68**, 2777 (1964).

24) D. O. HAYWARD, Chap. 4, in ref. 14.

25) W. A. CROSSLAND and J. PRITCHARD, Surf. Science, **2**, 217 (1964).

26) T. A. DELCHAR, Surface Science, **27**, 11 (197).

27) L. WHALLEY, D. H. THOMAS and R. L. MOSS, J. Catalysis, **22**, 302 (1971).

28) O. JOHNSON, J. Chem. Educ., **47**, 431 (1970).

29) R. V. CULVER and F. C. TOMPKINS, *Adv. in Catalysis*, **11**, Acad. Press, N. Y., 1959, p. 104.

30) D. O. ELEY and D. SHOOTER, J. Catalysis, **2**, 259 (1963).

Appendix

The distance of the adsorbed atom from the ion cores of the metal surface cannot be determined experimentally and must be estimated. This is commonly done by considering ionic or covalent radii of metal ions and adsorbed atoms. In the view of chemical binding used in this series of papers the adsorptive (A) at equilibrium is looked upon as having a binding region of $\bar{e}$ between the positive nucleus (A^+) of the adsorbed atom and the adjacent metal ion cores (M^+). Since in principle this is no different from the binding of the same atom in a diatomic molecule (MA) or solid $(MA)_n$, the M–A distance will be taken as similar to the latter values.

For a series of metal hydrides the values of M–H are compared in Table 3 to the M–M distance in the metal. It is seen that for both solid

TABLE 3. Interatomic distances in metal hydrides and oxides

Compound	M-H or M-O distance[a] in Å	M-M distance in metal, in Å (=a)	M-H or M-O distance relative to M-M distance
K_2ReH_9	1.68	2.74	0.61a
$H(CO)Rh(P\phi_3)_3$	1.60	2.69	0.60a
$HMn(CO)_5$	1.6	2.54	0.63a
$[(C_5H_5)Mo(CO)_3]_2$	1.8 (H to 2M)	2.72	0.7 a
ScH_2	1.98	3.21	0.6 a
YH_2	2.18	3.56	0.61a
LaH_2	2.45	3.76	0.65a
TiH	2.20	2.94	0.75a
TiH_2	1.92	2.94	0.64a
ZrH	2.39	3.20	0.74a
ZrH_2	2.87	3.20	0.64a
VH_1	1.68	2.62	0.64a
NbH_1	1.72	2.85	0.60a
CrH	1.67	2.49	0.67a
CuH	1.73	2.56	0.69a
KH	2.85	4.51	0.63a
CaH_2	2.35	3.94	0.60a
K_2O	2.79	4.51	0.62a
Cu_2O	1.84	2.56	0.72a
Ag_2O	2.05	2.88	0.70a
MgO	2.10	3.20	0.69a
CaO	2.40	3.94	0.62a
SrO	2.58	4.30	0.60a

a) M-N distance in TiN is 1.581 Å; ratio is 0.63a.

hydrides and metal hydride complexes the M-H distances are in the range 0.6a–0.75a. The above M-H values correspond very closely to the distances of centers of oct and tet interstices[9] from M^{n+} (0.71a and 0.61a, respectively).

A similar comparison of M-O distances, also shown in Table 3, show these distances to be in the range 0.60a–0.75a for solids. The relatively few data for nitrides and carbides give ratios in the range 0.63a–0.75a. Thus, it is concluded that the most probable distance of H, N, CO or O adsorbed on the metal surface is in the range 0.6a–0.7a. Further, since there are oct and tet interstitial positions at 0.71a and 0.61a, respectively, the adsorption sites are taken as identical to these interstitial positions which are associated with 2 or 3 metal ion cores (See Part II).

Adsorption directly over M^{n+} would place the adsorbed atom 0.6a–0.7a above the metal surface which, according to the model developed in Part II, is well above the $\bar{e}$ layer and may be less likely to lead to chemical binding.

The question of position of adsorbed atoms can be also approached from an assessment of sizes of metal ion core and adsorbate, similar to use of covalent or metallic radii. In part II the ion cores were shown to have $\bar{e}$ density extending to at least 0.4a. For an ion core extension of 0.4a the space between ion cores (at the intermetallic distance, a) relatively free of $\bar{e}$ density is only 0.2a. Diameters of atoms such as N and O are considered to be approximately 1.2–1.5 Å (0.5a to 0.6a for a=2.5 Å) and hydrogen, approximately 0.6–0.7 Å (0.2a-0.27a). Thus, it is not reasonable to expect that N or O atoms would occupy positions between ion cores at the distance of closest approach. For the 100 face of BCC where the M–M distance is 1.16a, the available space between ion cores is 0.36a; for the 110 face of CCP the longest M–M distance is 1.414a, and the available space between these ion cores is 0.61a. It would appear that only on the 110 plane of CCP lattice can atoms such as N or O enter the metal surface between adjacent ion cores. Placement of an adsorbate between 2 metal ion cores at the largest distance, *i.e.*, on the 110 face of CCP leads to a M–A distance of 0.71a which is also compatible with the estimate from metal compounds.

A reasonable conclusion is that generally a chemisorbed atom or molecule can be expected to be a distance of 0.6a–0.7a from the metal ion cores of the surface. Usually this places the adsorbate in interstitial positions above the surface, but on lattice planes with large M–M distances the adsorbate can be between metal ion cores in the surface.