The Bond-Energy Bond-Order (BEBO) Model of Chemisorption

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The bond-energy bond-order (BEBO) model of chemisorption allows an estimate to be made of the interaction energy between a gaseous specie and a solid surface as a function of either bond length or bond order, i.e., the length or order of either the gas–surface bond being formed or the bond of the gaseous molecule being broken. The relationship between bond energy and either bond length or bond order is deduced from spectroscopic correlations for gaseous molecules, and a linear relationship between bond energy and bond order is assumed for the surface–adsorbate interaction. The geometry of the surface orbitals is taken to be that predicted by the crystal field model. The model allows a prediction of several relevant quantities in gas–surface interactions, namely: (1) binding energies for molecular adsorbed species, (2) binding energies for atomically adsorbed species, (3) activation energies to chemisorption, and (4) activation energies to dissociative chemisorption. The model is illustrated for the adsorption of H_2, CO, NO and O_2 on Pt, W and Ni surfaces.

Introduction

Although a reliable quantum mechanical theory of covalent chemisorption on metal surfaces does not presently exist, it would nevertheless be highly desirable to be able to make predictions concerning the way in which adsorbates interact chemically with solid surfaces. Evidently what is needed is an empirical model description of chemisorption—the formation of chemical bonds between a gaseous specie and a solid surface—in the spirit of the empiricism used by Pauling to describe molecular bonding over forty years ago. Such an approach has recently been formulated in which the variation of bond energy in chemical bonds being broken or formed is given by spectroscopic correlations for gaseous species, and a linear relationship is assumed for the variation of bond energy with bond order for surface–gas bonds.[1-6] Electrons, or equivalently chemical bonds, are conserved and the geometry of the surface orbitals is taken to be that predicted by crystal field theory.[7]

This model has been applied to the adsorption of H_2 on (111) Pt;[1] O_2, CO, and CO_2 on (111) Pt and Ni;[2] N_2, NO, and N_2O on (111) Pt[3] and Ni; and O_2 on both clean and carbon contaminated (111) Pt.[4] The model can also be applied to simple surface reactions, and in particular has been used to describe the reaction of O_2 and CO, NO and CO, and H_2 and O_2 on (111) Pt,[5] as

well as the hydrogenation of C_2H_4 and the nucleation of graphitic carbon on (111) Pt and Ni.[6] In this communication the BEBO model is described, and selected results for the adsorption of H_2, O_2, CO, and NO on Pt, Ni, and W surfaces are presented.

Attention will be focussed on the (111) crystallographic orientation of Pt and Ni (both face-centered cubic metals) and a brief word will be mentioned concerning the (100) crystal face of W (a body-centered cubic metal). The geometries of (111) fcc (face-centered cubic) metals and (100) bcc (body-centered cubic) metals are shown in Fig. 1. There are two distinct bonding sites on the (111) fcc plane and three non-equivalent bonding sites on the (100) bcc plane. On the (111) fcc plane these sites are termed the e_g and t_{2g} sites in accordance with the symmetry of the d orbitals from which they derive,[1-6] and on the (100) bcc plane the sites are termed the A, B and C sites. Thus, it is seen that germane features of the crystal field theory (i.e., surface orbital geometry) introduces into the model the possibility of multiple binding states of an adsorbate on a given surface plane. Such multiple binding states are a well established experimental fact.

In order to calculate the electron occupancy of the surface orbitals, it is assumed that the available bonding electrons are equally divided (in a time-averaged sense) over all the pertinent orbitals (d, p, or s orbitals). The

FIGURE 1(a). The (111) plane of an fcc metal showing the e_g and t_{2g} adsorption sites. (b) The (100) plane of a bcc metal showing the A, B and C adsorption sites.

├──── 1 Å (Pt)

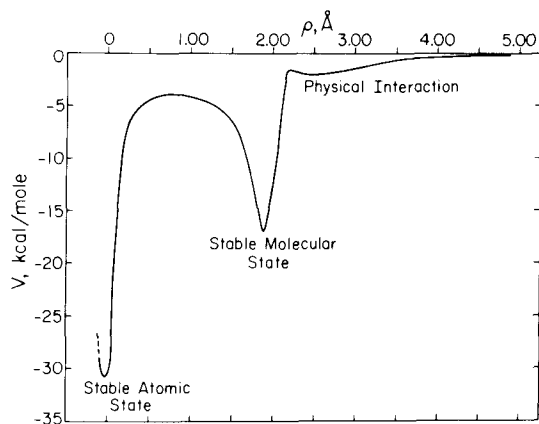├──── 1 Å (Ni)   (a)

├──── 1 Å (W)   (b)
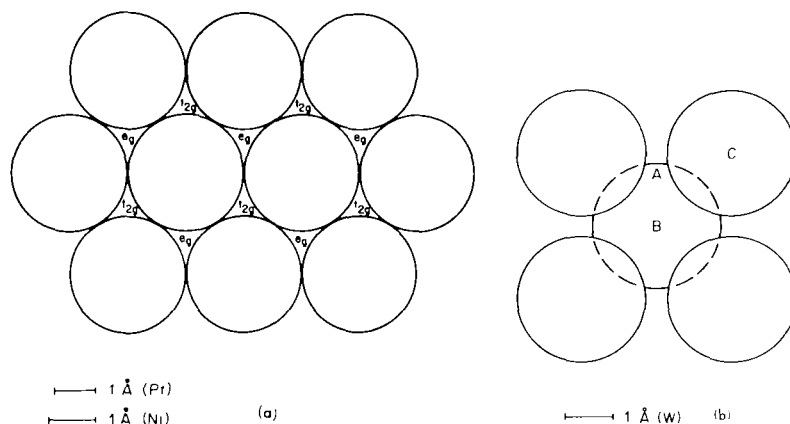
FIGURE 2. The interaction energy of H_2 with Pt (111) as a function of reaction coordinate which is set equal to zero at the minimum of the stable atomic well.

electronic configuration used is that predicted by the Engel–Brewer rules,[8] namely $d^{n-1}s$ for bcc metals and $d^{n-3} sp^2$ for fcc metals where n is the number of outer shell electrons. Thus, the electronic configuration of Pt and W is expected to be $5d^7 6sp^2$ and $5d^5 6s$, respectively.

By combining the BEBO concepts with the crystal field theory (the latter gives the surface orbital geometry and occupancy), it is possible to make rather detailed predictions concerning the way in which simple adsorbates interact with metal surfaces. For example, it is possible to predict in certain cases the following quantities: (1) the activation energy to adsorption, (2) the binding energy of both molecularly and dissociatively adsorbed species, and (3) the activation energy to dissociative chemisorption.

I. BEBO Model

The philosophy of how the BEBO model is used in connection with describing the chemical interaction of gases with surfaces has been given in the Introduction. A more detailed description of the model will now be presented. When a diatomic gas molecule interacts with a surface, the energetics involved may be thought of in terms of a Born–Haber cycle. For example, consider that the molecule AB is adsorbed on a metal surface M. The binding energy V of an adstate (in the most general case, a molecular state) is equal to the following contributions: (1) the dissociation energy of AB, D_{AB}, (2) the binding energies of both A and B to the surface, E_{M-A} and E_{M-B}, and (3) the energy in the AB molecule while in the adstate on the surface, $E_{Sur, AB}$. This cycle may be written in the following way (assuming the zero of energy is the infinitely separated gas and surface)

$$V = D_{AB} - E_{M-A} - E_{M-B} - E_{Sur, AB}. \tag{1}$$

The dissociation energy of the AB molecule is a known quantity; and the energies of the gas–metal bonds are assumed to obey the following relationship,

$$E_{M-i} = E_{M-i,s} n_{M-i}, \tag{2}$$

where $E_{M-i,s}$ is the *single order bond energy* between the two chemical species M and i, and n_{M-i} is the bond order between M and i. The single order bond energy is often available in the literature[9,10] or may be estimated empirically.[1-6] The energy in the AB bond while adsorbed on the surface may be calculated from an equation of the form[11]

$$E_{AB} = E_{AB,s} n_{AB}^p, \tag{3}$$

where $E_{AB,s}$ is the *single order bond energy* in the AB molecule, n_{AB} is the bond order of the AB molecule, and p is an empirical exponent which normally has a value very close to unity. Alternatively, spectroscopic correlations relating the energy in the AB bond to its bond order may be used.[11]

When applying the BEBO model to actual gas–surface interactions, the knowledge of the surface orbital geometry derived from the crystal field model of a surface is used. This can lead to interesting results, and in particular the possibility of multiple bonding states of a gas even on a low-index plane of a metal single crystal. The model will now be illustrated for the case of several specific examples.

II. Calculated Results

A. Hydrogen Adsorption on Platinum (111) and Tungsten (100)

1. $H_2 + Pt$ (111)

The e_g and t_{2g} sites on a Pt (111) surface are not equivalent. The triad of orbitals comprising the e_g site makes an angle of 35°16′ with the surface plane while the triad of orbitals comprising the t_{2g} site makes an angle of 54°44′. This geometry thus favors the t_{2g} sites as possible molecular sites for H_2 and the e_g sites as possible atomic sites for the hydrogen adsorbate.[1] In fact, H_2 can interact with two of the three individual t_{2g} orbitals of the t_{2g} site. The H–H bond is stretched (an endothermic process) while the Pt–H bonds are formed (an exothermic process). This continues until either of two events occur: (1) the electrons available in the surface orbitals are depleted, or (2) the hard sphere radius of the Pt–H complex is reached (1.685 Å). The occupancy of the t_{2g} surface orbitals of platinum is 0.6 electron.[1] After a molecular state is formed, dissociation of the H_2 may occur via surface diffusion of the two atoms to the atomic bonding e_g sites. Since the geometry of these interactions is known (both that of the surface orbitals and molecular hydrogen), the potential energy of interaction of H_2 with a Pt (111) surface may be calculated as a function of "reaction (i.e., adsorption) coordinate," ρ.

For this purpose Eq. (1) is rewritten as

$$V = D_{H_2} - 2E_{Pt-H} - E_{Sur, H_2}. \tag{4}$$

The chemical interaction commences when the H–H bond begins to stretch and the two Pt–H bonds begin to form. The energy in the H_2 molecule is known from the bond energy–bond length (BEBL)[1,11] correlation, i.e.,

the potential energy of interaction is calculated as a function of bond length or reaction coordinate. The term E_{Pt-H} of Eq. (4) is calculated in the following way. The bond order in the H_2 on the surface is calculated from the equation (with all energy units in kcal/mole)

$$E_{H_2} = 103.2 n_{H_2}^{1.041},\qquad(5)$$

since E_{H_2} is known as a function of p. From conservation of chemical bonds, it follows that

$$n_{Pt-H} = 1 - n_{H_2}\qquad(6)$$

and thus E_{Pt-H} may be calculated from the following equation

$$E_{Pt-H} = 67 n_{Pt-H},\qquad(7)$$

since $E_{Pt-H,s}$ is known to be 67 kcal/mole.[1] The dissociation energy of H_2, D_{H_2}, is 103.2 kcal/mole. This allows the interaction energy $V(p)$ to be calculated, and the result is shown in Fig. 2. The physical interaction well [calculated assuming a Lennard-Jones (3–9) potential] is shown for completeness together with both the molecular and atomic chemical wells. The former has a binding energy of 17 kcal/mole, while the latter has a binding energy of 31 kcal/mole. The molecular well occurs when $n_{Pt-H} = 0.6$, and the Pt–H bond length is 1.81 Å as opposed to the hard sphere of 1.68 Å. No activation energy relative to the energy zero is predicted for the adsorption or the dissociation of H_2 by Pt (111).

2. $H_2 + W$ (100)

A general reaction coordinate picture of the H_2–W (100) interaction may be calculated just as was done for the case of $H_2 + Pt$ (111) given above.[12] From orbital overlap considerations it would be excepted that a molecular interaction would occur on the A sites of Fig. 1(b), whereas atomic adsorption would occur on the B sites (and perhaps on the C sites at quite high coverages). Since the surface orbital occupancy is greater for W than Pt the molecularly adsorbed state at the A sites occurs at the hard sphere radius of the W–H complex, namely 1.66 Å. At this point the H_2 bond length is 1.23 Å, and the H_2 bond order may be calcu-
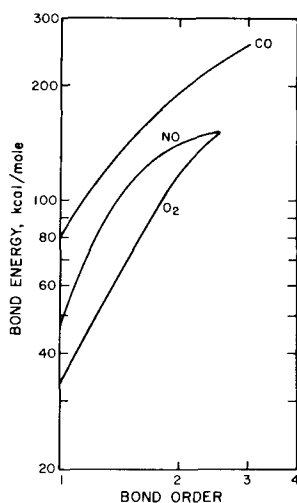
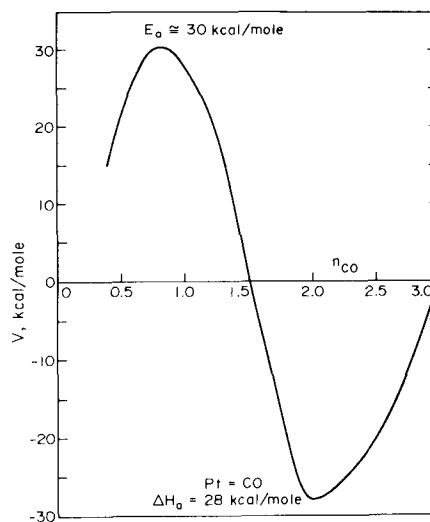Figure 3. BEBO correlation for O_2, CO, and NO bonds.

Figure 4. Calculated interaction energy for CO adsorption on Pt (111).

lated from the Pauling relationship[13] for H_2,

$$R = R_s - 0.26 \ln n_{H_2}\qquad(8)$$

and in the present case $R = 1.23$ Å and R_s, the single order bond length, is 0.74 Å. Thus the bond order for H_2 adsorbed in the molecular A sites is 0.15. Equations (4) and (5) may now be used together with the analogue to Eq. (7) for H_2–W (100) interactions, namely[12]

$$E_{W-H} = 67.7 n_{W-H},\qquad(9)$$

to give both the molecular binding energy of H_2 on (100) W ($n_{H_2} = 0.15$ and $n_{W-H} = 0.85$) and also the atomic binding energy ($n_{H_2} = 0$, $n_{W-H} = 1$). The binding energies for the molecular state and atomic state are calculated to be 26.2 and 32.2 kcal/mole, respectively.

B. Carbon Monoxide Adsorption on Platinum (111)

Due to orbital overlap considerations, CO is expected to adsorb on Pt (111) at the e_g sites; and elementary quantum chemical considerations[14,15] coupled with empirical infrared spectroscopy results[16] indicate the interaction is between the Pt and the C atom of the CO molecule. The potential energy of interaction may be written in analogy with Eq. (1) as

$$V(n) = D_{CO} - E_{Pt-CO} - E_{Sur, CO},\qquad(10)$$

where $D_{CO} = 256$ kcal/mole and $E_{Sur, CO}$ may be obtained as a function of n_{CO} (and equivalently as a function of n_{Pt-CO} through the appropriate bond conservation relationships[2]) from the spectroscopic correlation shown in Fig. 3. The Pt–CO bond energy is given by

$$E_{Pt-CO} = 46 n_{Pt-CO},\qquad(11)$$

since the single bond energy of Pt–CO is 46 kcal/mole.[2]

The calculated interaction energy of CO with Pt (111) is shown in Fig. 4. There is a stable molecularly adsorbed state with a binding energy of 28 kcal/mole at which point $n_{CO} = n_{Pt-CO} = 2.00$. The calculated acti-
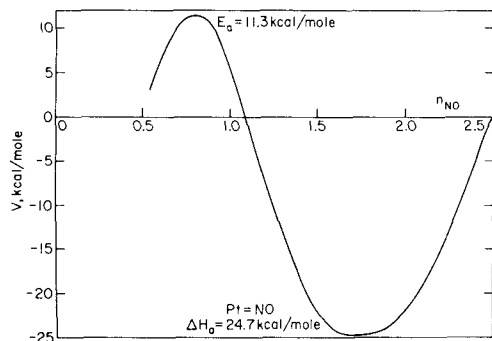
FIGURE 5: Calculated interaction energy for NO adsorption on Pt (111).

vation energy to dissociation is ~ 30 kcal/mole. The calculated molecular state is a result of the BEBO relation for CO (Fig. 3), and not, for example, a result of electron depletion of surface orbitals. Thus, it would be expected that on relatively smooth low index planes of Pt the binding energy should be rather constant, approximately 28 kcal/mole. On rougher surfaces of Pt it is possible *simultaneous* interaction of both the C and O atoms in the CO molecule with surface orbitals could lead to dissociative adsorption with an activation energy much less than 30 kcal/mole. Further details concerning the CO–Pt (111) interaction may be found in Reference 2.

C. Nitric Oxide Adsorption on Platinum (111)

The interaction between NO and Pt(111) is expected to be very similar to that of CO, namely adsorption through the N atom at an e_g site on the Pt surface.[3] Equation (1) may be written in the following form for the NO–Pt interaction

$$V(n) = D_{NO} - E_{Pt-NO} - E_{Sur, NO}, \qquad (12)$$

where $D_{NO} = 151$ kcal/mole and $E_{Sur, NO}$ is given as a function of n_{NO} in Fig. 3. The bond energy between a Pt atom and an NO molecule is given by[17]

$$E_{Pt-NO} = 32 n_{Pt-NO}, \qquad (13)$$

with the single order bond energy of Pt–NO given by 32 kcal/mole and with elementary bond conservation relations relating n_{NO} to n_{Pt-NO}.[3,17]

The interaction energy $V(n_{NO})$ may be calculated using Eqs. (12) and (13) together with Fig. 3, and the result is shown in Fig. 5. There is a molecularly adsorbed
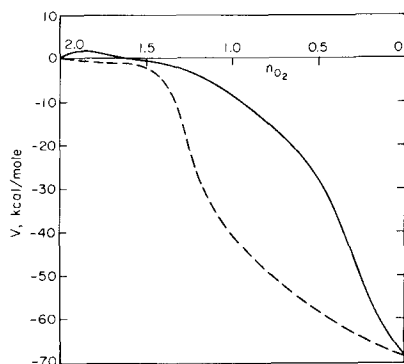

FIGURE 6. Calculated interaction energy for O_2 adsorption on both Pt (111) [——] and Pt (111) contaminated by C [- - -].

state of NO on Pt (111) with a binding energy of 24.7 kcal/mole which occurs when $n_{Pt-NO} = 1.5$ and $n_{NO} = 1.75$. The calculated activation energy to dissociation of the NO molecule on the Pt surface is 11.3 kcal/mole (relative to gaseous NO), and this energy barrier occurs at $n_{NO} = 0.775$. The calculations indicate no activation energy for adsorption into the molecular state.

D. Oxygen Adsorption on Platinum (111), Nickel (111), and a Platinum (111) Surface with Adsorbed Carbon

1. $O_2 + Pt$ (111)

The initial interaction of O_2 with Pt (111) is also expected to occur through an e_g site for overlap reasons.[2,4] The potential energy of interaction is given by

$$V(n) = D_{O_2} - E_{Pt-O_2} - E_{Sur, O_2}, \qquad (14)$$

where $D_{O_2} = 118$ kcal/mole and E_{Sur, O_2} is given in Fig. 3 as a function of n_{O_2}. The bond energy between Pt and O_2 is given by[2,4]

$$E_{Pt-O_2} = 46.6 n_{Pt-O_2}, \qquad (15)$$

since the single order Pt–O bond energy is 46.6 kcal/mole.[2,4,18] A plot of the interaction energy V as a function of bond order in the O_2 molecule is shown in Fig. 6. There is a calculated activation energy to adsorption of ~ 3 kcal/mole, and the dissociative heat of adsorption is predicted to be 68 kcal/mole. The BEBO model does not predict the existence of a stable molecularly adsorbed state.

2. $O_2 + Ni$ (111)

The interaction of O_2 with Ni (111) may be treated in an analogous way to that of Pt(111) given above.[2] The important differences are that the lattice spacing is smaller on Ni as compared with Pt (which modifies the relative positions of the adsorption sites on the surface), and the Ni–O bond energy is given by the following equation [the analogue of Eq. (15)],[2,18]

$$E_{Ni-O_2} = 58 n_{Ni-O_2} \qquad (16)$$

since the single order bond energy of Ni–O is 58 kcal/mole. The calculated interaction energy for O_2 and Ni (111) is different from that for O_2 and Pt (111) in the following ways: (1) There is no predicted activation energy to adsorption on Ni; and (2) the calculated heat of dissociative chemisorption is greater, approximately 114 kcal/mole. A similarity in the two results is that the BEBO model predicts no stable molecularly adsorbed state of O_2 on Ni (111).

3. $O_2 + (111)$ PtC

The BEBO model can also be used to predict the chemisorption properties of O_2 on a carbon contaminated Pt (111) surface.[4] The O_2 initially interacts with the free valence of the adsorbed C atom, with the final

TABLE I.   Comparison of BEBO predictions with experimental data.

Gas–Surface	Ea, ads., kcal/mole		Molecular ΔHa, kcal/mole		Ea, dis., kcal/mole		Dissociative ΔHa, kcal/mole	
	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
H$_2$/Pt (111)	0	~0[a]	17	~18[a]	0	~0[a]	31	~31[a]
H$_2$/W (100)	0	~0[b,c]	26.2	26.3[b] 25.2[c]	0	~0[b,c]	32.2	32.3[b,c]
CO/Pt (111)	0	~0[d,e,f]	28	~28[d,e,f]	~30	"large"[d,e] >10[f]	...	...
NO/Pt (111)	0	~0[g]	24.7	~25[g]	11.3	~12[g]	...	...
O$_2$/Pt (111)	~3	~3[d,e,h,i,j]	...	...	0	~0[h,i,j,k]	68	64[k]
O$_2$/Ni (111)	0	~0[k]	...	...	0	~0[k]	114	107[k]
O$_2$/PtC	0	~0[i]	...	...	0	~0[i]	68	ND[l]

[a] Reference 26.   [d] Reference 29.   [g] Reference 17.   [j] Reference 32.
[b] Reference 27.   [e] Reference 30.   [h] Reference 2.   [k] Reference 33.
[c] Reference 28.   [f] Reference 31.   [i] Reference 4.   [l] ND = No data.

adstate being an O atom bound to a Pt site and a CO molecule also bound to a Pt atom. The interaction energy may be written as

$$V(n) = D_{O_2} - E_{PtC-O_2} - E_{Sur, O_2} \qquad (17)$$

and the BEBO relationships (Fig. 3) for both CO and OO bonds are used together with equations (11) and (15). The number of bonding electrons, i.e., the number of chemical bonds, is conserved in the usual fashion. The calculated interaction energy is shown in Fig. 6. The BEBO model predicts no activation energy to adsorption, no stable state of molecularly adsorbed O$_2$, and a dissociative heat of adsorption of 68 kcal/mole (Pt = CO + Pt = 0). That is fortuitously the same value for the dissociative heat of adsorption of O$_2$ on clean Pt (111).

III. Summary

The BEBO model has been described and applied to the chemisorption of several atomic molecules on various surfaces, i.e., H$_2$ on Pt (111) and W (100), CO on Pt (111), NO on Pt (111), and O$_2$ on Pt (111), Ni (111) and a Pt (111) surface contaminated by carbon. The calculated results are shown in Table I together with a comparison with relevant experimental results. It is clear that the BEBO model describes very well these gas–surface interactions; and it has also been used to successfully elucidate the chemisorption of several other molecules on various metal surfaces,[1-4] and to predict the energetics of several heterogeneously catalyzed surface reactions.[5,6]

Perhaps the greatest uncertainties in the BEBO model are the following: (1) The single order bond energy to be used in calculating the gas–surface bond energy, i.e., $E_{M-i,s}$ of Eq. (2); (2) the appropriate BEBO relationship for the surface–gas bonds, i.e., the exponent of the bond order in Eq. (2) may not be exactly unity; (3) the geometry of the surface orbitals may not be that predicted by the crystal field model; and (4) the electronic structure of the surface orbitals may not be precisely that predicted by the Engel–Brewer rules. It is probable that the uncertainty in $E_{M-i,s}$ leads to the greatest source of error in the BEBO calculations. It has been argued previously that the

surface–gas bond energy should be very nearly linear with bond order.[1-3] The success of the model especially for the case of H$_2$ adsorption strongly suggests that the surface orbitals (at least in the presence of an adsorbing gas) have approximately the geometry as in the bulk solid and the Engel–Brewer rules have been shown to be quite reliable in predicting the electronic structure of both metals and alloys.[7,19] In the most unfavorable case a value of $E_{M-i,s}$ may have to be derived by fitting empirical chemisorption data, but generally its value can be deduced either from available thermochemical data (e.g., heats of sublimation or heats of formation) or empirical mixing rules.[1-3]

The BEBO model implicitly implies the formation of a localized "surface molecule" as a result of chemisorption. This is a very attractive concept which has recently been given a theoretical foundation.[15,20,21] Experimental evidence for this proposition is derived from the studies of Sachtler et al.[20,21] on Cu–Ni alloys who have shown that an adsorbing gas molecule actually can discriminate between a surface Ni and Cu atom, i.e., the chemisorption is evidently not governed by collective properties such as the structure of the d-band or the position of the Fermi energy. In addition, Boudart[22] has shown that the chemisorption properties of gas molecules are identical on both very dispersed metal particles whose diameter is only ~10 Å (i.e., the particles are essentially totally surface) as well as on metal conglomerates whose diameter is on the order of hundreds of Ångstroms (i.e., particles with a small surface-to-volume ratio). If collective electronic properties of the metal are important, differences in the experimental results for these two radically different surfaces would be expected, but none were noted. These results tend to support the BEBO approach.

It is useful to briefly compare the BEBO method with previous thermochemical calculations aimed at estimating initial heats of adsorption. The latter approaches have generally been confined to the interaction of H$_2$ with metal surfaces[23]; however, Higuchi et al. have also considered the adsorption of O$_2$, N$_2$, and CO on various transition metals.[24] Eley has assumed that the metal–hydrogen bound energy is given by (with

energy units in kcal/mole)

$$E_{M-H,s} = \tfrac{1}{2}(D_{MM} + D_{H_2}) + 23.06(\chi_M - \chi_H)^2 \quad (18)$$

where D_{MM} is the metal–metal single order bond energy, D_{H_2} is the dissociation energy of H_2 and, χ_M and χ_H are the electronegativities of the M and H atoms respectively.[23] A value of D_{MM} is obtained by multiplying the bulk heat of sublimation of the metal by a factor which accounts for the multiple bonding in the bulk metal; this factor is normally $\tfrac{1}{6}$. A value of $\chi_M - \chi_H$ is obtained from experimental surface potential or work function measurements. The (dissociative) heat of adsorption of H_2 on the metal surface is given by

$$\Delta H_a = D_{H_2} - 2E_{M-H,s}, \quad (19)$$

with the value of $E_{M-H,s}$ obtained from Eq. (18).

The BEBO model draws on the approach of Eley, but extends it and thus renders the method considerably more powerful. This is easily recognized when one realizes that Eqs. (18) and (19) give only the dissociative heat of chemisorption. The BEBO model not only yields a value for the binding energy of the dissociated adspecie, but also gives the entire potential energy of interaction as a function of bond order. Thus activation energies to both molecular and dissociative chemisorption are obtained as well as the prediction of whether or not a stable molecular adstate exists on the surface. The BEBO model also takes account of surface geometry (anisotropic adsorption on different crystallographic orientations of the same metal), a feature lacking in the older thermochemical models.[23]

The application of the BEBO model to chemisorption on transition metal surfaces has been demonstrated in this communication as well as other work.[1–4] It seems likely that the BEBO model can also be applied to adsorption on Group IV or III–V semiconductor surfaces where localized bonding should be important.[25] The treatment is probably not amenable to highly ionic solids such as oxides or alkali halides where long range electrostatic interactions are certainly non-negligible. The BEBO model would probably also fail at describing metallic bonding, e.g., the adsorption of metal atoms on metal substrates. An exciting application of the BEBO model is to heterogeneous surface reactions.[5,6] The energetics of various simple surface reactions can be calculated, and in favorable instances a choice may be made between Rideal–Eley and Langmuir–Hinshelwood kinetics.

Acknowledgment

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