

Theory of chemisorption of hydrogen on transition metals and their alloys

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THEORY OF CHEMISORPTION OF HYDROGEN ON TRANSITION METALS AND THEIR ALLOYS

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A theoretical discussion is given of the changes in the heat of chemisorption of a hydrogen atom upon alloying a group-VIII metal with a group-IB metal. The emphasis is on two concepts: the ensemble effect and the ligand effect. The ensemble effect ascribes the changes in the heat of chemisorption primarily to changes in the geometry of the adsorption complex, whereas the ligand effect also takes into account changes in bond strength due to a different intrinsic activity of the bonding metal atoms.

1. Introduction

In view of the increasing interest in the use of alloys as catalysts, the properties of alloys relevant to catalysis are currently the subject of intensive studies [1]. We propose to discuss the changes in the heat of chemisorption by alloying. Since the surface composition of an alloy will in general differ from the bulk composition, one has to know the surface composition of the alloy [1,2]. Then the heat of chemisorption of a molecule on the alloy can be usefully compared with that on the unalloyed metal and a difference may be found [3]. This study is concerned with these changes in the heat of chemisorption.

Alloying can cause a change in the number of metal atoms to which the adsorbate is coordinated. The ensemble effect [4] ascribes changes in heat of chemisorption exclusively to a change in geometry of the adsorption complex, such as a change in number of neighbours. In addition to the ensemble effect alloying can cause a change in bond strength of the metal–adsorbate bond. This so-called ligand effect [4a] has to be ascribed to a change in the electronic nature of the bonding metal as a result of changes in its environment. These effects are illustrated in fig. 1. We apply the ensemble effect to the chemisorption of a single atom to a substrate and therefore it is to be considered as a specialization of the concept of the ensemble effect as originally introduced [4a] to explain selectivity changes in hydrocarbon conversions upon alloying. Unlike the ligand effect, the ensemble effect cannot change the heats of chemisorption of single coordinated adsorbates.

In order to assess the relative contributions of these two effects to an actual change in the heat of chemisorption, we have made some simple model calculations,

the results of which can be easily interpreted. We have studied the adsorption of hydrogen as atoms, being the most simple adsorbate.

In the ligand effect two counteracting phenomena can be discerned. Calculations on quasi-infinite alloys have been performed in order to estimate their relative magnitudes.

2. The adsorption model

Attention is focussed on the adsorption on a hydrogen atom on a transition metal. Of the valence electrons, the d-electrons are placed in a rather narrow band and the s,p-electrons in an overlapping, very broad band [5]. The extent of hybridization between the d- and the s,p-band is small [6] and can, therefore, be neglected. For our calculations we chose the Anderson [7] model of adsorption. The metal atoms contain one orbital with energy α_m ; they interact with each other by the hopping integral β . The full repulsion (γ) of two electrons on the hydrogen is

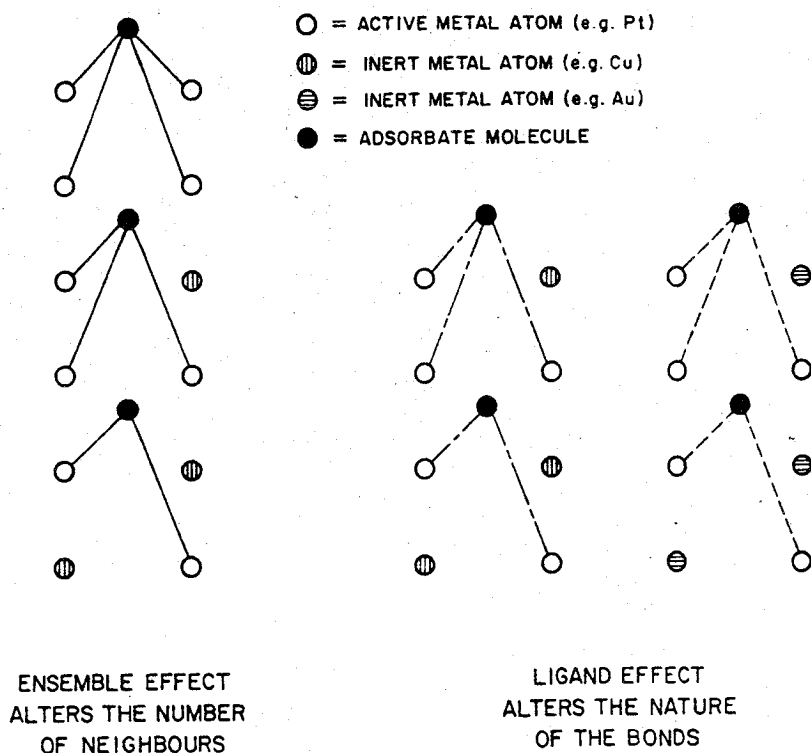


Fig. 1. The ligand versus ensemble effect.

taken into account. The energy of one electron on the hydrogen atom is α_H ; the interaction with a neighbouring metal atom is the hopping integral β' .

Newns [8a] arrived at solution of this model in the Hartree–Fock approximation [8b] for an infinite metal lattice in one dimension. Using a different method we will study exact and approximate solutions for a multi-dimensional lattices. The use of only one orbital per atom implies that the chemisorption model of Bond [9], based on ligand-field splitting, cannot be incorporated into our calculations. Moreover, Bond's chemisorption model is based on Goodenough's [10] model for a metal, which is no longer acceptable.

We performed the calculations for various values of the bond width of the metal. Chemisorption is then to be discussed in terms of a parameter μ defined by:

$$\mu = \beta'/\beta. \quad (1)$$

If μ is large, the metal–adsorbate bond will be strong compared with the metal–metal interaction. A good first approximation to the adsorption energy is then given by the bonding energy of the surface complex formed between the adsorbate and the metal atoms to which it is coordinated [11]. It is now favourable to compute the heat of adsorption according to the following formula:

$$E_{\text{ads}} = E_{\text{compl}} + E_{\text{reads}} - E_{1\text{oc}}. \quad (2)$$

Chemisorption is considered to comprise three imaginary steps: (a) Localization of electrons on the metal atoms to which the hydrogen atom becomes bonded; the energy cost is $E_{1\text{oc}}$, defined in eq. (6). (b) Formation of a chemical bond between these metal atoms and the adsorbate; the energy gain is E_{compl} . (c) Readsorption of this complex into the lattice; the energy gain is E_{reads} .

In fig. 2 the calculated heat of adsorption for cluster *a* shown in fig. 3 is given as a function of μ . Each atomic orbital contributes one electron. In order to calculate the heat of adsorption on cluster *a* we have explicitly made use of the assumption that the hydrogen atom interacts only with the metal atom in the center. Therefore, only eigenfunctions of the metal cluster that are totally symmetric with respect to the binding metal atom, contribute to the binding of the hydrogen atom. Two of these eigenfunctions are found, with energy difference $2\sqrt{Z}\beta$, where Z is the number of metal atoms neighbouring the binding metal atom. In the particular case that each atom contributes one electron, the problem to be solved reduces to the solution of the problem of three electrons distributed over three orbitals, two orbitals on the metal cluster and one on the hydrogen. The full repulsion of the two electrons on the hydrogen can be taken into account by solving this problem using configuration interaction, which now is restricted to only 8 states. Within the Anderson model the resulting value for the ground state is the exact solution. Fig. 2 also shows $E_{\text{compl}} (1.33\beta')$, the energy of one metal atom bonded to a hydrogen atom found by using a similar configuration-interaction calculation. It is seen that

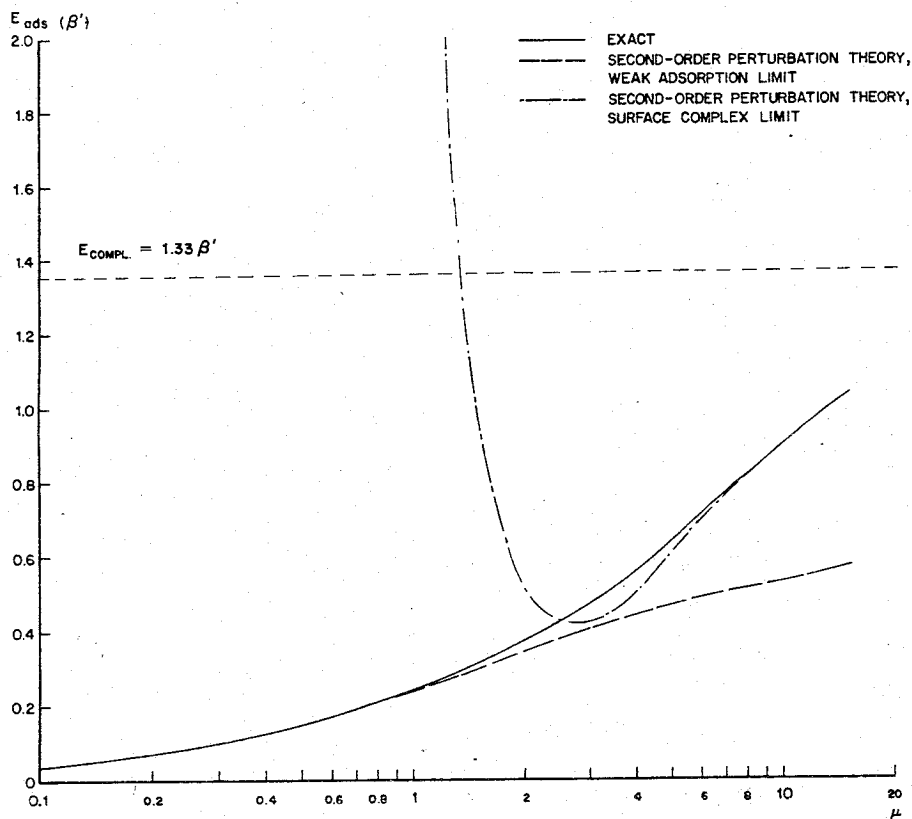
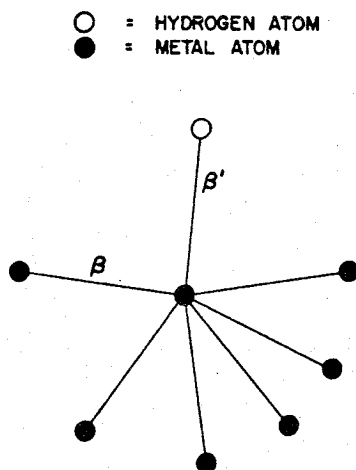


Fig. 2. Chemisorption energy as a function of μ for cluster *a*.

at high values of μ E_{ads} approaches E_{compl} . Representative values of μ for interaction with a d-band and an s,p-band are approximately 8 and 2, respectively. Thus, the heat of chemisorption is found to differ by a factor of 4. This large difference supports an earlier suggestion [12] that binding to a transition metal surface is dominated by the interaction of the adsorbate with the d-band. This, or course, is not the case for bonding of a single metal atom to a hydrogen atom. Indeed, it is found [13] that the bond strength of CuH is larger than that of NiH, whereas the heat of adsorption of a hydrogen atom on Cu is less than that on Ni [14]. Although alloying will undoubtedly change the s,p-band structure, we will assume that changes due to the altered d-band are dominant.

Fig. 2 also shows E_{ads} computed with E_{reads} from second-order perturbation theory. At $\mu = 2.5$ the surface-complex approximation is found to break down. The values of the parameters used are:

$$(\alpha_m - \alpha_H)/\beta' = -2.12 \quad \text{and} \quad \gamma/\beta' = -3.44.$$



These values are representative of chemisorption on a transition metal.

The other extreme is a very small value of μ . The heat of chemisorption is low and can be computed using the charge-transfer no-bond model of Mulliken [15,16]. This situation applies for instance to the adsorption of xenon to a transition metal [17]. The result obtained by using second-order perturbation theory is also shown in fig. 2.

3. The alloy model

Ultra-violet photoelectron spectroscopy (UPS) [18] and ESCA [19] have recently shown that not only the d-band filling, but also the shape of the d-band can change upon alloying.

The theory in which this effect is satisfactorily taken into account is the coherent potential approximation [20].

If a transition metal is alloyed with a metal containing a filled d-band and the average energy of this band is much lower than that of the transition metal, this will lead to a decrease in the band width of the d-electrons of the transition metal. The palladium-silver [18b] and nickel-copper alloys [18a] provide examples of this behaviour, which is caused by a decrease in bonding between the d-electrons of the transition metal and those of the alloying metal. One can compare this behaviour with band narrowing due to a decrease in the number of effective neighbours, as is illustrated in Appendix I for a one-dimensional chain.

Upon alloying there will also be a transfer of electrons from the s,p-band into the d-band.

Therefore the effects of alloying will be simulated in two ways: (a) by a change in number of neighbours, which contribute effectively to the d-band relevant to chemisorption, and (b) by a change in the number of electrons per atom; this is simulated by a change in Fermi level (E_F).

4. The ensemble effect

If the only effect of alloying is the dilution of the surface, such that the probability of finding active neighbouring metal atoms decreases, then the heat of chemisorption depends only on the number of coordinating atoms (Z) of the adsorbate.

We studied this effect using clusters of various sizes, for which the heat of adsorption can be exactly calculated in a way similar to that of cluster *a*. The hydrogen atom is supposed to be bonded to a varying number of neighbours ($Z = 3$ to 6 ; see fig. 1). Each metal atom bonded to the adsorbate has six other neighbouring metal atoms as in cluster *a* (fig. 3). In table 1 the results are presented. The heat of adsorption divided by the heat of adsorption for $Z = 1$ is given as a function of Z and μ . For any value of μ the heat of chemisorption proves to decrease with decreasing Z . It is found that for strong adsorption (μ high) the heat of adsorption becomes proportional to the square root of Z , in accordance with theoretical expectations, whereas for weak adsorption (μ low) it is found to be proportional to Z . The deviation from the linearity in Z at high values of μ is due to the competition of the metal atoms with each other to bind the electron on the hydrogen atom. At low

Table 1
The ensemble effect – comparison of relative adsorption energies

Z	μ							
	0.5	0.6	0.7	0.8	0.9	1	2	3
6	5.62	5.56	5.48	5.40	5.33	5.27	4.74	4.31
5	4.73	4.69	4.63	4.56	4.52	4.46	4.06	3.71
4	3.82	3.80	3.76	3.71	3.67	3.64	3.34	3.07
3	2.90	2.88	2.86	2.83	2.81	2.78	2.58	2.39

Z	μ						
	4	5	6	7	8	9	10
6	3.93	3.64	3.41	3.24	3.12	3.02	2.94
5	3.41	3.16	2.98	2.84	2.73	2.65	2.59
4	2.84	2.65	2.51	2.40	2.32	2.25	2.20
3	2.22	2.09	1.99	1.91	1.85	1.81	1.77

values of μ bonding is so weak, that the bonds do not influence each other. This also explains why changes in coordination have a larger influence on weak adsorbates than on strong adsorbates.

Since $\mu = 8$ is typical of adsorption of a hydrogen atom on a transition metal, the heat of adsorption will vary with \sqrt{Z} . Obviously, this is true only if the distance between the hydrogen atom and the metal atoms does not vary with the size of the ensemble.

An assumption basic to this section is that multiple bonding gives a larger binding energy than single bonding [21]. This will only be true if the distance between metal atoms coordinated with the hydrogen atom is so small that the increase in coordination is not cancelled by a much larger increase in repulsive forces. The particular configuration can become extremely important if hybridization plays a role. If the singly coordinated metal atoms are highly unsaturated it can occur that they have a stronger binding force than a plane formed by atoms which are less highly unsaturated [22].

5. The ligand effect

5.1. Cluster calculations

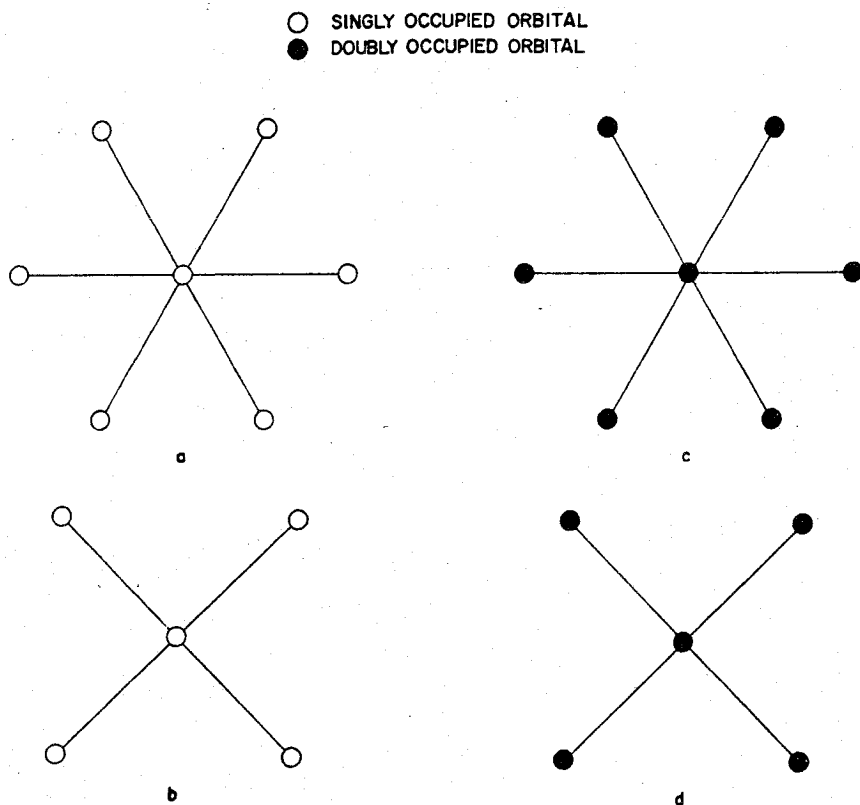
The ligand effect ascribes the change in heat of chemisorption to a change in the nature of the chemical bond with the metal atoms. For this reason we have studied this effect in the absence of a geometric effect, by using models in which the hydrogen atom is bonded to only one metal atom. Table 2 compares for each value of μ , the heat of chemisorption of various metal clusters with that of cluster *a* (fig. 3). Fig. 4 shows the four metal clusters used, drawn without the hydrogen atom. The hydrogen atom is supposed to be adsorbed on the central atom.

We have used similar configuration-interaction calculations as for cluster *a*.

In cluster *b* the number of metal neighbours of the central atom is reduced from six to four. The heat of chemisorption is found to increase. Just as with the ensemble

Table 2
The ligand effect – comparison of relative adsorption energies

	μ					
	5	6	7	8	9	10
Cluster a	1.00	1.00	1.00	1.00	1.00	1.00
Cluster b	1.12	1.11	1.10	1.09	1.08	1.07
Cluster c	0.88	0.79	0.71	0.66	0.63	0.59
Cluster d	0.86	0.76	0.69	0.65	0.62	0.59

Fig. 4. Clusters *a*, *b*, *c* and *d*.

ble effect, the largest variations are found at the lowest values of μ . This isolation effect is truly a ligand effect because the extent of narrowing of the density of states of the binding atom will depend on the metal used for alloying (see Appendix I).

In cluster *c* the number of neighbours of the central metal atom is again six, but the metal orbitals are doubly filled. Here the largest *decrease* is observed at the highest value of μ . The decrease in heat of chemisorption becomes smaller at lower values of μ and the heat of adsorption is even found to increase at values of $\mu < 5$. (The results for μ values < 5 have not been included in table 2 because at these low values it would be better to speak of ionosorption. Moreover, electrostatic forces should then be explicitly taken into account.)

The behaviour of the heat of chemisorption as a function of μ in cluster *c* is opposite to that found in cluster *a* (fig. 2), because here the negative ion of the MH molecule is the best zero-order approximation, even at low values of μ . In this case

the localization energy for two electrons on a metal is zero. The stronger the metal-metal interaction the more energy is gained because now the only additional contribution to the heat of adsorption comes from rebonding. The large increase in the heat of adsorption at low values of μ is due to this increasing probability of rebonding of negative ions.

If the number of metal atoms neighbouring the central atom now decreases from six to four, as in cluster *d*, the heat of adsorption will, of course, show a decrease instead of an increase.

These considerations suggest that if the electron density on the central metal is gradually changed, the decrease in heat of chemisorption due to electron transfer can, in principle, be counteracted by a narrowing of the density of states, as a result of a decrease in d-electron delocalization upon alloying. For this reason we made some calculations on a semi-infinite lattice in which the band occupation can be gradually changed.

5.2. Semi-infinite lattice calculations

We calculated the heats of chemisorption for the adsorption of singly coordinated hydrogen atoms for three lattices.

In lattice 1 the hydrogen atom is bonded to one metal atom which has six neighbours. These atoms in their turn have eight metal-atom neighbours, including the metal atom participating in adsorption. These neighbouring atoms in their turn also have eight neighbours, and so on.

Lattice 2 differs from lattice 1 only in the number of neighbours of the metal atom to which the hydrogen atom is bonded. This metal atom has four metal-atom neighbours.

In lattice 3 the metal atom to which the hydrogen is bonded has four metal-atom neighbours, but here the number of neighbours of the other metal atoms in the lattice is reduced to five.

We calculated the chemisorption energy using the *surface complex* and *weak adsorption approximations*.

Before presenting the results we will deal with a few new approximations, which we have introduced in the calculations. At high values of μ the surface complex approximation is valid and E_{ads} is calculated from eq. (2). We did not calculate E_{reads} using the second-order perturbation theory because this yields diverging results as soon as the band becomes filled with electrons. Convergence is maintained up to high electron band filling and moderate values of μ by solving eq. (3) for E_{reads} :

$$E_{\text{reads}} = 2 \left[\int_{E_{\text{F}}}^{E_{\text{max}}} dE \frac{0.50 \Gamma'(E)}{-2.43 \beta' + E + E_{\text{reads}}} - 2 \int_{E_{\text{min}}}^{E_{\text{F}}} dE' \frac{0.88 \Gamma'(E')}{-1.33 \beta' + E - E' + E_{\text{reads}}} \right]$$

$$+ \int_{E_{\min}}^{E_F} dE \left[\frac{0.43 \Gamma'(E)}{0.71 \beta' - E + E_{\text{reads}} - 2 \int_{E_F}^{E_{\max}} dE' \frac{0.71 \Gamma'(E')}{-1.33 \beta' + E' - E + E_{\text{reads}}}} \right] \quad (3)$$

The derivation of this equation is briefly discussed in Appendix II. E_{\min} and E_{\max} are the minimum and maximum energy of the metal electron band, respectively. The spectral function $\Gamma'(E)$, defined in eq. (II-11), Appendix II, reduces to eq. (4):

$$\Gamma'(E) = Z\beta^2 \rho'(E), \quad (4)$$

if the number of metal atoms in the surface complex equals Z and these atoms are not interconnected, as is the case in the lattices we want to study. The symbol $\rho'(E)$ stands for the density of states on the metal atoms neighbouring the metal atom used in adsorption before rebonding.

In order to solve eq. (3) we have chosen the local densities of state to be of the form:

$$\rho_i(E) = C_1^i + C_2^i (E - \alpha_m)^2. \quad (5)$$

The determination of the coefficients C_1^i and C_2^i following a method due to Haydock, Heine and Kelly [23] is discussed in Appendix III.

After substitution of eqs. (4) and (5) into eq. (3), the function was integrated. The resulting equation was numerically solved using Mueller's iterative method [24].

The localization energy on atom j was calculated from the formula:

$$E_{\text{loc}}^j = E_{\text{coh}}^j - (x - 1)(E_F - \alpha_m), \quad (6)$$

with

$$E_{\text{coh}}^j = 2 \sum_{i=1}^N \int_{E_{\min}^b}^{E_i^b} dE (E - \alpha_m) \rho_i^b(E) - 2 \sum_{i=1}^N \int_{E_{\min}^a}^{E_F} dE (E - \alpha_m) \rho_i^a(E), \quad (7)$$

where E_{coh}^j is the cohesive energy of atom j and x is the number of electrons present per atom ($2 \geq x \geq 1$). N is the number of metal atoms present in the metal; the indices b and a mean before and after localization of an electron, respectively. In our calculations N includes only the surface atoms together with the nearest and next-nearest neighbours a and b denote functions after and before localization.

In order to ensure convergence upon band filling in weak adsorption we solved eq. (8):

$$E_{\text{ads}} = \int_{E_F}^{E_{\max}} dE' \Gamma(E') \left[E' - \alpha_H + E_{\text{ads}} - 2 \int_{E_{\min}}^{E_F} dE'' \frac{\Gamma(E'')}{E_{\text{ads}} + E' - E''} \right]^{-1}$$

$$+ \int_{E_{\min}}^{E_F} dE' \Gamma(E') \left[\alpha_H + \gamma - E' + E_{\text{ads}} - 2 \int_{E_F}^{E_{\max}} dE'' \frac{\Gamma(E'')}{E_{\text{ads}} + E'' - E'} \right]^{-1} \quad (8)$$

The derivation of this equation is given in Appendix II.

If the hydrogen atom is bonded to only one metal atom the spectral function $\Gamma(E)$, defined in eq. (II-9) of Appendix II, reduces to:

$$\Gamma(E) = \beta'^2 \rho(E), \quad (9)$$

where $\rho(E)$ is the density of states on a metal surface atom, before it is bonded to the hydrogen atom. $\rho(E)$ is computed using eq. (5).

After substitution of eq. (5) and (9) into eq. (8), the latter can be integrated

Table 3
The relative adsorption energy Q as a function of electron density ρ (semi-infinite lattice)

μ	l	ρ								
		0.5	0.6	0.7	0.8	0.9	0.95	0.98	0.99	1
3	1	1	0.984	0.942	0.835	0.747	0.668	0.694	0.694	0.694
	2	1.01	0.998	0.944	0.849	0.731	0.664	0.655	0.655	0.655
	3	1.41	1.394	1.326	1.190	0.872	0.786	0.638	0.638	0.638
4	1	1	0.989	0.960	0.871	0.832	0.775	0.592	0.567	0.567
	2	1.01	1.0004	0.962	0.881	0.778	0.716	0.553	0.553	0.553
	3	1.267	1.259	1.210	1.112	0.888	0.827	0.662	0.548	0.546
5	1	1	0.991	0.968	0.894	0.856	0.808	0.635	0.539	0.516
	2	1.01	1.0017	0.969	0.913	0.816	0.763	0.620	0.508	0.508
	3	1.197	1.191	1.154	1.076	0.898	0.831	0.710	0.615	0.504
6	1	1	0.993	0.973	0.911	0.877	0.834	0.684	0.590	0.488
	2	1.01	1.0029	0.975	0.917	0.845	0.800	0.662	0.548	0.483
	3	1.155	1.151	1.121	1.057	0.909	0.852	0.749	0.667	0.481
7	1	1	0.994	0.976	0.923	0.892	0.854	0.721	0.636	0.471
	2	1.01	1.0040	0.978	0.931	0.866	0.825	0.698	0.601	0.467
	3	1.127	1.245	1.100	1.046	0.919	0.870	0.780	0.708	0.466
8	1	1	0.997	0.982	0.935	0.906	0.872	0.754	0.675	0.460
	2	1.01	1.0066	0.983	0.942	0.885	0.848	0.736	0.647	0.458
	3	1.108	1.106	1.085	1.039	0.937	0.884	0.804	0.740	0.456
9	1	1	0.997	0.983	0.943	0.915	0.886	0.779	0.705	0.452
	2	1.01	1.0069	0.986	0.949	0.899	0.866	0.771	0.684	0.450
	3	1.09	1.092	1.074	1.034	0.935	0.896	0.831	0.766	0.449
10	1	1	0.997	0.985	0.948	0.925	0.898	0.801	0.731	0.446
	2	1.010	1.0076	0.990	0.955	0.909	0.880	0.795	0.714	0.444
	3	1.084	1.082	0.066	1.029	0.969	0.906	0.839	0.757	0.443

* l = lattice.

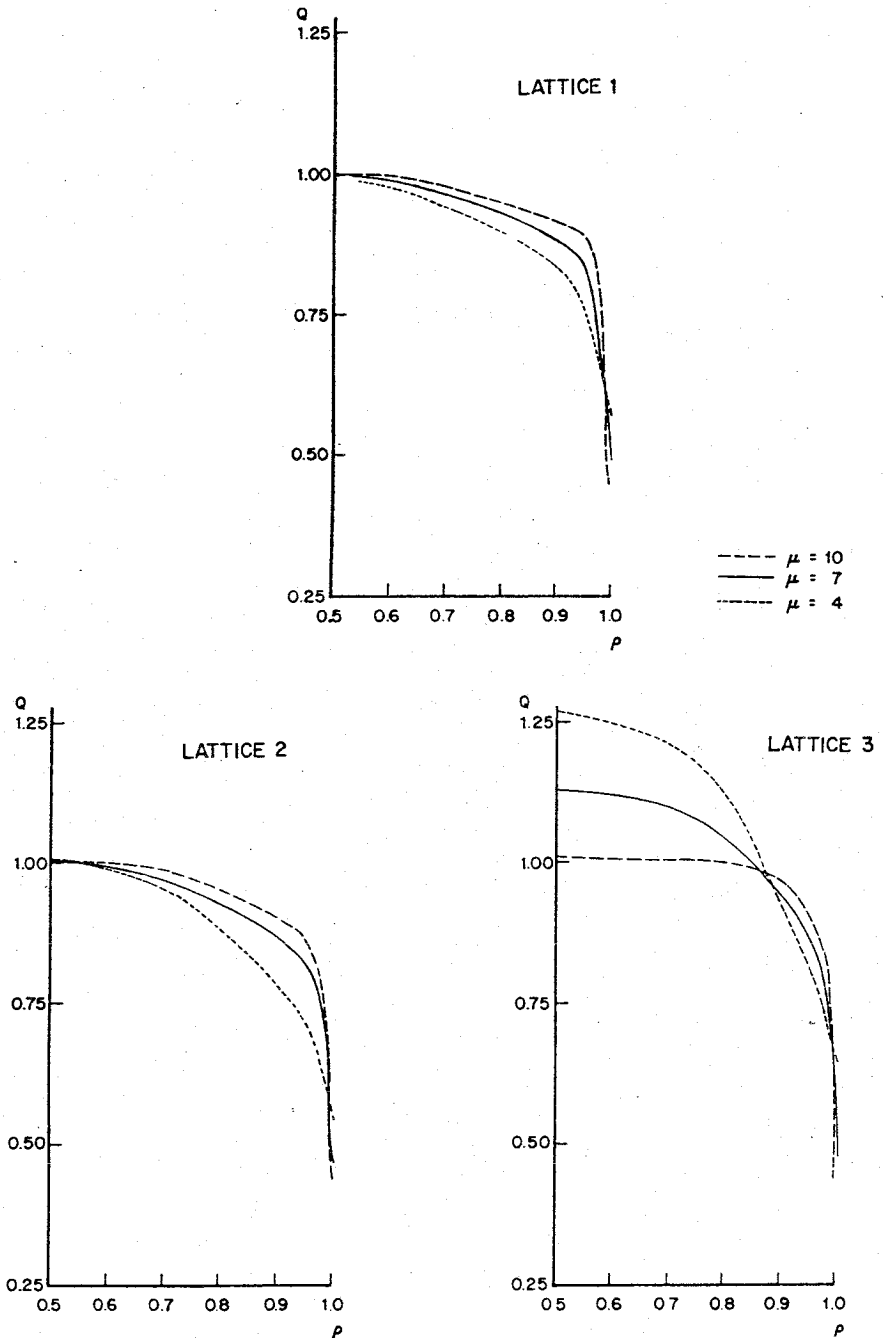


Fig. 5. The relative adsorption energy Q as a function of electron density ρ for a few values of μ .

and then numerically solved. E_{ads} calculated from eq. (8) becomes exact if the electron band is completely filled.

The results of the calculations are presented in table 3. Q , the chemisorption energy relative to that calculated for lattice 1 when $\rho = 0.5$, is tabulated as a function of ρ , the electron density in the band, and μ , the bond strength parameter. Of the energies computed with the two approximations the highest value is used. Most of the data in table 3 have been derived from surface-complex calculations, except for a few at large fillings of the d-band. In fig. 5 Q has been plotted as a function of ρ for three values of μ .

It is seen from the calculations on lattice 1 that the heat of adsorption decreases if the band becomes filled and the d local density of states does not change. Similar results were found by Newns [8], Schrieffer [25] and by Cyrot-Lackmann et al. [21]. The latter, however, did not consider the filling of the d-band separately from that of the adatom. As long as the band is not completely filled, this decrease is less pronounced at high values of μ . Only if the band is nearly completely filled does the relative change in the heat of adsorption increase if μ decreases. This is most clearly seen from the crossing of the curves in fig. 5 at ρ values approaching 1.

Comparison of the results of lattice 2 with those of lattice 1 shows that at high values of μ an increase in electron density by 0.1 is already sufficient to cancel the increase in heat of adsorption due to the change in the number of metal neighbours from six to four. If $\rho = 0.9$, decreasing Z only enhances the decrease in chemisorption energy owing to the increase in electron density.

Comparison of these results with those of lattice 3 shows — particularly at low values of ρ — large difference in behaviour between changes in the heat of adsorption caused by a monolayer of inactive atoms and changes induced by alloying in several outer layers.

Whereas in the first case (lattice 2) changes in metal—adsorbate bond strength are very small, in the second case (lattice 3) the effect of atom isolation is found to be comparable to that of band filling. Only for large filling is the effect of atom isolation cancelled.

At low values of ρ the heat of adsorption is found to increase upon alloying. The increase is largest at the lowest values of μ . At high values of ρ the heats of chemisorption are found to decrease. At intermediate values of ρ this decrease is largest at the lowest values of μ . If the band is completely filled, the decrease in heat of chemisorption is largest at high values of μ .

6. Conclusion

Both the ensemble and the ligand effect are found to change the heat of chemisorption.

If the metal orbitals are partly empty they both have the same dependence on μ : at high values of μ the changes in heat of chemisorption are smaller than at low val-

ues of μ . Changes due to the ligand effect are then small compared with changes due to the ensemble effect. Considering μ to be a measure of the relative strength of adsorbates we can conclude the following: With adsorption complexes of equal geometry alloying changes the heat of chemisorption of weak adsorption complexes to a larger extent than that of strong adsorbates as long as there remain holes in the d-band. We have demonstrated that singly coordinated adsorbates can in principle become more strongly bonded upon alloying as long as d-band filling is absent.

If the d-band becomes completely filled the ligand effect predicts the largest decrease in heat of chemisorption at the highest value of μ , i.e. for the most strongly bonded adsorbates. If band filling is accompanied by a decrease in the number of coordinating metal atoms, the decrease due to the ligand effect can become equal to, or even larger than, the decrease due to the ensemble effect at high values of μ . As a result, it is now possible that even with multiple bonding at similar sites weak adsorbates are less strongly influenced by alloying than strong adsorbates.

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Appendix I

The energy bands in a one-dimensional A-B chain

The eigenvalues of an infinite, one-dimensional, ordered chain containing an equal number of atoms A and B, carrying one orbital characterized by energies α_A and α_B respectively, are given by [26]:

$$E_k = \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}\sqrt{(\alpha_A - \alpha_B)^2 + 16\beta^2 \cos^2 2\pi k}, \quad (\text{I-1})$$

where β is the hopping integral between atoms A and B. If the atoms are equal, the bandwidth W is 4β .

If $|\alpha_A - \alpha_B| \neq 0$, the band is split symmetrically around $\frac{1}{2}(\alpha_A + \alpha_B)$ with gap $|\alpha_A - \alpha_B|$. The width of the separated band becomes:

$$\frac{1}{2}\sqrt{(\alpha_A - \alpha_B)^2 + 16\beta^2} - \frac{1}{2}|\alpha_A - \alpha_B| < 2|\beta|. \quad (\text{I-2})$$

The width of the bands decreases of $|\alpha_A - \alpha_B|$ increases. In the limiting case where $(\alpha_A - \alpha_B)/4\beta$ approaches infinity the bandwidth becomes zero. A similar conclusion is reached from the density of states $\rho(k)$:

$$\rho(k) = \left| \frac{\sqrt{\Delta^2 + 16\beta^2 \cos^2 2\pi k}}{4\pi\beta^2 \sin 4\pi k} \right| \quad (\text{I-3})$$

with $\Delta = |\alpha_A - \alpha_B|$. The local density of states on atom A is:

$$\rho_A(k) = |C_A(k)|^2 \rho(k), \quad (\text{I-4})$$

where

$$C_A(k) = \langle \phi_A | \psi_k \rangle, \quad (\text{I-5})$$

in which ϕ_A is the atomic wave function and ψ_k the eigenfunction of the chain.

If $\alpha_A < \alpha_B$ the quotient $C_A(k)/C_B(k)$ is:

$$\frac{C_A(k)}{C_B(k)} = \left[\frac{\alpha_B - \alpha_A}{4\beta \cos 2\pi k} \pm \sqrt{\frac{(\alpha_B - \alpha_A)^2}{16\beta^2 \cos^2 2\pi k} + 1} \right]^{-1}. \quad (\text{I-6})$$

If $|(\alpha_B - \alpha_A)/4\beta|$ increases, it is seen that, depending on the value of k , the electron becomes localized on atom A or B. If $0 \leq |k| \leq \frac{1}{4}\pi$ the electron becomes localized on atom A; if $\frac{1}{4}\pi \leq k \leq \frac{1}{2}\pi$ the electron becomes localized on atom B.

Hence, if this model represents an alloy with a contribution of one electron by atom B and two electrons by atom A (the analogue of a copper–nickel alloy), it is seen that if:

$$|(\alpha_A - \alpha_B)/4\beta| \geq 1, \quad (\text{I-7})$$

the electron on atom B has roughly energy α_B , but bandwidth $4\beta^2/|\alpha_A - \alpha_B|$, which is much smaller than 4β , the width before alloying. The localization energy which is $4\beta/\pi$ before alloying decreases to $-2\beta^2/|\alpha_A - \alpha_B|$ upon alloying, resulting in a large decrease in localization energy and therefore in an increase in heat of chemisorption of an atom bound to the B atom, as is explained in the text.

Appendix II

Derivation of eqs. (3) and (8) for E_{reads} and E_{ads}

Eqs. (3) and (8) of the main text are derived in a similar way. The derivation of eq. (8), the heat of chemisorption for weak adsorption, being the less elaborate of the two, will be presented in detail.

In the zero-order state ϕ_0 there is no interaction between adsorbate and substrate:

$$\phi_0 = \prod_{\sigma} \prod_{k=0}^{k_F} a_{k\sigma}^{\dagger} b_{\sigma'}^{\dagger} \phi_{\text{vac}}, \quad (\text{II-1})$$

where k labels the eigenstates of the substrate, σ and σ' are the spin states, $a_{k\sigma}^{\dagger}$ the

creation operator for an electron in state k, σ ; b_{σ}^{\dagger} is the creation operator for an electron on the hydrogen atom with spin σ' , and k_F is the quantum of the highest occupied level in the substrate. The zero-order Hamiltonian is:

$$H = \sum_{k, \sigma} \epsilon_k a_{k\sigma}^{\dagger} a_{k\sigma} + \sum_{\sigma} \epsilon_0 b_{\sigma}^{\dagger} b_{\sigma} - \frac{1}{2} \gamma \sum_{\sigma, \sigma'} (\delta_{\sigma, \sigma'} - b_{\sigma}^{\dagger} b_{\sigma'}) b_{\sigma}^{\dagger} b_{\sigma}, \quad (\text{II-2})$$

where ϵ_k is the eigenvalue of the substrate, ϵ_0 the eigenstate of the hydrogen atom and γ the repulsion integral of two electrons on the hydrogen atom.

The interaction between adsorbate and substrate is given by the interaction Hamiltonian H' :

$$H' = \sum_{k\sigma} (\beta'_k a_{k\sigma}^{\dagger} b_{\sigma} + \beta_k^* b_{\sigma}^{\dagger} a_{k\sigma}). \quad (\text{II-3})$$

Interaction of ϕ_0 with the following states is taken into account:

$$\phi_{1, \lambda_i} = b_{\sigma}^{\dagger} a_{\lambda_i \sigma} \phi_0, \quad (\text{II-4})$$

with $E_{1, \lambda_i} = \epsilon_0 + \gamma - E_{\lambda_i}$; $\lambda_i \leq k_F$. An electron is transferred from the metal to the hydrogen:

$$\phi_{0, k_i} = a_{k_i \sigma}^{\dagger} b_{\sigma} |0\rangle, \quad (\text{II-5})$$

with $E_{0, k_i} = E_{k_i} - \epsilon_0$; $k_i > k_F$. An electron is transferred from the hydrogen to the metal.

$$\phi_{0, k_i, \lambda_j}^{(1)} = a_{k_i \sigma'}^{\dagger} b_{\sigma}^{\dagger} b_{\sigma'} a_{\lambda_j \sigma} \phi_0;$$

$$\phi_{0, k_i, \lambda_j}^{(2)} = a_{k_i \sigma}^{\dagger} a_{\lambda_j \sigma} \phi_0;$$

$$\phi_{0, k_i, \lambda_j}^{(3)} = a_{k_i \sigma'}^{\dagger} a_{\lambda_j \sigma'} \phi_0; \quad (\text{II-6})$$

$$E_{0, k_i, \lambda_j}^{(1)} = E_{0, k_i, \lambda_j}^{(2)} = E_{0, k_i, \lambda_j}^{(3)} = E_{k_i} - E_{\lambda_j}; \quad k_i > k_F; \quad \lambda_j \leq k_F.$$

$\phi_{0, k_i, \lambda_j}^{(2)}$ and $\phi_{0, k_i, \lambda_j}^{(3)}$ are states where a single excitation takes place in the substrate; $\phi_{0, k_i, \lambda_j}^{(2)}$ describes excitation in the substrate accompanied by spin exchange with the hydrogen atom.

Using these states one derives the secular equations:

$$-EC_0 + \sum_{k_i > k_F} \beta_{k_i}^* C_{0, k_i} + \sum_{\lambda_i \leq k_F} \beta'_{\lambda_i} C_{1, \lambda_i} = 0,$$

$$\begin{aligned}
& \left\{ E_{0,k_i} - E - 2 \sum_{\lambda_i \leq k_F} \frac{1}{E_{0,k_i,\lambda_i} - E} |\beta'_{\lambda_i}|^2 \right\} C_{0,k_i} \\
& - \sum_{\lambda_i \leq k_F} \frac{1}{E_{0,k_i,\lambda_i} - E} \beta'_{\lambda_i} \beta'_{k_i} C_{1,\lambda_i} = -\beta'_{k_i} C_0, \\
& \left\{ E_{1,\lambda_i} - E - 2 \sum_{k_i > k_F} \frac{1}{E_{0,k_i,\lambda_i} - E} |\beta'_{k_i}|^2 \right\} C_{1,\lambda_i} \\
& - \sum_{k_i > k_F} \frac{1}{E_{0,k_i,\lambda_i} - E} \beta'^*_{\lambda_i} \beta'^*_{k_i} C_{0,k_i} = -\beta'^*_{\lambda_i} C_0. \tag{II-7}
\end{aligned}$$

If the coupling between the coefficients C_{1,λ_i} and C_{0,k_i} of the states defined in (II-4) and (II-5) is neglected and we use identities as exemplified by:

$$\sum_{\lambda_i \leq k_F} |\beta'_{\lambda_i}|^2 \frac{1}{E_{1,\lambda_i} - E} = \int_{E_{\min}}^{E_F} dE' \sum_k |\beta'_{0k}|^2 \frac{\langle \psi_k | \delta(E' - H_m) | \psi_k \rangle}{E' - E}, \tag{II-8}$$

in combination with the definition (II-9) for the spectral function $\Gamma(E)$:

$$\Gamma(E) = \sum_k |\beta'_{0k}|^2 \langle \psi_k | \delta(E - H_m) | \psi_k \rangle, \tag{II-9}$$

ψ_k is an eigenfunction of the Hamiltonian H_m , which gives the energy of the metal substrate. Eq. (8) of the main text is readily derived.

The derivation for E_{reads} [eq. (3)] is entirely analogous.

To allow for spin polarization not only charge-transfer states, but also excited singlet and triplet states of the surface complex have to be taken into account.

One finds:

$$\begin{aligned}
E_{\text{reads}} = & 2 \sum_{\alpha} \int_{E_F}^{E_{\max}} dE \frac{a_{\alpha} \Gamma'(E)}{E_{\alpha}^{+} + E + E_{\text{reads}} - 2 \sum_i \int_{E_{\min}}^{E_F} dE' \Gamma'(E') \frac{a_{\alpha}(i)}{E_i + E - E' + E_{\text{reads}}}} \\
& + 2 \sum_{\beta} \int_{E_{\min}}^{E_F} dE \frac{b_{\beta} \Gamma'(E)}{E_{\beta}^{-} - E + E_{\text{reads}} - 2 \sum_i \int_{E_F}^{E_{\max}} dE' \Gamma'(E') \frac{b_{\beta}(i)}{E_i + E' - E + E_{\text{reads}}}} \tag{II-10}
\end{aligned}$$

E_{α}^{+} is the energy of a positive ion of the surface complex, a_{α} the square of the over-

lap integral between the surface complex ground state and the two-electron parts of the ion eigenstates yielding this state, and $a_\alpha(i)$ the square of the overlap integral from this state to an excited state of the complex with energy E_i . E_β is the energy of a negative ion state of the surface complex, b_β the square of the overlap integral between surface complex ground state and the two electron parts of ion eigenstates yielding this state, and $b_\alpha(i)$ the square of the overlap integral leading from this state to the excited state i of the complex.

With our parameter choice only one positive and one negative charge transfer state contribute appreciably. For them we derive the values:

$$a_1 = 0.50, \quad E_1^+ = -2.43 \beta';$$

$$b_1 = 0.43, \quad E_1^- = +0.71 \beta'.$$

The only excited state of the surface complex that contributes is the triplet state. We find:

$$a_1(T) = 0.88, \quad b_1(T) = 0.71, \quad E_T = -1.333 \beta'.$$

The spectral function $\Gamma'(E)$ is defined by:

$$\Gamma'(E) = \sum_k |\beta_{0k}|^2 \langle \psi'_k | \delta(E - H'_m) | \psi'_k \rangle. \quad (\text{II-11})$$

ψ'_k is an eigenfunction of the Hamiltonian H'_m , which gives the energy of the metal surface without the atom used in the surface molecule.

Appendix III

Calculation of the density of states

The density of states on atom i is given by:

$$\rho_i(E) = \langle \phi_j | \delta(E - H) | \phi_j \rangle, \quad (\text{III-1})$$

where ϕ_j is the atomic orbital on atom i and H the Hamiltonian of the metal.

To determine the parameters C_1^i and C_2^i in eq. (5) of the main text we calculated $\rho_i(E)$ by expanding (III-1) using the resolvent method [23]. Eq. (III-1) can be rewritten to give:

$$\rho_j(E) = \lim_{\epsilon \rightarrow 0} \frac{i}{\pi} \text{Im} \left\langle \phi_j \left| \frac{1}{E - H + i\epsilon} \right| \phi_j \right\rangle. \quad (\text{III-2})$$

By defining $\phi'(k)$ as the wave function on the atoms other than j , eq. (III-1) can be

reformulated again to given identity:

$$\rho_j(E) = \lim_{\epsilon \rightarrow 0} \frac{i}{\pi} \text{Im} \left[E - \alpha_m + i\epsilon - \beta^2 \sum_k \langle \phi'_k | \frac{1}{E - H + i\epsilon} | \phi'_k \rangle \right]^{-1}.$$

Approximation:

$$\langle \phi'_k | H | \phi'_k \rangle \approx \alpha_m$$

results in the lowest-order approximation of $\rho_j(E)$:

$$\rho_j(E) = \frac{1}{2} \{ \delta(E - \alpha_m + \sqrt{Z} \beta) + \delta(E - \alpha_m - \sqrt{Z} \beta) \}. \quad (\text{III-4})$$

We use the values of $\rho_j(E)$ found by repeating the process of continued fractions three times. The general form of $\rho_j(E)$ is:

$$\rho_j(E) = \sum_i a_j^i \delta(E - E_i), \quad (\text{III-5})$$

where a_j^i is the probability of finding the electron on atom j with energy E_i . The quotient of the weight factors in front of the δ -function in eq. (III-5) is put equal to the quotient of the local density of states in eq. (5):

$$\rho_j(E_k) / \rho_j(E_l) = a_k^j / a_l^j. \quad (\text{III-6})$$

From this relation together with the normalization of the local density of states, C_1^j and C_2^j can be calculated.

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