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CHEMISORPTION BONDS ON METALS^{*)}

By

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(Reproduced from "Shokubai" (Catalyst), 4, 47 (1962))

Summary

Recent results on the physical nature of chemisorption bonds on metal surfaces are reviewed and discussed. Attention is mainly focussed on three points

1. Chemisorption can imply a weakening or rupture of intermetallic bonds in the adsorbing surface. At a certain stage the heat of chemisorption becomes equal to the heat of formation of a bulk compound.
2. Positive and negative adsorption states are observed simultaneously at low temperatures for the majority of adsorbates. Topographical and quantum-mechanical considerations are invoked to understand the various adsorption complexes.
3. The rate-determining step in heterogeneous catalysis is, for the majority of reactions, associated with the most stable chemisorbed complex.

I. Introduction

The nature of the bond between a metal surface and adsorbed atoms or groups has been studied in recent years by a number of methods. Most of these are based on some physical property of the adsorbing metal which is changed in a characteristic way when adsorption takes place. The following properties have been found useful.

1. Work function (photoelectric, thermionic or field emission, contact potential)¹⁻⁶⁾
2. electric conductivity of thin metal layers^{1,4,7,8)}
3. magnetization, in particular of finely dispersed metals^{4,9)}
4. X-ray absorption at the K-edge of the metal¹⁰⁾
5. Accommodation coefficients^{11,12)}.

While these techniques concentrate on the adsorbent, it is also possible to follow the fate of the adsorbed molecule by means of *e.g.* infra-red spectro-

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scopy^{13,14}), by kinetic studies of adsorption and, in general, of heterogeneous catalysis. Finally, the development of sensitive calorimeters¹⁵⁻¹⁹) has provided useful data on the heats of adsorption and their dependence on the degree of coverage.

The methods based on a comparison of clean and gas-covered surfaces require good vacuum conditions so that a gas-free surface can be prepared and maintained for a sufficient time. Modern ultra-high vacuum technique which allows of obtaining pressures below 10^{-12} mmHg has provided this prerequisite²⁰). Among the techniques to prepare clean surfaces the flashing of filaments and the deposition of films by sublimation from thoroughly degassed samples are of importance. The flashed clean filaments have the advantage of presenting a well-defined crystallographic surface with a low concentration of lattice faults. This technique is, however, restricted to a small number of high-melting metals such as tungsten, molybdenum, tantalum and rhenium, where all impurities can be evaporated from the surface at temperatures below the melting point of the metal. Another restriction of this method results from the small area of the thus cleaned surfaces; only certain elaborate methods allow quantitative measurements of *e. g.* the adsorbed amounts, and—although the first measurements of heat of adsorption ever made have been obtained for flashed filaments (ROBERTS,²¹)—a direct calorimetric determination is difficult. Films, on the other hand, can be prepared from almost every metal and their surface areas are much higher. But the crystallographic nature of their surfaces is less well defined. Other techniques for preparing clean surfaces include ion bombardment²²) and evaporation from metal tips under the action of very high electric fields⁵). Some of the methods listed above require finely dispersed metals. These are prepared by impregnation or coprecipitation with a support such as silica gel¹). The dried compound is reduced and degassed under vacuum. These supported metals are highly thermostable and easy to regenerate by reduction at a temperature up to $\sim 500^{\circ}\text{C}$. Their surface areas are so large that small amounts of contaminants can be tolerated for most measurements.

Only very rigorous vacuum techniques provide reproducible results. Before modern ultra-high vacuum techniques were generally accepted, widely different results were often obtained in different institutes. The resulting controversies, although highly stimulating for the experimentors, had the by-effect of reducing the confidence of non-experts in the new methods. Fortunately, these experimental difficulties have now been overcome and the data obtained in the last five years by various schools are generally consistent. It seems, therefore, that now the time has come for inspecting the experimental evidence and inquiring what general conclusions can be drawn for the understanding of chemisorption

and catalysis on metals. Some of these will be discussed in the present article. It does not pretend to completeness; where a selection had to be made the authors have confined themselves to those methods with which they have personal experience. The reader who desires more complete information is referred to some recent review articles *e. g.* by CULVER and TOMPKINS²³, or GUNDRY and TOMPKINS²⁴.

II. Strength of Adsorption Bonds, Weakening of Metal Bonds

a. Heats of adsorption

Data for the heats of chemisorption of a number of diatomic molecules on transition metals have been compiled in Table I. The majority were measured by BRENNAN, HAYWARD and TRAPNELL¹⁹. As the heat of adsorption depends on the degree of coverage, the initial heat has been used where data are available. In Table I the heats of adsorption are compared with the heats of formation of bulk compounds (metal hydrides, nitrides, oxides), the heats of formation being taken per mole H₂, N₂ or O₂ introduced into the compound. In the case of polyvalent metals the stable compounds with the lowest valency were chosen. This is not an essential restriction, because the heats of formation per mole of H₂, N₂ or O₂ are only slightly dependent on the valence state of the metal²⁵. It is well known that in all cases, the diatomic molecules undergo dissociation when chemisorption occurs or when the bulk compound is formed. As the heats of dissociation are known with high precision, it is possible to include them and consider a property

$$Z = \frac{1}{2}(Q - D_{X-X})$$

where Q is the heat of either adsorption or formation of the bulk compound per mole of the diatomic molecule; D_{X-X} is the heat of dissociation of the latter.

In Fig. 1 the Z values of chemisorption are plotted versus the Z values of the corresponding bulk compounds. A straight line is included in the graph which would be valid if both values were equal.

It is seen from Table I and Fig. 1, that there is a striking parallelism between the heats of adsorption and the corresponding heats of formation. In many cases the initial heats of adsorption are definitely higher. This was to be expected, because the metal surface is highly unsaturated. At the initial stage of adsorption little or no energy is required for a rupture of metal-metal bonds, while for the formation of a bulk compound the original metal lattice has to be broken down. Z_{ads} is therefore expected to be very strongly exothermic

TABLE 1. Heats of adsorption and heats of formation of bulk compounds

Metal	Gas	ΔH_{ads} (kcal/mole)	Comp.	ΔH_f (kcal/mole)	
Cr	H ₂	45	Cr ₇ H ₂	3.7	Beeck <i>et al.</i> ²⁶⁾
Ni	H ₂	30	NiH ₂	6.2	Beeck <i>et al.</i> ²⁶⁾ Schuit <i>et al.</i> ⁴⁾ Wahba, Kemball ²⁷⁾ Baker <i>et al.</i> ²⁸⁾ Klemperer, Stone ¹⁶⁾
Co	H ₂	26	CoH ₂	10.2	Schuit <i>et al.</i> ⁴⁾ Rudham & Stone ²⁹⁾
Pd	H ₂	27	Pd ₂ H	18	Ritchie ³⁰⁾ Schuit <i>et al.</i> ⁴⁾
Ta	N ₂	138	TaN	116	Beeck <i>et al.</i> ³¹⁾
Cr	N ₂	105	CrN	60	Beeck <i>et al.</i> ¹⁵⁾
Fe	N ₂	70	Fe ₂ N	1.8	Beeck <i>et al.</i> ¹⁵⁾ Bagg & Tompkins ¹⁷⁾
Pt	O ₂	67	PtO	34	Brennan <i>et al.</i> ¹⁹⁾
Pd	O ₂	67	PdO	42	Brennan <i>et al.</i> ¹⁹⁾
Rh	O ₂	76	RhO	43	Brennen <i>et al.</i> ¹²⁾
Ag	O ₂	108	Ag ₂ O	15	Gonzales, Paravano ³²⁾
Mo	O ₂	172	MoO ₂	131	Brennan <i>et al.</i> ¹⁹⁾
W	O ₂	194	WO ₂	134	Brennan <i>et al.</i> ¹⁹⁾
Co	O ₂	100	CoO	114	Brennan <i>et al.</i> ¹⁹⁾
Ni	O ₂	107	NiO	116	"
Fe	O ₂	136	FeO	127	"
Mn	O ₂	150	MnO	184	"
Cr	O ₂	174	Cr ₂ O ₃	180	"
Nb	O ₂	208	Nb ₂ O ₅	182	"
Ta	O ₂	212	Ta ₂ O ₅	193	"
Ti	O ₂	236	Ti ₂ O ₃	245	"

Chemisorption Bonds on Metals

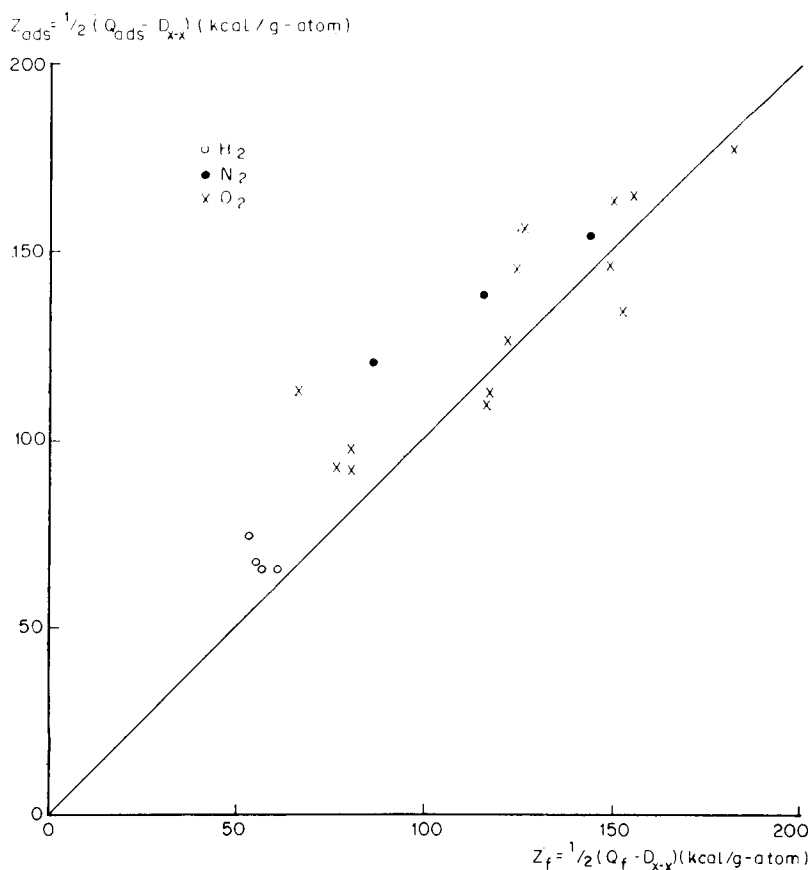


Fig. 1. Comparison of "Bond strengths" for the adsorbed state and the bulk compound.

with respect to $Z_{b.lk}$.

For a number of metals, however, grouped together in the second half of Table I, the initial heats of oxygen adsorption are of the same order as the heats of formation of the oxides. For these metals, moreover, the heats of adsorption are nearly independent of coverage, while the coverage extends considerably beyond the monolayer coverage. Apparently for these metals there is a close correspondence between adsorption and formation of bulk compounds³³. This is a very striking result. In order to explain the similarity of the two heat effects one can assume that also upon chemisorption a considerable rupture of metal-metal bonds occurs. An alternative explanation is possible by assuming that the adsorbed layer, when compared with the bulk compound, has the same degree of unsaturation as the metal surface has in comparison to the bulk metal.

The question arises to what extent the various effects balance and what conclusion can be drawn about the metal-metal bonds in the surface layer of a metal covered by a chemisorbed layer. The unprejudiced expectation is that adsorption at very low degrees of coverage may use the same surface bond electrons which would also be used when the metal lattice would be extended by several layers. In a clean metal surface these "dangling" surface bonds are possibly combined with each other, hence the metal-metal bond strength exceeds the bond strength in the interior of the metal. Schematically the metal surface thus has a "polyolefinic" rather than a "polyradical" character:



These "olefinic" bonds must be opened when the adsorption bond is established. At higher degrees of coverage, these easily available electrons will be exhausted, and further adsorption bonds can only be formed by weakening the normal metal-metal bonds. The point where this occurs will depend on the bond number of the adsorption bond, *i.e.* on the valency of the adsorbate, and on the nature of the adsorbing metal. The adsorption of *e.g.* oxygen on calcium will engage all the valence electrons of the calcium atoms in the surface and leave no electrons for metal-metal bonds in the surface, if a monolayer of oxygen is adsorbed. The situation is different for a transition metal such as nickel. The 10 available electrons might allow of simultaneously filling the bonding orbitals to the adsorbate and to the neighbouring metal atoms.

For the adsorption of *e.g.* oxygen on nickel the available data allow a rough comparison of the energy terms involved. For this purpose we shall treat the energy of cohesion as the sum of bond strengths between adjacent atoms. The symbol $v/n B_{M-A}$ will be used for the energy of bonds of bond number v/n between M and A, where v is the valency and n the ligancy. In this notation the heat of sublimation of nickel becomes.

$$-\Delta H_s = 6^{7/2} B_{Ni-Ni} = 102 \text{ kcal/g atom.}$$

PAULING³⁴⁾ ascribes a value of $v = 6$ to the metallic valency of nickel, for the present treatment this numerical value is of no importance. The heat of formation of one mole of bulk nickel oxide $\Delta H_{b,ik}$ from one gram-atom of metallic nickel and half a mole of gaseous oxygen then becomes:

$$-\Delta H_{\text{bulk}} = 6^{2/6} B_{\text{Ni-O}} - 6^{7/12} B_{\text{Ni-Ni}} - \frac{1}{2} B_{\text{O=O}}.$$

58 219 102 59

The numerical values, rounded off to integers are written under the symbols.

The heat of adsorption of $\frac{1}{2}$ mole of oxygen on a (111) face of nickel where each oxygen atom contacts three nickel atoms and, hence, forms three Ni-O bonds of bond number $2/3$ becomes

$$-\Delta h_{\text{ads}} = 3^{2/3} B_{\text{Ni-O}} - \frac{1}{2} B_{\text{O=O}} - \Delta_+ - \Delta_-$$

where a small h is used to avoid confusion with the normal convention of expressing heats of adsorption per *mole* of adsorbate, and where Δ_+ and Δ_- are the energies of rupture of "normal" and "olefinic" bonds in the nickel surface.

The heat of adsorption decreases with increasing coverage. At a certain point it reaches the value

$$\Delta h_{\text{ads}} = \Delta H_{\text{bulk}}$$

from which we obtain

$$\Delta_+ + \Delta_- = 3^{2/3} B_{\text{Ni-O}} - 6^{2/6} B_{\text{Ni-O}} + 6^{7/12} B_{\text{Ni-Ni}}.$$

The bond strength $^{2/3} B_{\text{Ni-O}}$ is unknown. Two extreme assumptions will be considered:

- a. $^{2/3} B_{\text{Ni-O}} = 2^{2/6} B_{\text{Ni-O}}$; *i.e.* the total bond energy per oxygen atom is equal in the oxide (distributed over six bonds) and the adsorbate (distributed over 3 bonds). The assumption leads to $\Delta_+ + \Delta_- = -\Delta H_s = 102$ kcal/g atom.

The same amount of bond rupture occurs as in the formation of the bulk oxide. The opposite extreme to assumption (a) would be:

- b. $^{2/3} B_{\text{Ni-O}} = ^{2/6} B_{\text{Ni-O}}$; *i.e.* the bond strength is independent of the bond number. In this case we obtain:

$$\Delta_+ + \Delta_- = -8 \text{ kcal/g atom.}$$

The truth will lie somewhere within the range between assumption (a) and (b). A rough estimate of the real bond strength of the adsorption bond can be obtained in the following way.

We consider the initial adsorption at $\theta=0$. At this stage, adsorption will make use only of the "olefinic" bonds, or

$$\Delta_- = 0.$$

On the (111) face every nickel atom has 9 neighbours compared to 12 in the

interior. This provides an upper limit for Δ_+ , namely

$$\Delta_+ \leq 3/12 |\Delta H_S|.$$

In the treatment of ELEY³⁵⁾ and STEVENSON³⁶⁾, the surface was considered as a polyradical, *i. e.*

$$\Delta_+ = 0.$$

It might be a good guess to assume a value midway between these extremes, namely

$$\Delta_+ = 15 \text{ kcal/mole.}$$

The initial heat of adsorption exceeds the heat of formation by an amount which will not be higher than 30 kcal/mole or 15 kcal/g atom. With these values we find

$$-\Delta h_{\text{ads}} - (-\Delta H_{\text{bulk}}) = 15$$

which leads to

$${}^{2/3}B_{\text{Ni-O}} = 1.34^{2/6} B_{\text{Ni-O}}.$$

If this is used instead of assumptions (a) or (b), we find for the total amount of metallic bond rupture at the coverage where $\Delta h_{\text{ads}} = \Delta H_{\text{bulk}}$:

$$\Delta_- + \Delta_+ = 30 \text{ kcal/g atom} = 0.3 |\Delta H_S|.$$

This value is probably too high, since the mutual repulsion of adsorbed atoms was disregarded, in other words, the actual decrease of the metal-oxygen bond strength with increasing coverage was neglected.

A consequence of these considerations is that the heat of adsorption might drop below the value for the heat of formation of the bulk compound, before the monolayer is full.

This will, in particular, happen on metals with a low number of available electrons such as calcium or titanium. Unless special precautions are taken, adsorption will be followed by corrosion, even before the monolayer is established. The difficulty to separate adsorption and surface corrosion experimentally, mentioned in discussing Table I, might find its origin just in this circumstance.

The near equality of heats of adsorption and formation can be used in theoretical treatments of heterogeneous catalysis²⁵⁾. In order to understand the catalytic activities of various metals, it is essential to know the strengths of the bonds which are formed and broken when the reacting molecules interact with the catalyst surface. In many cases direct experimental data are not available. Fig. 1 shows that a reasonable approximation can be found by substituting the

known values of bulk compounds. This approximation appears particularly justified, since only differences in bond strengths are important when the adsorption of a given molecule is compared on various catalysts such as in the theory of the "volcano-shaped curves"^{37,38,25}.

The formation of adsorption bounds will modify the physical properties of the adsorbing surface in various ways. Some of these phenomena will be reviewed in the next few paragraphs, and it will be seen that, generally, the surface loses its typical metallic character. This is true even under circumstances, where no rupture of normal metallic bonds occurs.

b. Magnetization of dispersed metals

When a ferromagnetic metal such as nickel is dispersed on a non-magnetic support, a particle size of the nickel crystals can be attained which is smaller than the WEISS domains in bulk nickel. No BLOCH walls other than the particle boundaries are present in these "superparamagnetic" systems^{39,40}. Chemisorption on the metal surface causes a measurable change in the magnetization. In all cases studied under reliable vacuum conditions a decrease in magnetic moment is observed (see SCHUIT & VAN REIJEN⁴¹, SELWOOD⁹). The result is consistent with the view that upon chemisorption the surface atoms cease to contribute to the collective phenomenon of magnetism. A new compound is formed at the surface which includes both the adsorbate and the metal atoms of the original surface.

c. Electric resistance of metal films

The resistance of clean metal films undergoes a measurable change when adsorption takes place on the surface^{1,7,41,42}. Again, all reliable data show that all metalloidal adsorbents cause effects of the same sign: the resistance is increased. Sometimes a second and third resistance change is observed at higher coverages^{7,8,43} which may reduce the initial effect, but never does the resistance of the covered film drop below the value of the clean film⁴⁴. In some cases (H_2 on Ta⁴², Ti⁴¹, Pd⁴⁶, Pt⁴⁷) the adsorption effect is accompanied by a diffusion into the bulk which causes an additional resistance change. But since the latter process requires a higher activation energy than adsorption, it can usually be separated experimentally by selecting an appropriate working temperature. The resistance measurements will be discussed in more detail in a later section; for the moment it is sufficient to state that all metalloidal adsorbates cause a rise in resistance and that the amount of this rise is consistent with the view that approximately one atomic layer of metal surface atoms is de-metallized, since

it becomes part of a two-dimensional compound.

d. X-ray absorption at the K-edge

This method was introduced by LEWIS⁽¹⁹⁾. It is based on the principle that the shape of the X-ray absorption curve at the K-edge is characteristic for the nature of the bond. Only one result is known at present, it concerns the chemisorption of oxygen on dispersed nickel. The same deviations from the curve of bulk nickel are found to occur for chemisorption and for bulk oxidation. The deviations occur at exactly the same wave lengths, only the absolute amounts of the deviations are different because, evidently, more nickel atoms are involved in bulk oxidation than in chemisorption. LEWIS concludes that the nature of the Ni-O bond is equal for chemisorption and oxidation.

e. Surface corrosion

When TAMARU⁽²⁰⁾ studied quantitatively the adsorption of formic acid vapour on nickel catalysts he found that more formate ions were adsorbed than could be accommodated on the nickel surface if all metal atoms had stayed at their positions. The same result was confirmed by FAHRENFORT, VAN REIJEN & SACHTLER⁽²¹⁾ who showed that a surface formate was formed. This conclusion was based on infra-red and calorimetric evidences and on the material balance of the gas. More extensive studies which included resistance measurements and experiments with the field emission microscope⁽²²⁾ showed that three stages can be distinguished when formic acid vapour reacts with a metal surface at low temperatures:

1. Adsorption on the intact metal surface; this adsorption is dissociative yielding formate groups and hydrogen atoms, the latter are driven off the surface when more formic acid vapour is admitted, so that a surface covered with formate groups results.
2. Surface corrosion, *i.e.* the surface metal atoms leave their places and a two-dimensional metal formate is formed.
3. Bulk corrosion.

On nickel, the second process is very fast at 0°C and probably starts before stage 1 is completed. On tungsten which has a much higher heat of sublimation than nickel, the first and second stages are separated by a break in the plot of resistance versus time plot. In the field emission microscope it is seen that the second stage starts, as expected, on the crystallographically "open" areas of the surface, where the number of metal-metal bonds to be broken is smaller than in the closely packed planes.

These results show that upon forming the adsorption bond with formate

ions the metal atoms can easily migrate to more favourable positions at low temperatures. Even metal atoms below the surface can become mobile, as was found by MÜLLER⁵⁰⁾ for oxygen adsorption.

In conclusion of section II we can state that numerous independent data provide consistent evidence for an at least partial dissociation of surface metal-metal bonds upon chemisorption. The degree of this bond loosening will vary for various adsorbates. It will be small for hydrogen and very pronounced for such aggressive agents as formic acid. Moreover, it will depend on the strength of the intermetallic bonds, *i.e.* on the heat of sublimation, and on the number of available electrons. For a given metal and a given adsorbate, it depends on the surface coverage and consequently may be one of the reasons, why differential heats of adsorption always decrease with increasing coverage.

III. Differentiation of Various Chemisorbed States

Some seven years ago one of the writers⁴²⁾ measured the resistance effects of hydrogen adsorption on nickel films by admitting a dose of hydrogen to a fresh film at 0°C. A rise in resistance was observed. Then the excess hydrogen was pumped off. To the great surprise of the experimentors, a second resistance increase was registered. It seemed reasonable to assume that two species of adsorbed hydrogen were present, one of which caused an increase and the other, less strongly bound, a decrease in resistance. Removal of part of the latter complex by pumping would explain the second resistance rise. A support for this interpretation was seen in MIGNOLET's^{2,51)} earlier finding that a "negative" and a "positive" species of hydrogen on nickel could be discerned by their surface potentials, although much lower temperatures had been used by MIGNOLET to detect his "positive" complex.

In order to investigate this phenomenon in greater detail, resistance measurements were done in an apparatus which allowed a very slow and continuous gas admission by KNUDSEN diffusion⁷⁾. It was found that the plot of resistance versus time indeed showed a maximum at 0°C. At -78°C the curve showed two extrema, indicating three adsorbed hydrogen complexes, as is seen from Fig. 2. Upon pumping at -78°C the third weak complex is removed and resistance drops; at 0°C pumping also removes part of the second complex and resistance, consequently rises. The results have been confirmed by SUHRMANN *et al.*⁵²⁾, by ODA *et al.*⁸⁾ and by KNOR and PONEC⁴³⁾, under varying conditions of temperature and film preparation. ODA *et al.*⁸⁾ found that the sticking coefficient sharply drops after the completion of the first species layer. For hydrogen on tungsten HICKMOTT⁵³⁾ also found two adsorbed hydrogen species by means of flash filament techniques: a weakly bound α -type, desorbing below room tem-

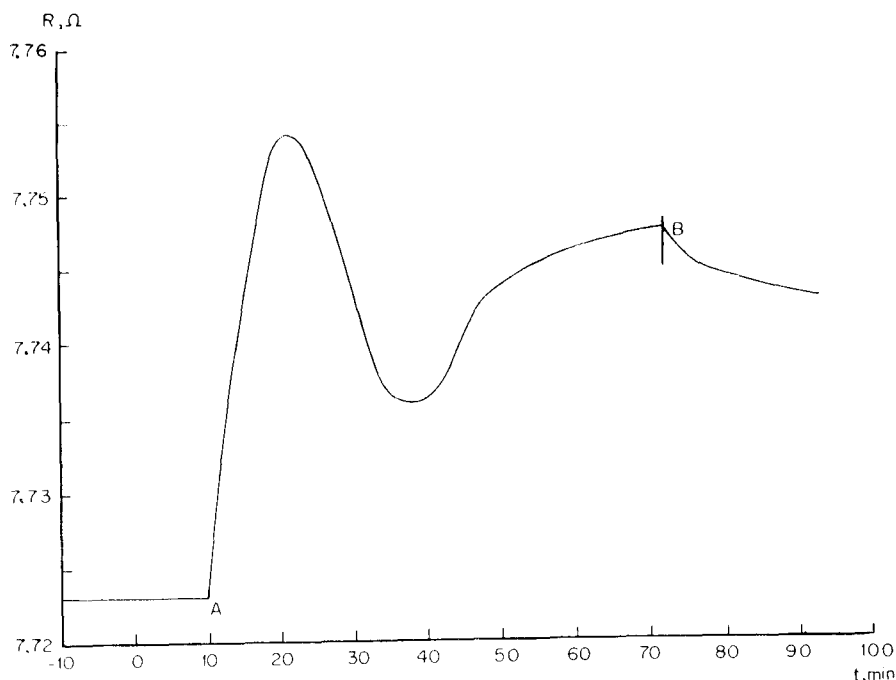


Fig. 2. Resistance change on hydrogen adsorption at -78°C .

A = Hydrogen admitted.

B = Hydrogen pumped off.

perature and a much more strongly bound β -type. BECKER⁵⁴⁾ investigated various forms of hydrogen adsorbed on tungsten in the field emission microscope. The phenomenon of composite adsorption is not confined to hydrogen. EISCHENS *et al.*⁵⁵⁾ found two species of CO on nickel in the infra-red and DORGELO & SACTLER⁵⁶⁾ by means of the surface potentials. YANG & GARLAND⁵⁷⁾ found three CO species on rhodium, using again the infra-red method. For CO adsorption on tungsten EHRLICH⁵⁸⁾ distinguished two complexes using the flash filament technique and three states were detected in this way for nitrogen chemisorbed on tungsten⁵⁹⁾. It seems that the occurrence of more than one chemisorbed state is quite a general phenomenon at low temperatures.

The important question how these different adsorption states must be understood physically has not yet been answered satisfactorily. There is convincing evidence that all the species listed above are truly chemisorbed. For hydrogen on nickel BEECK, GIVENS & RITCHIE⁶⁰⁾ could show that physical adsorption sharply decreases above 20°K . At the much higher temperatures (*e.g.* 200°K) at which the three above-mentioned chemisorbed hydrogen complexes on nickel

were detected, no physical adsorption can occur. Also the heats of adsorption which EHRlich⁵⁹⁾ determined for the three nitrogen species on tungsten from their desorption rates are higher than the heat which would result from a pure VAN DER WAALS-LONDON interaction. Some of the chemisorbed complexes will, nevertheless, be molecular as no complete dissociation occurs⁵²⁾,

It should be mentioned that the number of states which can be distinguished for a given adsorption system depends on the method used. For hydrogen on nickel, the resistance method detects three, the contact potentials two and the magnetization method only one species. This shows that various adsorbed species may be different with respect to a certain physical property, but indistinguishable, when another property is regarded.

The attempts for a physical interpretation of the different adsorption states can, roughly be classified in two groups

1. Those which are based on the microtopography of the adsorbing surface. All atoms on a clean metal surface are chemically equal, their only differentiation results from their surrounding, in one crystal plane or another, at the edge or corner of a crystal, next to a dislocation or vacancy *etc.*
2. Those which consider the possibility of successively appearing chemical bond types in terms of quantum chemistry. There is also a topographic element in the latter treatment, as the direction of unfilled *p*- and *d*-orbitals depends on the location of the other ligands, *i. e.* on the crystal geometry.

In each case one can focus the interpretation on *a priori* differences or on induced effects, caused by the preceding adsorption.

A purely topographical analysis of hydrogen adsorption on tungsten was given by BECKER⁵⁴⁾. Adsorption sites are characterized by the number of tungsten atoms which contact an adsorbed hydrogen atom, and the tungsten atoms are classified by their degree of unsaturation, *i. e.* by the number of first neighbours compared to complete surrounding as given for a tungsten atom in the interior. Field emission currents are registered as a function of adsorption time and breaks in the resulting plots are attributed to the completion of the covering of a family of equivalent adsorption sites.

A topographic approach was also attempted by SACHTLER & DORGELO^{7,61)}. They compare adsorption to crystal growth and assume that those sites which are actually used in crystal growth will also be favourable for chemisorption. As a hydrogen molecule needs two sites for dissociative adsorption it may occur at high coverage that only one or no site of the favourable type is available for an impinging molecule, so that less favourable sites have to be used.

MIGNOLET's²⁾ approach is very similar, it rejects, however, the "*a priori*" differentiation in SACHTLER's approach and replaces it by an induced differen-

tiation. On a (111) plane of a fcc lattice *e.g.*, all points between three metal atoms are potential adsorption sites, they are favourable when their distance from an already covered site is equal to an even number of atomic steps and unfavourable when the number is uneven. When adsorption zones expand from various independent starting points, they will finally meet and may be in misfit with respect to each other. This is supposed to give rise to a second type of adsorption.

EISCHENS¹⁴⁾ assumes that adsorption sites are not necessarily pits between metal atoms. The two complexes of CO on nickel are attributed to (1) adsorption above one Ni atom, causing a linear Ni-C-O complex and (2) adsorption between two nickel atoms, giving a bridged complex. This interpretation is supported by comparison of the infra-red spectra with those of mono- and binuclear metal carbonyls.

An essentially non-topographical approach was brought forward by DOWDEN⁶²⁾. He distinguishes three types of *e.g.* hydrogen chemisorption on transition metals. Type A implies a rupture of intermetallic bonds; the chemisorption makes use of the *dsp* bonding orbitals of the metal and is very stable, so that no exchange of H atoms thus adsorbed and gaseous D₂ molecules is possible at 90°K. Type B is located at the immediate rear of the surface layer. It is bound by vacant *d*-orbitals and comparable to absorbed hydrogen. It cannot catalyse hydrogen reactions and is absent on *sp* metals such as Cu. Type C, finally, makes use of unfilled *d*-orbitals which protrude above the surface. The heat gain is rather small. This type of hydrogen adsorption is responsible for a hydrogen-deuterium exchange mechanism at 90°K. These three species allow a consistent interpretation of the hydrogen catalysis observed on *sp* and *spd* metals, of the heats of adsorption, the surface potentials and the magnetic effects.

TOYA'S⁶³⁾ interpretation is similar to DOWDEN'S but his approach is based on BLOCH'S wave function for the metal electrons. He discusses two adsorbed species, one of which (*r*-type) is adsorbed *on* the surface, similar to DOWDEN'S type A, the other (*s*-type) is located *in* the surface and comparable to bulk adsorption, sharing therefore many characteristics with DOWDEN'S type B adsorption. The potential energies of the forms M⁺-H⁻ and M⁻-H⁺ which both contribute to the actual bonding states depend on the distance between the hydrogen nucleus and the electronic surface. The potential energy minimum for M⁺-H⁻ is located at a greater distance from the surface than M⁻-H⁺, and consequently there is a strong contribution of M⁺-H⁻ to the *r*-type complex which, therefore, exhibits a negative surface potential; the form M⁻-H⁺ contributes mainly to the *s*-type complex which therefore has a positive surface

potential.

TOYA⁶⁴⁾ is able to give a consistent interpretation of some of the resistance effects. Since the mean free path of the electrons in a metal exceeds the thickness of films at low temperature, electronic reflection at the surface is an important factor for electric conduction. From the observed temperature dependences of the resistance effects⁶⁵⁾ TOYA concludes that *r*-type adsorption reduces the reflection coefficient at the surface while *s*-type adsorption only modifies the number of quasi-free electrons.

It does not seem possible at present to decide which of the approaches is most likely to be able to interpret the totality of the experimental evidence in an unambiguous way. There is good hope that further research by means of the field emission microscope will show the potentialities of the topographic aspect, while adsorption experiments on alloys with systematically varied filling of *e.g.* *d*-orbitals may elucidate the function of various orbitals in chemisorption.

IV. Implication of Different Adsorption States for Catalysis

The discovery of loosely bound adsorption complexes has stimulated speculations on the role of such complexes in fast catalytic reactions. There are, however, some limitations for such a possibility;

1. In the steady state of a catalytic reaction, labile and stable states should be in equilibrium.
2. Most reactions are carried out at temperatures where the concentration of labile complexes on the catalyst surface is exceedingly small.
3. Many reactions proceed at highly covered surfaces. The production of free sites, necessary for a continuous process is controlled by a removal of the most tightly bound species present.

Only a small number of catalytic reactions is known which may proceed without strongly adsorbed intermediates. These reactions are observed at very low temperatures (90°K *e.g.*). The *o*, *p*-conversion of hydrogen and the exchange reaction of hydrogen and deuterium on transition metal catalysts are possible candidates as is argued by DOWDEN⁶²⁾ and by BORESKOV *et al.*⁶⁶⁾.

For numerous catalytic reactions a stable chemisorbate could be shown to be an intermediate. This was demonstrated for the H₂/D₂ exchange reaction on transition metals at *e.g.* room temperature⁹⁾. Also for the ammonia synthesis a stable adsorption of hydrogen and nitrogen on *e.g.* iron is generally assumed⁶⁷⁻⁶⁹⁾. The decomposition of formic acid vapour on metal catalysts is another example. For nickel³⁸⁾ the rate of this reaction is equal to the rate at which the two-dimensional nickel formate on the catalyst surface is decomposed as

could be proven by spectrokinetic measurements. The hydrogen-deuterium exchange proceeds via chemisorbed atoms even on gold and germanium; these metals do not favour a dissociation of H₂ molecules under normal conditions; catalytic exchange is therefore found to be absent on these metals unless chemisorbed atoms are brought to the surface by some experimental trick, such as adsorption of mono-deuteroformic acid on gold^{70,71}, or simultaneous decomposition of GeH₄ and GeD₄ on germanium⁷².

It therefore seems that for the majority of the catalytic reactions, labile adsorption, although very interesting as potential precursor and intermediate, will have no direct influence on the overall kinetics.

For a better understanding of catalytic activity of metals, a precise knowledge of the stable chemisorbed intermediate under steady-state conditions appears to be of greater significance.

Amsterdam, 10 th February 1962

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