THE MECHANISM OF HETEROGENEOUS CATALYTIC ORGANIC REACTIONS. I

CATALYTIC HYDROGENATION[1]

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The process of catalytic hydrogenation of organic compounds is of great interest, not only industrially but also scientifically. It comprises the hydrogenation of fatty substances, the hydrogenation of carboxides with formation of methanol, and a host of other important chemical processes. In order to master these reactions the most important step is to understand their mechanism.

In hydrogenating fatty oils one or more double bonds between carbon atoms are converted into single bonds; in hydrogenating carboxides one or more double bonds between carbon and oxygen atoms are reduced. This seems to be a close analogy; nevertheless the mechanism of the two processes is probably quite different, as we shall see later.

We consider first the mechanism of the hydrogenation of multiple carbon bonds. For a long time I have adhered to the theory (1) that catalytic hydrogenation of multiple carbon bonds belongs to the great class of catalytic reactions that are produced by ions. I am glad now to have the opportunity of surveying the facts which seem to me to prove that ionic catalysis is involved in this type of hydrogenation.

But first, what is ionic catalysis?

Ostwald (2) and Arrhenius (3) were the first to find that ions

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[1] This is the first of a series of three articles. II, The Dissociation of Carbon Bonds, is scheduled for publication in Volume XIII of This Journal, and III, The Formation of Carbon Bonds, in Volume XIV.—Editor.

[2] Written in English by the author.

are catalysts. Ostwald showed that the velocity of saponification of esters and that of inversion of cane sugar are much accelerated by adding inorganic or organic acids. Then Arrhenius found that there is a direct relation between the electrical conductivity of the acids and the acceleration of the reaction. Electrical conductivity is, as Ostwald found, a measure of dissociation. In aqueous solutions of acids we have as dissociation products the various anions, the radicals of the acids, and the hydrogen cation. This last is the only ion present in all these catalytic reactions, and therefore we conclude that the hydrogen ion is the catalyst. This conclusion is confirmed by the fact that the concentration of the hydrogen ions is, to a first approximation, proportional to the acceleration of the velocity of reaction, as Ostwald, Palmaer, and Goldschmidt have found (4).

But what is the mechanism of these reactions, in which the positively charged hydrogen atom, the proton, is the catalyst?

The proton is the smallest ion we know; its radius is perhaps smaller than 10^{-13} cm., while the radius of Na^+ is 10^{-8} cm. (1 Å.). The field power, F, equals Q/r^2; therefore F of the spherical proton is at least 10^{10} times larger than that of the sodium ion. Therefore the proton strongly deforms all known ions, dipoles, and molecules.

On bringing it into water, the proton combines with water molecules to form a complex, namely, the especially stable H_3O^+, surrounded by spherical layers of water dipoles, which are directed toward the central ion. All the reactants in the hydrolysis of cane sugar or in the hydrolysis or formation of esters, i.e., water, cane sugar, alcohols, esters, and undissociated acids, are dipoles and can substitute each other in the complex formed by the H_3O^+ ion; all these dipoles are reinforced by the electric field of the central ion,—reinforced, polarized, deformed, and *activated*.

And now we have in a single complex each participant in the reaction beside the other. The activated water and the activated cane sugar molecule are thus joined for a relatively long time. They combine and react to give glucose and fructose.

Born and Franck (5) have shown in a very important paper that the catalyst is characterized by two properties,—the *deform-*

ing of the reactants and thus the activating of them, and the *bringing them closely together for a time*. These are the two significant features of our picture of the hydrolysis of cane sugar.

The most important property of the catalyst is its power of deformation. It is not sufficient that the participants in the reaction merely lie together for a time. Charcoal absorbs hydrogen and ethylene in fairly large amounts, but they do not combine. We suppose that the activation of hydrogen by deformation is in this case not sufficient.

By the polarization of the reactants their centers of electric gravity are separated. We get dipoles, the electric field of which is much stronger than that of an undeformed organic compound. In many cases this deformation leads to dissociation, as, for instance, Meerwein (6) has shown in the reaction between zinc chloride and water:
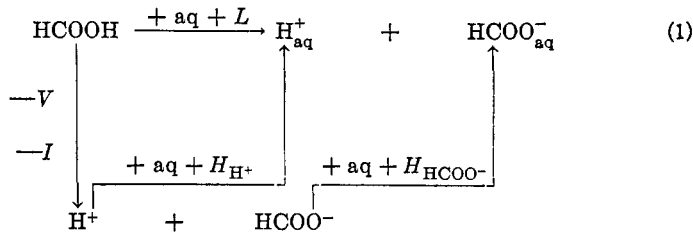
$$ZnCl_2 + H_2O = (ZnCl_2OH)' + H^{\cdot}$$
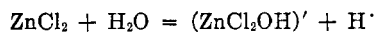
By forming the complex $(ZnCl_2OH)'$ the dipole water is ionized and gives the $H^{\cdot}$ ion, which is much more active than the hydrogen of the water molecule itself.

The substances which take part in a catalytic reaction are generally very inert. Thus we find that inversion of cane sugar does not take place in an aqueous solution which is free of catalyst. This means that the energy of activation is so large that it cannot be delivered under these conditions. Cane sugar is a dipole and has therefore a certain activity; homopolar gases, such as hydrogen, oxygen, and nitrogen, are much more inactive. In agreement with the quantum-mechanical investigations, made by London, Heitler, and Polanyi (7), we must suppose that the molecules are surrounded by a potential wall which knocks off other molecules coming along. We need the activation energy for surmounting the potential wall. Since the catalyst lowers the energy necessary for activation, we presume that its action consists of a deformation of the participants in the reaction.

Work is needed to lower the potential wall. If we bring a typically heteropolar substance, such as an acid, into water then the acid is dissolved in water and is dissociated into its ions.

Born's cyclic diagram represents the factors as follows:

$$\text{HCOOH} \xrightarrow{\ +\ aq\ +\ L\ } \text{H}^+_{aq} \quad + \quad \text{HCOO}^-_{aq} \qquad (1)$$

with $-V$ and $-I$ on the left branch, $+\ aq\ +\ H_{H^+}$ and $+\ aq\ +\ H_{HCOO^-}$ on the lower branches, leading to

$$\text{H}^+ \quad + \quad \text{HCOO}^-$$

$$L = H - V - I \qquad (2)$$

$$H = H_{H^+} + H_{HCOO^-} \qquad (2a)$$

where L is the heat of solution, H the heat of hydration of the ions, V the heat of evaporation, and I the heat of ionization. L and V generally have values of several Calories and I of some hundred, so that H, the sum of the energies of hydration, must have a large value and delivers the energy needed for the ionization of the acid.

Born has shown that the energy of solution can be calculated approximately by a very simple method (8). He finds

$$H = 1/2 \left(1 - \frac{1}{k}\right) \frac{z^2 e^2}{r_i} N \cdot F \text{ Cal.} \qquad (3)$$

where k is the dielectric constant of the solvent, z is the charge on the ion, r_i is its radius, F is the equivalent value of the erg in Calories (2.388×10^{-11}), and N is Avogadro's number (6.06×10^{23}). Therefore the heat of solution is greater at high values of k and z and at small values of r_i. Because the heat of solution furnishes the energy needed for ionization the three important factors are: *greatness of k and of z and smallness of r_i.*

The two types of catalysis, i.e., homogeneous catalysis in water, produced by hydrogen ions, and heterogeneous catalysis in metals with hydrogen, both occur in media of high dielectric constant. The value of k for water is 81; the value for metals is not determinable, but is very high. In formula 3 we can therefore neglect the value of $1/k$ which is very small, and we get very large values for H if r_i is less than 1×10^{-8} cm. and z has a higher value than 1.

In homogeneous catalytic reactions, in which the hydrogen ion is the real catalyst, we have seen that the ion activates the reactants by deforming (polarizing, ionizing) them and that it brings together the activated participants for a long enough time to allow them to react.   The mechanism of heterogeneous hydrogen catalysis is not identical with this but the principal features are obviously the same.   We ask, what ion is here the catalyst? But before we answer this question we must discuss another explanation.

It is generally supposed that hydrogen is sorbed by metals in the form of atoms and that therefore the hydrogen atoms are the active factors in this type of catalysis (10).   This is based on the fact that the sorption of hydrogen by metals often follows the square root relation,

$$c = k \sqrt{p} \tag{4}$$

where c is the quantity of sorbed hydrogen, p the pressure in the gas phase, and k a constant.   According to the distribution law, the molecular hydrogen is so distributed between the solid and gaseous phases that for a given temperature and pressure the concentration in the two phases has a fixed proportion

$$[H_2]_{gas}/[H_2]_{solid} = k_1 \tag{5}$$

On the other hand the molecular hydrogen, dissolved in the solid phase, is in equilibrium with its products of dissociation:

$$[H]^2_{solid}/[H_2]_{solid} = k_2 \tag{6}$$

Therefore we have

$$[H]^2_{solid} = k_3[H_2]_{gas} \tag{7}$$

For a given temperature the concentration of a gas in the gas phase is proportional to its pressure, so that we have

$$[H]_{solid} = k_4 \sqrt{p} \tag{8}$$

If we assume that the dissociation of hydrogen is practically

complete in the solid phase, then [H] is a measure of the total quantity of sorbed hydrogen and we have

$$H_{\text{dissolved}} = k \sqrt{p} = kp^{1/2}$$

which is equation 4, as found empirically.

This is the usual explanation of the validity of the square root relation. If there is dissociation, we must have this relation; but the reverse conclusion does not necessarily follow. Equation 4 is only a special form of the general equation of the isotherm of adsorption, given by Freundlich:

$$p = kp^{1/n} \tag{9}$$

where $1/n$ is a proper fraction and n can have values from 10 to 1 (11).

We ignore the physical significance of n in this empirical formula and it seems therefore impossible to draw conclusions from the fact that in the above cases n is often equal to 2, as Sieverts and his coworkers found (12).

Not in all cases of sorption of hydrogen by metals is n exactly equal to 2. Thus Sieverts (13) found that for palladium the following equation is valid:

$$c = k \sqrt{p} + k'p \tag{10}$$

In this case one might suppose that a part of the hydrogen is dissociated and the rest is not. By contracting equation 10 we find a value for $1/n$ which lies between 1 and 1/2. But $1/n$ can also have values smaller than 1/2. Chappuis has found, for instance, that $1/n$ has a value of 0.184 in the sorption of ammonia by meerschaum (14). It is of course impossible to give a rational explanation on the above basis for a value of $1/n$ which is smaller than 1/5.

There are still other substances which sorb hydrogen according to the square root relation, e.g., charcoal, as found by McBain (15). But charcoal is not a catalyst for hydrogenation; it is quite indifferent at moderate temperatures.

On the other hand we know that double bonds are easily at-

tacked by atomic hydrogen, as v. Wartenberg and Schulze (16) and also Bonhoeffer and Harteck (17) have found. In the gaseous state the reaction is complex. Ethylene gives not only the product of hydrogenation, ethane, but also acetylene; by the enormous development of heat, caused by the reaction of atomic hydrogen, a portion of ethylene is dehydrogenized and gives acetylene. It is probable that in the solid phase the reaction is not so complex because the heat of reaction is here conducted away much more easily.

Since charcoal, nevertheless, has no catalytic action in the hydrogenation of ethylene, it seems improbable that the hydrogen sorbed by charcoal is to an appreciable extent in the atomic state. We therefore cannot agree with the conclusions drawn by Winkelmann and by Coehn from the square root relation (10, 74).

On the other hand I do not imply that there is no possibility that atomic hydrogen is present on or in catalytic metals. On the contrary we shall see that it is often present. That explanation of catalysis seems, however, to be wrong.

One of the reactants, the unsaturated hydrocarbon, has a moderate dipole moment when unsymmetrical; but the other, hydrogen, has none. The heat of activation is very large for hydrogen, small for the unsaturated hydrocarbons. It is often sufficient to activate only hydrogen; e.g., atomic hydrogen hydrogenates the double bonds of carbon, as Bonhoeffer has shown (18). Therefore it seems sufficient to investigate the manner of activating hydrogen in this type of catalysis.

First we ask which elements, or compounds of elements, are able to hydrogenate multiple carbon bonds.

THE CATALYTIC ELEMENTS ARE EFFECTIVE ESSENTIALLY AS SUCH

There is no doubt that the hydrogenating properties of catalysts are connected with the metallic state. Bedford and Erdmann (19) for a time advanced the opinion that the suboxides of metals, and especially Ni_2O, are catalysts; but this opinion was an error and their Ni_2O was only a mixture of NiO and Ni. Oxides of metals are effective only at a temperature at which they are reduced by

hydrogen. Nevertheless we must emphasize that it is not at all necessary that the whole catalyst or the greater part of it be present as metal. In many cases the catalyst is effective even when large amounts of unreduced oxides or sulfides are present.

The simple technical catalysts for hydrogenating multiple carbon bonds are made by employing compounds of elements, the oxides of which are easily reducible. Hydrogen is the reducing agent and the compounds are oxides or such other compounds as easily go over into oxides by heating, viz., carbonates, nitrates, oxalates, etc. Thus the metals are obtained in a finely divided state, very favorable for hydrogenation. The reduction of the easily reducible oxides involves mostly *development of heat* and follows the equation:

$$MeO + H_2 = Me + H_2O + Q$$

The reduction of the difficultly reducible oxides requires *absorption of heat.*

In order to determine the conditions for obtaining these metals from the oxides we employ the Nernst theorem. We use it in the approximate formula and always write the equations so that the reaction takes place with the development of heat as read from left to right. Thus for a reaction which absorbs heat we write

$$Me + H_2O = MeO + H_2 + Q_1$$

In the first case

$$K_p = p_{H_2}/p_{H_2O}$$

in the second

$$K_p = p_{H_2O}/p_{H_2}$$

If we set $p_{H_2} = 1$, we have $K_p = 1/p_{H_2O}$, or p_{H_2O}, respectively. The approximate formula of Nernst's theorem

$$\log K_p = -\frac{Q}{4.571\ T} + \Sigma\ \nu\ 1.75 \log T + \Sigma\ \nu\ C$$

is in this case simplified, because the second member on the right side is zero; $\Sigma\nu C$ is equal to -2 or to $+2$ respectively. Table 1

gives the heat of formation, B, of the oxides of metals, the heat of reaction, Q, and the value p_{H_2O}/p_{H_2} for $p_{H_2} = 1$ for a number of oxides of metals.

Table 1 shows that the partial pressure of water vapor is very small in the state of equilibrium for the difficultly reducible oxides. For hydrogen, saturated with water vapor, we find the proportion p_{H_2O}/p_{H_2} at 18°C. and 1 atmosphere to be 2×10^{-2}A. Therefore it is impossible to reduce ferrous oxide at 400° A. with moist hydrogen.

For thermodynamic reasons it is impossible that in the state of equilibrium an oxide be only partly reduced to metal at a given

TABLE 1

Heat of formation, B, heat of reaction, Q, and p_{H_2O}/p_{H_2} in the state of equilibrium

| OXIDE OF METAL	B	Q	p_{H_2O} FOR $p_{H_2} = 1$	
			$T = 400°$A.	$T = 800°$A.
	Calories	*Calories*		
Ag₂O..........................	+6.5	+51.4	1×10^{30}	1×10^{16}
CuO..........................	+37.8	+20.1	1×10^{13}	3.2×10^7
PbO..........................	+52.7	+5.2	6.9×10^4	2.6×10^3
NiO..........................	+54.7	+3.2	5.6×10^3	7.5×10^2
CoO..........................	+57.5	+0.4	1.7×10^2	1.3×10^2
FeO..........................	+65.0	−7.1	1.3×10^{-2}	1.2
ZnO..........................	+83.0	−25.1	1.9×10^{-12}	1.4×10^{-5}
MnO..........................	+90.8	−32.9	1×10^{-16}	1×10^{-7}
CaO..........................	+145.0	−87.1	2.5×10^{-46}	1.6×10^{-22}

temperature; above the equilibrium pressure we have only oxide, below it only metal, provided there are two solid phases and not a solution. But in many cases the normal progress of the reduction is hindered by sintering, which may be considerable, as I have shown in the case of finely divided nickel (20). Thereby inertness is produced and a part of the oxide is not reduced. In some cases the reduction of nickel oxide, NiO, or ferrous oxide, FeO, leads to final states which are still rather far from the quantitative reduction to metal, as Taylor and Starkweather have shown (21).

Sieverts (27) has found that the solubility of gases is often greater in an oxide of a metal than in the metal itself. Hence the

presence of an oxide promotes sorption and therefore the catalytic activity, as Willstätter has shown (22).

But in what manner can we produce finely divided elements, the oxides of which are hard to reduce? This must be known in order to solve the question as to what elements have hydrogenating properties, since hydrogenation is caused not only by the presence of a suitable metal, but also by its finely divided state, i.e., its great exterior or interior surface.

The figures of table 1 are valid for the state of equilibrium. But the reaction

$$MeO + H_2 = Me + H_2O$$
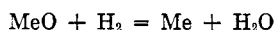
can also be employed when the equilibrium is unfavorable. We must then quantitatively remove the water formed by reduction. But the speed of this reaction is generally very small. It is only at high temperatures (1000–2000°C.) and pressures that the difficultly reducible oxides such as Cr_2O_3, V_2O_3, Nb_2O_5, can be reduced, as v. Wartenberg, Broy, and Reinicke have shown (23).

But such methods cannot be used because they give crystallized metals of small surface which are unable to catalyze the hydrogenation. However, the reduction of an oxide which is accompanied by absorption of heat can be effected at lower temperature, provided we bring this oxide together with another one that is easier to reduce and provided that the metal of the second oxide gives an alloy or a mixed crystal with the metal of the first. In this case the absorption of heat is lowered by the heat of formation of the alloy or of the mixed crystal, and therefore the partial pressure of steam in the equilibrium rises.

Thus zinc oxide is much more easily reduced by hydrogen in the presence of cupric oxide than when alone. The reason is that the heat of formation of an alloy of zinc and copper is positive and especially large if the content of copper is large, as Baker has shown (24). v. Wartenberg and his coworkers have found (23) that even oxides which are very hard to reduce, such as the oxides of yttrium, zirconium, and thorium, are reducible in the presence of metals with which they can alloy. In practice we often use mixtures of easily and difficultly reducible oxides of

metals.   The latter are known as promotors or activators, e.g., the oxides of chromium, molybdenum, tungsten, and vanadium.

It has not been known whether these elements in a state of large surface have catalytic properties for hydrogenation, because we did not know methods for producing them.   However, in some cases we can get these finely divided metals by heating the amalgams at moderate temperatures in a high vacuum for a long time (25).   Thus we can get chromium in a finely divided state. It is a hydrogenating catalyst of high activity.   The amalgam of manganese also gave a strongly active metal.

The elements of the first and second group, i.e., the metals of the alkalies and alkaline earths, can be prepared in an active state if the metals are sublimed in high vacuum, then diluted in dry, liquid ammonia and precipitated on quartz beads by evaporating the ammonia (25).   Pease and Stewart have applied a similar, though not so effective, method (26).

WHAT ELEMENTS HAVE HYDROGENATING PROPERTIES IN A STATE OF LARGE SURFACE AREA?

We shall investigate the hydrogenating properties of metals in a state of large surface area by using them as catalysts in the hydrogenation of ethylene.   We test only the simple elements without any additions, because it is otherwise impossible to determine which component of a mixture is really effective and which is the activator.   We use only mild conditions of reaction: $t = 0$ to 200°C., $P = 1$ atmosphere.

A large number of papers has been published on the hydrogenation of ethylene at moderate temperature and pressure.   The results are given in table 2.

Ethylene is very easily reduced by hydrogen; an active nickel catalyst hydrogenates ethylene at −100°C. with great velocity (25).   So this reaction is useful in revealing even a slight activity.   Column 2 of table 2 gives a rough evaluation of the activity of the element in question; this evaluation is only a rough approximation, and serious objections might be raised against it because it is often impossible to get two different elements into comparable states for hydrogenation.

Yet though it is often impossible to establish fine distinctions, we find in many cases differences large enough to justify the above rough evaluation. Of course, it is necessary to make sure in every case that no contact poisons or sintering effects have inadvertently lowered the activity and that no undoubtedly active elements have increased it. In most cases the evaluation of the activity

TABLE 2

The activity of finely divided metals in the hydrogenation of ethylene

0 = inactive; 1 = slightly, 2 = moderately, 3 = strongly active

METAL	ACTIVITY	REFER-ENCE	METAL	ACTIVITY	REFER-ENCE
Group 1			**Group 4**		
Na................	0	(28)	Pb...............	0	(36)
K.................	0	(28)	**Group 5**		
Rb................	1	(25)			
Cs................	2	(29)	As................	0	(37)
Cu................	3	(30)	Bi................	0	(38)
Ag................	0	(31)	**Group 6**		
Au................	0	(32)			
Group 2			Cr................	3	(25)
			Group 7		
Ca................	2	(33)	Mn...............	3	(25)
Sr................	2	(25)	Re...............	2	(39, 25)
Ba................	2	(25)	**Group 8**		
Zn................	0	(34)			
Hg................	0	(35)	Fe................	2	(40)
Group 3			Co................	3	(41)
			Ni................	3	(42)
Ce................	0 (?)	(25)	Pd...............	3	(43)
Tl................	0	(25)	Pt................	3	(44)

was based not only on the measurements of other authors, but also on my own.

The situation concerning zinc is not clear. Zinc has a high affinity for oxygen; when finely divided it goes rapidly over into zinc oxide in the presence of oxygen. Zinc oxide is not reducible with hydrogen under mild conditions, as we have seen. Maxsted

(34) has found that zinc is a contact poison for platinum and palladium.

On the other hand, Mittasch (34) has found that a contact mass made by reducing a mixture of zinc oxide, chromic oxide, and uranium trioxide is an excellent catalyst for hydrogenating ethylene. In a previous paper (34) I have reported that finely divided zinc, made by a reaction between zinc chloride and magnesium in alcoholic solution, hydrogenates ethylene. In a more recent investigation (25) I was unable to repeat this result when using a well-cleaned zinc chloride. Other methods also did not give an active zinc, so that I now believe that pure, finely divided zinc is not able to hydrogenate ethylene under mild conditions.

If we locate the active elements in the curve of atomic volumes, given in figure 1, we find them in two opposite places. (1) At the maxima of the curves of the long periods, the alkali elements with large atomic volumes and the alkaline earths. In this series the activity increases with increase of atomic volume. However, the activity of these elements is low or moderate. (2) At the minima of the curves of the long periods, the elements of the eighth group and copper, chromium, and rhenium. The activity of these elements is high and generally increases with decrease of atomic volume. The atomic volume decreases in the series iron, cobalt, nickel, while the activity increases (1).

The atomic volume, V, is determined by the relation $V = A/D$, where A is the atomic weight and D the density. The dimensions of the space required by a single atom are given by the expression $f = \sqrt[3]{V/N}$ where N is Avogadro's number. In many cases f corresponds approximately to the distance between the atoms of the crystallized element (47).

If we assume that the atoms are spherical, we have, according to Meg Nad Saha (60), the simple relation:

$$I_1/I_2 = r_2/r_1 \qquad (11)$$

where I_1 and I_2 are the ionization potentials of the elements E_1 and E_2 and r_1 and r_2 are their radii.

This relation is exact only if the elements compared have a similar electron structure. But for our rough calculation it is
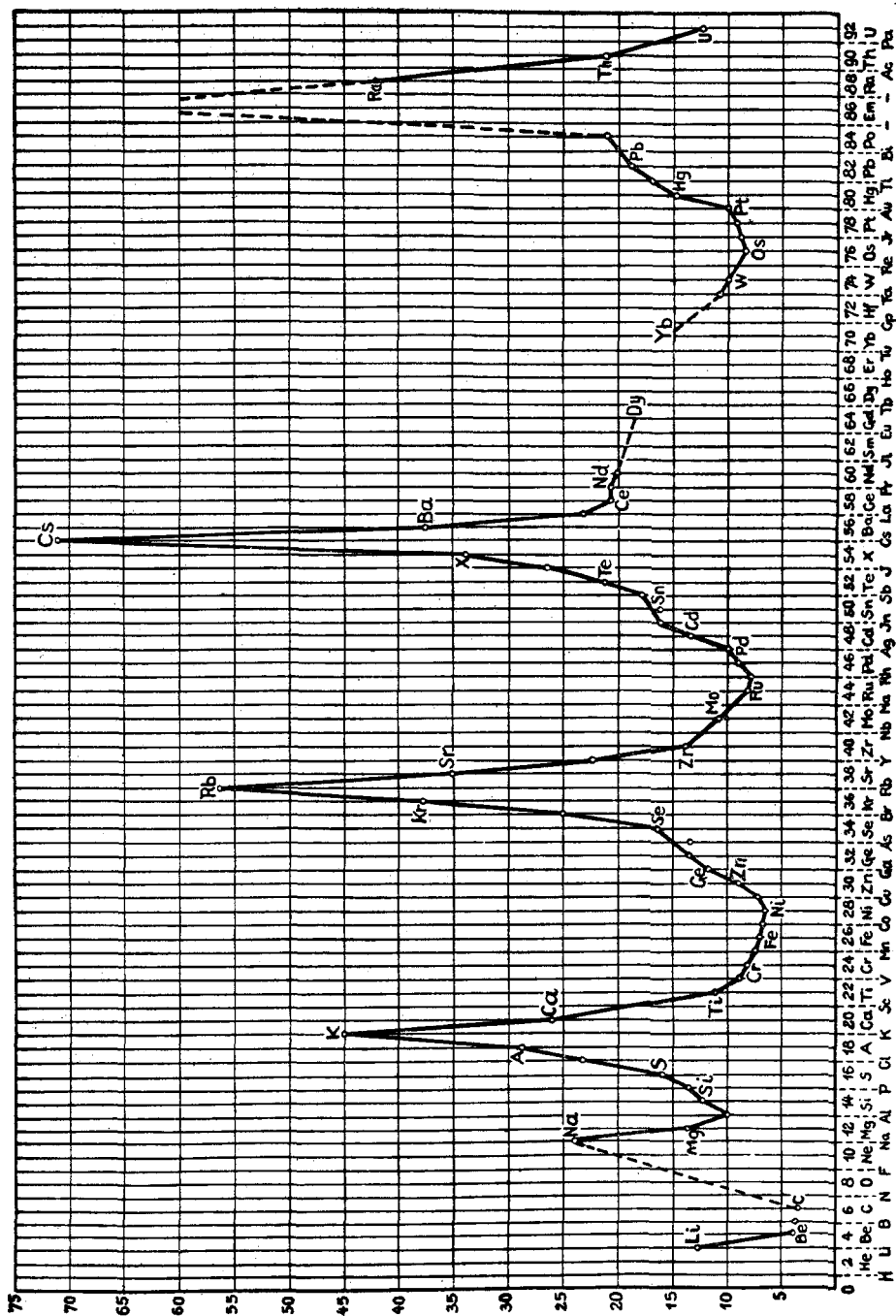
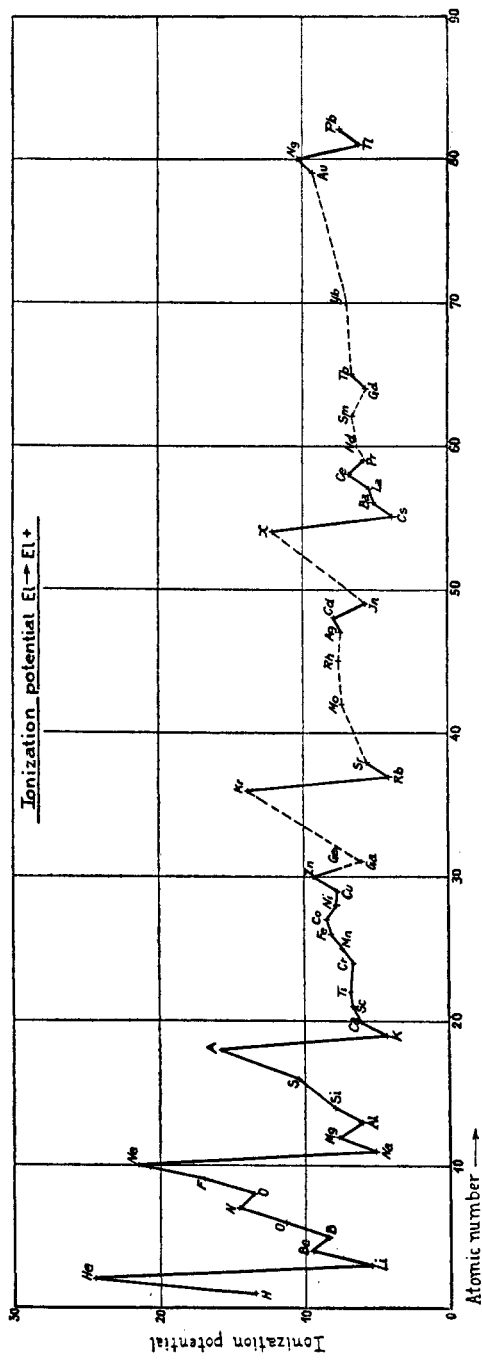Fig. 1. Relation of Atomic Volume to Atomic Number

FIG. 2. RELATION OF IONIZATION POTENTIAL TO ATOMIC NUMBER

permissible to assume that large atomic volume means a large atomic radius and therefore, according to equation 11, also a low ionization potential.   The relation between r and f is not exactly $1:2$, but we may assume it as a first approximation.   Then the ionization potentials of the elements of the first class would be much smaller than those of the second.   This, indeed, is the case, as shown in figure 2.

Generally the work function ϕ, i.e. the work needed to remove an electron from a metallic surface, is smaller than the ionization potential I.   There is a similar difference between the work functions of the elements of the first and second class; the work function is small in the first class and large in the second.

The values for I and ϕ in equivalent volts ($\phi = eV$) for the two groups of metals are:

	Na	K	Rb	Cs	Ca	Ba	Fe	Co	Ni	Cu	Pt
I	5.1	4.3	4.2	3.9	6.1	5.2	8.1	7.8	7.6	7.7	8.9
ϕ	1.8	1.6	1.5	1.4	2.2	1.9	4.0	4.3	4.4	4.0	5.5

The work function, ϕ, of the elements of the first class is lowered in mixtures of metals and oxides, as is the case in the oxide cathode tubes (47) which contain mixtures of elements and oxides of the first class.   The work function for the Siemens tube O. C. No. 4 is 0.83 volt and for B. O. No. 585 is 0.64 volt, as Rothe found (48).   These energies are of the order of heats of adsorption, and thus can easily be attained.

While the work function in these elements is small so that electrons are easily emitted from their surfaces, the situation on the surface of a metal of the second class is quite different, for the work function is large.   If we bring a volatile metal of the first class, such as rubidium, on to the heated surface of a metal of the second class, then the rubidium atom loses its electron and leaves the surface as a positive ion.   Therefore heating an element of the first class produces electron emission at low temperature; heating a metal of the second class produces at low temperature (400–500°C.) emission of positive ions of the alkalies, which are always present in commercial metal.

In the interior of a metal we have free electrons, according to

the electron theory of metals; the number of these electrons corresponds to the number of valency electrons, as Houston (50) has found.

Because the alkali metals are univalent, the charge on their ions is only 1; their radius is large and therefore the force of the electric field, F, is weak.

Table 3 gives the values of the ionic radii, using the figures of Goldschmidt, (G), (51) and Pauling, (P), (52).   Because $F = Q/r^2$, the field in the immediate vicinity of Ba^{++} would be 3.6 times weaker than in that of Ni^{++}, if we can consider the ion as a charged sphere, the charge of which is concentrated at the center. But we can do so only when the number of exterior electrons is

TABLE 3
Values of the ionic radii

	Li^+	Na^+	K^+	Rb^+	Cs^+	
(G)...............	0.78	0.98	1.33	1.49	1.65	
(P)...............	0.60	0.95	1.33	1.48	1.69	
	Mg^{++}	Ca^{++}	Sr^{++}	Ba^{++}		
(G)...............		0.78	1.06	1.27	1.43	
(P)...............		0.65	0.99	1.13	1.35	
	Fe^{++}	Co^{++}	Ni^{++}	Cu^{++}	Zn^{++}	
(G)...............		0.83	0.82	0.78	0.83 (extra-polated)	0.83

large, as in the case of Ni^{++}, where there are 16.   For Ba^{++} there are only 8 and therefore the field of Ba^{++} in its immediate vicinity is still weaker, because the potential of repulsion is equal to b/r^n and n is a function of the number of exterior electrons (58). Barium belongs to the first, nickel to the second class; the stronger electric fields are always in the second class.

There is still another important difference between the two classes.   All elements belonging to Class 2 are "gap elements" in the sense of Thomson and Bohr, as shown in figure 3.   In this figure the "gap elements" are enclosed in brackets.   They are those in which the last interior electron shell is not yet filled, though there are already electrons in the exterior shell.

A characteristic property of the salts of these "gap elements" is the formation of colored solutions in water. As Fajans has shown (45), the color of the aqueous solution is produced by the deformation of water molecules by the ions of these metals. Copper, which is not enclosed by brackets in figure 3, also belongs
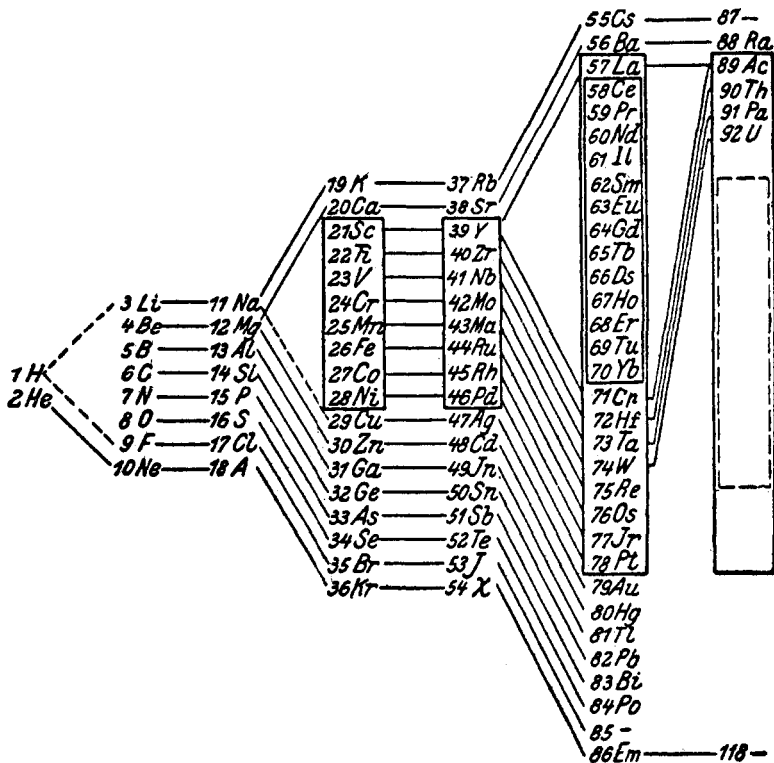

FIG. 3. PERIODIC SYSTEM OF THE ELEMENTS BASED ON ATOMIC STRUCTURE
(J. J. Thomson, N. Bohr)

to this class of elements. It gives colored solutions in the divalent state, though solutions of univalent copper are colorless. In the spectrum of atomic copper part of the lines correspond to an alkali type with a complete M shell and only one valence electron. The arrangement of electrons is:

| 2 | 2 | 6 | 2 | 6 | 10 | 1 |

The other lines belong to an atomic type which is produced by the passing of a $3d$ electron out of the M shell to $4s$, with this arrangement of electrons resulting:

$$2 \mid 2 \quad 6 \mid 2 \quad 6 \quad 9 \mid 2$$
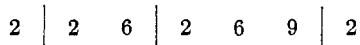
This type corresponds to the "gap elements."

Colored solutions are characteristic of multiply charged ions. In Class 2 we have only multivalent elements; the ions carry a charge of at least 2. They also have small ionic radii, shown in table 3. A small radius, together with multiple charges on the ion, produces a strong electric field and a strong polarization of the atoms and molecules. This gives the conditions necessary for the deformation and activation of participants in a reaction.

TABLE 4

Values of the heat of formation, Q, of the hydrides of the alkalies and alkaline earths

| HYDRIDE	Q/H_2	AUTHOR
LiH	43.2	Moers (51)
NaH	25.6	Hagen and Sieverts (52)
CaH$_2$	46.6	
SrH$_2$	42.2	Guntz and Benoit (53)
BaH$_2$	41.0	

Elements of Class 1, on the other hand, have weak electric fields. They presumably operate in hydrogenation by a mechanism quite different from that of Class 2.

We have still to discuss one last important difference between the two classes. In the first class hydrides are formed easily and are solids with the properties of real salts, as Moers has found (51). The heat of formation of several hydrides is known (see table 4).

In the second class, on the other hand, only copper hydride is known as a well-defined compound; but under *extreme conditions* a series of hydrides of the metals have been spectroscopically found and measured by Mecke (54). The heat of formation of cuprous hydride is negative; Sieverts found it to be -10.2 Cal. and showed that it is a derivative of univalent copper (55).

The existence of other hydrides of this class formed at room temperature seems to be doubtful. According to Schlenck and Weichselfelder, nickel hydrides, NiH_2 and NiH, may be formed by the reaction between nickel chloride, phenylmagnesium bromide, and hydrogen in ether (56). I was unable to verify the formation of these compounds. In any case, if they exist, all hydrides of the second class are very unstable. The probability of their formation from the elements under ordinary reaction conditions is very small.

For calculating the dissociation pressure of these hydrides by the Nernst theorem the equation of dissociation is written:

$$2CuH = 2Cu + H_2 + 10,240 \text{ cal.}$$
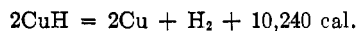
$$\log K_p = -\frac{Q}{4.571\ T} + 1.75\ \Sigma\nu \log T + \Sigma\nu C$$

where

$$\Sigma\,\nu = -1$$

and

$$\Sigma\nu C = -1.6;\ K_p = \frac{1}{p_{H_2}}$$

The resulting dissociation pressure at the absolute temperature, T, is:—

$T =$	300	373	473
$p_H =$	10^{13}	10^{12}	10^{11}

Therefore at equilibrium the cuprous hydride must be completely dissociated into hydrogen and copper at the above temperatures and at the pressure of 1 atmosphere. At high temperatures the formation of cuprous hydride, CuH, is possible, but at low temperatures it is very improbable.

The nature of the hydrides of the second class can be determined by measuring the exponents of the potentials between the metal and the hydrogen atoms   In the molecule, MeH, forces of attraction and repulsion are effective; their dependence on the

distance, r, between the two nuclei is a very different function of r in the two cases.   The potential, P, is the sum of the potential P_p of the attractive forces and the potential P_q of the repulsive forces.   Assuming that the forces are purely radial, we have

$$P = P_p + P_q = -e^2 \frac{C_p}{r^p} + e^2 \frac{C_q}{r^q}$$

where e is the charge of the electron, C_p and C_q constants, p the exponent of attraction, and q that of repulsion.   If we have attraction according to Coulomb's law, then p is equal to 1.   This is the case if we have a heteropolar binding of ions with complete shells of electrons. q is a number greater than 1.

The evaluation of spectroscopic data of the hydrides, MgH, CuH, AuH, gives the figures $p = 1$, $q = 3$ to 4.   Thus quasipolar binding must be assumed (Mecke).   The halogen hydrides give the same values.   The halogen hydrides in the gaseous state are not purely heteropolar compounds.   We must suppose that the proton has largely deformed the halogen ion and has entered into it.   The molecule of the halogen hydride in the gaseous state is thus an intermediate stage between a heteropolar and a homopolar compound; we call it quasipolar and express by this term that it is nearly polar.

In most cases hydrogen is sorbed by the metals of the second class with formation of a solid solution, as Hoitsema has proved for the system PdH_x (57).

Now we can characterize the two classes of catalysts.   (1) To the first class belong uni- and multi-valent elements, including the alkalies and the alkaline earths, which form stable, solid, salt-like hydrides, and which lie at the maxima of the atomic volume curve.   Their atomic radius is large, their ionization potential low, their work function small.   Among the alkali metals the catalytic activity increases with increase of atomic radius and varies from 0 to 2.   (2) To the second class belong the divalent elements of the iron and platinum groups and other members of these groups which (like iron) have a minimum valence of 2, or (like copper) a maximum of 2.   They do not give stable, solid hydrides but form solid solutions of hydrogen, such

that the content of hydrogen for a given piece of metal depends on the pressure and the temperature, and such that there is a reversible equilibrium of adsorption or solution under definite conditions of volume and surface of the metal, temperature, and pressure. These elements lie at the minima of the long periods of the atomic volume curve. Their atomic radius is small, their ionization potential high, their work function large. All elements lying at the minima of the long periods—and therefore the elements of Class 2—are "gap elements" in which the last interior shell of electrons is incomplete. In the iron group the activity increases with decreasing atomic radius, and is always large, with a value of about 3.

THE RELATION OF THE TWO CLASSES OF ACTIVE ELEMENTS TO THE PERIODIC SYSTEM

The two classes of active elements are on opposite sides of the atomic volume curve, the first at the maxima, the second at the minima of the long periods. There remain two minima in the short periods, including the elements beryllium, boron, carbon, magnesium, aluminum, and silicon. These have no catalytic properties under ordinary conditions. They are not "gap elements" and therefore are not included in the definition of the second class. It seems probable that the activity of the "gap elements" is due to the presence of unshared electrons in the incompleted inner shell.

Furthermore, the elements at the minima of the short periods have a valency of more than 2 and do not form solid hydrides. Their hydrides are gaseous, as are those of tin, lead, phosphorus, arsenic, and antimony. All these elements have no catalytic properties, whether their atomic volume be large or small. The reason for their inactivity is thus not only the lack of unshared electrons but also the inertness of their hydrides. Nearly all solid elements which give gaseous hydrides have a valence of 3 or 4.

Since there is a continuous transition from the heteropolar to the homopolar state in the halogen hydrides, for instance, we may consider the metal hydrides as a first approximation to be hetero-

polar.   We may assume that the ions are rigid spheres.   Then in a molecule, MeX_n, the central ion will be more protected the more enveloping ions there are, and the larger is the ratio of the radius of the enveloping ion to the radius of the central ion.   For methane we find $r_{H^-} = 2.08$ (Goldschmidt) and $r_{C^{4+}} = 0.2$, whence the value of the ratio is 10.   Therefore we must assume that the field of the central ion is largely protected by the four negative ions, and that this central ion can no longer exert a noticeable attraction on the negative ions or electrons of a neighboring molecule.   The attraction is weak and can be broken by heat vibration.   Such compounds therefore will have a low boiling point and show the inert behavior of methane.

To this class of hydrides belong the volatile stannic hydride, SnH_4, and lead hydride, PbH_4.   Once they are formed they cover and then poison the catalyst by their inertia.   The enveloping of the central ion is of course most complete with the hydrides of the type MeH_4.   Here the ions are arranged around the central ion in the form of a tetrahedron; owing to the symmetrical structure the dipole moment is equal to zero.

With compounds of the type MeH_3 the H^- ions are distributed at the corners of a triangle.   In this case a complete envelopment is scarcely possible, and we therefore find higher boiling points than with the MeH_4 hydrides.   The dipole moment is no longer equal to zero (see table 5).

A high energy of dissociation accompanies the symmetrical configuration of the inactive hydrides of the type MeH_4.   The work needed to remove an atom of hydrogen from the molecule of methane is about 90(115) Cal., as Mecke (p. 393) has shown, which is about as great as the work needed to dissociate the hydrogen molecule.   Therefore carbon has no catalytic properties at moderate temperatures.

We have seen that there are three groups of elements which react with hydrogen in a different manner:—the first group gives solid hydrides, the second gives solid solutions or adsorption, the third gives gaseous hydrides.   If we add as a fourth group those elements which do not react with hydrogen, then we can arrange all elements according to their behavior with hydrogen.   If we

TABLE 5

Boiling points and dipole moments of volatile hydrides

HYDRIDE	BOILING POINT	DIPOLE MOMENT
	degrees C.	
CH_4	−161	0
SiH_4	−112	0
GeH_4	−90	0
SnH_4	−52	0
NH_3	−33	1.5
PH_3	−86	0.55
AsH_3	−55	0.15
SbH_3	−17	0.1

TABLE 6

Periodic system of the elements in Staigmüller's arrangement

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Number of period	1	Li	Be	B											C	N	O	F	He
	2	Na	Mg	Al											Si	P	S	Cl	Ne
	3	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ca	Ce	As	Se	Br	Ar
	4	Rb	Sr	Y	Zr	Nb	Mo	−	Ru	Rh	Pd	Ag	Cd	Jn	Sn	Sb	Te	J	Kr
	5	Cs	Ba	Seltene Erden	Ta	W	−	Os	Jr	Pt	Au	Hg	Tl		Pb	Bi	Po	−	X
	6	−	Ra	Ac	Th	Pa	U												Em

Class 1   Class 2   Class 3   Class 4

TABLE 7

Energy of formation of hydrides

| METAL	GRAM ATOMS Me ON ONE MOLECULE OF HYDROGEN	ENERGY OF FORMATION PER MOLE OF HYDROGEN
		calories
Li	2	43,200
Na	2	25,600
Ca	1	46,600
Sr	1	42,200
Ba	1	40,960
Ce	0.75	42,260
Pr	0.74	39,520
La	0.75	40,090

use the periodic system in the form given by Staigmüller (59), then these groups fall into definite positions, as Paneth has already shown (60), and as is evident from table 6.

The two classes of active elements correspond to Staigmüller's Groups 1 and 2. The first class and the first group are almost identical except for the elements of low atomic weight. They contain the elements which give salt-like hydrides of the type of lithium hydride, LiH; but, as Sieverts has found (61), there are also salt-like hydrides in the family of rare earths. The energy of formation per mole of hydrogen is almost the same for the hydrides of the alkaline earths as for those of the rare earths, as shown in table 7. On the basis of the energy of formation of the hydrides and their stability, the elements cerium, praseodymium, and lanthanum, which are in Staigmüller's second group, belong to his first. The atomic volume curve shows that the atomic volumes of these elements are much smaller than those of the alkalies and alkaline earths. The work function is larger and amounts to 3.0–3.3 volts in the series cerium to lanthanum. In accord with the point of view here developed, I was unable to effect hydrogenation of ethylene with cerium as catalyst at a temperature of 200°C.[3] The activity of the rare earth elements, if existent, is therefore small.

The fundamental difference between the two classes of active elements is given by the value of their atomic volume and their structure (i.e., as gap elements). The atomic volume is roughly proportional to the atomic radius and is inversely proportional to the ionization potential and to the work function.

MECHANISM OF REACTION IN CLASS 1.—AFFINITY OF THE
HYDROGEN ATOM FOR THE ELECTRON

The work, D_{H_2}, needed to dissociate H_2 into $2H$, amounts to 100 Calories and is so large that it cannot be supplied under ordinary conditions in the gas phase.

$$H_2 \rightarrow 2H - Q; Q = 100 \text{ Cal.}$$

_____
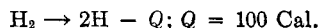
[3] British patent 325,695, however, states that cerium is a hydrogenation catalyst at 300°C.

If there are free electrons, Q is reduced by the affinity of the hydrogen atom for electrons, E_H, provided that it is positive:

$$H_2 + 2\bar{e} \rightarrow 2H^- - Q'; Q - 2E_H$$
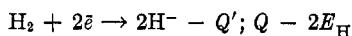
Until recently the value of E_H was in doubt. Joos and Hüttig (64) made the first calculation and gave a value of $+$ 23 Cal. But Kasarnowsky and Proskurnin (65) were able to show that this calculation was in error, because it made use of an incorrect value for the density of sodium hydride. They found $E_H = -$ 1 Cal. But this figure also was of dubious value because it was based on very doubtful figures for the heat of sublimation of the alkali metals. At last Hylleraas (66) has calculated this value by the use of wave mechanics and has found $E_H = +16.3$ Cal. This value was confirmed by Bethe (67) and is very well founded theoretically. We shall use it in the following. If we set $E_H = 16.3$ Cal., we have

$$H_2 + 2\bar{e} = 2H^- - 67.4 \text{ Cal.} \tag{13}$$

in the gas phase.

Reaction 13 will start more easily if H_2 is deformed by an electric field. In this case the polarized molecule H_2^* is involved and the energy needed according to equation 13 is lowered.

It is very probable that the electron takes part in the activation of hydrogen in Class 1, for we have seen that only those elements of this class are active whose work function is small enough to be available under mild conditions. The heat of formation of the alkali hydrides is about 10 Cal., excepting for lithium hydride, for which it is 21.6 Cal. (68). The dissociation according to the equation:

$$MeH = Me + 1/2\ H_2 - Q''$$

must take place easily because Q'' is small. But this reaction does not give atomic hydrogen; the work required for producing 2H in the gas phase in this way is still $2Q''$ in excess of 100 Cal.

But in the solid phase the situation is different. The hydrides of the alkalies crystallize in the type of sodium chloride, though it is possible that cesium hydride crystallizes in the similar type of

cesium chloride. The hydrogen has the function of a negative ion. The affinity, E, of the hydrogen atom for the electron is, however, distinctly less than that of halogen atoms:—

$$\begin{array}{ccccc} \text{H} & \text{F} & \text{Cl} & \text{Br} & \text{I} \\ E = 0.71 & 4.0 & 3.8 & 3.0 & 3.1 \text{ volts} \end{array}$$

Therefore the attraction of the second electron of H^- is small. H^-, according to Goldschmidt, has a radius, r_i, as large as that of the iodide ion.

$$\begin{array}{ccccc} \text{H}^- & \text{F}^- & \text{Cl}^- & \text{Br}^- & \text{I}^- \\ r_i = 2.08 & 1.36 & 1.81 & 1.95 & 2.16 \end{array}$$

The structure of H^- is therefore very loose.

Fajans has shown that in the series

$$\begin{array}{cccc} \text{CuF}_2 & \text{CuCl}_2 & \text{CuBr}_2 & \text{CuI}_2 \\ \text{colorless} & \text{yellow-brown} & \text{brown-black} & \text{unstable} \end{array}$$

the color becomes gradually more dark; he explains this by the increasing deformation of the electron envelopes, caused by the strong field of the doubly charged small ion of copper. The increase of coloring is the consequence of the tendency of the ions to become deformed, which increases from F^- to I^- and can be measured by refractometric data. At the end of the series is cupric iodide, which is unstable. Here the deformation of I^- has become so great that the electron is split off and neutral atoms, and hence molecules, are formed:[4]

$$2Cu^{++} + 4I^- \rightarrow 2CuI + 2I \rightarrow 2CuI + I_2 \tag{14}$$
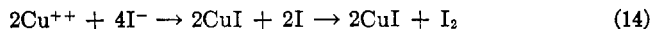
Because the affinity of H for the electron is much less than that of I, and the volumes of the two ions are nearly the same, we should expect a hydride to be still less stable than an iodide, provided the electric field of the cation is the same. From this point of view it is very interesting that cuprous hydride, CuH, is a derivative of monovalent copper, as Sieverts has shown (55), and that cupric hydride, CuH_2, does not exist. In the latter the electric field of the copper ion is much stronger.

[4] The radius of Cu^+ is much greater than that of Cu^{++} (i.e., 1.27 and 0.83 Å respectively).

It therefore seems very improbable that a hydride of nickel, NiH_2, can exist, as Schlenck and Weichselfelder suppose (56). In the strong field of Ni^{++}, H^- cannot exist and must be converted immediately into H or H_2. Indeed I could find no indication of the existence of a nickel hydride in repeating the above experiments.

The dissociation

$$MeH_2 \rightarrow MeH + H \rightarrow Me + 2H$$

which we must assume in analogy with equation 14, will occur in every case to a greater or less extent,—the more easily when the energy needed is small. The energy is especially small in a medium of high dielectric constant.

Hüttig and Krajewski conclude from measurements of the dissociation pressure of lithium hydride that a part of the hydrogen ions are free and mobile in the lattice structure. They use the expression "vagabond hydrogen" (69). We have in the interior of the hydride crystal an equilibrium

$$H^- \rightleftarrows H + \bar{e}$$
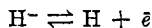
since the work needed to dissociate is small even in the gas phase and is still smaller in a medium the dielectric constant of which is much greater than 1. H travels much more easily than H^-, because its radius is 0.5 Å, only a fourth of that of H^- (2.08 Å, according to Goldschmidt).

In the series of alkali metals only rubidium and cesium proved to be active. In the alkaline earth series all the elements are active, i.e., calcium, strontium, and barium.

It is very probable that hydrides are intermediate products in the action of metals of the first class as catalysts for hydrogenating ethylene. The dissociation pressures of these hydrides are considerably under 100 mm. at temperatures under 350°C., as Ephraim and Michel have established (77). Therefore they are stable at a pressure of 1 atmosphere and a temperature of 150–250°C.

Hill and Kistiakowsky have found that cesium hydrogenates ethylene at room temperature, but that this reaction is hindered

after a short time by formation of cesium hydride, CsH (29). Cesium hydride is very stable at room temperature and reacts only slowly with ethylene, though more quickly at higher temperature. I have found that cesium reacts rather quickly with a mixture of ethylene and hydrogen at 200°C. and gives ethane. At this temperature this hydrogenation can be carried on with sufficient velocity for a long time. The stability of cesium hydride at room temperature seems to me not incompatible with the supposition that it delivers the active hydrogen to the hydrogenation at 200°C.

Therefore we may expect that formation of hydrides takes place at the surface, but that the formation of active hydrogen occurs at any distance beneath the visible surface in the interior of the crystal, where the active points of the catalyst are located. We presume that the active form of hydrogen for hydrogenation with the first class of catalysts is the *hydrogen atom*.

We therefore formulate the hydrogenation of ethylene in this class as follows:—

$$C_2H_4 + 2H = C_2H_6$$

THE MECHANISM OF THE REACTION FOR ELEMENTS IN CLASS 2

In the first class of active elements we have formulated the process of activation with regard to the ease of formation of free electrons at the surface:

$$H_2 + 2\bar{e} = 2H^-$$

$$2H^- + 2Me^+ = 2MeH$$
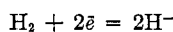
and have seen that the hydrides dissociate in the interior of the lattice to give H^- and H.

In the second class a similar reaction is impossible since the work function is large and the concentration of electrons at the surface must be extremely small or equal to zero. The probability of the formation of hydrides is also very small.

In the interior of a metal the valence electrons are free and mobile; hence the atoms themselves must be present as ions. The ions of the second class carry strong electric fields in their vicinity.

We may expect the following reactions:

$$H_2 \rightarrow H_2^*$$

$$H_2^* \rightarrow H_2^+ + \bar{e}$$
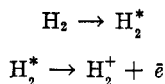
Here H_2^* means a deformed hydrogen molecule. H_2^+ is unstable. With an energy of 2.5 volts, it dissociates according to the equation
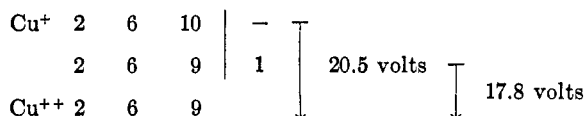
$$H_2^+ \rightarrow H^+ + H$$

The whole process

$$H_2 \rightarrow H^+ + H + \bar{e} \tag{15}$$
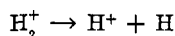
requires 17.88 volts, as Birge has shown (69).

It is very remarkable that this amount of energy is nearly identical with the second potential of ionization in this class, as is shown in table 8 (70).
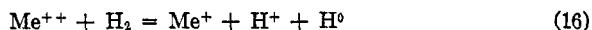
TABLE 8

Ionization potentials of the elements of the second class

	FIRST POTENTIAL	SECOND POTENTIAL
Cr...	6.74	16.6
Fe...	8.06	16.5
Co...	7.81	
Ni...	7.64	18.2
Cu...	7.69	17.8 (20.5)
Pd...	8.1	19.8 (?)

For copper two second potentials of ionization are known (71). They correspond to the transitions:

$$
\begin{array}{llll}
Cu^+ \ 2 & 6 & 10 \\
\ \ \ \ \ \ \ 2 & 6 & 9 & 1 \\
Cu^{++} \ 2 & 6 & 9
\end{array}
$$

20.5 volts   17.8 volts

The process

$$Me^{++} + H_2 = Me^+ + H^+ + H^0 \tag{16}$$

in the above cases therefore requires no energy or only a small amount. Kallmann and Rosen have shown that in the gaseous phase a reaction of exchange between charged and uncharged cor-

puscles takes place when the ionization potentials of both are nearly equal (78). We are inclined to suppose that the equality of the ionization potentials of H_2 according to equation 15 and of $Me^+ \rightarrow Me^{++}$ in this class is not merely accidental.

THE PRESENCE OF POSITIVE IONS IN THE INTERIOR OF THE METALS OF THE SECOND CLASS

There is no doubt that there are positive ions of hydrogen in the solution of hydrogen in some metals, especially in metals of Class 2. Thus Janitzky concluded, from his measurements of the resistance of wires charged with gas, that the gases dissolved in the metal are dissociated into positive ions and electrons and participate in the conduction of current (72). Similar observations were made by Smith who employed hydrogen (73). But Coehn and Specht and Coehn and Jürgens were the first to furnish incontestable experimental proof that hydrogen dissolved in palladium travels with the positive current and must be present, at least in part, in the form of positive ions (74, 75). Coehn and his coworkers used wires of palladium or of an alloy of palladium and silver, which were electrolytically charged with hydrogen. The possibility thus remains that the protons taken up electrolytically were the cause of the traveling effect. I was able to show (25) that molecular hydrogen, dissolved by the wire at room temperature under pressure, shows the same phenomena as electrolytic hydrogen.

Positively charged hydrogen molecules, H_2^+, have a volume of the magnitude of molecular hydrogen and cannot travel in many lattices because the interstices are too small. They are dissociated at the expense of a small amount of energy,

$$H_2^+ \rightarrow H^+ + H_0$$
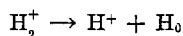
with the formation of protons and atomic hydrogen.

The stability of the solution of hydrogen in the metal at ordinary temperature is very remarkable. The dissolved hydrogen does not leave the metal, even though it sometimes travels in various directions with the current, and even though the wire may be in a medium free of hydrogen.

Similar observations could not be made with other metals. The phenomena with platinum, copper, iron, and nickel are different; if hydrogen comes into contact with these metals, either in molecular form under pressure or electrolytically in the form of ions, no noticeable change of resistance is found (25). It is evident from figure 4 that the amount of hydrogen dissolved in
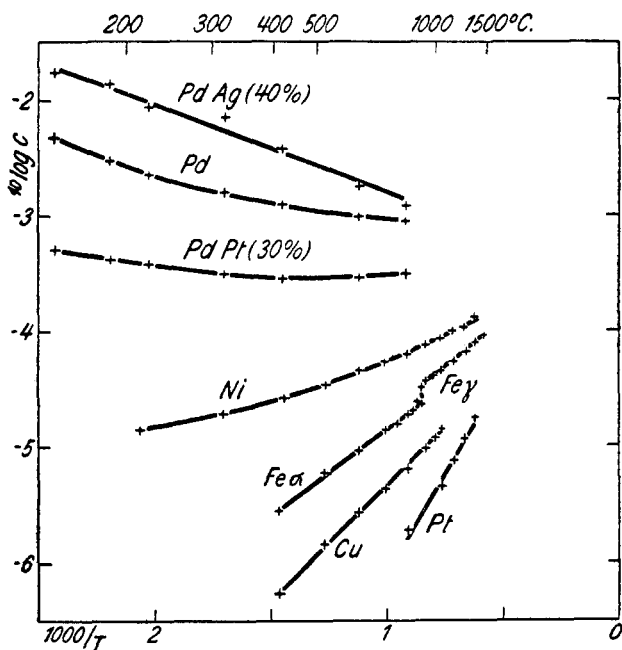

FIG. 4. RELATION OF SOLUTION PRESSURE OF HYDROGEN TO TEMPERATURE FOR VARIOUS METALS

these metals at moderate temperatures is very small in comparison with palladium–silver and palladium. (The figure is taken from Borelius who used the data of Sieverts (76).) Therefore the question whether positively charged hydrogen ions are present in these metals cannot be answered exactly by resistance measurements. However, there are other reasons to suppose that dissolved hydrogen forms ions in other metals also.

### THE EFFECT OF THERMIONS AND OTHER PHYSICAL PROPERTIES

It has long been known that the physical properties of metals, especially of those of Class 2, are considerably changed by taking up hydrogen.

Atoms of gases and vapors are ionized by the fields of atomic and image forces on heated surfaces and under certain conditions leave them in the form of ions. Catalytic processes, especially those of hydrogenation, ordinarily take place at higher temperatures because they are nearly always exothermal and thus lead to a rise of temperature at the surface. Hence conditions are often such as lead to the ionization of certain atoms. It is therefore important in elucidating the mechanism of hydrogenation to know the conditions at which the different atoms are ionized.

Kunsman deduced from his investigations the general rule that an element is evaporated at a surface in the form of an ion only when the work function of an electron, ϕ, is greater than the ionization potential, P, of the element, where ϕ and P represent work per mole (102).

The experiments of Langmuir and Kingdon (103) with tungsten wires in an atmosphere of cesium, conform to this rule. These investigators found that a tungsten wire which is heated to 1200°C. or higher in an atmosphere of cesium will convert *all* atoms of cesium which strike the wire into ions, which leave the surface as such.
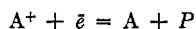
Now the ionization potential, P, of atomic cesium is 3.88 volts and is therefore, according to the above rule, smaller by 0.65 volt than the work function, ϕ, of the clean tungsten surface, which amounts to 4.53 volts. The rule therefore establishes that the reaction

$$\overline{Me^+} + A = \overline{Me} + A^+ + Q \tag{17}$$
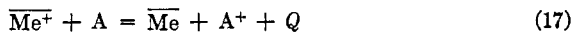
takes place from left to right only when Q has a positive value. $\overline{Me^+}$ here means a surface with affinity for electrons.

Eggert (104), Meg Nad Saha (105), and finally Langmuir and

Kingdon (106) have shown that the degree of thermal dissocia-
tion of a gas, which follows the equation:

$$A^+ + \bar{e} = A + P$$

can be calculated from the ionization potential, P, by using the
Nernst theorem.

The exact equation of the third principal heat theorem can
be written:—

$$\log K_p = -\frac{U}{4.571\ T} + \Sigma\, \nu\, 2.5 \log T + \Sigma\, \nu\, j \tag{18}$$

if only monoatomic gases take part in the reaction (107). Here
$U = P$, $P_{\text{cal.}} = V\ 23{,}028$, $\Sigma\nu = 1$, $\Sigma\nu j = -6.483$, because

$$j_e = -1.587 + 1.5 \log M_{\text{electron}}$$

As $K_p = K_c \cdot RT$, $R = 0.082$ liter atmosphere, we find

$$\log K_c = -\frac{P}{4.571\ T} + 3/2 \log T - 6.483 + 1.086 \tag{19}$$

If we convert from the number of gram molecules per liter to the
number of atoms per cubic centimeter, i.e., so that

$$K_n = \frac{n_e \cdot n_p}{n_a} \tag{20}$$

where n_e, n_p, n_a are the number of electrons, positive ions, and
atoms in a cubic centimeter, we find:

$$\frac{K_c \cdot 6.06 \cdot 10^{23}}{10^3} = K_n; \quad K_c = \frac{K_n}{6.06 \cdot 10^{20}}$$

$$\log K_n = -\frac{P}{4.571\ T} + 3/2 \log T + 15.385 \tag{21}$$

To determine the degree of thermal dissociation $n_p\, n_a$, we calcu-
late n_e by using Richardson's equation

$$I = AT^2\, e^{-\frac{b}{T}}$$

where $A = 60.2$ amperes per cm^2. degree^2, and $b = 52,600$ for tungsten. The density of electrons, n_e, in a volume with walls of the metal concerned is:

$$n_e = \left(\frac{2\pi m}{e^2 kT}\right)^{1/2} \times I = 4.034 \times 10^{13}\, \frac{I}{\sqrt{T}} \qquad (23)$$

This gives for tungsten at 1200°C., $n_e = 9.25$. Now the degree of ionization, $\frac{n_p}{n_a}$, may be calculated from equations 21 and 23.

Langmuir and Kingdon (106) found that for cesium on a surface of tungsten at 1200°K. and at a pressure of 0.001 bar, the value of the above fraction is 577:1; that is, 99.8 per cent of the cesium atoms which strike the surface are ionized. This is an experimental value. Under the same conditions the fraction for H^+/H would be 1.7×10^{-38}, and for H_2^+/H_2 would be similar. Therefore under these conditions no measurable emission of H_2^+ and H^+ can be obtained. Contrary observations by Hüttemann (108) are incorrect, as I was able to show (80).

The phenomena at the surface of platinum and tantalum are similar because the values of ϕ are in the neighborhood of that for tungsten.

From equations 20 and 21 we obtain:

$$\log \frac{n_p}{n_a} = -\frac{P}{4.571\ T} + 3/2 \log T + 15.385 - \log n_e \qquad (24)$$

From equations 24, 22, and 23 we have:

$$\log \frac{n_p}{n_a} = \frac{\phi - P}{4.571\ T} + 1.779 - \log A$$

Because the last two members of this equation are practically identical for $A = 60.2$ amperes per cm.^{2} degree,^{2} i.e., for the cleanest metal of the second class, we find:
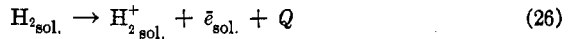
$$\frac{n_p}{n_a} = e^{\frac{\phi - P}{RT}} \qquad (25)$$

a result which Beeker has obtained by a quite different method (109). Thus for $\phi = P$, we get $n_p = n_a$. But if the ionization

potential surpasses the work function by 1 volt, the fraction $\frac{n_p}{n_a}$ amounts to 5×10^{-7} at $800°A.$, i.e., of 10^8 atoms there are only fifty ionized. Kunsman's rule is therefore theoretically justified, but it is not an exact expression of the phenomena.
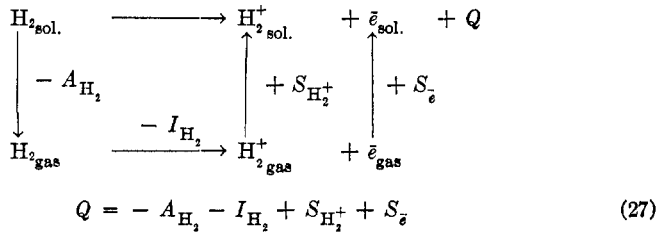
Equation 25 gives the composition of the gas phase beyond the sphere of the image forces.

From the experiments of Coehn and his coworkers the conclusion must be drawn that hydrogen, sorbed by palladium, travels with the positive current as positive ion. The energy of ionization needed for the reaction $H_2 \rightarrow H_2^+$ amounts to 15.4 volts or 354 Cal., and it is clear that this energy cannot be delivered by the simple sorption energy of H_2.

But it can be delivered by the heat of solution of the ions formed. If we consider the ionization process in the metallic solution

$$H_{2\,sol.} \rightarrow H_{2\,sol.}^+ + \bar{e}_{sol.} + Q \qquad (26)$$

then we find by Born's cycle process:

$$
\begin{array}{ccccc}
H_{2sol.} & \xrightarrow{\hspace{2cm}} & H_{2\,sol.}^+ & + \bar{e}_{sol.} & + Q \\
\downarrow{-A_{H_2}} & & \uparrow{+S_{H_2^+}} & \uparrow{+S_{\bar{e}}} & \\
H_{2gas} & \xrightarrow{-I_{H_2}} & H_{2\,gas}^+ & + \bar{e}_{gas} &
\end{array}
$$

$$Q = -A_{H_2} - I_{H_2} + S_{H_2^+} + S_{\bar{e}} \qquad (27)$$

where A_{H_2} is the pure heat of sorption of H_2; I_{H_2} is the ionization potential of H_2, $S_{H_2^+}$ and $S_{\bar{e}}$ the heat of solution of H_2^+ and of $\bar{e}$. $S_{\bar{e}}$ is numerically identical with the work function, ϕ.

We set

$$Q + A_{H_2} = Q' \qquad (28)$$

where Q' is the total amount of heat produced by the process of solution of hydrogen in the metal. Then

$$Q' = S_{H_2^+} + S_{\bar{e}} - I_{H_2} \qquad (28a)$$

As has been mentioned, Born has given a very simple method for calculating the heat of solvation, S, of an ion. He finds (8)

$$S = 1/2 \left(1 - \frac{1}{\epsilon}\right) N \times 2.388 \times 10^{-11} \frac{e^2 z^2}{r_i} \text{ Cal.} \tag{29}$$

where ϵ is the dielectric constant, N Avogadro's number, and r_i the radius of the ion. Because ϵ of those metals has a high value, we can neglect $\frac{1}{\epsilon}$. If we take, for instance, platinum, then $S_{\bar{e}}$ is 5.5 volts, I_{H_2} is 15.4 volts and Q' was found to be 1.3 volts. That gives $I_{H_2^+} = 11.2$ volts. If we set r_i^2 0.5 Å., we get $I_{H_2} = 14.3$ volts, which is too high.

But equation 29 is no longer valid at such small distances, as Webb has shown (9). The dielectric constant is really not a constant, but is a function of field force and temperature. It diminishes with decreasing ionic radius. Also the compression of the solvent, the electrostriction, changes the result. Therefore the values obtained by using equation 29 are too high. It is probable that the real values are in the neighborhood of 11.2 volts.

The concentration of the hydrogen ions at the surface must be extremely small. As Langmuir and Kingdon have shown (103), the concentration of ions in the sphere of image forces, i.e., at a distance of 10^{-6} cm. or less from the surface, depends on that outside this sphere and is proportional to it if the concentration is not too high. In our case the concentration of hydrogen ions in the gas phase is practically zero, as we have seen, and therefore the concentration of hydrogen ions at the surface can be neglected.

Rupp concludes from his experiments with electronic rays (81) that in the (111) plane of the nickel crystal, atoms of hydrogen are embedded at double the distance of the atoms of nickel. Also with iron we find a surface lattice of adsorbed hydrogen. E. Müller and K. Schwabe likewise concluded from their investigations on the nature of hydrogen sorbed by metals of the platinum group that the hydrogen at the surface is atomic (82). Nevertheless nickel in the crystalline form is completely inactive; the presence of atomic hydrogen on the surface, as found by Rupp, is not sufficient for hydrogenating purposes.

We therefore suppose that catalytic hydrogenation in this class is an ionic reaction in the metal phase between the ions of hydrogen and of ethylene. Ethylene adds electrons, as Loeb had found (112). We have

$$H_2^+ \rightarrow H^+ + H$$

$$C_2H_4^{2\bar{e}}{}_{sol.} + 2H^+_{sol.} = C_2H_6$$
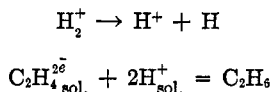
In an aqueous solution an ionic reaction usually proceeds when the product of the reaction is slightly soluble or insoluble, for example:

$$Ba^{++} + SO_4^- = BaSO_4$$

Now C_2H_6 is generally less soluble in metals than is C_2H_4, as I have found (83), and its volume is greater. By hydrogenating ethylene the distance between the carbon atoms is increased from 1.2 Å to 1.6 Å. It is therefore removed from the small pores, which are the seat of activity of the catalyst, as we shall see.

Bancroft has called attention to the fact that hydrogen ions, dissolved in water, have no reducing properties (113); therefore, according to Bancroft, a hydrogenation by positively charged hydrogen ions seems to be improbable. But in aqueous solution there is competition between the water molecules, which are dipoles of large moment, and the organic molecules, which in most cases have a much smaller moment. H^+ does not exist in aqueous solution; it forms H_3O^+. The formation of HR^+, where R is the organic compound, is quite improbable. H_3O^+ does not react as ionized hydrogen, but as a complex ion of water. Its effect is one of hydration, not of hydrogenation.

Some years ago Bonhoeffer called attention to the fact that at the surface of different metals atomic hydrogen recombines to form hydrogen molecules at different velocities (84). Arranging the metals according to their velocity of recombination gives the following series:

Pt, Pd, W, Fe, Cr, Ag, Cu, Pb, Hg
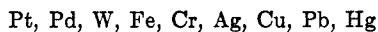
Here the elements at the left easily effect recombination, while those at the right do so with difficulty or not at all. This series

corresponds approximately to the activity of these metals as hydrogenating catalysts, except that in the above series silver precedes copper though it falls behind copper in its hydrogenating properties.

The order in which these elements show overpotential in electrolysis corresponds closely with the above. Thiel and Hammerschmidt (85) give the following sequence:

$$\text{Pd, Pt, Ag, W, Fe, Cr, Cu, Pb, Hg}$$

In this case also silver is in the wrong place from the point of view of hydrogenation.

That lead hinders the recombination of H to H_2 is easy to understand from the discussion of the stability of the PbH_4 on its surface. It protects the metal as well as the atomic hydrogen, so that no more recombination of atomic hydrogen can take place.

One may perhaps conclude that in the process of hydrogenation in the second class atomic hydrogen is the real intermediate product of hydrogenation, just as in the first class, because the elements which catalyze the process $2H \rightarrow H_2$ also catalyze the reverse process $H_2 \rightarrow 2H$. This argument seems to be obvious at first sight, but it is not conclusive. We have seen that in the solution of hydrogen in palladium there are hydrogen ions. Since ionic reactions generally proceed with infinitely great velocity, the reaction with atomic hydrogen, being one of smaller velocity, will be left behind if there is a noticeable concentration of positively charged hydrogen ions at the active points of the catalyst.

This leads to these questions: Where are the active places of the catalyst, on the visible surface or in the interior? How is it possible for the participants in the reaction to reach the points where the ions of hydrogen are located? We shall try to answer these questions by studying the events at the surface in the process of sorption.

PROCEEDINGS AT THE SURFACE IN THE PROCESS OF SORPTION;
ACTIVE PLACES OF THE CATALYST

If hydrogen is taken up by metals the process of course begins at the surface; then we call it *adsorption*. The quantity of ad-

sorbed hydrogen at uniform conditions of temperature and pressure is proportional to the surface area of the body.

In the course of time hydrogen travels from the surface to the interior of the metal and at last fills uniformly the whole interior, provided the time is long or the velocity of diffusion is great enough. We call this process *absorption*. If now the extent of the surface is small in comparison with the weight of the particle, or if the solubility of hydrogen is large in comparison with the adsorption, then the quantity of absorbed hydrogen is no longer a function of the surface, but of the volume or the weight of the piece of metal.

This is shown by the experiments of Sieverts and his coworkers (86), who measured the absorption with compact pieces of metals and with sintered metallic powders and found that the quantity of hydrogen absorbed by a unit of weight of the metal between 400°C. and 1650°C. depends only on the pressure and the temperature and is independent of the surface area (87).

Between the initial state of pure adsorption, which, at low temperature and small velocity of diffusion, may be prolonged, and the final state of pure absorption or solution at higher temperatures, there are numerous intermediate states which McBain has described (88). If it is uncertain which form is involved, the process is called sorption.

If it is of importance for the hydrogenating process that the hydrogen reach the interior of the metal, this will be facilitated if the metal is porous. It is very remarkable that all hydrogenating catalysts are porous. This is especially evident with the catalyst for ammonia synthesis which is made by smelting together the lower oxide of iron and the oxides of aluminum and potassium, cooling and reducing with hydrogen; in this way pieces of metal with indefinitely many pores are obtained. As early as 1910 Bosch and Mittasch expressed the idea that aluminum oxide in this catalyst protects the finely porous structure of the iron and therefore conserves its catalytic power.

The catalysts used for the hydrogenation of organic compounds are also finely divided, porous metals. Numerous technical methods are used to obtain great porosity; one of the methods

most used is the addition of inert porous materials, such as alumina, infusorial silica, and pumice stone, in the preparation of the catalyst. These carriers are not always completely inert. Mittasch and Keunecke have shown that iron oxide and alumina form mixed crystals, which diminish the possibility of reduction and augment the activity of the catalyst (89).

One might suppose that porous catalysts are only a convenient form of procuring a mass with a very large surface. That, however, is wrong. It is true that a porous mass has an enormous surface in a small volume. A crystal of chabasite, weighing 1 g., has after dehydration an interior surface of many hundred m². But the mere area of the surface is not decisive; its form and position are also involved. We have many reasons to suppose that surfaces which are completely free from pores have no catalytic properties.

This follows, for instance, from the researches of Bredig and Allolio (90). These investigators produced a metallic surface on a carrier by dispersing platinum, palladium, and nickel in hydrogen. In the case of platinum they obtained beautifully brilliant surfaces, but all these metals in this form were inactive or nearly so. The nickel was still inactive at a temperature of 350°C. It is also well known that smooth sheets or nets of the active metals are completely inactive for hydrogenating purposes.

Taylor adheres to the view that the corners, tips, and edges of the surface are the active places of the catalyst (91). From this point of view the negative results of Bredig and Allolio are easy to understand, since the surfaces used by them were wanting in the development of corners, tips, and edges. However, the edges and tips of the exterior surface doubtless do not represent the most active points of the catalyst. There, it is true, atomic hydrogen can exist, but the ionized hydrogen can not, as we have seen.

Smekal has shown in a series of papers the importance of faults of structure in the crystal. The firmness, conductivity of electricity and heat, and the interior electric properties depend enormously on the presence or absence of such "loose places." Thus the firmness, i.e., the resistance to disruption, of an ordi-

nary crystal which has these faults, is 100 to 1000 times smaller than that of the ideal crystal. According to Smekal these "loose places" are the active centers of the interior of the crystal. In crystals composed of ions these are the points at which the ions are connected lightly and are loosened to take part in the transport of current. At low temperatures the loosened ions can be conductive ions. *These "loose places" are the active places of the catalyst.* According to this theory it is at the "loose places" of the crystals of hydrides of the alkalies and alkaline earths that the ions of these metals and H^- are loosened. Here we should expect that dissociation into Me^+ and H^- would take place when the heat vibration is sufficient. As we have seen, H^- is unstable and can easily be dissociated into H and $\bar{e}$, so that we have active forms of hydrogen at the "loose places" of these hydrides.

Especially the catalysts of the second class are characterized by their enormous content of "loose places." We must suppose that at these places free ions of the metals, with single or double charge are present, and *that the pores accessible from the outside are the really active places of the catalyst.*

IMPORTANCE OF THE SIZE OF PORES

There is no doubt that the size of the pores of solid substances has a large influence on the sorption of gases and therefore on the catalysis. The best object for studying this influence is dehydrated chabasite, as I have shown (93). Tammann has called attention to the fact that chabasite belongs to a class of minerals which remain transparent after dehydration (94). Brill has established that the lattice of chabasite is not changed by dehydration; the pores which are produced by dehydration are therefore of quite extraordinary regularity. They constitute, so to speak, a natural gauge.

Now I have shown that with inert porous sorbents, such as dehydrated chabasite, dehydrated gypsum, silicious acid, and charcoal, the sorption of a series of gases,—including hydrogen, nitrogen, carbon monoxide, argon, oxygen, methane, ethylene, ethane, carbon dioxide, and ammonia,—at constant temperature

and at a pressure of 1 atmosphere, and in a range of temperature between 0 and 150°C. follows the simple equation:

$$\log c = a \sqrt{\lambda} + b$$

where c is the sorbed volume of gas in cc. under normal conditions, λ is the heat of evaporation, and a and b are constants, which are invariable for different gases at the same conditions of temperature and pressure for the same sorbent, but vary with the conditions and the sorbents (93).

This logarithmic relation was justified by many experiments with the above sorbents and gases. Therefore it was extremely surprising that a series of gases and vapors did not follow the above equation and gave no or little sorption. These gases and vapors were propylene, butylene, butadiene, ether, benzene, and hexamethylene. The last three were not sorbed at all.

The results of these experiments are shown in the fourth column of table 9; in the fifth column are the calculated values, in the second the molecular volume, and in the third the diameter, σ, calculated by the usual methods. The calculated and the observed values begin to differ notably at a fixed value of the molecular volume or diameter. Down to ethylene, the molecular volume of which is 44, the sorption follows the formula. But propylene, with a molecular volume of 67, gives a sorption of only 13 per cent of the calculated value. The sorption of butylene and butadiene is only 1 per cent and that of the remaining gases is practically zero. Ethane is at the dividing line; some sorbents give low values for it.

The reason for this phenomenon is that the pores of chabasite have fixed dimensions and therefore the molecules of gases which are too large cannot enter the crystal and cannot be absorbed.

In sorbing gases in many other sorbents, experiment and theory deviate, beginning with propylene. The actual sorption lags increasingly behind the calculation as the molecular volume rises. But while the sorption of dehydrated chabasite is equal to zero for gases of molecular volume greater than 90, that is not the case with the other sorbents. Thus it is known that charcoal absorbs both benzene and ether to a large extent. It is

easy to understand that sorbents such as dehydrated gypsum, vanadium oxide, uranium oxide, charcoal, and amorphous silicious acid do not show such a typical effect of gauge. The dimensions of their pores are not so exactly defined as in the case of dehydrated chabasite; they vary between wide limits.

If we pass from solid, porous, inorganic substances to organic colloids, such as rubber, the rigid fixation of the pores vanishes

TABLE 9

Sorption of gases by dehydrated chabasite

FORMULA	MOLECULAR VOLUME	$\sigma \times 10^9$	QUANTITY OF SORBED GAS PER 0.2 G. OF DEHYDRATED CHABASITE AT 100°C. AND 760 MM.	
			Found	Calculated
NH_3	25.2	—	37.0	41.5
O_2	28.0	29	0.6	1.5
Ar	28.3	28	0.4	1.3
H_2	28.6	23	0.1	0.1
N_2	34.5	31	1.2	1.0
CO	35.3	32	1.6	1.2
CO_2	35.1	32	13.3	17.0
CH_4	33.0	28.3	1.9	2.5
C_2H_4	44.0	32.9	8.3	10.3
		36.0		
C_2H_6	55.0	39.9	6.6	12.4
C_3H_6	67.0	—	4.0	29.7
C_4H_6	90	—	0.8	64.4
C_4H_8	88	38.9	1.4	72.4
C_6H_6	96	41.0	0.0	251
C_4H_9OH	102	—	0.3	407
$(C_2H_5)_2O$	107	48	0.0	126
C_6H_{12}	117	—	0.0	251

and therefore the size of the pores does not prevent the sorption from following the logarithmic relation. I found no deviation between the observed and the calculated values for the gases sulfur dioxide, butadiene, butylene, methyl chloride, and ethyl chloride in using natural rubber.

The conclusion from these experiments is that the sorption in porous materials takes place especially in the pores and that the

ratio of the diameter of the pores to the diameter of the gas molecules is of decisive influence on the sorption and the catalytic effect.

While relatively small molecules must be considered as spherical, organic molecules having a long chain of carbon atoms show a quite different behavior. This becomes evident in the hydrogenation of organic chain molecules containing a $C=C$ bond. Here the position of the double bond in the chain is decisive and not the value of the molecular volume. If the double bond is in the 1, 2 position, the unsaturated compound is easily hydrogenated. So also if the molecule is large, as in the esters of undecylenic acid. In these cases the velocity of hydrogenation practically does not differ from that of small molecules such as allyl alcohol and the ester of acrylic acid. But if the double bond lies in the middle of a long chain, as in oleylic alcohol, the ester of oleic acid, and elaidic acid, the reaction velocity is less by about two powers of ten (25) for nickel as catalyst.

The explanation of these phenomena on the basis of our theory is that it is necessary for the reaction group to enter into the pores, and that for mechanical reasons this is easier when the double bond is at the end of the molecule.

The pores, but not the tips and edges of the exterior surface, are the reactive points of the catalyst. We identify the small pores with the "loose places" of Smekal.

OTHER PHENOMENA OF SORPTION; EXCEPTIONAL POSITION OF HYDROGEN

We have seen that the sorption of gases by porous bodies and solid colloids such as rubber is given by the logarithmic relation

$$\log c = a \sqrt{\lambda} + b \tag{4}$$

Passing from solid colloids to liquids, every resistance to the penetration of gas molecules has vanished and we must suppose that our equation is exactly valid. Indeed we find that in alcohol there is in most cases excellent agreement between theory and experiment, using the data given by Carius (95). (Figure 5-1.)
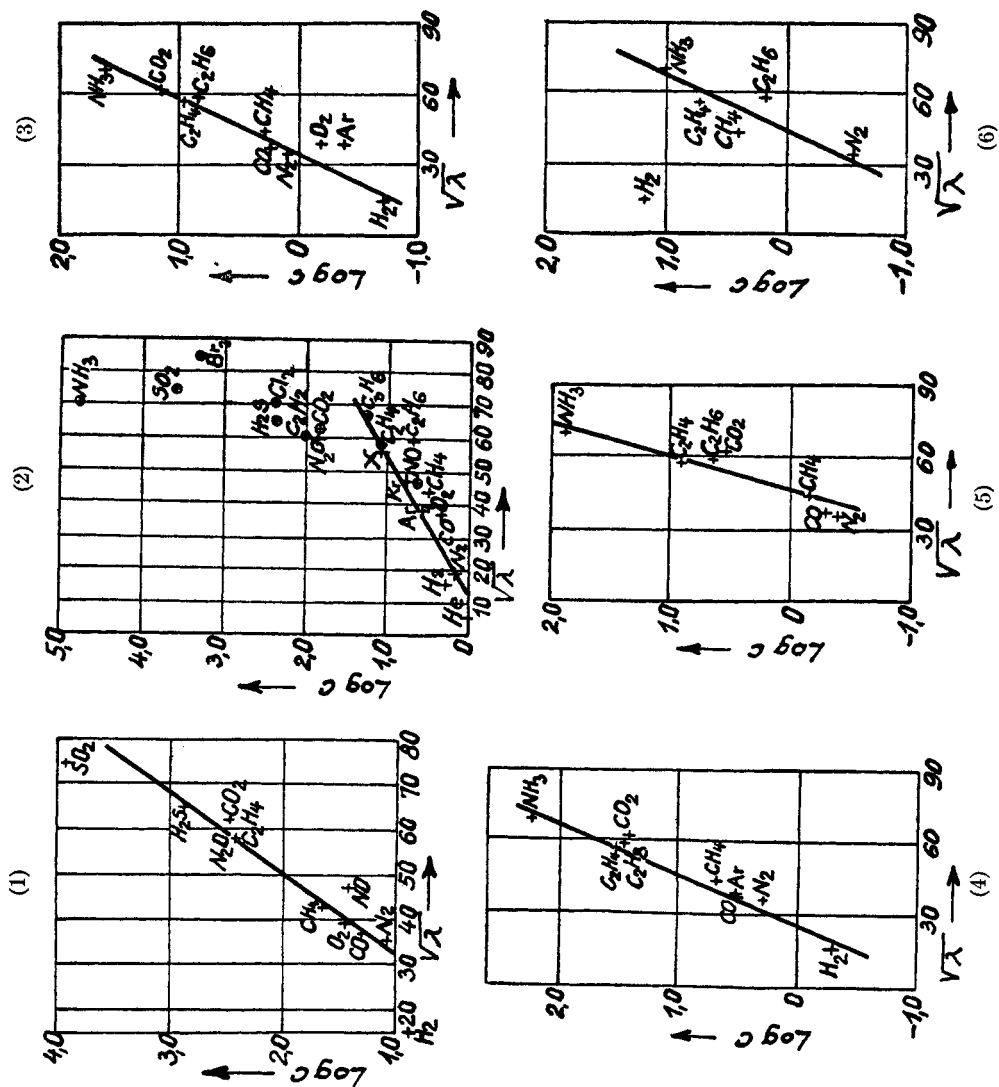
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FIG. 5. RELATION OF SOLUBILITY AND SORPTION OF GASES TO HEATS OF EVAPORATION

1. Solubility in 100 cc. of alcohol at 20°C. and 760 mm.
2. Solubility in 100 cc. of water at 20°C. and 760 mm.
3. Sorption by 0.2 g. of chabasite at 100°C. and 760 mm.
4. Sorption by silicic acid at 40°C. and 760 mm.
5. Sorption by charcoal at 20°C. and 760 mm.
6. Sorption by 10 g. of powdered nickel at 20°C. and 760 mm.

But the sorption in water, calculated with data from the tables of Landolt-Börnstein, in many cases gives large deviations from the theoretical values, as is shown in figure 5-2. In this case only the noble gases and the mono-olefins follow the logarithmic relation exactly, while all those gases which form ions in water, such as carbonic acid, ammonia, hydrogen sulfide, and sulfurous acid are excessively sorbed, the excess increasing with the concentration of ions in the solution under the conditions of the reaction. Nitrous oxide and the halogens also show a large increase of the constants. Nitrous oxide and the halogens are among the gases which easily add electrons (96).

It is this facility in adding negative charges which explains the increase of the sorption constants in the case of water. In the case of gases which give ions on solution, the energy of the van der Waals' forces of attraction is augmented by the energy of hydration of the ions produced by forces of Coulomb's attraction; therefore we have an exaltation.

SORPTION OF GASES BY METALS

My investigations of the sorption of gases in metals have given the following results. Metals of the second class show a great increase in the sorption of hydrogen, which in the case of nickel is more strongly absorbed than ammonia. This increase of sorption is much greater, indeed of another order of magnitude, than the small increase which often occurs with hydrogen and can be explained by the small diameter of its molecule. Mixtures of iron and nickel gave a smaller increase than did nickel alone. The sorption of the other gases follows the logarithmic relation, as is shown in figure 5-6.

The sorption of hydrogen is quite normal with aluminum and silver, which are not catalysts and do not belong to the second class.

With regard to the increased sorption of ionizable gases in water and the large sorption of hydrogen in nickel, we conclude by analogy that hydrogen is ionized on solution in nickel. Then the situation in nickel is the same as in palladium, where the existence of ionized hydrogen was established.

OTHER THEORIES

Hedwall and his coworkers have advanced the view that the ability of a crystallized material to react reaches a maximum at temperatures at which the material suffers crystallographical changes (97). Ch. Slonim showed that the transition of one type of crystal into another goes through the amorphous state (98). These transitions therefore involve intermediate forms, the energy content of which is larger than of the crystals.

In the transition state some substances show a maximum of catalytic activity, as Hüttig and Brühl have found (99). Therefore one may assume that the finely divided state of some active catalysts is the cause of their activity, since they are in this state of transition and the heat of the change from one type to the other furnishes the necessary energy of activation.
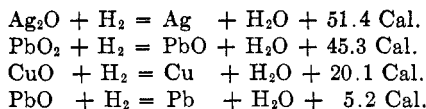
It seems probable that this heat of change can not be neglected in the interpretation of the mechanism of the process of hydrogenation, but it is certain that it cannot explain the real activation, for the hydrogenating catalysts, e.g., that of the ammonia process, are not amorphous but are crystallized and endure a very long time. It is very improbable that the heat of change can be of great importance in such a catalyst.

B. THE HYDROGENATION OF MULTIPLE BONDS BETWEEN CARBON, OXYGEN, AND OTHER ELEMENTS

The catalysts which are able to hydrogenate the multiple bonds of carbon are not always the same as those which hydrogenate the multiple bonds between carbon and other elements. Thus, for instance, copper is an excellent catalyst for the hydrogenation of the $C=O$ bond but it is unable to effect the hydrogenation of the $C=C$ bond in stilbene and of the aromatic bonds in benzene, toluene, etc. (100). Furthermore, Brown and Henke have shown (101) that aromatic compounds containing nitro groups, such as nitrobenzene and nitrotoluene, can be reduced to the amines with good yields by hydrogen with the use of lead and silver as catalysts. Yet in the hydrogenation of the multiple bonds of carbon, lead is a poison and silver is completely inactive.

Only such metals are able to reduce nitro compounds as have oxides which are reduced by hydrogen with the development of heat.

$$Ag_2O + H_2 = Ag \quad + H_2O + 51.4 \text{ Cal.}$$
$$PbO_2 + H_2 = PbO + H_2O + 45.3 \text{ Cal.}$$
$$CuO \quad + H_2 = Cu \quad + H_2O + 20.1 \text{ Cal.}$$
$$PbO \quad + H_2 = Pb \quad + H_2O + 5.2 \text{ Cal.}$$

That is easy to understand, for when absorption of heat is involved the reduction of the metallic oxides is no longer possible under normal conditions of reaction. Therefore the metallic catalysts would go over irreversibly into the inactive oxides.

In this case, too, the metal is the catalyst; but as intermediate product we find here a metal oxide, if the nitro group is reduced. It is probable that the nitro group gives its two oxygen atoms to the catalyst in forming the radical, $C_6H_5N:$, which is then reduced to aniline. However, the manner in which this reduction takes place is doubtful at this time.

The $C\!=\!O$ bond is hydrogenated either by conserving the oxygen in the molecule or by eliminating it. Of the metals, copper, nickel, cobalt, the oxides of which are reduced with development of heat, copper is the most effective because it gives the highest heat value (20.1 Cal.), while nickel and cobalt often reduce oxygen compounds to hydrocarbons, for instance C_6H_5CHO to $C_6H_5CH_3$ (101).

It is easy to understand that copper is especially able to conserve the $C\!=\!O$ binding. The large development of heat in the reduction of its oxide with hydrogen shows that the firmness of the binding between oxygen and metal is here less than in the above metallic oxides and also smaller than that of the bond between carbon and oxygen.

The affinity for oxygen of the active metals therefore decides the course of the process.

SUMMARY

The mechanism of catalytic hydrogenation of *multiple carbon bonds* is as follows:

The active elements, which act essentially as such, are divided into two classes.

To the first class belong mono- and bi-valent elements, including the alkalies and alkaline earths, which form stable, solid, salt-like hydrides. These elements are at the maxima of the long periods of the atomic volume curve, and have a large atomic volume. Their catalytic activity is small. Among the alkali metals the activity increases with the diameter of the atom. It is very probable that hydrides are intermediate products of the reaction, which then give negatively charged ions and atoms of hydrogen by dissociation in the interior of the catalyst.

To the second class belong the bivalent elements or those which have a minimum valence of 2 (Fe), or a maximum of 2 (Cu), which do not form solid hydrides but do form solutions with hydrogen, which have a small atomic volume and are "gap elements" in the periodic system. They are at the minima of the long periods of the atomic volume curve and are the more active the smaller is their atomic or ionic radius. Their ionization potential, $Me^+ \rightarrow Me^{++}$, amounts to about 18 volts and corresponds surprisingly with the work of ionization of $H_2 \rightarrow H^{++} + H + \bar{e}$. To this class belong the elements of the iron and platinum groups, and also copper, chromium, manganese, and rhenium. In the interior of these metals, when charged with hydrogen, there are positive hydrogen ions, as is proved by the experiments of Coehn and his coworkers, the phenomena of the thermionic effect, and those of sorption of hydrogen by metals.

The elements of these two classes differ markedly in their atomic volume, in the atomic or ionic radius, and in the work function. The principal properties of the two classes are quite different and the mechanism of their action must also be different.

Catalytic hydrogenation is an ionic catalysis. The ions of the catalysts,—electrons in the first class, ions of metal in the second,—are the real catalysts. In the first class the work function is small and the field of the metallic ions is weak; electrons are easily formed at the surface of the metal. Then molecular hydrogen is dissociated by the free electrons because the affinity for electrons of the atomic hydrogen favors the dissociation. It seems probable that atomic hydrogen, formed by the decomposition of hydrides, is an intermediate product of hydrogenation.

In the second class the work function is large and the field of the metallic ions is strong. In the strong fields hydrogen is ionized to form positively charged ions. Because the energy of these ions is greater than that of atomic hydrogen, it is probable that these ions are intermediate products of reaction in this class.

The process of hydrogenation takes place at the "loose places" of the metal crystal or of metallic hydrides in which the ions are loosely bound. The small pores which are accessible from the outside are such "loose places" in the sense of Smekal.

The mechanism of the hydrogenation of multiple carbon bonds differs from that of the C$=$O bond. In the latter case the affinity of the catalyst for oxygen decides the course of hydrogenation.

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