JOURNAL OF CATALYSIS 3, 7–21 (1964)

A Mathematical Interpretation of Catalysis Derived from Infrared Spectroscopy

R. A. GARDNER

From The Standard Oil Company (Ohio), Research Department, Cleveland, Ohio

Received July 19, 1963

For the class of adsorbates designated as intermedions, the change in vibration frequency upon chemisorption can be related by equations to a change in the number of valence electrons associated with these adsorbates. This leads to numerical measurements of the chemical reactivity of intermedions and the polarizing effect of the adsorbent. Mathematical interpretations are made of the catalyzed reactions of CO oxidation to CO_2 and carbonate, acetylene hydrogenation and hydration, peroxide decomposition, and several reactions of hydrogen and oxygen. The metallic components of these catalysts are chromium, iron, cobalt, nickel, copper, rhodium, palladium, silver, iridium, and platinum. The results of these calculations coincide with the known catalytic reactions of these metals with respect to valence state as well as with respect to heterogeneous or homogeneous systems. The polarizing effect of the metallic component of the adsorbent shows an indication of periodicity when the metals are arranged according to atomic number.

I. INTRODUCTION

A mathematical relationship between spectroscopy and catalysis is proposed on the basis of an interpretation of data from an infrared study of chemisorption. The hypotheses which are the foundations of this work give numerical descriptions of (1) the energy state of adsorbates, (2) the "polarizing" or "activating" influence of the adsorbent or catalyst, and (3) the energy relationships which lead to reaction. In order to account for the interactions in an area as complex as catalysis, many detailed assumptions are necessary. In some instances, the experimental methods and instrumentation may not exist at this time to test these ideas directly. Such assumptions must be evaluated on the basis of their utility and by the new experiments which they suggest. For example, to consider reactants in addition to carbon monoxide, the necessary proposals are advanced to extend the mathematical relationships to systems that have not been studied by means of the infrared spectra of chemisorbed species and to other systems that do not produce infrared spectra.

II. DISCUSSION

An interpretation (*1*) of the data from an infrared study of the chemisorption of carbon monoxide on several metals and compounds was based on the following equation

$$(\nu_{CO} - 2269.96)(E_{CO} - 12.1182) = 268.309 \qquad (1)$$

This equation was derived to relate the vibration frequencies ν and numbers of valence or outershell electrons E of gaseous CO species, viz., the neutral molecule and the ions. The species which can exist in the gas phase have integral numbers of electrons. On the basis of Eq. (1), the vibration frequencies of the chemisorbed CO species correspond to nonintegral numbers of valence electrons. However, some of the CO species on adsorbents containing the same metallic component produced infrared bands whose vibration frequencies correspond to nonintegral numbers of electrons with different integers but a *constant fraction.*

The neutral gaseous CO molecule, 10 valence electrons, has a vibration frequency of 2143.27 cm^{-1} (*2*). The infrared bands for CO on copper oxide which correspond to numbers of electrons with a constant fraction were at 2173 cm^{-1} (9.35 electrons) and 2121 cm^{-1} (10.32 electrons). On cobalt, infrared bands for chemisorbed CO were observed at 2160 cm^{-1} (9.68 electrons) and 2091 cm^{-1} (10.62 electrons). On a partially decomposed silver nitrate adsorbent, CO produced an infrared band at 2165 cm^{-1} (9.56 electrons). The addition of hydrogen caused the appearance of a band at 2099 cm^{-1} (10.55 electrons). Eischens and Pliskin (*3*) report an infrared band for CO on iron at 1960 cm^{-1} which was replaced, upon the addition of oxygen, by a band at 2127 cm^{-1}. According to Eq. (1), these vibration frequencies correspond to 11.25 and 10.24 valence electrons respectively. These chemisorbed species which produce infrared bands corresponding to a constant fractional number of electrons were named "intermedions" and the fraction, which seems to be a characteristic of each metal, was named the "polarization fraction." The infrared bands due to chemisorbed species not assigned as intermedions were considered to result from the carbonyl type of adsorbates described by other investigators. A complete description of the development of these interpretations is presented in the previous paper (*1*).

Constant Value of Polarization Fraction

The polarization fraction remained constant despite changes in the electronic environment of the metallic component of the adsorbent. In the above example of the adsorbent containing silver, the addition of hydrogen changed the surface from an electron acceptor to an electron donor. The addition of oxygen to the iron adsorbent produced a significant change in the electron donor character of the surface. The fact that the fraction remains constant in these examples is an indication that the polarization fraction is a numerical expression of the effect on adsorbates of the "polarizing" or "activating" influence of the metallic component of the adsorbent and an indication that this fraction may remain constant with other adsorbates. It follows that if the equation relating vibration frequency and number of valence electrons is known for a molecule and if the polarization fraction of the metallic component of the adsorbent is known, then it should be possible to calculate the vibration frequencies of the intermedions that may be formed by chemisorption.

Myers Hypothesis

It is the Myers (*4*) hypothesis which proposes a relationship between vibration frequency and catalytic reactions. He observed a coincidence between the vibration frequencies assigned to the normal modes of gaseous ethylene and the vibration frequencies of several reactive catalyst complexes. For example, the ν_7 mode of gaseous ethylene has a vibration frequency of 950 cm^{-1} and the gaseous Ag–O diatomic molecule has a vibration frequency of 481 cm^{-1} (a first harmonic* of 962 cm^{-1}). The match of these frequencies was interpreted by Myers to explain why silver is a catalyst for the epoxidation of ethylene. The several examples of this type of correlation led Myers to propose that certain reactions are facilitated when the vibration frequencies of the reactants coincide.

On the basis of this proposal by Myers, the discovery of intermedions and the polarization fraction generates many catalytic possibilities through the interaction of two constants. These are a *constant* polarization fraction for each metal and a *specific* equation for the vibration frequencies of each reactant. A given reactant will have different vibration frequencies when chemisorbed on adsorbents containing different metal components and thus show different reactions. Similarly, different reactants on a single adsorbent will have different vibration frequencies and different reactions. The extension of these concepts to reactants other than CO and the establishment of the necessary mathematical relationships requires the following detailed interpretation of the available experimental data relating to intermedions.

---

* It may be necessary to multiply one of the frequencies by 2, 4, 8 . . . 2^n, where n is integral, to compare it with the other frequency.

Interpretation of Experimental Data Relating to Intermedions

Intermedions have been detected on only those adsorbents whose metallic components possessed partially vacant orbitals. No intermedions were detected on adsorbents of supported metallic copper or a vacuum-evaporated copper film. It is possible that the partially vacant orbitals combine to form some type of delocalized surface orbital which can bond intermedions in a π-type or charge transfer configuration. Since a single equation describes both gaseous species and intermedions,* they seem to be bonded in a gaslike state, at least with respect to vibration frequency. Intermedions may be constrained with respect to rotation since no evidence of a vibration–rotation doublet has been detected upon the examination of the infrared bands of CO intermedions with a grating spectrometer.

Intermedions may reside on specific lattice faces. Cunningham and Gwathmey (*5*) observed that with copper crystals, other lattice faces were reoriented to the (111) face upon exposure to hydrogen and oxygen during the catalytic formation of water. It is possible that the (111) face may be the site of residence of the chemisorbed hydrogen and oxygen intermedions which react to form water. The highly exothermic character of this reaction and the concurrent large decrease in free energy would be expected to be more than sufficient to promote the rearrangement of the lattice faces to facilitate the formation of water.

The type and number of intermedions may be proposed on the basis of the presence of two states of the atoms of the metallic component. While the conventional representation of copper (II) as $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^9$ suggests that only one electron can be transferred between the $3d$ orbital and CO, to form intermedions possessing 9 or 11 electrons, the experimental data indicates the presence of two copper species with partially vacant orbitals capable of electron transfer. If the 2121 cm^{-1} band observed with the grating spectrometer for CO on copper oxide is assumed to be the more accurate,† then the polarization fraction of copper is 0.32 and the observed CO vibration frequencies of 2173 and 2121 cm^{-1} are equivalent to 9.32 and 10.32 valence electrons. These two intermedions could be formed from two types of copper species—having 0.32 and the other 1.32 electrons available for exchange in the partially vacant d orbital, i.e., $3d^{8.32}$ and $3d^{9.32}$. Since these two species with different numbers of electrons are analogous to upper and lower oxidation states, they are believed to correspond to cupric and cuprous, respectively.

The electron transfers which appear to take place during the formation of intermedions by the chemisorption of CO on copper are:

1. those in which the surface accepts electrons to fill the partially vacant orbital and
2. those in which the surface donates electrons to empty the partially vacant orbital.

These are "apparent" electron transfers since the adsorbate is polarized only when it is bound in the surface field. Since a single orbital may contain up to two electrons, the maximum range for the number of valence electrons on an intermedion will be two greater or less than the number of valence electrons on the neutral species. In the following equations, the superscripts are the number of electrons; the experimental vibration frequencies are included:

$$\text{(CO)}^{10} \text{ donates 1.68e to } \text{Cu}^{8.32} \rightleftarrows \text{Cu}^{10} + \text{(CO)}^{8.32} \quad (2)$$

$$\text{(CO)}^{10} \text{ donates 0.68e to } \text{Cu}^{9.32} \rightleftarrows \text{Cu}^{10} + \text{(CO)}^{9.32}\ 2173 \text{ cm}^{-1} \quad (3)$$

$$\text{(CO)}^{10} \text{ accepts 0.32e from } \text{Cu}^{8.32} \rightleftarrows \text{Cu}^{8} + \text{(CO)}^{10.32}\ 2121 \text{ cm}^{-1} \quad (4)$$

$$\text{(CO)}^{10} \text{ accepts 1.32e from } \text{Cu}^{9.32} \rightleftarrows \text{Cu}^{8} + \text{(CO)}^{11.32} \quad (5)$$

Accordingly, the partial orbital vacancy of the surface metal atoms is transferred by chemisorption from the metal to the adsorbate. Equations (2–5) indicate that a

---

[*] Gaseous species may be considered as intermedions with integral numbers of electrons.

[†] In addition to the increased resolution of the grating over the NaCl prism, Eq. (1) changes more rapidly with respect to number of electrons at 2173 cm^{-1} than at 2121 cm^{-1}, i.e., 2174 cm^{-1} corresponds to 9.32 electrons.

maximum of four intermedions can be formed from the chemisorption of CO as a result of electron exchange with the upper and lower states of a single delocalized orbital. The nonintegral numbers of electrons associated with CO intermedions will be composed of the polarization fraction, a number from 0.00 to 1.00, of the metallic component of the adsorbent plus the integers 8, 9, 10, and 11. The CO intermedions detected on adsorbents containing copper were those with integers of 9 and 10. The infrared bands reported by Eischens and Pliskin (*3*) for CO on adsorbents containing iron correspond to the intermedions with intergers of 10 and 11. While a CO intermedion with an integer of 8 has not been identified, the experimental observation of intermedions with integers of 9, 10, and 11 gives support to the electron exchanges indicated by Eqs. (2–5). It seems likely that the intermedions which can be proposed but were not observed may be present at concentrations below the limit of detection of the spectrometers.

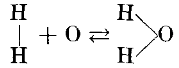
The similar exchange of electrons between the neutral oxygen molecule (12 valence electrons) and the upper and lower states of a single orbital will generate four oxygen molecule intermedions with nonintegral numbers of valence electrons composed of the polarization fraction of the adsorbent metal and the integers 10, 11, 12, and 13 with a total range from 10 to 14 electrons. The four oxygen atom intermedions will have numbers of electrons with integers of 4, 5, 6, and 7 (total range from 4 to 8). The nitrogen atom intermedions will have integers of 3, 4, 5, and 6 (a total range from 3 to 7) since the neutral nitrogen atom has 5 valence electrons. Only three intermedions with integers of 5, 6, and 7 may be formed with OH, and H_2O can only donate electrons to form intermedions with integers of 6 and 7. These limits on OH and H_2O result from the fact that 8 is the maximum number of electrons that can be accommodated by OH and H_2O.

Vibration Frequency and "Energy Level"

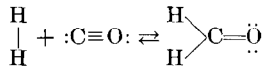
While the concept of matching vibration frequencies can be applied to reactions across the bonds of molecules, it is not applicable to reactions of atomic intermedions or at one atom of a molecule. The addition of a hydrogen molecule as shown in the following equation

$$\mathrm{H{-}H} + \mathrm{:C{\equiv}O:} \rightleftarrows \mathrm{H{-}}\underset{\cdot\cdot}{\ddot{\mathrm{C}}}\mathrm{{-}O{-}H} \qquad (6)$$

should occur on a catalyst containing that metal which because of its particular polarization fraction changes the gaseous molecules by chemisorption so that their vibration frequencies are equal. A mathematical interpretation of such reactions as



$$\begin{matrix}\mathrm{H}\\ |\\ \mathrm{H}\end{matrix} + \mathrm{O} \rightleftarrows \begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\!>\!\mathrm{O} \qquad (7)$$



$$\begin{matrix}\mathrm{H}\\ |\\ \mathrm{H}\end{matrix} + \mathrm{:C{\equiv}O:} \rightleftarrows \begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\!>\!\mathrm{C{=}}\underset{\cdot\cdot}{\ddot{\mathrm{O}}} \qquad (8)$$

requires the numerical expression of an "energy" or reactivity of the oxygen atom to be compared with the vibration frequency of the hydrogen molecule and a similar "energy" to express the reactivity at the carbon atom of carbon monoxide. Although this energy cannot at present be measured directly, it may be derived from the following interpretation of vibration frequencies.

The vibration frequency of a diatomic molecule can be related to its capacity to accept or donate electrons. Since the addition of electrons to carbon monoxide decreases the vibration frequency, it is proposed that the vibration frequency is related to the capacity of carbon monoxide to accept electrons. On the contrary, the addition of electrons to the OH diatomic molecule increases the vibration frequency. The vibration frequencies of (OH), seven valence electrons, and $(OH)^+$, six valence electrons are given by Herzberg (*6*) as 3569.59 and approximately 2955 cm^{-1}, respectively. The vibration frequency of OH can be related, therefore, to its capacity to donate electrons. As electrons are added to CO and its electron acceptor capacity decreases, there should be a corresponding increase in its electron donor capacity and vice versa for OH. It is proposed that the term "energy level" be used to describe the electron donor capacity of CO and the electron acceptor capacity of OH. The sum of the vibration frequency represented by ν(C–O), and the energy level represented by ν(—CO) is a constant as indicated by the following equation for the example of carbon monoxide

$$\nu(\text{C–O}) + \nu(\text{—CO}) = k_{\text{CO}}. \qquad (9)$$

Whereas the vibration frequency is represented by ν(C–O), the energy level will be represented by ν(—CO) and in the example of carbon monoxide will refer to reaction at the carbon atom. The energy levels of atomic species can be related in a similar manner to their electron acceptor or donor capacity to provide a numerical measurement of their reactivity. The derivations of the equations to characterize atomic and molecular intermedions in terms of energy levels and number of electrons are presented in the last section of this paper.

Mathematical Interpretation of Catalytic Reactions

As indicated by Eqs. (6) and (8), the energy terms to be matched depend upon the reaction mechanism. The specific mechanisms of the following reactions are those proposed by other investigators or generally accepted with the exception that the intermedions are not considered to be bonded to specific catalyst atoms, but rather to delocalized orbitals. The mechanisms are for reversible reactions of the Langmuir-Hinshelwood type, i.e., with both reactants chemisorbed. In the case of those reactions which are decompositions, according to the principle of microscopic reversibility, the catalyst which promotes the decomposition should form the appropriate intermedions with matching energy since the position of the equilibrium depends on the free energy change. Although the preceding discussion has considered only solid adsorbents and catalysts, some of the reactions listed below involve catalysis by dissolved salts, i.e., homogeneous systems. A later section will show the extension of this interpretation of catalysis to homogeneous systems. For those reactions that are catalyzed by many metals, or their compounds, all metals whose polarization fractions occur as solutions to the equations are presented in Table 1. These reactions are the formation of water from $H_2 + O$ and $H + OH$, the oxidation of carbon monoxide by O and O_2, and the hydrogenation of acetylene, by addition of H_2 across the triple bond. In addition, several reactions that require a specific metal component in the catalyst are included. Some of the reactions that have been described in the literature and those that require special comments are briefly noted in the following section.

The reactions in Table 1 known to be catalyzed by chromium compounds are the hydrogenation of acetylene to ethylene and the oxidation of carbon monoxide to carbon dioxide. Another reaction between oxygen and carbon monoxide presented in Table 1 is the formation of a carbonate species. Little and Amberg (*7*) assigned some of the spectral bands that they observed in an infrared study of the chemisorption of carbon monoxide on chromia-alumina to a surface carbonate species. It is likely that this carbonate species will decompose to yield carbon dioxide. Thus, this reaction will also contribute to the oxidation of carbon monoxide. The reaction of a hydrogen atom intermedion and a hydroxyl intermedion to form water may be an example of a reaction not previously described that is predicted by this type of analysis of catalytic reactions.

The reactions catalyzed by iron and its compounds are well known. In addition to the formation of water and the oxidation of carbon monoxide, the decomposition of peroxide to form an oxygen atom intermedion and a hydroxyl intermedion coincides with the mechanism proposed by Jarnagen and Wang (*8*) and by Koefoed (*9*) for the homogeneous liquid phase reaction. The combination of a hydrogen molecule intermedion with a carbon monoxide intermedion to form an HCOH species is an initial step in the Fischer-Tropsch synthesis in the mechanism proposed by Emmett and Kummer (*10*) and by Storch, Golumbic, and Anderson (*11*).

One of the most interesting reactions in Table 1 is the formation of water from hydrogen and oxygen catalyzed by copper. The Atomic Energy Commission sponsored a search by McDuffie *et al.* (*12*) for a soluble compound to catalyze this reaction in homogeneous nuclear reactors. After investigations of compounds of some 20 metals, they found that cupric salts were optimum for the regeneration of the water that had been decomposed by the radiation. The oxidation of carbon monoxide by oxides of copper has been investigated by Ritchey and Calvert (*13*). They observed that a particular cuprous oxide preparation did not catalyze the oxidation in the dark and that exposure of the system to light caused the oxidation to occur. They proposed that the reaction is catalyzed by cuprous oxide which is activated by the cupric ions which are generated in the surface by the radiation. The oxygen atom and carbon monoxide intermedions in Table 1 are those which would be present on cuprous copper. Finally, the hydration of acetylene to acetaldehyde (*14*) is a commercial reaction catalyzed by dissolved cuprous salts.

The reactions catalyzed by silver are the formation of water and the homogeneous oxidation of carbon monoxide by hydroxyl. This latter reaction has been studied by Nakamura and Halpern (*15*), who proposed a mechanism which includes the insertion of OH into a silver –CO complex, then subsequent decomposition of this intermediate to yield carbon dioxide. It is to be noted that not only is the polarization fraction of silver a solution to the equations for reaction between (C–O) + (—OH), but that the polarization fraction of silver is *not* a solution for the reactions of O + (—CO) or (O–O) + (—CO). This type of mathematical analysis provides a clear distinction between the mechanisms that are possible for this reaction.

The reactions known to be catalyzed by cobalt are the formation of water, oxidation of carbon monoxide, hydrogenation of acetylene, and the addition of H_2 across CO as an initial step in the Fischer-Tropsch synthesis. It is indicated in Table 1 that cobalt will catalyze the reaction of hydrogen atom and hydroxyl intermedions to form water as well as the reaction of hydrogen molecule and oxygen atom intermedions to form water.

The reactions catalyzed by platinum are the two reactions for the formation of water, the oxidation of carbon monoxide and the hydrogenation of acetylene.

The two reactions catalyzed by nickel are the formation of water from hydrogen molecule and oxygen atom intermedions and the combination of oxygen molecule and carbon monoxide intermedions to form a carbonate species. Courtois and Teichner (*16*) have assigned infrared bands to a carbonate species formed in the presence of oxygen, carbon monoxide, and nickel oxide. Since the fractions for nickel and iron do not appear as solutions to the equations for the addition of H_2 across the triple bond of acetylene, it is concluded that this reaction does not proceed by this mechanism in the presence of catalysts whose metallic components are nickel or iron.

The vibration frequencies and energy levels of the intermedions in the reactions considered in Table 1 are calculated from the following equations:

$$[\nu(\text{C–O}) - 2269.96][E(\text{CO}) - 12.1182] = 268.309 \tag{1}$$

$$\nu(\text{C–O}) + \nu(\text{—CO}) = 2204.81 \tag{10}$$

$$[\nu(\text{O–H}) - 6080.64][E(\text{OH}) - 0.1862] = -17109.7 \tag{11}$$

$$\nu(\text{O–H}) + \nu(\text{—OH}) = 3890.95 \tag{12}$$

$$[\nu_3(\text{H}_2\text{O}) - 5925.03][E(\text{H}_2\text{O}) - 0.1123] = -17109.7 \tag{13}$$

$$\nu_3(\text{H}_2\text{O}) + \nu_3(\text{—OH}_2) = 3755.79 \tag{14}$$

$$[\nu(\text{HC}{\equiv}\text{CH}) - 3530.43][E(\text{HC}{\equiv}\text{CH}) - 14.2018] = 712.441 \tag{15}$$

$$[\nu(\text{O–O}) - 2920.16][E(\text{O–O}) - 15.7525] = 5117.58 \tag{16}$$

$$\nu\text{H} = 4161.14E(\text{H}) \tag{17}$$

$$\nu\text{H}_2 = 2080.57E(\text{H}_2) \tag{18}$$

$$\nu\text{O} = 778.19[8 - E(\text{O})] \tag{19}$$

These equations are derived from the published experimental data for the vibration frequencies of gaseous molecules, ions, and radicals that have been determined by infrared, Raman, or electronic emission spectra. These data have been obtained at conditions of high resolution with an accuracy that is generally greater than has been achieved in the determination of the spectra of chemisorbed species. The increased gain and/or increased optical slits that may be necessary to detect some of the bands of chemisorbed species diminish the resolution of the spectrometer. Therefore, the spectra of chemisorbed CO have been used to provide approximate values of the polarization fractions, with the more accurate values being determined from computations of reactions based on the equations.

An analysis of the silver-catalyzed reaction of a hydrogen molecule intermedion and an oxygen atom intermedion to yield water might take the form of the following equation where the subscripts are the vibration frequencies calculated by the above equations for the indicated number of valence electrons. The polarization fraction of silver determined from the chemisorption of carbon monoxide is 0.55 from the infrared band at 2099 cm^{-1}.

$$\begin{array}{ccccc} H_2^{0.55} & + & O^{6.55} & \rightleftarrows & H_2O \\ 1144.31 & & 1128.38 & & \end{array} \tag{20}$$

This type of matching of the vibration frequencies and energy levels depends upon the values of the polarization fractions calculated from the spectra of chemisorbed CO. An analysis independent of the spectra of chemisorbed species can be accomplished by determining the "optimum" fraction for a perfect match of the vibration frequencies of the intermedions as shown in the following equation:

$$\begin{array}{ccccc} H_2^{0.544} & + & O^{6.544} & \rightleftarrows & H_2O \\ 1131.83 & & 1133.04 & & \end{array} \tag{21}$$

The "optimum" fractions for a perfect match of the vibration frequencies of the reacting intermedions are presented in Table 1. If the preceding hypotheses are valid, then the optimum fractions for reactions catalyzed by each metal will be constant within the limits of the accuracy of the equations and approximately equal to the polarization fraction determined from the chemisorption of carbon monoxide.

The agreement between theory and calculation is satisfactory, particularly in view of the fact that small differences in the equations of the intermedions will make large differences in the values of the optimum fractions. The fractions seem to be sufficiently constant and to agree with the polarization fractions determined from CO chemisorption to a degree that the differences may be attributed to small errors in the vibration frequencies used in the derivations of the equations. For example, the equation of CO intermedions was derived from the vibration frequencies reported in the literature for $(CO)^{10}$, the neutral molecule, and $(CO)^{9}$, the positive ion. Plyler, Blaine, and Connor (*2*) state the value of $\nu(C\text{–}O)^{10}$ as 2143.274 ± 0.0015 cm^{-1} from precise infrared determinations. The value for $\nu(C\text{–}O)^{9}$ of 2183.90 cm^{-1} is given by Herzberg (*17*) from electronic emission spectra. Techniques are not available at this time to provide as accurate a measurement of the vibration frequency of the positive ion as can be obtained for the neutral molecule. In addition, any error in the value of $\nu(C\text{–}O)^{9}$ is magnified in Eq. (1) by the large value of $dE/d\nu$ in the region of $(CO)^{9}$. Investigations are continuing in this entire area to determine the limit of significance of decimal places in the polarization fractions and the effects of slight differences of vibration frequency between reactants on the rates of reaction.

In addition to the new experimental data presented in Table 1 from infrared studies of the chemisorption of CO on adsorbents containing chromium, platinum, or nickel (*18*), the three fractions, 0.779, 0.798, and 0.809 are tentatively assigned to the group of metals, palladium, iridium, and rhodium. This assignment is based in part on the solutions of the equations for the hydrogenation of acetylene since infrared bands have not been observed that can be designated as CO intermedions on these metals. The following section will describe in detail the solutions to these equations.

Calculation of Optimum Fractions

The calculation of optimum fractions for the reaction of a hydrogen molecule intermedion with an oxygen atom intermedion involves the determination of each fraction for which the ratio of the vibration frequencies (and energy levels) of any pair of the H_2 and O intermedions is equal to 2^n where

TABLE 1
ANALYSES OF CATALYTIC REACTIONS

Reaction		"e" Optimum fraction	Component of catalyst	Polarization fraction from CO chemisorption[a]
$H^{1+e} + (\text{—}OH)^{7+e}$	$\rightleftarrows H_2O$	0.098	Chromium	2203 cm^{-1} $(CO)^{8.11}$
$H_2^{e} + (HC\equiv CH)^{11+e}$	$\rightleftarrows C_2H_4$	0.099		2181 cm^{-1} $(CO)^{9.10}$
$O^{4+e} + (\text{—}CO)^{9+e}$	$\rightleftarrows CO_2$	0.099		2134 cm^{-1} $(CO)^{10.14}$
$(O\text{–}O)^{12+e} + (\text{—}CO)^{9+e}$	$\rightleftarrows CO_3$	0.100		
$H_2^{e} + O^{5+e}$	$\rightleftarrows H_2O$	0.257	Iron	2127 cm^{-1} $(CO)^{10.24}$
$O^{7+e} + (\text{—}CO)^{8+e}$	$\rightleftarrows CO_2$	0.264		1960 cm^{-1} $(CO)^{11.25}$
$O^{6+e} + (O\text{–}H)^{5+e}$	$\rightleftarrows OOH$	0.260		
$H_2^{e} + (C\text{–}O)^{10+e}$	$\rightleftarrows HCOH$	0.256		
$H_2^{e} + O^{6+e}$	$\rightleftarrows H_2O$	0.315	Copper	2121 cm^{-1} $(CO)^{10.32}$
$O^{7+e} + (\text{—}CO)^{11+e}$	$\rightleftarrows CO_2$	0.312		2173 cm^{-1} $(CO)^{9.35}$
$\nu_3(\text{—}OH_2)^{7+e} + (HC\equiv CH)^{11+e}$	$\rightleftarrows CH_3CHO$	0.315		
$H_2^{e} + O^{6+e}$	$\rightleftarrows H_2O$	0.544	Silver	2165 cm^{-1} $(CO)^{9.56}$
$(C\text{–}O)^{8+e} + (\text{—}OH)^{7+e}$	$\rightleftarrows CO_2 + H$	0.539		2099 cm^{-1} $(CO)^{10.55}$
$H_2^{e} + O^{4+e}$	$\rightleftarrows H_2O$	0.630	Cobalt	2160 cm^{-1} $(CO)^{9.68}$
$H^{1+e} + (\text{—}OH)^{7+e}$	$\rightleftarrows H_2O$	0.638		2091 cm^{-1} $(CO)^{10.62}$
$O^{5+e} + (\text{—}CO)^{10+e}$	$\rightleftarrows CO_2$	0.631		
$H_2^{1+e} + (HC\equiv CH)^{8+e}$	$\rightleftarrows C_2H_4$	0.635		
$H_2^{1+e} + (C\text{–}O)^{11+e}$	$\rightleftarrows HCOH$	0.641		
$H^{e} + (\text{—}OH)^{6+e}$	$\rightleftarrows H_2O$	0.779	(Rhodium)	
$O^{7+e} + (\text{—}CO)^{11+e}$	$\rightleftarrows CO_2$	0.772		
$H_2^{e} + (HC\equiv CH)^{11+e}$	$\rightleftarrows C_2H_4$	0.778		
$H_2^{1+e} + O^{6+e}$	$\rightleftarrows H_2O$	0.798	(Iridium)	
$H_2^{e} + (HC\equiv CH)^{10+e}$	$\rightleftarrows C_2H_4$	0.798		
$(O\text{–}O)^{11+e} + (\text{—}CO)^{9+e}$	$\rightleftarrows CO_3$	0.803		
$H_2^{1+e} + (O\text{–}O)^{10+e}$	$\rightleftarrows H_2O_2$	0.811	(Palladium)	
$(O\text{–}O)^{11+e} + (\text{—}CO)^{11+e}$	$\rightleftarrows CO_3$	0.812		
$H_2^{e} + (HC\equiv CH)^{9+e}$	$\rightleftarrows C_2H_4$	0.809		
$H_2^{e} + O^{5+e}$	$\rightleftarrows H_2O$	0.817	Platinum	2063 cm^{-1} $(CO)^{10.82}$
$H^{e} + (\text{—}OH)^{5+e}$	$\rightleftarrows H_2O$	0.816		
$O^{7+e} + (\text{—}CO)^{10+e}$	$\rightleftarrows CO_2$	0.818		
$H_2^{e} + (HC\equiv CH)^{8+e}$	$\rightleftarrows C_2H_4$	0.817		
$H_2^{e} + O^{6+e}$	$\rightleftarrows H_2O$	0.856	Nickel	2058 cm^{-1} $(CO)^{10.85}$
$(O\text{–}O)^{10+e} + (\text{—}CO)^{11+e}$	$\rightleftarrows CO_2$	0.857		1230 cm^{-1} $(CO)^{11.86}$

[a] This column presents the vibration frequencies from CO chemisorption and the corresponding CO intermedions.

n is an integral number. Hydrogen molecule intermedions can have numbers of valence electrons with integers of 0 and 1, i.e., H_2^{e} and H_2^{1+e} where e, the polarization fraction, is different for each metal. On any one metal, four oxygen atom intermedions may be formed with numbers of valence electrons having integers of 4, 5, 6, and 7. The vibration frequencies of the hydrogen molecule intermedions are given by the equation

$$\nu H_2 = 2080.57 E_{H_2} \tag{18}$$

where E_{H_2} equals e and $1 + e$. The energy levels of the oxygen atom intermedions are given by the equation

$$\nu O = 778.19(8 - E_O) \tag{19}$$

where E_0 equals $4 + e$, $5 + e$, $6 + e$, and $7 + e$. If the polarization fraction e of a metal is known, then the vibration frequencies of the two H_2 intermedions and the energy levels of the four 0 intermedions can be calculated and the values compared to determine if any pair composed of one H_2 intermedion and one 0 intermedion have equal energy levels.* As proposed by Myers (*4*) it may be necessary to multiply one of the energy levels by 2, 4, 8, 16 . . . 2^n to bring it to a magnitude that is comparable to the other energy level. As an example, the hydrogenation of acetylene to ethylene catalyzed by platinum may be considered. The polarization fraction of platinum from Table 1 is 0.817, therefore, acetylene and hydrogen molecule intermedions with the following vibration frequencies may exist on platinum or its compounds: $(HC{\equiv}CH)^{8.817}$, 3398.12; $(HC{\equiv}CH)^{9.817}$, 3367.95; $(HC{\equiv}CH)^{10.817}$, 3319.95; $(HC{\equiv}CH)^{11.817}$, 3231.69; $(H_2)^{0.817}$, 1699.83; $(H_2)^{1.817}$, 3780.40. The catalytic reaction is shown in the following equation:

$$\underset{\substack{1699.83\\(3399.66)}}{H_2^{0.817}} + \underset{3398.12}{(HC{\equiv}CH)^{8.817}} \rightleftarrows H_2C = CH_2 \qquad (22)$$

Multiplication of the vibration frequency of the H_2 intermedion by 2 produces a satisfactory match with the vibration frequency of the acetylene intermedion. The opposite example is provided by a test of silver as a catalyst for the same reaction. From Table 1, the polarization fraction of silver is 0.541. Acetylene and hydrogen molecule intermedions with the following vibration frequencies may exist on silver or its compounds: $(HC{\equiv}CH)^{8.541}$, 3404.57; $(HC{\equiv}CH)^{9.541}$, 3377.57; $(HC{\equiv}CH)^{10.541}$, 3335.85; $(HC{\equiv}CH)^{11.541}$, 3262.68; $(H_2)^{0.541}$, 1125.59; $(H_2)^{1.541}$, 3206.16. There is no match of the vibration frequencies nor multiples of 2, 4, 8, etc. of the acetylene and hydrogen molecule intermedions on silver. Therefore, 0.541 is not an optimum fraction for the reaction of acetylene and hydrogen molecule intermedions and silver will not catalyze this reaction of these intermedions in the ground electronic state.

The equations and reactions considered in this paper are limited to intermedions in the ground electronic state since the vibration frequencies used to derive the equations are for molecules, ions, and radicals in this state. Excitation to higher electronic states changes the vibration frequencies and, therefore, changes the equations. Intermedions in excited electronic states could be described by equations, if sufficient accurate data were available.

A "search" for catalysts for a particular reaction is conveniently programmed for a computer. The fraction e is the variable and is incremented from 0 to 1.00. The energy levels of the two reactants are determined for each value of e, for each of the possible intermedions and multiplied by 2, 4, 8, etc. and compared. The answers are "optimum" fractions, i.e., those fractions for which the energy levels of the intermedions are equal. If from independent experimental data the fractions can be related to particular metals, then these metals should catalyze the reaction. There are, of course, many other factors that enter into an actual catalytic reaction, e.g., the metal must be in the appropriate valence state and compound to generate the pairs of intermedions that will react, and the rate and yield will be determined by the temperature, pressure, and thermodynamic properties of the system.

In the example of the reaction of

$$H_2 + O \rightleftarrows H_2O \qquad (7)$$

if the multiplicative factors are limited to 1, 2, 4, and 8, there are 56 equations which can be written of the type:

$$M_1 2080.57(A + e) = M_2 778.19(8 - B - e) \qquad (23)$$

where M_1 and M_2 are the multiplicative factors, i.e., either M_1 or M_2 equals 1 and the other equals 1, 2, 4 or 8; A equals 0 or 1 and B equals 4, 5, 6, or 7. Only 26 of these equations give positive fractions for e. Of these 26 "optimum" fractions, the following 6 have been assigned from analyses of the infrared spectra of chemisorbed CO: Fe 0.257, Cu 0.315, Ag 0.544, Co 0.630, Pt 0.817, and Ni 0.856. Some of the other 20 "optimum" fractions correspond to other metals that also catalyze this reaction by this

---

* It is convenient to use a single term for both "energy level" and "vibration frequency." Energy level seems to be the more general designation.

mechanism. Among these 20 unassigned fractions, there will also be those which do not correspond to any metal. The number of optimum fractions varies greatly from one reaction to another, e.g., there are only four solutions for the reaction:

$$\nu_3(H_2O) + HC{\equiv}CH \rightleftarrows H_2C{=}CHOH \qquad (24)$$

Tentative assignments of the polarization fractions of rhodium, iridium, and palladium are suggested by the optimum fractions for the reaction of a hydrogen molecule intermedion and an acetylene molecule intermedion to form ethylene. When multiplicative factors of 1 and 2 are used, there are 8 optimum fractions of which 2 have been assigned to metals from infrared studies of chemisorbed carbon monoxide. The 8 fractions with the assigned metals are: 0.567, 0.602, 0.622, 0.635 Co; 0.778, 0.798, 0.809, and 0.817 Pt. In addition to cobalt and platinum, three metals that are known to be good catalysts for the hydrogenation of acetylene are rhodium, iridium, and palladium (*19*, *20*). In view of the close similarities of these metals of the platinum group, it seems likely that the fractions 0.778, 0.798, and 0.809 correspond to these three metals. It will be difficult to assign these fractions to the individual metals from the spectra of chemisorbed CO. The vibration frequencies for the CO intermedions with these fractions and integers of 10 differ in vibration frequency by only 4 cm^{-1}, i.e., $(CO)^{10.78} = 2068$ and $(CO)^{10.81} = 2064$. However, the individual assignments are suggested by the reactions presented in Table 1.

Of the three fractions, only 0.798 is a solution of the reaction:

$$H_2 + O \rightleftarrows H_2O \qquad (7)$$

Iridium is the one of these three metals that readily catalyzes the formation of water from hydrogen and oxygen. Hofmann (*21*) describes iridium as "the ideal detonating-gas catalyst." Iridium is, therefore, tentatively assigned the fraction 0.798.

The high activity of palladium as a catalyst for the formation of hydrogen beroxide is attributed by Pospelova and Kopozev (*22*) to the catalysis of the direct synthesis from hydrogen and oxygen while maintaining the O—O bond. The fraction 0.811 is the only solution to the equations for the addition of a hydrogen molecule intermedion across an oxygen molecule intermedion that can be related at this time to a specific metal. In addition, although palladium will catalyze the formation of water from hydrogen and oxygen, it has been demonstrated to selectively oxidize low concentrations of carbon monoxide in hydrogen (*23*). This reaction is used commercially to remove trace quantities of carbon monoxide from ammonia synthesis gas. Since the fraction 0.811 is an optimum fraction for the equations for the reaction of oxygen molecule and carbon monoxide intermedions to oxidize carbon monoxide, an optimum fraction for the synthesis of hydrogen peroxide, and an optimum fraction for the hydrogenation of acetylene, it is tentatively assigned to palladium. The third fraction, 0.778, is assigned to rhodium. Additional evidence will be required to support these tentative assignments.

Homogeneous and Heterogeneous Catalysis

The numerical analyses of reactions provides a means for determining which reactions may be catalyzed by a dissolved salt of the appropriate metal, i.e., in a homogeneous system, and establishes the relationship between heterogeneous and homogeneous catalytic reactions. Eqs. (2) and (4) above indicate that the formation of intermedions on the higher oxidation state (or "ic" state) of the metal can occur either by the donation of $2 - e$ electrons, e.g., $2 - 0.32 = 1.68$ for copper, Eq. (2), or by the acceptance of e electrons, Eq. (4), by the adsorbate. The lower oxidation state (or "ous" state) forms intermedions by the donation of $1 - e$ electrons, Eq. (3), or by the acceptance of $1 + e$ electrons, Eq. (5), by the adsorbate. It is proposed that if a single complexed atom of the metal possesses a delocalized orbital, then it should be able to bond the donor and acceptor pair of intermedions that can exist on the same oxidation state. For example, in Table 1, the oxygen and hydroxyl intermedions with matching energy levels on iron are O^{6+e} and $(OH)^{5+e}$. The neutral oxygen atom has six valence electrons; an O^{6+e} has accepted e. The neutral hydroxyl diatomic molecule has seven valence electrons; an $(OH)^{5+e}$ has donated $2 - e$ electrons. The acceptance of e and donation of $2 - e$ are the electron exchanges that can occur on the "ic" state. Therefore, as is observed experimentally, ferric ion catalyzes the homogeneous decomposition of peroxide. While, on this basis, the reaction

$$H_2 + CO \rightleftarrows HCOH \qquad (6)$$

on iron should also be a homogeneous reaction catalyzed by complexed ferric ion, it is not reported in the literature. The equilibrium is undoubtedly shifted far to the left since HCOH is an unstable intermediate incapable of more than fleeting existence when separated from the adsorbent or catalyst. This is an example of a reaction that does not occur in a homogeneous system because of the thermodynamic instability of the product. In a heterogeneous system, further reactions of HCOH with CO and/or H_2 lead to stable products.

The formation of water catalyzed by copper corresponds to the donation of $2 - e$ electrons by H_2 and the acceptance of e electrons by O. This reaction is observed to be catalyzed by aqueous solutions of cupric salts. Accordingly, from the observations by Cunningham and Gwathmey, it appears that the (111) lattice plane of copper becomes a "cupric" lattice face (perhaps by epitaxial oxidation) and is the site of residence of both H_2^e and O^{6+e} intermedions at these experimental conditions. The hydration of acetylene to vinyl alcohol which tautomerizes to acetaldehyde is indicated in Table 1 to proceed on copper by the formation of an $(H_2O)^{7+e}$ intermedion by the donation of $1 - e$ electrons and an $(HC{\equiv}CH)^{11+e}$ intermedion by the acceptance of $1 + e$ electrons. This electron exchange corresponds to the cuprous state and cuprous copper is observed to catalyze the homogeneous hydration of acetylene (*14*).

Both of the reactions in Table 1 catalyzed by silver require the "ic" state; in each, the electron exchanges are e and $2 - e$. Both reactions are observed to be catalyzed by homogeneous solutions of silver salts. If the fraction 0.798 corresponds to iridium, then iridium in the higher oxidation state should catalyze the hydrogenation of acetylene in a homogeneous system. The formation of water from H_2 and O catalyzed by nickel requires the "ic" state. McDuffie *et al.* (*12*), did not observe the catalysis of this reaction by nickel salts in aqueous solution. However, they may have had the lower valence state, since they took no precautions to test all oxidation states of the metals.

The foregoing discussion indicates a fundamental difference between heterogeneous and homogeneous catalytic reactions. When the catalyst is a solid, more than one oxidation state of the metal may be present on adjacent lattice faces. Reactions may take place on the lattice face, edge, or corner where the intermedions with matching energy-levels meet. This may result in several reaction paths or mechanisms for a single product and several products when more than one is possible. In homogeneous systems, when a single dissolved complexed metal ion acts as a single catalytic site, only the specific pair of intermedions is formed and the selectivity of the reaction may be 100%. The homogeneous catalyst is observed to function as a simple electron exchange site, accepting electrons from one reactant and donating to the other, forming intermedions with matching energy levels.

Periodicity of the Polarization Fraction

The foregoing discussion has presented the hypothesis that the polarization fractions are characteristic constants for, at least, these several metals. The possibility that the polarization fractions may be related to fundamental properties of metals is indicated by the comparison of the polarization fractions and the atomic numbers of the metals presented in Table 2. Those polarization fractions which have been tentatively assigned from known reactions are included in Table 2.

A limited periodic relationship seems to exist between the polarization fractions and

TABLE 2

POLARIZATION FRACTIONS AND ATOMIC NUMBERS

24	25	26	27	28	29
Cr	Mn	Fe	Co	Ni	Cu
0.099		0.257	0.635	0.856	0.315
			45	46	47
			Rh	Pd	Ag
			0.778	0.810	0.544
			77	78	
			Ir	Pt	
			0.798	0.817	

the atomic numbers of these metals. The fractions increase from chromium to nickel and, with the exception of nickel, increase with atomic number within the groups. The narrow range of the fractions for Rh, Ir, Pd, and Pt, 0.039 electrons, is consistent with the qualitative similarity of their behavior as catalysts. However, as indicated in the preceding discussion, there are sufficient differences in the catalytic activity of these metals to enable distinctions to be made. Frequently, these differences are magnified at reaction conditions of low conversion and low temperature, e.g., the selective oxidation of low concentrations of CO in H_2 streams catalyzed by Pd takes place in the temperature range of 100°C. At elevated temperatures, this selectivity is lost. In addition to the continuing experimental efforts to obtain the polarization fractions of other metals, attempts are under way to establish a fundamental interpretation of this fraction on the basis of current theories of the metallic state.

Derivations of Equations of Intermedions

The mathematical functions which relate the vibration frequencies (or energy levels) and the number of valence electrons of intermedions are of only two types; the straight line and the hyperbola. The equations for atomic intermedions are straight lines and the equations for diatomic intermedions are hyperbolas except for the H_2 intermedion. The curvature of the equations for diatomic intermedions results from changes in the bond order and/or changes in the relative distribution of electrons between two unlike nuclei as electrons are added or removed. Changes in bond order are changes in the number of molecular orbitals which contribute to the bond. Such changes cannot occur with the H_2 intermedion since the $1\sigma g$ molecular orbital is the only bonding orbital available (in the electronic ground state). The relative distribution of electrons between the two protons cannot change since H_2 is a homodiatomic molecule. Therefore, the equation which describes H_2 intermedions is a straight line, while the equations for all other diatomic molecules are hyperbolas. The general method used for the derivation of the equations of atomic intermedions is based on the following relationship between the equations for hydrogen molecule and hydrogen atom intermedions.

Hydrogen atom and molecule intermedions. The vibration frequency of the hydrogen molecule, H_2, represents its electron donor capacity. As electrons are removed, the vibration frequency decreases, becoming zero for 2 protons. The equation for hydrogen molecule intermedions is the straight line defined by the points $\nu H_2{}^2 = 4161.14$ cm^{-1} (*24*) and $\nu H_2{}^0 = 0.0$, viz., Eq. (18). The hydrogen atom with one valence electron is also an electron donor, with its energy level decreasing as electrons are removed, becoming zero for the proton. It is proposed that the donor capacity of a hydrogen atom, a proton and one electron, is equal to the donor capacity of a hydrogen molecule, two protons with two electrons:

$$\nu H = \nu H_2{}^2 = 4161.14 \qquad (25)$$

The equation for hydrogen atom intermedions is the straight line defined by the points $\nu H^1 = 4161.14$ cm^{-1} and $\nu H^0 = 0.0$, viz., Eq. (17).

Oxygen atom intermedions. The derivation of the equation for oxygen atom intermedions is similar to the preceding derivation for hydrogen atom intermedions. The ground state vibration frequency (*25*) of the oxygen molecule (O_2) with 12 valence electrons is 1556.38 cm^{-2}. Since this vibration frequency represents a measurement of the electron acceptor ability of the neutral oxygen molecule, it is proposed that one oxygen atom with 6 valence electrons will have the same electron acceptor capacity or energy level:

$$\nu O^6 = \nu O_2^{12} = 1556.38 \qquad (26)$$

The addition of electrons to the oxygen atom should decrease its electron acceptor capacity and "energy level" until both reach zero at the electron saturated O^{2-} ion.

The equation for oxygen atom intermedions is the straight line defined by the points $\nu O^6 = 1556.38$ cm^{-1} and $\nu O^8 = 0.0$, viz., Eq. (19).

The derivation of Eq. (10) to describe the "energy level" of CO intermedions requires the evaluation of k in Eq. (9). As electrons are removed from CO, the vibration frequency ν(C—O), bond order, and electron acceptor capacity increase. It is proposed that the limit is $(CO)^8$. If more than 2 electrons are removed from the neutral CO molecule, it is thought that the C to O bond is weakened and Eq. (1) is no longer applicable; ν(—CO) decreases as electrons are removed becoming zero at $(CO)^8$. Therefore,

$$k_{CO} = \nu(\text{C–O})^8 = 2204.81 \text{ cm}^{-1} \qquad (27)$$

Oxygen molecule intermedions. The equation for oxygen molecule intermedions is derived similarly to the equation for carbon monoxide intermedions. The vibration frequencies of the neutral O_2 molecule, 12 valence electrons, and the positive ion, 11 valence electrons, are 1556.38 and 1843.34 cm^{-1} (*26*), respectively. It is proposed that the O_2 intermedion with 14 valence electrons (the double negative ion) dissociates. The equation for oxygen molecule intermedions is the right hyperbola defined by the points $\nu O_2^{11} = 1843.34$ cm^{-1}, $\nu O_2^{12} = 1556.38$ and $\nu O_2^{14} = 0.0$, viz., Eq. (16).

OH intermedions. The vibration frequency of (O–H) corresponds to an electron donor capacity since it decreases as electrons are removed. The form of the relationship between the vibration frequencies of OH intermedions, ν(O–H), and the number of valence electrons, E(OH), is hypothesized to be the hyperbola (Curve A) shown in Fig. 1. In addition to the single point shown, two other points are necessary to define Curve A.

A second curve can be proposed to represent the energy levels of the OH species as a function of the number of valence electrons, i.e., ν(—OH) vs. E(OH) (Curve B). It is assumed that the energy level of the electron-saturated $(OH)^8$ equals zero. The sum of these two, viz., ν(—OH) and ν(O–H) is a constant and the two functions are related by the following equation:

$$\nu(\text{O–H})^m + \nu(\text{—OH})^m = \nu(\text{O–H})^8 \qquad (28)$$

where m may be an integral or nonintegral number. The third curve necessary is ν(O) vs. E(O) from Eq. (19). These relationships are indicated in Fig. 1. When electrons are removed from the OH intermedion, Curve A decreases and becomes zero at an integral number of electrons. If the hypothesis is made that the OH intermedion decomposes to form a positive oxygen atom intermedion and a proton at Point 1, then the oxygen atom intermedion formed by the decomposition is now described by a point (Point 2) on Curve C. It is identical in number of electrons with one of the oxygen atom intermedions on Curve C possessing an

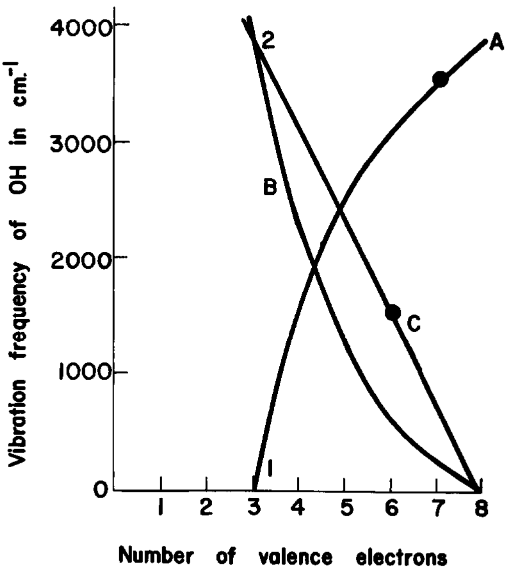


FIG. 1. Suggested curves characterizing OH intermedions. Curve A is ν(O—H) vs. E(OH); B is ν(—OH) vs. E(OH); C is ν vs. E(O).

integral number of electrons. Further, since

$$\nu(\text{O–H})^m + \nu(\text{—OH})^m = \nu(\text{O–H})^8 \quad (28)$$

and letting the number of electrons at decomposition equal n, where n is an integral number, we may write

$$\nu(\text{O–H})^n = 0.0 \text{ (Point 1)} \quad (29)$$

and

$$\nu(\text{—OH})^n = \nu(\text{O–H})^8 = \nu\text{O}^n \text{ (Point 2)} \quad (30)$$

That is, the integral number of electrons possessed by the OH intermedion at decomposition is equal to the number of electrons possessed by one of the oxygen ions. The appropriate value of n can be chosen on the bases of the above-mentioned requirements, viz., (1) the curvature of $\nu(\text{O–H})$ vs. $E(\text{OH})$ must be positive with increasing $E(\text{OH})$ and (2) since $\nu\text{O}^n = \nu(\text{O–H})^8$ and $\nu(\text{O–H})^8$ must be greater than $\nu(\text{O–H})^7$, νO^n must be greater than 3569.59 cm^{-1}. The value $n = 3$ satisfies both of these requirements. The three vibration frequencies and number of electrons used to establish the hyperbola for OH intermedions are:

$$\nu(\text{O–H})^8 = 3890.95 \text{ cm}^{-1},\ \nu(\text{O–H})^7 = 3569.59 \text{ cm}^{-1}, \text{ and } \nu(\text{O–H})^3 = 0.0$$

The equations characterizing OH intermedions are Eqs. (11) and (12).

Water intermedions. The water molecule has three normal vibration modes. The frequencies of these vibrations for the neutral water molecule $(H_2O)^8$ are: $\nu_1 = 3656.65$, $\nu_2 = 1594.78$, and $\nu_3 = 3755.79$ cm^{-1} (*27*). A second point on each hyperbola of the three normal modes is the point of dissociation of the water intermedion at three valence electrons. In the absence of published data of the vibration frequencies of H_2O ions, it was necessary to derive a third constraint for the equations of H_2O intermedions. The hyperbolas for OH and H_2O intermedions describe the energy levels and vibration frequencies of O to H bonds as functions of the number of valence electrons. It was assumed that these four equations differ by a translation of the axes while maintaining a constant curvature, k, equal to k_{OH}. The equations of the hyperbolas of the three normal modes of H_2O are:

$$[\nu_1(H_2O) - 5810.14][E(H_2O) - 0.0552] = -17109.7 \quad (31)$$

$$[\nu_2(H_2O) - 3265.83][E(H_2O) + 2.2390] = -17109.7 \quad (32)$$

and Eq. (13).

Acetylene intermedions. The equation of the vibration frequency of acetylene intermedions was derived on the bases that chromium and platinum catalyze the hydrogenation by the addition of a hydrogen molecule intermedion and that the vibration frequency of the C to C bond of acetylene decreases with the addition of electrons, becoming zero at 14 valence electrons. Values of 0.0991 and 0.8167 were used for the polarization fractions of chromium and platinum, respectively. The hydrogen molecule intermedions and the corresponding acetylene intermedions with matching vibration frequencies are shown in the following two equations:

$$\underset{\substack{206.19\\(3299.04)}}{H_2{}^{0.0991}} + \underset{3299.04}{(\text{HC}{\equiv}\text{CH})^{11.0991}} \rightleftarrows C_2H_4 \quad (33)$$

$$\underset{\substack{1699.20\\(3398.40)}}{H_2{}^{0.8167}} + \underset{3398.40}{(\text{HC}{\equiv}\text{CH})^{8.8167}} \rightleftarrows C_2H_4 \quad (34)$$

The hyperbola relating vibration frequency and number of valence electrons for the C–C bond of acetylene intermedions is Eq. (15).

III. SUMMARY

The foregoing discussion has presented the development of empirical relationships leading to quantitative mathematical interpretations of many diverse catalytic reactions. The simplicity of the functions—the straight line and the right hyperbola—and the wide variety of reactions that are correlated on these bases imply that more fundamental relationships precede the hypotheses presented. It was necessary to propose the several new concepts in order to generate the relationships to test the applicability of "intermedions," "the polarization fraction," and "the Myers hypothesis" to the interpretation of catalytic reactions. The delineation of steps of the reaction mechanisms, the designation of homogeneous catalysis as a "restricted" area of heterogeneous catalysis, the determination of the valence state of the catalytic metal, and the indication of a periodicity of the polarization fraction support the hypotheses and, at the same time, demonstrate the need for further exploration in these areas.

ACKNOWLEDGMENT

The author wishes to acknowledge the advice and assistance to Dr. H. A. Strecker, Dr. R. H. Petrucci, and Mrs. R. Krizan in this study, and to thank the Standard Oil Company (Ohio) for permission to publish this work.

REFERENCES

1. GARDNER, R. A., AND PETRUCCI, R. H., *J. Phys. Chem.* **67**, 1376 (1963).

2. PLYLER, E. K., BLAINE, L. R., AND CONNOR, W. S., *J. Opt. Soc.* **45**, 102 (1955).

3. EISCHENS, R. P., AND PLISKIN, W. A., *Advan. in Catalysis* **10**, 20 (1958).

4. MYERS, R. R., *Ann. N. Y. Acad. Sci.* **72**, 341 (1958).

5. MEELHEIM, R. Y., CUNNINGHAM, R. E., LAWLESS, K. R., AZIM, S., KEAN, R. H., AND GWATHMEY, A. T., *in* "Proc. 2nd Intern. Congr. on Catalysis, Paris, 1960," Vol. 2, pp. 2005–19. Éditions Technip, Paris, 1961.

6. HERZBERG, G., "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules," 2nd ed., p. 560. D. Van Nostrand, Princeton, New Jersey, 1955.

7. LITTLE, L. H., AND AMBERG, C. H., *Can. J. Chem.* **40**, 1997 (1962).

8. JARNAGIN, R. C., AND WANG, J. H., *J. Am. Chem. Soc.* **80**, 6477 (1958).

9. KOEFOED, J., *Acta. Chem. Scand.* **9**, 283 (1955).

10. KUMMER, J. T., AND EMMETT, P. H., *J. Am. Chem. Soc.* **75**, 5177 (1953).

11. STORCH, H. H., GOLUMBIC, N., AND ANDERSON, R. R., "The Fischer-Tropsch and Related Syntheses," p. 592. Wiley, New York, 1951.

12. McDUFFIE, H. F., COMPERE, E. L., STONE, H. H., WOO, L. F., AND SECOY, C. H., *J. Phys. Chem.* **62**, 1030 (1958).

13. RITCHEY, W. M., AND CALVERT, J. G., *J. Phys. Chem.* **60**, 1456 (1956).

14. MILLER, S. A., *Chem. and Ind.*, p. 12 (Jan. 5, 1963).

15. NAKAMURA, S., AND HALPERN, J., *J. Am. Chem. Soc.* **83**, 4102 (1961).

16. COURTOIS, M., AND TEICHNER, S. J., *J. Catalysis* **1**, 121 (1962).

17. HERZBERG, G., *loc. cit.*, p. 522.

18. GARDNER, R. A., *J. Catalysis* **3**, 22–24 (1964).

19. BOND, G. C., "Catalysis by Metals," p. 297. Academic Press, New York, 1962.

20. BOND, G. C., DOWDEN, D. A., AND MACKENZIE, N., *Trans. Faraday Soc.* **54**, 1537 (1958).

21. HOFMANN, K. A., *Ber. Deut. Chem. Ges.* **56B**, 1165 (1923).

22. POSPELOVA, T. A., AND KOBOZEV, N. I., *Zhur. Fiz. Khim.* **35**, 535 (1961).

23. MARS, P., AND VAN DE MOND, TH., *Nature* **191**, 1003 (1961).

24. HERZBERG, G., AND HOWE, L. L., *Can. J. Phys.* **37**, 636 (1959).

25. BABCOCK, H. D., AND HERZBERG, L., *Astrophys. J.* **108**, 167 (1961).

26. HERZBERG, G., *loc. cit.*, p. 560.

27. KHACHKURUZOV, G. A., *Optics and Spectroscopy* **6**, 294 (1959).