



Unified explanation of catalyzed and non-catalyzed chemical reactions

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Abstract

A right hyperbola, specific for each molecule, is used to convert vibrational frequencies from infrared spectra into numbers of electrons. This conversion greatly increases the information to be obtained from spectra and has led to the discovery of a third type of interaction of a gas with a solid surface, neither physical nor chemical adsorption. This discovery along with the Myers' Hypothesis that a synchronization of the vibrational frequencies of reactants would facilitate reaction has led to 14 publications in catalysis. Combining the hyperbolas, one from each reactant provides a quantitative interpretation of catalysis by specifying the catalytic metal, its numerical oxidation state, the mechanism of the reaction and the necessary structure of the catalyst, heterogeneous or homogeneous (enzyme). Ions that have low-lying electronic states, below 4000 cm^{-1} , in the Atomic Energy Levels (AELs) tables from NIST produce an electric field, which serves as a site for catalysis. The electric field at the catalyst affects the reactants as if electron density has been added or removed. For homogeneous or enzyme catalysis both reactants are altered the same way. In the case of heterogeneous catalysis both reactants may be altered the same way or one reactant may be altered as if it has gained and the other as if it has lost electron density. Reactants in non-catalyzed reactions are positive and negative ions generated by solution in ionic solvents or generated by increases in temperature.

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1. Introduction

In the past, circa 1950, researchers wrote papers describing experiments in catalysis. Although these studies were very scientifically performed, measured, and reported, they seemed at that time to be anecdotal. The results that one investigator obtained bore little or no relation to the study reported by the next person. This situation seemed to reflect some lack of knowledge of the field of catalysis. A study based on

principles different from those that others were using might be more fruitful.

Investigators in the field of heterogeneous catalysis had decided that physical adsorption was inappropriate as a significant contributor to catalysis because it is a very weak reaction, such as, steam condensing on a mirror and thus could not produce the large changes in reactivity observed in catalysis. Thus, they were left with the only other interaction known at that time between a gas and the surface of a solid, chemical adsorption, that is, the formation of a chemical bond attaching the gaseous molecule to an atom embedded in the surface of the solid. Therefore, when using the Eischens and Pliskin [1] infrared spectroscopic technique,

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after exposing their catalyst sample to the subject gas, most investigators thoroughly evacuated the catalyst to remove any bands due to physisorbed species and then proceeded to study the chemisorbed species.

In an effort to not follow the path of others, attention was paid to all bands in the spectra, whether produced by species that were readily removed by evacuation or that were strongly attached to the surface of the catalyst. A trace of gas was added to the cell, four spectra were run with each addition of successively larger amounts until bands due to gaseous species appeared. Then successive evacuations were performed with multiple spectra at each step.

During this study of adsorption by infrared spectroscopy, five bands were observed from carbon monoxide, CO, on catalysts containing copper oxide and on cobalt that could not be classified as neither chemisorbed nor physisorbed, but could only be considered to be both at once. These bands were immediately removed by evacuation of the adsorbing gas as if physisorbed but showed large changes in frequency from gaseous CO as if chemisorbed. Adding CO gas to the in situ cell caused the reappearance of these bands and evacuation removed them. A change in frequency indicates a change in energy and should be related to a corresponding change in reactivity. "This third type of interaction of a gas with the surface of a solid, neither physisorption nor chemisorption, but something that appeared to have properties of both, would seem to be exactly that which is necessary for catalysis". The reactants can contact the catalyst, be altered, react, and leave immediately at rates as great as the 30 million reactions per second estimated for the enzyme carbonic anhydrase.

The discovery of the third type of interaction of a gas with the surface of a solid was combined with the Myers' [2] Hypothesis, namely, that a matching or synchronization of the vibrational frequencies of reactants would facilitate their reaction. This union led to the following descriptions of heterogeneous catalysis with the special conditions for the subsets of homogeneous or enzyme catalysis and non-catalyzed reactions.

2. Background

Eischens [1] pioneered in the study, by infrared spectroscopy, of the interaction of molecules from

the gas phase with the surfaces of solids. Using the Eischens' technique infrared spectra were obtained of CO in contact with copper oxide and with cobalt supported on Cab-o-sil, a high surface area silica aerogel Gardner and Petrucci [3]. Spectral bands at 2173, 2127, 2000 and 1932 cm^{-1} on copper oxide and 2179, 2160 and 2091 cm^{-1} on cobalt were removed by evacuation of the gas and reappeared upon readmission of gas at room temperature. A re-examination of CO on copper oxide with a grating spectrometer, which was more accurate than the original prism instrument, showed the band at 2127 to be at 2121 cm^{-1} . Because these spectral bands were readily removed by evacuation, other investigators may have considered these to be physisorbed species and thus unimportant in catalysis. However, the critical temperature, the temperature above which a gas cannot be liquefied, of CO is -136°C . This temperature is much too far below room temperature for any phenomenon analogous to physisorption to be observed in these experiments. Therefore, bands that were readily removed by evacuation were attributed to CO on the surface in a *gas-like state*. Thus, the frequencies of these bands should bear some relationship to the vibrational frequencies of gaseous species of carbon monoxide. The measured vibrational frequencies of species of gaseous carbon monoxide, published by Herzberg [4], are the gaseous neutral molecule at 2143.27 and the gaseous unipositive ion at 2183.90 cm^{-1} .

A theoretical mechanism of chemisorption proposed by Wolkenstein [5], suggests that the number of electrons assigned to the surface carbon monoxide species noted above might be at one-electron intervals. As is illustrated in Fig. 1, Wolkenstein, viewed the interaction of a hydrogen atom with an ionic surface, such as sodium chloride, as initially forming a one-electron bond between the proton and a sodium ion at the surface as shown in Fig. 1B. He considered this configuration, namely two positive centers held together by a single electron, as similar to that found in the positive hydrogen molecule ion, H_2^+ . Wolkenstein suggested that this site might be a trap for free electrons or holes in the solid. If another electron becomes localized at this site, an electron pair bond is formed as shown in Fig. 1C. If a hole migrates to this site, that is, a chlorine atom at the surface, the electron from the hydrogen atom would be lost to the surface to form a chloride ion and an

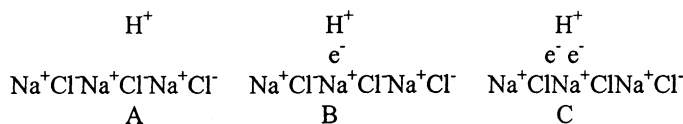


Fig. 1. Representation of Wolkenstein's mechanism of adsorption of a hydrogen atom on an ionic surface.

ionic bond would be formed between the positive proton and the negative chloride ion as shown in Fig. 1A. The numbers of electrons associated with the proton are 0, 1 and 2 in the three configurations, respectively.

The ionic bond and the one and two-electron bonds in Wolkenstein's mechanism were not considered applicable to this study since all of the species that are important in this study are in a gas-like state. The only information taken from Wolkenstein's mechanism of adsorption was that these surface species might differ by one electron from each other. It was on this basis alone that the following relationship was established between the gaseous species of CO from Herzberg and the surface species that were readily removed by evacuation Gardner and Petrucci [6]. Since the frequency of 2173 cm^{-1} is between 2143.27 cm^{-1} , the frequency of the neutral CO molecule with 10 electrons and 2183.90 cm^{-1} , the frequency of the unipositive ion with 9 electrons, 2173 cm^{-1} corresponds to $(9 + x)$ valence electrons where 'x' is a fraction. "The concept of non-integral numbers of electrons throughout the following discussion does *not* mean that electrons are fractionated but simply that some phenomenon is

occurring that gives the appearance of a fraction of electrons, such as, partial ionic character". Continuing by analogy with the example proposed by Wolkenstein, the band at 2121 cm^{-1} corresponds to $(10 + x)$ and one of the bands at 2000 and 1932 cm^{-1} corresponds to $(11 + x)$ valence electrons. The bands on cobalt at 2160 and 2091 cm^{-1} correspond to $(9 + y)$ and $(10 + y)$ valence electrons, respectively, with the 'y' of cobalt being different from the 'x' of copper. On the following graph, Fig. 1, of vibrational frequency ' ν ' in cm^{-1} , as a function of the number of valence electrons ' η ', the two gaseous carbon monoxides from Herzberg and the five surface carbon monoxide species (at one electron intervals) formed the curve Gardner and Petrucci [6] in Fig. 2. This curve appears to be a section of a right hyperbola, of the form,

$$(\nu_{\text{CO}} - V)(\eta_{\text{CO}} - N) = k \quad (1)$$

wherein the constants 'V' and 'N' are asymptotes and 'k' is the curvature.

The next step is to derive the equation of the curve in Fig. 2. Three data points are needed to define the three constants in Eq. (1). Only Herzberg's two data points,

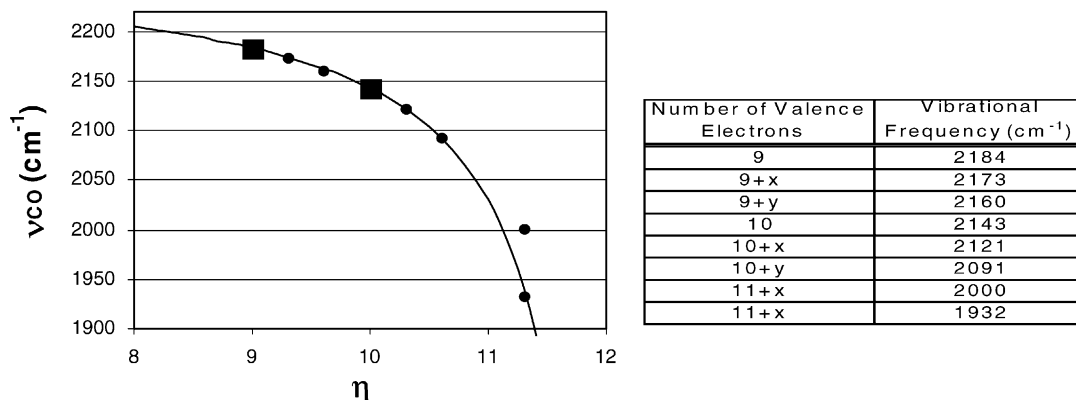


Fig. 2. Graph of vibrational frequency of CO vs. number of valence electrons constructed from experimental data.

2143.27 and 2183.90 cm^{-1} , accurate to six significant figures could be found in the literature. Fig. 1 indicates that the vibrational frequency of CO decreases as electrons are added to the positive ion. The only other point at which the frequency is known to 6 significant figures is the point of dissociation; at this point the vibrational frequency is zero. Dissociation must occur at an *integral* number of electrons since electrons cannot be fractionated. This point required an extraordinarily long extrapolation from 2200 and 2000 to 0.00. Since the curve in Fig. 2 is already past 11 electrons, a value of 12 was used for a first trial. Eq. (2) was derived from the three frequencies, 2183.90, 2143.27 and 0.00 cm^{-1} at 9, 10 and 12 valence electrons, respectively.

$$(\nu_{\text{CO}} - 2269.96)(\eta_{\text{CO}} - 12.1182) = 268.309 \quad (2)$$

Testing Eq. (2) with data from CO in contact with copper oxide and cobalt gave the following numbers of electrons for the IR bands: (9.35, 2173); (10.32, 2121); (11.12, 2000) and (11.32, 1932) for copper oxide and (9.17, 2179); (9.68, 2160) and (10.62, 2091) for cobalt. Without the bands at 2000 on copper and 2179 on cobalt, that obviously did not fit the pattern proposed by Wolkenstein, the presence of different integers but a constant fraction showed a precision within 0.06 of an electron for the other five bands. At that time, these results were considered to be more than sufficient to encourage gathering additional data from the literature on IR spectra of CO in contact with various surfaces.

It was not always obvious from the descriptions of others whether the spectra were obtained before evacuation or after. Thus, some data may be due to chemisorbed species and therefore not expected to fit the pattern. Equations similar to Eq. (2) for CO were derived from literature and experimental values for the three normal modes of vibration of carbon dioxide, CO_2 [7]. These data for CO_2 are included in the lists below because, despite different integers, they show the same fractions as CO. Bands due to CO_2 are distinguished by asterisks for the three normal modes and by integers of 16 and 17. Bands from CO and CO_2 observed by other investigators on the following surfaces are:

2127, 2020 and 1960; Fe and Fe oxide; Eischens and Pliskin [8];

2165 and 2099; Ag and Ag oxide; Huber et al. [9] and Gardner and Petrucci [6];
2203, 2184 and 2134; Cr oxide; Gardner [10];
2188, 2058, 1965, 1230 and 1635***; Ni and Ni oxide; Eischens and Pliskin [11], Little and Amberg [12], Pickering and Eckstrom [13], O'Neill and Yates [14], Filimonov [15];
2174 and 2198***; zinc oxide; Taylor and Amberg [16];
2288***, 1379***, 658.3*, 657.2*, 630.9*, 630.9*;
NaCl; Kozirovsky and Folman [17];
2146, 2074 and 2040; Ru and Ru oxide; Abhivantanaporn and Gardner [18];
1807***, 356** and 850*; gold; Huber et al. [19].

Very little analysis or interpretation can be made of these data, no more than that some bands are above or below the data from Herzberg of 2183.90 for the positive CO ion and 2143.27 for the neutral CO molecule and below the three normal modes of gaseous CO_2 at: $\nu_1(1336.9)$, $\nu_2(667.3)$, $\nu_3(2349.3)$ cm^{-1} . When the spectral bands are translated by Eq. (2) for CO and the corresponding equations for CO_2 , into numbers of electrons, the same pattern observed for the data of CO on copper oxide and on cobalt becomes evident, namely, two or more bands on each metal corresponding to different integers but a constant fraction.

Applying Eq. (2) to these data gives;
10.24, 11.04 and 11.25; Fe and Fe oxide;
9.56 and 10.55; Ag and Ag oxide;
8.11, 9.10 and 10.14; Cr oxide;
8.84, 10.85, 11.25;
11.86 and 17.86; Ni and Ni oxide;
9.32 and 17.34; zinc oxide;
16.89, 17.91, 17.896, 17.899, 17.904 and 17.904;
NaCl;
9.94 and 10.94; Ru and Ru oxide;
17.80, 17.79 and 17.82; gold.

The precision within 0.04 electrons of all of these fractions is a tribute to the experimental accuracy of these scientists who had no idea that their data would be used in this manner as well as substantial support for the validity of Eq. (2), the right hyperbola relating vibrational frequency as a function of the number of electrons on CO and the similar equations for CO_2 .

One of the two data that is particularly important is the band on chromium at 2203 corresponding to

8.11 electrons. This band gives support to Eq. (2) to within 0.11 electrons of the double positive CO ion. The other band of extra significance is at 1230 cm^{-1} for CO on nickel oxide corresponding to 11.86 electrons in agreement with 8.84 and 10.85 for CO and 17.86 for CO₂. This datum for CO supports Eq. (2) to within 0.14 electrons of 12, the number of electrons chosen to correspond to dissociation of CO into negative ions. (Dissociation at the -2 ion is observed in equations representing vibrational frequency versus number of electrons for several other molecules, namely, Cl₂, N₂, O₂, CO₂, C₂H₂, HCN, and NO). The data for CO₂ on sodium chloride suggests that the molecule may be rotating. A more complete analysis of CO₂ is given in the paper by Gardner [7]. Up to this point these fractions have been observed but not yet explained.

Selover [20], a long-time friend, had done a considerable amount of research that involved use of the Atomic Energy Levels (AELs) tables [21] published by the National Bureau of Standards, presently the National Institute of Standards and Technology (NIST). These tables list the energy that must be supplied to make an electron jump from the ground state in an atom or ion to the first available higher level, then to the next, etc. in terms of wave numbers. When asked where electrons might be found, the AEL tables were suggested [22]. The element, chromium, that is, the neutral chromium atom, I Cr was first chosen. Since these are tables prepared by physicists, their notation places the Roman numeral indicating the ionization state in front of the atomic symbol. For each atom or ion, the energy of the ground state is always zero. Values are also given of ' J ' where ' $2J + 1$ ' is the multiplicity of each level as shown in the excerpt from the AEL tables (Table 1).

Seeing the four low-lying levels in the double positive ion lead to the following suggestion, "an electron spending a fraction of time in these levels would look like a fraction of an electron." This would create an electric field with a fractional charge. Here, was the answer that explained the presence of the characteristic fractions observed from the spectra of CO on various metals. The phenomenon of catalysis immediately became obvious. Each metal and oxidation state that can function as a catalyst has a different set of low-lying levels. The appropriate catalyst has the particular set of levels that will create the proper field

Table 1
Excerpts from Atomic Energy Levels of chromium

J	E (cm ⁻¹)
Atom I Cr	
3	0.00
2	7593.16
0	7750.78
Positive ion II Cr	
5/2	0.00
1/2	11962.00
3/2	12032.72
5/2	12148.00
Double positive ion III Cr	
0	0.00
1	62.22
2	183.16
3	356.55
4	576.08
0	16771.36
1	17168.56
2	17851.18

to change reactants that do not match into reactants that match to satisfy the Myers Hypothesis. Tables 1 and 2 tie catalysis to the most fundamental property, namely, the energy of the electrons of the catalyst. This explains the 30 million reactions per second estimated for the enzyme carbonic anhydrase. An electric field with a partial charge would certainly be capable of greatly altering the electric field of an atom or molecule. A partial analogy considers the situation in which a person is a little more dense than water and therefore will not float. The person weighs 180 pounds on a scale. Now the person and the scale are at the bottom of a pool 8 ft deep. The person weighs 9 pounds. This is a tremendous change in the person's weight but the person has not interacted with the water to become attached and can jump out at will. This is a 'field effect' just as the change in vibrational frequency of CO is caused by the electric field without attachment.

In order to compare one set of levels for one metal with the levels of another, it was necessary to express each set of levels by a single number. The four low-lying levels in III Cr from the AEL tables, namely, 59.9, 181.8, 355.8 and 575.0 were summed along with the $2J + 1$ values using the following truncated Partition Function; truncated by omitting the contribution

to the sum by the ground state.

$$U = \sum_{\substack{n=1 \\ n \neq 0}}^{n=\infty} (2J_n + 1) \exp\left(\frac{-hc\bar{\nu}_n}{kT}\right) \quad (3)$$

In Eq. (3), h is Planck's constant, c the speed of light, k the Boltzmann's constant, $T = 298.16$ K, the temperature of the AEL tables. The ground state was omitted since we are concerned only with levels above the ground state.

There were four metals for which the fractions from CO spectra had been determined (this fraction has been named the Perturbation Fraction, PF, since it is the fractional amount by which the molecule is perturbed by the metal) that also showed low-lying levels in the AEL tables. Data used to determine “ U ” for cobalt and chromium were from my experiments while data used for iron and nickel were from the experiments of others. The following plot of ‘ $\log U$ ’ versus the fraction, PF, clearly establishes an electric field with a partial charge as the source of the fractions and the source of catalysis [21].

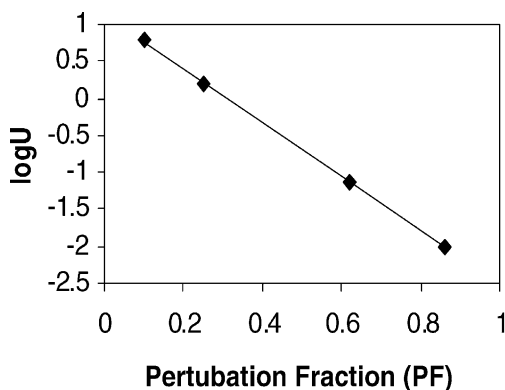
The straight line relationship between $\log U$, over three decades, and PF, over most of the range of fractions in Fig. 3 indicates that the perturbation fraction, the single property of a metal that will be shown to determine its activity as a catalyst, is the result of the fractional population of the low-lying excited electronic states of metal ions. Fig. 3 relates catalysis to the most fundamental of atomic properties, namely, the energies of electrons of the catalyst and indicates

that the IR spectra of adsorbed species are sensitive to the fractional occupancy of these low-lying electronic states. The carbon positive ion, II C, shows low-lying electronic states in the Atomic Energy Levels tables and thus carbon in certain compounds may be active as a catalyst as may also any other non-metallic ions with similar low-lying electronic states.

To see that perfectly straight line over three decades often and over almost the entire range of fractions from 0 to 1, was incredible. There is no way that such a direct relationship can exist between these fractions that are obtained by (1) determining the infrared spectra of CO in contact with a metal or compound containing the metal, (2) choosing spectral bands that are readily removed by evacuation, (3) calculating the number of electrons corresponding to the frequency of the bands, (4) discarding the integers and (5) plotting the fraction against the log of the Boltzmann sum of the low-lying energy levels, (6) truncated by omitting the ground state. . . unless it is all true.

Intermediations are considered to be neutral species at all times that are perturbed by the electric field of the adsorbent to have the vibrational frequency and other properties corresponding to the calculated number of electrons.

In order to account for the integers of the number of electrons associated with intermediations, ‘we will speak, in this section, of ‘donating and accepting fractions of electrons’ realizing that these designations are only an artificial accounting procedure’. Neutral CO has 10 electrons, therefore, the 10.86 intermedion on



PF	Metal Ion	U	Log U
0.1	III Cr	6.144	0.788
0.25	II Fe	1.552	0.191
0.62	II Co	0.074	-1.131
0.86	III Ni	0.01	-2.000

Fig. 3. Relationship between Atomic Energy Level tables and perturbation fractions.

nickel must have emptied an orbital containing 0.86 electrons. An orbital containing 0.86 electrons could be filled up to two electrons by accepting 1.14 electrons generating an 8.86 intermedion. Similarly, the 11.86 intermedion emptied an orbital containing 1.86 electrons that could be filled by accepting 0.14 electrons generating a 9.86 intermedion. By proposing two orbitals of nickel on the surface containing 0.86 and 1.86 electrons and allowing the acceptance of electrons by the intermedion to empty the orbital or the donation of electrons to fill the orbital to two (not both at once) four intermedions can be generated with integers of 8, 9, 10 and 11 along with the characteristic fraction of the metal, as shown in the following Fig. 4.

The three intermedions that were observed are 8.86 (2188), 10.86 (2058) and 11.86 (1230 cm^{-1}), the fourth 9.86 (2152 cm^{-1}) might have present but at such a low concentration as to not be detected. Proposing two species of metal differing by one electron, i.e. 0.86 and 1.86 prompts the designation of ‘ic’ as the higher oxidation state of the 0.86 and ‘ous’ to the lower oxidation state of 1.86. The ‘ic’ state corresponds to the even integers and the ‘ous’ state to the odd integers because CO is an ‘even’ molecule containing an even number of protons. For ‘odd’ molecules such as hydroxyl, OH or nitric oxide, NO, the designations are the opposite. “Thus, the number of electrons, by the integer designates the oxidation state of the surface at the site with respect to ic or ous and the fraction specifies the active component, metal or non-metal”.

A project for a graduate student [18] was to test to determine if this entire process was reversible. So far the process had been from spectra of CO to atomic energy levels. It should be possible to proceed in the

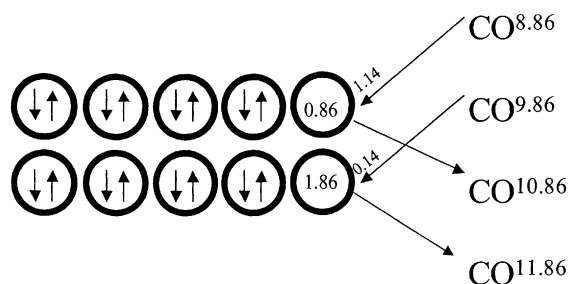


Fig. 4. The four intermedions and apparent electron transfers for CO on an adsorbent containing nickel.

reverse, that is, to predict the infrared spectra of CO, the bands readily removed by evacuation, starting from data in the AEL tables.

Ruthenium showed low-lying levels in the AEL tables but had not been investigated with CO in the in situ cell. In the tables there were low-lying levels for two ionization states, II Ru and III Ru. (1) Log U was calculated from the AEL tables for each of the two physicists’ ionization states. (2) The graph of Fig. 1 was used to convert each log U to the corresponding PF, namely, ‘ f_1 ’ and ‘ f_2 ’. (3) The integral numbers of electrons were assigned to each of the four intermedions for each PF, namely, $8 + f_1$, $9 + f_1$, $10 + f_1$ and $11 + f_1$ and $8 + f_2$, $9 + f_2$, $10 + f_2$, and $11 + f_2$. (4) The vibrational frequencies of the eight intermedions were calculated. (5) Spectra were determined of CO in contact with reduced and then oxidized ruthenium. Of the eight intermedions listed, the frequencies of two were outside the range of the grating and filters of the infrared spectrometer. Three of the remaining six were detected in the experiment at frequencies that matched the calculated values within one wave number.

All of the above leads to the explanation or prediction of catalytic reactions. To utilize the Myers’ Hypothesis, in Eq. (1) replace ‘ η ’ by ‘ $I + f$ ’ where the values of ‘ I ’ are the four integers for each intermedion. The equations of the two reactants are solved to determine the fraction ‘ f ’ that makes the ratio of the vibrational frequencies of the two reactants correspond to 2^n (Harmonics are powers of 2). Whatever metal has the fraction, ‘ f ’, as its PF will catalyze the reaction by producing intermedions with matching vibrational frequencies.

$$(v_1 - V_1)[(I_1 + f) - N_1] = K_1 \quad (4)$$

$$(v_2 - V_2)[(I_2 + f) - N_2] = K_2 \quad (5)$$

$$\frac{v_1}{v_2} = 2^n \quad (6)$$

The only unknown is ‘ f ’ in the quadratic equation. When ‘ f ’ is the same as the ‘PF’ of one of the metals, that metal will function as a catalyst because it will produce matching intermedions producing resonance, allowing electron pairing, sharing and exchange to form and break chemical bonds. The reaction will proceed in the direction of a favorable value of ‘ ΔG ’, the Gibbs free energy change for the overall reaction, provided there is microscopic reversibility of each

elementary step of the reaction sequence. Symmetry restrictions also may be important for complex reactants.

Expressing vibrational frequencies in term of numbers of electrons elevates infrared spectroscopy to a new level of utility as an analytical technique. In this manuscript, the benefits to be derived from expressing vibrational frequencies in terms of numbers of electrons extend to applications such as:

1. a quantitative evaluation of the changes in electron density of bonds as atoms or groups of atoms are combined to form molecules such as hydrogen peroxide;
2. a quantitative interpretation of catalysis in terms of explicit designations of:
 - 2.1. the catalytic entity, i.e. metal or non-metal;
 - 2.2. the oxidation number of the catalyst;
 - 2.3. the mechanism of the reaction at the instant of the catalytic event;
 - 2.4. the necessary structure of the catalyst, i.e. whether heterogeneous or homogeneous (enzyme);
3. this same functional form, a right hyperbola, relates vibrational frequency to numbers of electrons for all other molecules so far tested, such as OH, CO₂, Cl₂ and O₂.

2.1. Physicists ionization states related to chemists oxidation states and oxidation numbers

In order to specify the exact numerical oxidation state of the catalyst, it was necessary to develop, [21] Gardner, the following relationship between physicists' ionization states and chemists' numerical oxidation states. This relationship is based on the following rules and is presented in examples of iron, cobalt, chromium, nickel and manganese in Tables 3 and 4:

1. physicists designate ionization states by Roman numerals as a prefix to the atomic symbol;
2. the atom, designated by physicists by '*I*', always corresponds to the chemists' '0' oxidation state even if this state has low-lying electronic levels;
3. each successive physicists' ionization state that does not have low-lying energy levels corresponds to a single chemists' oxidation state;

Table 2

The relationship of physicists' ionization states in Roman numerals to chemists' oxidation states in Arabic numerals

I M M 0	I M M 0	I M M 0
II M ous M 1+	II M M 1+	II M M 1+
II M ic M 2+	III M ous M 2+	III M M 2+
III M ous M 3+	III M ic M 3+	IV M ous M 3+
III M ic M 4+	IV M ous M 4+	IV M ic M 4+
	IV M ic M 5+	V M ous M 5+
Iron	Chromium	V M ic M 6+
Cobalt	Nickel	VI M ous M 7+
		VI M ic M 8+
		Manganese

4. the first physicists' ionization state with low-lying energy levels has a perturbation fraction as well as successive states with low-lying levels;
5. each perturbation fraction corresponds to two oxidation states, identified as 'ous' for the lower of the two oxidation states and 'ic' for the higher;
6. chemists' oxidation numbers increase sequentially.

For example, the first ionization state of manganese having low-lying levels is IV Mn, therefore, I Mn is the chemists' 0; II Mn is the chemists' 1+; III Mn is the chemists' 2+; IV Mn 'ous' is the chemists' 3+; and IV Mn 'ic' is the chemists' 4+; V Mn 'ous' is the chemists' 5+ and V Mn 'ic' is the chemists' 6+; VI Mn 'ous' is the chemists' 7+ and VI Mn 'ic' is the chemists' 8+ (if it exists, perhaps only on a surface).

The oxidation number 2+ assigned to iron and cobalt corresponds to an 'ic' state since II Fe and II Co have low-lying electronic levels. If the 1+ oxidation state was not observed at the historical time when assignments of 'ic' and 'ous' were made then it could not have been taken into account at that time.

2.2. Derivation of equations of carbon dioxide intermedions [7] Gardner

Since carbon dioxide has three normal vibrational modes, there are three equations, one for each normal mode. The vibrational frequencies of the neutral molecule are: ν_1 (1336.9 cm⁻¹), ν_2 (667.3 cm⁻¹) and ν_3 (2349.3 cm⁻¹). Filimonov [15] monitored the decomposition of nickel carbonate, NiCO₃, by infrared spectroscopy and observed several bands in the spectra. A band at 1635 cm⁻¹ was the only one removed

by evacuation at room temperature. This experimental observation satisfies one criterion to be considered an intermedion, namely, facile removal by evacuation at room temperature. The other essential criterion is that the vibrational frequency must correspond to a non-integral number of electrons, the fraction of which is the PF of the adsorbent metal. Assuming the PF of nickel to be 0.857, if the band at 1635 cm^{-1} is the ν_3 vibration of a CO_2 intermedion on nickel, this band should correspond to 17.857 valence electrons. The two points, $\nu_3\text{CO}_2^{16.00} = 2349\text{ cm}^{-1}$ and $\nu_3\text{CO}_2^{17.857} = 1635\text{ cm}^{-1}$, together with the third point of decomposition, $\nu_3\text{CO}_2^{17.854} = 0.0\text{ cm}^{-1}$ are sufficient to derive the following equation [7] for the ν_3 mode of CO_2 intermedions.

$$(\nu_3\text{CO}_2 - 2431.1)(\eta_3\text{CO}_2 - 18.070) = 170.18 \quad (7)$$

Because the three vibrational modes of CO_2 involve only the same bonds between the same atoms, it was considered that the constant 'k', the curvature of the right hyperbola, is the same for all three equations. Thus, from $\nu_1\text{CO}_2^{16} = 1336.9\text{ cm}^{-1}$, $\nu_1\text{CO}_2^{18} = 0.0\text{ cm}^{-1}$ and $k = 170.18$; and from $\nu_2\text{CO}_2^{16} = 667.3\text{ cm}^{-1}$, $\nu_2\text{CO}_2^{18} = 0.0\text{ cm}^{-1}$ and $k = 170.18$; the equations for the ν_1 and ν_2 modes of CO_2 intermedions are:

$$(\nu_1\text{CO}_2 - 1418.2)(\eta_1\text{CO}_2 - 18.120) = 170.18 \quad (8)$$

$$(\nu_2\text{CO}_2 - 742.1)(\eta_2\text{CO}_2 - 18.229) = 170.18 \quad (9)$$

2.3. Role of intermedions in chemical reactions, infrared spectrum of CO oxidation to CO_2 on zinc

Taylor and Amberg [16] reported the infrared spectrum of CO in contact with zinc oxide at 25°C . Admission of CO into the cell produced a band at 2174 cm^{-1} . Upon standing, the band at 2174 was replaced by a band at 2198 cm^{-1} . According to Eq. (2), $\nu\text{CO}^{9.322} = 2174\text{ cm}^{-1}$ and according to Eq. (7), $\nu_3\text{CO}_2^{17.34} = 2198\text{ cm}^{-1}$. This agreement, within 0.02 electrons of the perturbation fractions calculated for CO and CO_2 intermedions on zinc:

1. supports Eq. (7) for $\nu_3\text{CO}_2$ intermedions;
2. indicates that the perturbation fraction for zinc is 0.322 (the fraction from the CO intermedion is chosen because the equation for CO intermedions is considered the more accurate);

3. indicates that zinc functions as a catalyst for the oxidation of carbon monoxide;
4. defines the oxidation state at the catalytic site as the 'ous' or lower state since the integers of both intermedions are odd.

2.4. Infrared spectrum of CO_2 on sodium chloride

Kozirovsky and Folman [17] report the following infrared bands from a study of carbon dioxide on sodium chloride: 2288, 1379, 668.3, 647.2, 630.9 and 629.3 cm^{-1} . According to Eq. (7), $\nu_3\text{CO}_2^{16.89} = 2288\text{ cm}^{-1}$ and $\nu_3\text{CO}_2^{17.91} = 1379\text{ cm}^{-1}$. According to Eq. (8), $\nu_1\text{CO}_2^{17.896} = 658.3\text{ cm}^{-1}$, $\nu_1\text{CO}_2^{17.899} = 647.2\text{ cm}^{-1}$, $\nu_1\text{CO}_2^{17.904} = 630.9\text{ cm}^{-1}$ and $\nu_1\text{CO}_2^{17.904} = 629.3\text{ cm}^{-1}$. The cluster of fractions about 0.90 identifies this as the perturbation fraction of sodium. It is quite remarkable that the ν_1 mode of CO_2 , which is inactive in the infrared for the linear $D_{\infty h}$ symmetry in the gaseous molecule, has become infrared active for this intermedion. According to Walsh [23], the addition of electrons to CO_2 is expected to change its structure from linear to bent C_2v for which all normal modes are active in the infrared. In this instance, the intermedion has not only the vibrational frequency corresponding to the calculated number of valence electrons, but also the structure as well. An analysis Gardner [7], of the four bands in the 600 cm^{-1} region suggests that the intra-molecular angle is approximately 60° and that the intermedion may be rotating.

2.5. Infrared spectra of CO_2 from CO and O_2 on gold

Huber et al. [19] studied the interaction of CO and O_2 on gold at 4 K by infrared spectroscopy. They made a matrix of a mixture of CO and O_2 , cooled it to 4 K and sputtered gold onto the surface. They observed infrared bands in the ranges of 2190–2180 and 2180–2170 cm^{-1} (depending on the conditions of deposition) and at 1807, 850, 448, 416 and 356 cm^{-1} . Warming the sample to 35–40 K removed the bands in the range of 2190–2180 cm^{-1} and those at 1807, 850 and 356 cm^{-1} and produced an increase of CO_2 in the gas phase. Substituting these last three frequencies into Eqs. (7)–(9), respectively gives: $\nu_3\text{CO}_2^{17.80} = 1807$, $\nu_1\text{CO}_2^{17.82} = 850$ and $\nu_2\text{CO}_2^{17.79} = 356\text{ cm}^{-1}$.

This is the second experimental observation that provides all three normal modes of vibration of a single intermedion.

The clustering of fractions around an average of 0.803 strongly suggests that this is the perturbation fraction of gold. As in the preceding example of CO₂ on sodium chloride, ν_1 CO₂ is infrared active on gold. The CO₂ intermedions on sodium chloride and on gold correspond to the apparent acceptance of electrons, 1.90 on sodium chloride and 1.80 on gold. Infrared spectra of the ν_1 normal mode indicate that the carbon dioxide molecule is no longer linear. These results support the proposal by Walsh [23], that the addition of electrons to carbon dioxide changes its structure from linear to bent.

2.6. Intermedions in hydrogen peroxide

The foregoing successful descriptions of infrared spectra and chemical reactions in terms of intermedions suggests that infrared spectra may be predicted if parts of a molecule can be expressed as intermedions. The symmetrical and unsymmetrical O–H stretching modes of water are assigned at 3656 and 3755 cm⁻¹, respectively, by Herzberg [24]. The assignment of the symmetrical and unsymmetrical O–H stretching modes of hydrogen peroxide at 3417 and 3540 cm⁻¹, seemed questionable because in hydrogen peroxide the hydrogen atoms would be expected to be only minimally dependent on each other since they are attached to different oxygen atoms. Viewing the hydrogen peroxide molecule as composed of intermedions, allowed the calculation, Gardner [25], of the electron density in the bonds of hydrogen peroxide by considering the molecule as either an oxygen molecule with hydrogen atoms attached or as two attached hydroxyl molecules. To investigate this view of hydrogen peroxide required equations representing dioxygen and hydroxyl intermedions. The following equation of dioxygen intermedions was derived, Gardner [25], from data published by Herzberg [4], of the vibrational frequencies of the neutral O₂ molecule with 12 electrons at 1556.38 cm⁻¹, the positive ion with 11 electrons at 1843.34 cm⁻¹ and the hypothesis that the vibrational frequency becomes zero at 14 electrons. The derivation of the equation of hydroxyl intermedions necessary for the following discussion is more complex since data for neither positive nor

negative hydroxyl ions was available. This derivation though already published Gardner [26], is reviewed in Appendix A.

$$(\nu_{\text{O}_2} - 2920.16)(\eta_{\text{O}_2} - 15.7525) = 5117.58 \quad (10)$$

$$(\nu_{\text{OH}} - 6090.25)(\eta_{\text{OH}} - 0.16649) = -17256.8 \quad (11)$$

Electrons that are in anti-bonding orbitals of the oxygen molecule bond the hydrogen atoms of H₂O₂. Because the bonding orbitals of H₂O₂ are filled, electrons added to H₂O₂ occupy anti-bonding orbitals, thus strengthening the OH bonds and weakening the OO bond. Dissociation of the OO bond occurs, that is, the vibrational frequency of the OO bond becomes zero when two electrons are added, yielding two OH molecules each with eight electrons. When the six electrons in anti-bonding orbitals of H₂O₂ are removed, the OH vibrational frequency becomes zero and the hydrogen atoms dissociate as protons. This leaves an O₂ molecule with eight valence electrons. According to Eq. (11), the vibrational frequency of the hydroxyl molecule becomes zero at three valence electrons. Electrons associated with the OH and OO regions of the neutral H₂O₂ molecule with 14 valence electrons may be calculated by interpolation as shown in the following series of equations.

$$\begin{aligned} \nu_{\text{H-OO-H}}^{16} &= \nu_{\text{O-H}}^8; \\ \nu_{\text{H-OO-H}}^8 &= \nu_{\text{O-H}}^3 = 0.0; \\ \nu_{\text{H-OO-H}}^{14} &= \nu_{\text{OH}}^{6.75} \end{aligned} \quad (12)$$

$$\begin{aligned} \nu_{\text{HO-OH}}^{16} &= \nu_{\text{O-O}}^{14} = 0.0; \\ \nu_{\text{HO-OH}}^8 &= \nu_{\text{O-O}}^8; \quad \text{HO-OH}^{14} = \nu_{\text{O-O}}^{12.5} \end{aligned} \quad (13)$$

The two sets of equations indicate that when two OH molecules are bonded there is a shift in electron density corresponding to a loss of 0.25 electron from each OH group and a gain of 0.50 electron in the OO group. From Eqs. (10) and (11) the OH and OO stretching frequencies are calculated at 3474 and 1347 cm⁻¹, respectively.

2.7. Interpretation of the infrared spectrum of hydrogen peroxide

By suspending H₂O₂ in a matrix of solid nitrogen, Catalano and Sanborn [27] obtained a definitive

infrared spectrum with a minimum of hydrogen bonding and other inter-molecular interactions. The bands they reported at 3540, 3417, 1735 and 388 cm^{-1} were assigned as the unsymmetrical OH stretch, the symmetrical OH stretch, the OO stretch and the OO torsion modes, respectively. The assignment of the torsion mode to 388 cm^{-1} was supported by an assignment of $386 \pm 4 \text{ cm}^{-1}$ from a vapor-phase study Hunt et al. [29]. The combination of the calculated OO stretch at 1347 cm^{-1} and the torsion vibration at 388 cm^{-1} satisfy the symmetry requirements to produce the spectral band reported at 1735 cm^{-1} . The midpoint of the bands assigned at 3417 and 3540 cm^{-1} to the symmetrical and unsymmetrical OH stretching vibrations, respectively, is 3478 cm^{-1} . This value is close enough to the first overtone of the combination OO stretch and torsion, that is 3470 cm^{-1} , and is of the appropriate symmetry to produce the widely separated bands at 3540 and 3417 cm^{-1} as a result of Fermi Resonance, Fermi [28]. A more complete discussion of point groups and symmetry operations for this system is presented in a previous publication Gardner [26].

2.8. Requirements of oxidation state, electronegativity, and reaction at an atom

There are three additional characteristics of a chemical reaction that must be considered in order adequately to test the Myers Hypothesis. Chemical reactions, including catalysis, must be capable of being expressed as a sequence of elementary reversible reactions each of the form



As described above, the formation of an intermedion occurs because the fractional electron deficit of the electrical field at the catalyst is filled by interaction with the electric field of the adsorbate thereby transferring the electron deficit to the adsorbate. Therefore, each atom of the catalysis can contain only one intermedion. Thus, to satisfy the requirements of Eq. (14), the catalytic site must contain two atoms with orbitals that touch or overlap so that mass transfer can occur, either C dissociating to become A + B or A combining with B converting B to C. The higher or 'ic' oxidation state may be viewed as an orbital that would be empty except for the fractional electron population. The lower or 'ous' oxidation state may

be viewed as an orbital that already contains one electron. As shown in Fig. 4, both oxidation states become either empty or filled to two electrons upon forming intermedions. Oxidation state, that is, 'ic' or 'ous' is considered to be the property that must be identical to allow the overlap of two orbitals. That is, each of the two orbitals that overlap initially contains one electron plus the fractional electron population for the 'ous' state and each initially contains only the fractional population for the 'ic' state.

The differences in oxidation state on the planes of different crystal faces and at edges and comers are indicated by the differences in work function at different sites. As presented in Fig. 4, a particular oxidation state can function either as an electron donor or acceptor depending on the relative electronegativities of the adsorbate and the catalytic site. At different places on a surface, a heterogeneous catalyst, it may be possible to have orbital overlap between two catalytic atoms, one of which acts as an electron acceptor and the other as an electron donor. In solution, that is, homogeneous or enzyme, the metal atoms of a solute would be expected to all have not only the same oxidation state but also the same electronegativity, that is, the same direction of apparent electron transfer to form an intermedion.

2.9. Reactions at an atom in a molecule

At this point, as complete as this analysis has been, it only applies to bond-to-bond reactions between two molecules. There are three times as many reactions between two molecules involving an atom in a molecule as the bond-to-bond reaction, that is, atom in molecule A with bond of molecule B, bond of A with atom in B and atom in A with atom in B. To consider reactions at an atom or at an atom in a molecule requires not only a new equation but also a conceptual change because there is no vibration at an atom. In order to continue to test or apply the Myers' Hypothesis all types of reactions that may take place at the catalytic site had to be considered. It was necessary to find some property at an atom that was on the same scale of energy as the vibrational frequency and that changes with a change of the number of electrons on a molecule. This property was thought to be related to the electric field of the molecule at the site of the atom. Next it was realized that the measurable property was the difference

Vibrational Frequency vs. Number of Valence Electrons

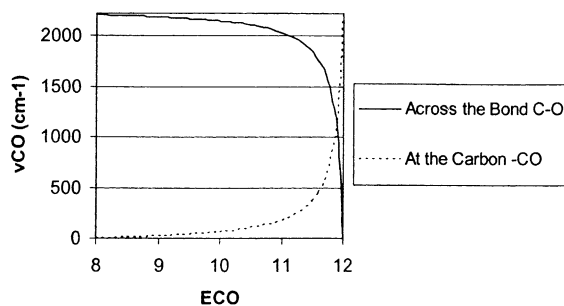


Fig. 5. The reciprocal relation of a reaction across the bond to reaction at the carbon atom of carbon monoxide.

in energy between two electronic states of the molecule.

The vibrational frequency of CO decreases as valence electrons are added beyond the ninth valence electron in Fig. 5 or as a result of electron pairing probably beyond the first eight. Thus, the vibrational frequency, over this interval, may be thought of as indicative of an ‘electron acceptor capacity’ that decreases as electrons are added. Conversely, there should be a function that increases as electrons are added, an ‘electron donor capacity’. Since these are two aspects of the same molecule, one is the reverse of the other and the two, together, should add to a constant. These relationships are indicated in Fig. 5.

A problem arises when a reaction is considered that involves an atom reacting at a bond. It does not seem reasonable to have an electric field matching a vibrational frequency because an electric field is an electrical entity and a vibrational frequency is a mechanical entity. However, it becomes reasonable if the absorption of light in infrared spectroscopy is actually the result of the interaction of light with the electric field of the molecule at the site of the bond. After all, light is an electric phenomenon and as such can only interact with an electric field. Otherwise, it would be possible to touch two wires from a battery to a bell and the bell would ring. This does not happen. The electric current must be transformed into mechanical energy to ring a bell. The Stokes lines in Raman spectroscopy are called vibrational states; however, these are the fine structure on an electronic transition and therefore must be electrical states. It may be that the molecule is

undergoing the vibrational motions assigned to these frequencies but the actual process of light absorption is due to the transition of the electrical field of the molecule from one electronic state to another.

The transition energy of the electric field at the bond will be indicated as EC–O while the transition energy at the carbon atom of CO will be indicated as E–CO. As a result of the symmetry of the two equations, EC–O and E–CO, the ordinate asymptote, ‘A’ equals the maximum value of ECO, that is, EC–O⁸ minus the ordinate constant in the EC–O equation, ‘V’ as shown in the following equation:

$$\Lambda_{\text{CO}} = \text{EC-O}^8 - V = 2204.81 - 2269.96 = -65.15 \quad (15)$$

The abscissa term remains the same and the sign of the curvature ‘k’ is reversed. The new equation is

$$(\text{E-CO} + 65.15)(\eta_{\text{CO}} - 12.1182) = -268.309 \quad (5)$$

The equations corresponding to reaction at an atom in the molecule are the following for oxygen and hydroxyl intermediations.

$$(\text{E-OO} + 660.120)(\eta_{\text{O}_2} - 15.7525) = -5117.58 \quad (16)$$

$$(\text{E-OH} + 2202.94)(\eta_{\text{OH}} - 0.16649) = 17256.78 \quad (17)$$

A brief review and summary of the concepts presented in the foregoing sections may facilitate the following mathematical descriptions of six catalytic systems.

1. The presence of low-lying excited electronic states in certain ions of a catalyst leads to the fractional population of these states by an electron of the ion, forming an orbital that is unsaturated with a partial or fractional charge.
2. The interaction of the electric field of an adsorbate with the electric field of the catalyst saturates that field by a shift of electron density either to empty the orbital or fill it up to two electrons.
3. The direction of the shift of electron density depends on the electronegativities of the adsorbate as compared to the catalyst and the environment at the catalytic site.
4. The ‘ous’ oxidation state with one electron more than the ‘ic’ state would be expected usually to

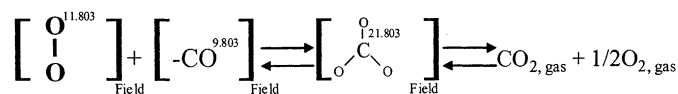


Fig. 6. Schematic of CO oxidation catalyzed by gold compound.

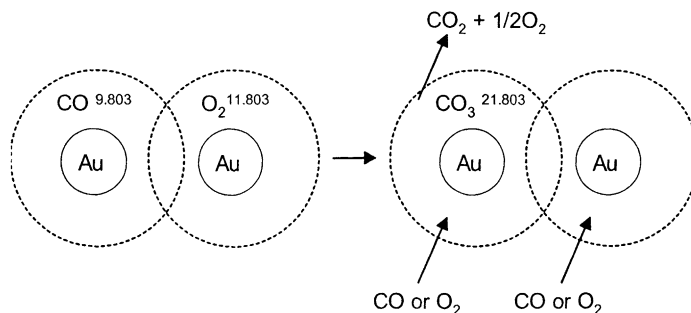


Fig. 7. Representation of reactants and orbitals during oxidation of CO catalyzed by gold.

function as an electron donor while the ‘ic’ state would be expected to be more of an electron acceptor. Thus, in Fig. 4, the 9.86 and 10.86 carbon monoxide intermediations on nickel would be expected to be somewhat less prevalent since the 9.86 requires the lower oxidation state of the catalyst, the electron donor state, to act as an electron acceptor and the 10.86 requires the higher oxidation state of the catalyst, the electron acceptor state, to act as an electron donor.

5. The matching or synchronization of the vibrational frequencies or more explicitly the transition energies, of the two reactants diminishes the ‘activation energy’ sufficiently close to zero, allowing resonance to occur leading to the sharing, pairing or exchange of electrons necessary to form or break chemical bonds.

2.10. Analyses of catalytic reactions

The equations used in this section are the most accurate known at this time. As presented in Fig. 4 above, there can be a maximum of four intermediations

that may form for each perturbation fraction. These four are: two for the higher or ‘ic’ oxidation state and two for the lower or ‘ous’ oxidation state. For each oxidation state there are two directions of apparent partial electron transfer as shown in Fig. 4. In the following tables vertical columns of intermediations correspond not only to the same perturbation fraction but also to the same oxidation state and same direction of apparent partial electron transfer. For molecules having an even number of protons, even integers correspond to the ‘ic’ state and odd integers correspond to the ‘ous’ state. For odd molecules the opposite designations apply. The transition energies of intermediations are normalized by harmonics, 2^n to a range of 500–1000 cm^{-1} to facilitate comparisons; those that match are underlined. In addition to the numerical analyses, to further assist the interpretation of the catalytic reaction for this first example, Figs. 6 and 7 present graphic illustrations. Similar relationships as shown in these figures apply to the remaining five analyses of catalytic reactions. The equations used in these calculations precede the tables (Figs. 8–12).

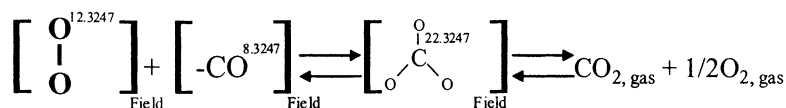


Fig. 8. Schematic of CO oxidation catalyzed by zinc compound.

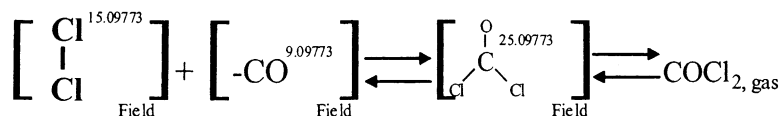


Fig. 9. Schematic of CO chlorination catalyzed by chromium compound.

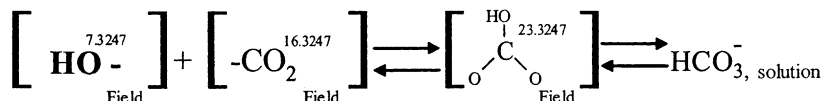


Fig. 10. Schematic of hydration of carbon dioxide catalyzed by zinc compound.

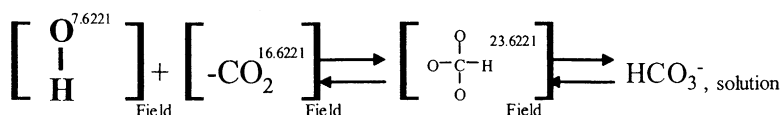


Fig. 11. Schematic of hydration of carbon dioxide catalyzed by cobalt compound.

2.11. CO + O₂ on gold

$$(\text{EC-O} - 2269.96)(\eta_{\text{CO}} - 12.1182) = 268.309 \quad (2)$$

$$(\text{E-CO} + 65.1521)(\eta_{\text{CO}} - 12.1182) = -268.309 \quad (15)$$

$$(\text{EO}_2 - 2920.16)(\eta_{\text{O}_2} - 15.7525) = 5117.58 \quad (10)$$

$$(\text{E-OO} + 660.12)(\eta_{\text{O}_2} - 15.7525) = -5117.58 \quad (16)$$

The data in Table 5 defines the reaction mechanism at the instant of the catalytic event as the attack of the carbon atom of the 9.8034 CO intermedion into the bond of the 11.8034 O–O intermedion forming a CO₃ molecule. This unstable molecule dissociates into CO₂ and an oxygen atom probably upon leaving the electric field of the catalyst.

The integers of the CO and O₂ intermedions that react on gold are odd and the CO₂ intermedions on gold also are odd, corresponding to the lower oxidation state. In Table 2, this corresponds to both

Table 3

The four CO intermedions and the four O₂ intermedions on gold
PF = 0.8034

CO intermedions on gold			
EC-O			
8.8034	9.8034	10.8034	11.8034
2189.03	2154.07	2065.95	1410.73
(547.26)	(538.52)	(516.49)	(709.36)
E-CO			
15.78	50.76	138.85	786.08
(504.99)	(812.16)	(555.41)	
O ₂ intermedions on gold			
EO-O			
10.8034	11.8034	12.8034	13.8034
1886.20	1624.41	1185.09	295.08
(943.10)	(812.20)	(592.55)	(590.17)
E-OO			
373.943	635.634	1074.94	1964.95
(747.88)		(537.47)	(982.48)

intermedions in the same vertical column. Intermedions having the same oxidation state, both ic or both ous, but in different columns require a heterogeneous catalyst. This analysis predicts that an aqueous

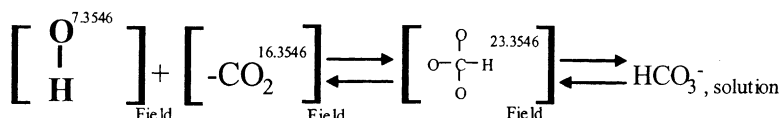


Fig. 12. Schematic of hydration of carbon dioxide catalyzed by cadmium.

solution of a gold compound with the appropriate electron donating anion, such as, cyanide will function as a homogeneous catalyst for the oxidation of a mixture of CO and O₂ to CO₂.

2.12. CO + O₂ on zinc

The experiment presented above by Taylor and Amberg [16] of carbon monoxide on zinc oxide indicated that zinc oxide catalyzed the oxidation of carbon monoxide.

$$(\text{EC-O} - 2269.96)(\eta_{\text{CO}} - 12.1182) = 268.309 \quad (2)$$

$$(\text{E-CO} + 65.1521)(\eta_{\text{CO}} - 12.1182) = -268.309 \quad (15)$$

$$(\text{EO-O} - 2920.160)(\eta_{\text{O}_2} - 15.7525) = 5117.58 \quad (10)$$

$$(\text{E-OO} + 660.120)(\eta_{\text{O}_2} - 15.7525) = -5117.58 \quad (16)$$

The data in Table 5 defines the reaction mechanism at the instant of the catalytic event as the attack of the carbon atom of the 8.3247 intermedion into the bond of the 12.3247 oxygen molecule intermedion forming a CO₃ molecule. This unstable molecule dissociates into carbon dioxide and an oxygen atom. As in the previous example of the gold catalyzed reaction, the integers of the reacting intermedions correspond to the same oxidation state. However, the previous assumption that the catalytic site as ‘ous’ is in error. This mistake was made because the CO and CO₂ intermedions reported by Taylor and Amberg [16], in are both in the ‘ous’ oxidation state. Table 5 defines the catalytic site as ‘ic’ because both reacting intermedions are ‘ic’ but correspond to different directions of apparent electron transfer, that is, the catalyst zinc atoms accept from CO and donate to O₂. Thus, the catalyst must be a solid to accommodate simultaneously the two directions of apparent electron transfer. (The two intermedions with normalized frequencies of 988 correspond to different oxidation states).

Table 4

The four CO intermedions and the four O₂ intermedions on zinc (PF = 0.3247)

CO intermedions on zinc				
EC-O				
8.3247	9.3247	10.3247	11.3247	
2199.23	2173.91	2120.36	1931.83	
(549.81)	(543.48)	(530.09)	(965.91)	
E-CO				
5.5765	30.8955	84.4487	272.981	
(713.79)	(988.66)	(675.59)	(545.96)	
O ₂ intermedions on zinc				
EO-O				
10.3247	11.3247	12.3247	13.3247	
1977.31	1764.37	1427.20	812.25	
(988.65)	(882.18)	(713.60)		
E-OO				
282.726	495.664	832.844	1447.79	
(565.49)	(991.32)		(723.89)	

2.13. Negative metal ions

It is not possible to assign the explicit oxidation number for zinc or gold catalysts because there are no low-lying electronic levels shown in the Atomic Energy Levels tables for ions of these metals. Nevertheless, since these metals demonstrate a perturbation fraction and function as catalysts, it is thought that the catalytic entity must have low-lying levels. The Atomic Energy Levels tables include only positive ions. It is possible that negative ions of these metals have the low-lying electronic states necessary for catalytic activity. Further support for the proposal of negative metal ions may be the observed time delay in the experiment by Taylor and Amberg [16] between the observation of the reactant CO intermedion and the appearance of the product CO₂ intermedion. This delay may have been due to the ‘extremely low concentration on negative zinc ions, of the electron accepting sites’ needed to form the required 8.3247 CO intermedion (see Fig. 3). The 12.3247 O₂ intermedion would be expected to be more plentiful on a negative ion than the 8.3247 CO intermedion because this O₂ intermedion requires electron transfer corresponding to electron donation from the negative surface. With a substantial quantity of O₂ intermedions present, if the appropriate CO intermedions were available, the oxidation reaction would have proceeded instantaneously and CO

intermedions would not have been detected. Thus, the appearance of CO intermedions coincides with the proposal that zinc negative ions are the catalytic state.

2.14. CO + Cl₂ on chromium +2 and +3

The destruction of phosgene, COCl₂ stored from WWI and WWII is a challenging project. The Gibbs free energy change, ΔG° , is -67.7 kJ/mol to form phosgene from CO and Cl₂. The destruction of phosgene could be accomplished with catalysis of the oxidation of CO to CO₂. Even though ΔG° for the decomposition of phosgene is $+67.7$ kJ/mol, ΔG° for the oxidation of CO is -257.2 kJ/mol, so that ΔG° for the overall reaction is -189.3 kJ/mol.

$$(\text{EC-O} - 2269.96)(\eta_{\text{CO}} - 12.1182) = 268.309 \quad (2)$$

$$(\text{E-CO} + 65.1521)(\eta_{\text{CO}} - 12.1182) = -268.309 \quad (15)$$

$$(\text{ECI-Cl} - 909.228)(\eta_{\text{Cl}_2} - 17.2631) = 1148.48 \quad (18)$$

$$(\text{E-CICI} + 123.984)(\eta_{\text{Cl}_2} - 17.2631) = -1148.48 \quad (19)$$

The data in Table 5 defines the reaction mechanism, at the instant of the catalytic event, as the attack of the

Table 5

The four CO intermedions and the four Cl₂ intermedions on chromium (PF = 0.09773)

CO intermedions on chromium +2 and +3			
EC-O			
8.09773	9.09773	10.09773	11.09773
2203.22	2181.13	2137.16	2007.03
(550.81)	(545.28)	(534.29)	(501.76)
E-CO			
1.5836	23.6781	67.6427	197.775
(810.81)	(757.70)	(541.15)	(791.10)
Cl ₂ intermedions on chromium +2 and +3			
ECl ₂			
12.09773	13.09773	14.09773	15.09773
686.88	633.51	546.40	378.84
			(757.68)
E-Cl ₂			
98.358	151.74	362.83	406.40
(786.87)	(606.95)	(725.65)	(812.80)

carbon atom of the 9.09773 CO intermedion into the bond of the 15.09773 Cl-Cl intermedion, forming a COCl₂ molecule on Cr + 2. The oxidation number of chromium is identified by the following relationship between oxidation and ionization. The III Cr is the first ionization state with low-lying electronic states and consequently a perturbation fraction. The I Cr is Cr 0; II Cr is 1+, III Cr 'ous' is 2+ and III Cr 'ic' is Cr 3+. Thus, the catalytic state is chromous. The intermedions that match are in different columns and therefore the catalyst must be a solid. The reaction mechanism suggested above to destroy phosgene by decomposition to Cl₂ and CO with oxidation of CO to CO₂ may be difficult to achieve since it requires maintaining chromium in the 2+ state in the presence of oxygen.

2.15. OH and v₂CO₂ on the enzyme zinc carbonic anhydrase

The enzyme, carbonic anhydrase, converts gaseous CO₂ into soluble bicarbonate, HCO₃⁻. The reaction rate of the native enzyme, containing zinc, is estimated to be 30 million per second. Zinc has been replaced by iron, nickel, cobalt and cadmium, all in the 2+ oxidation state yielding cobalt and cadmium enzymes, Pocker and Sarkanen [30] with activity diminished by a factor of ten Tibell and Lindskog [31] from the zinc enzyme and nickel and iron enzymes that are inactive. In the past enzymologists have thought that this enzyme acts by reacting water with CO₂ forming carbonic acid which then dissociates forming the bicarbonate anion [32]. Northrop, through analyses of isotope effects on reaction rates, concluded that hydroxyl rather than water was the hydrating agent. For the zinc, cobalt and cadmium catalyzed reactions the matching intermedions are in the same vertical column, thus satisfying the criterion for homogeneous or enzyme reactions. The following equations are used in Tables 6–8 to analyze these reactions on the basis of intermedions, Gardner and Willard [33].

$$(\text{EOH} - 6090.25)(\eta_{\text{OH}} - 0.16649) = -17256.8 \quad (11)$$

$$(\text{E-OH} + 2202.94)(\eta_{\text{OH}} - 0.16649) = 17256.8 \quad (17)$$

Table 6

Three of the four OH intermediations and the two CO₂ intermediations on zinc (PF = 0.3247)

OH intermediations on zinc			
	5.3247	6.3247	7.3247
EO–H	2744.74 (686.11)	3288.00 (822.00)	3679.48 (919.87)
E–OH	1142.57 (571.28)	599.31	207.83 (831.33)
ν ₂ CO ₂ intermediations on zinc ^a			
		16.3247	17.3247
Eν ₂ CO ₂		654.22	555.53
Eν ₂ –CO ₂		12.989 (831.30)	111.65

^a The ν₂CO₂ intermediations on zinc are placed to the right since both correspond to electron donation by the catalyst.

$$(E\nu_2\text{CO}_2 - 743.34)(\eta_{2\text{CO}_2} - 18.2283) = 169.704 \quad (9)$$

$$(E\nu_2\text{--CO}_2 + 76.16)(\eta_{2\text{CO}_2} - 18.2283) = -169.704 \quad (20)$$

The data in Table 7 defines the reaction mechanism at the instant of the catalytic event as the attack of the carbon atom of the 16.3247 CO₂ intermedion into the O–H bond of the 7.3247 OH intermedion forming HCO₃ in a single step.

For both cobalt and cadmium enzymes the reaction at the instant of the catalytic event is attack of the carbon of the CO₂ into the bond of OH forming an unstable intermediate, a carbon with three oxygen

Table 7

Three of the four OH intermediations and the two CO₂ intermediations on cobalt (PF = 0.6221)

OH intermediations on cobalt +1 and +2			
	5.6221	6.6221	7.6221
EO–H	2927.12 (731.78)	3417.10 (854.28)	3775.64 (943.91)
E–OH	960.19	470.21 (940.42)	111.67 (893.36)
ν ₂ CO ₂ intermediations on cobalt**			
		16.6221	17.6221
ν ₂ CO ₂		637.68	463.39 (926.79)
Eν ₂ –CO ₂		29.50 (943.86)	203.79 (815.16)

Table 8

Three of four OH intermediations and the two CO₂ intermediations on cadmium (PF = 0.3546)

OH intermediations on cadmium			
	5.3546	6.3546	7.3546
EO–H	2764.03 (691.01)	3301.55 (825.39.28)	3689.51 (922.38)
E–OH	1123.28 (561.64)	585.76	197.80 (791.20)
ν ₂ CO ₂ intermediations on cadmium**			
		16.3546	17.3546
Eν ₂ CO ₂		652.76	549.10
Eν ₂ –CO ₂		14.412 (922.34)	118.08 (944.64)

atoms and a hydrogen atom. This intermediate would rearrange in a second step to form bicarbonate. This two-step reaction would be expected to be a contributor to the 10-fold difference in reaction rates from the single-step reaction of the zinc enzyme. The oxidation number can be assigned to the cobalt in the enzyme as 2+, however, this corresponds to an 'ic' state since II Co has low-lying electronic levels. If the 1+ oxidation state was not observed at the historical time when assignments of 'ic' and 'ous' were made then it could not have been taken into account. A brief discussion is presented in Appendix B of the usage in enzymology of the term 'co-factor' to describe the metallic component of certain enzymes.

2.16. Non-catalyzed reactions

Chemical reactions that do not require a catalyst are considered to involve neutral species and positive and negative ions. Eq. (17) for reaction at the oxygen of the OH molecule becomes zero at eight electrons, the hydroxide ion. The equation relating the transition energy, E_{tr} , for the hydrogen atom is zero for H⁺. Similarly, many ionic species such as Cl[−], Na⁺, Ag⁺, NO₃[−], etc. are all zero. This is the reason that the rates of some ionic reactions are diffusion controlled for there is no activation energy barrier to be overcome. Raising the temperature of a reaction increases the number of ions and excited electronic states either until a sufficient match occurs to enable the reaction to proceed or until thermal destruction of reactants occurs.

Current efforts are directed at an investigation of the rhodium-catalyzed destruction of NO in

automobile catalytic converters. The mechanism may involve several non-catalyzed steps in addition to the initial catalyzed step.

1. rhodium catalyzed reaction of N_2 with CO to form NNCO on the catalyst;
2. dissociation of NNCO into N plus NCO upon leaving the electric field of the catalyst;
3. thermal non-catalyzed ionization of NO to form $NO^+ + e^-$;
4. non-catalyzed reaction of NO^+ with NCO (at the nitrogen atoms) to form ONNCO $^+$;
5. addition of the electron from step 3 causing dissociation of ONNCO to N_2 and CO_2 .

This reaction will proceed by these steps if the N of NO^+ is a sufficient match to the N of NCO.

2.17. Evidence of the field of a single electron

Data in the Atomic Energy Levels tables involve excitation of a single electron. Transitions of an electron between different energy levels would be expected to create an electric field within an orbital. In the special case of catalysis, this field appears to have the following properties, namely,

1. a deficit or partial charge, quantitatively identified by a four digit number, that is made whole by interaction with the electric field of the adsorbate with transference of this partial charge to the adsorbate forming the intermedion;
2. electronegativity, depending upon the catalytic metal and its environment as compared with the adsorbate, the field may act as either an electron acceptor or electron donor;
3. energy density, the infrared band at 2201 cm^{-1} for CO on chromium oxide corresponds according to Eq. (2) to an intermedion with 8.1 electrons, 14.01 electron-volts Krupenie [34] are needed to remove one electron from carbon monoxide, thus the energy density in this field corresponds to some 30+ electron-volts. Additionally, data indicating the ν_1 vibration of CO_2 published by Kozirovsky and Folman [17] for CO_2 on NaCl and Huber et al. [19] for CO_2 on Au has been shown by Gardner [7] to suggest that CO_2 on these surfaces is changed from linear to bent at an angle of approximately 60° ;

4. quantization, the field appears to have the same effect on a hydroxyl, OH, molecule as on the much larger CO_2 molecule, that is, the same effect, to four significant figures. The constant Perturbation Fraction, independent of the size of the adsorbate, suggests that the field does not diminish by the reciprocal of the square of the distance from a point source, but is quantized. *This certainly suggests that the field is 'bound'.*

These four observed properties give for the first time, some insight into the interior of an orbital, at least an orbital that has a partial charge. The author suggests that this electric field, first identified Selover and Gardner [20] may be referred to as the 'Gardner–Chavis–Selover Field' or the GCS field. This field, produced by a single electron, appears to be the source of the type of catalytic reactions described in this paper by producing resonance between the two reactants allowing electron pairing, sharing and exchange as well as bond breaking and formation.

A paper in Science, December 24, 1999 titled "Fundamental Problem of Quantum Physics Solved" supports the proposal that the field is bound. These researchers McCurdy et al. [35] made a breakthrough in the 50-year quest for a quantum description of the interaction of three charged particles, namely, two electrons and a proton. Their solution required a mathematical transformation of the Schroedinger wave equation to treat the particles not as if their wave functions extend to infinity—as they are treated conventionally—but instead as if the wave functions become zero at some distance from the nucleus.

3. Summary

An investigation that started as a test of the Myers' proposal of the necessity of matching vibrational frequencies as a criterion of reaction has developed into a comprehensive theory capable of quantitative descriptions of diverse chemical and catalytic phenomena. Applications include:

1. predictions of stretching frequencies of bonds in hydrogen peroxide without reference to its spectra;
2. dissection of the action of the zinc containing enzyme carbonic anhydrase and two derivatives containing cobalt and cadmium including reaction

mechanisms at the instant of the catalytic event involving hydroxyl rather than water;

3. explicit descriptions of catalytic reactions involving CO, O₂, Cl₂, OH and CO₂ as reactants with catalysts containing gold, chromium, zinc, cobalt or cadmium as metals or compounds by designating the metal, oxidation state, reaction mechanism and structure of the catalyst;
4. demonstrating that the fundamental determining factor of this type of catalytic activity is the presence of electrons of the catalyst in the low-lying electronic states necessary to produce an electric field created by a single electron;
5. identifying the electric field not only as the source of catalysis but also as the orbital that alters the energy of the reactants so that resonance occurs allowing electron pairing, sharing and the formation and breaking of chemical bonds;
6. defining ‘intermedions’, the long-sought intermediates of catalysis, as a two-dimensional gas since, when data are available, all equations are derived from gaseous species;
7. by providing many different electric fields catalysts multiply the opportunities for reaction many times those provided by only neutral species and positive and negative ions;
8. data and relationships needed to extend these interpretations to other systems to provide mathematical explanations and predictions of chemical phenomena.

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Appendix A

Two data from Herzberg [4] and Walsh [23] are needed to approximate the equation of hydroxyl intermedions by relating the vibrational frequency as a function of the number of valence electrons. These

data are the value of 3569.59 cm⁻¹ for the vibrational frequency of the neutral OH molecule with 7 valence electrons and the value of 1556.38 cm⁻¹ for the vibrational frequency of the neutral dioxygen molecule with 12 valence electrons. The derivation of this equation has been published by Gardner [26] but is summarized here. An equation relating transition energy versus number of electrons for oxygen atoms is a straight line. The hypothesis was made that since a dioxygen molecule with two atoms and 12 electrons has a transition energy of 1556.38 cm⁻¹ a single oxygen atom with six electrons might also have a transition energy of 1556.38 cm⁻¹. When the oxygen atom is electron saturated at 8, the transition energy is considered to be zero. Thus, the equation characterizing oxygen atom intermedions is:

$$E_{\text{tr}o} = 778.19(8 - \eta_o) \quad (\text{A.1})$$

The shape of the right hyperbola of OH with increasing number of electrons curves upward to the right and passes through the point $\nu\text{OH}^7 = 3569.59 \text{ cm}^{-1}$. As electrons are removed from hydroxyl, the vibrational frequency decreases becoming zero at an integral number of electrons. The hydrogen drops off as a proton, leaving the oxygen ion with an integral number of electrons. This oxygen ion is therefore on the straight-line equation for oxygen atom intermedions with a transition energy adjacent to but greater than 3569.59, the value for OH⁷. The list of number of electrons and ‘E_{tr}o’ for oxygen atom ions are: 8(0.00), 7(778.19), 6(1556.38), 5(2334.57), 4(3112.76), 3(3890.95), 2(4669.14 cm⁻¹). The value of 3890.95 for the oxygen ion with three electrons satisfies the above criteria. Accordingly, the dissociation of OH occurs at three electrons and the vibrational frequency of the hydroxide ion with eight valence electrons is 3890.95 cm⁻¹. The equation for hydroxyl intermedions is derived from the three points, namely, $\nu\text{OH}^3 = 0.0$, $\nu\text{OH}^7 = 3569.59$ and $\nu\text{OH}^8 = 3890.95 \text{ cm}^{-1}$. This derivation is indicated in Fig. A.1.

A.1. Vibrational frequency versus number of valence electrons

$$\begin{aligned} &\text{Approximately}(E_{\text{O-H}} - 6080.64)(\eta_{\text{O-H}} - 0.18617) \\ &= -17109.9 \end{aligned} \quad (\text{A.2})$$

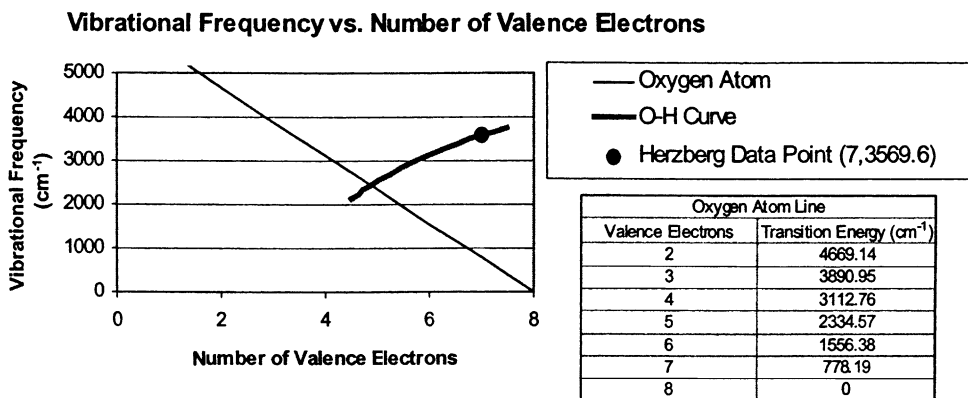


Fig. A.1. Elements used to derive an approximate equation for OH intermediations.

Appendix B

Metals or compounds of metals are ordinarily known to be catalysts except in the field of enzymology. Metals in enzymes are considered ‘co-factors’ because there are some enzymes that function as catalysts that do not contain a metal. The discussion in this paper clearly establishes the metals, zinc, cobalt and cadmium as the site of catalytic activity in the enzyme carbonic anhydrase and its derivatives. This slight difference in terminology becomes clarified when it is shown that the necessary requirement for catalysis is not a metal ion but the presence of an orbital with an electric field having a partial charge. Since certain ionization states of carbon have the necessary complement of low-lying electronic states required to produce a field with a partial charge, carbon may also show catalytic activity. The Atomic Energy Levels tables list only II C as a state with low-lying electronic levels. However, these tables list only positive ions. It is possible that carbon in certain negative ionization states also has the low-lying electronic states necessary for catalysis.

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