

# A Mathematical Interpretation of Catalysis Derived from Infrared Spectroscopy

## II. Reactions of H and H<sub>2</sub> with O, OH, and H<sub>2</sub>O

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Experimental data are presented on the activities reported for metals and compounds in the formation of water by catalysis of the reaction of hydrogen and oxygen and by reduction of metal oxides. The Intermedion Theory is used to predict metals which should catalyze reactions of H and H<sub>2</sub> with O, OH, and H<sub>2</sub>O. Predictions and experiment are in agreement with respect to the metals and in many cases with respect to chemical oxidation state as well. Other metals which are not good catalysts or components of oxidants to form water are not found among the metals predicted for these reactions. Restricting the reactants at the catalytic site to a single oxidation state limits the number of metals predicted to such an extent that differences in reaction mechanism become clearly apparent. Certain oxidation states of Cr, Fe, Cu, Ag, Co, and Ni catalyze the reaction of polarized chemisorbed hydrogen molecules and oxygen atoms to form water directly in a single step. Other metals, such as Mn, Ru, Ir, Pd, and Pt catalyze successive steps through OH and H<sub>2</sub>O<sup>+</sup> intermediates. The catalytic species active in these reactions are Cr<sup>4+</sup>, Fe<sup>4+</sup>, Co<sup>4+</sup>, Ru<sup>3+</sup>, and Ru<sup>2+</sup>, Mn<sup>3+</sup> and Mn<sup>4+</sup>, Mn<sup>6+</sup> and Mn<sup>7+</sup>, and Ni<sup>2+</sup>. The possibility that "intermedions" are one class of the long-sought activated intermediates of catalysis is supported by these results.

### INTRODUCTION

The following study considers the formation of water from the point of view of the Intermedion Theory. This provides a method for the selection of metals which, in metallic or combined form, are the most efficient catalysts for the synthesis of water from hydrogen and oxygen and whose oxides are the most readily reduced by hydrogen. The oxidation state of the metallic component of the oxide or catalyst is described and steps of the reaction mechanism are clearly specified.

The Intermedion Theory is based on the following three hypotheses:

(1) Chemisorbed intermedions are a group of adsorbates which may be described by equations relating their vibration frequencies to numbers of valence electrons.

(2) The polarization exerted on a chemisorbed intermedion by the metallic component of the adsorbent is, for certain oxidation states of the metal, a constant which may be expressed in terms of a fractional number of electrons.

(3) A catalyst for a reaction contains a metal (or its compound) which, because of its unique polarizing effect, forms intermedions with vibration frequencies which match or differ by factors of 2. The matching of vibration frequencies as a criterion for reaction was proposed by Myers (1).

A previous publication (2) presented a qualitative survey of the application of the Intermedion Theory to several catalytic reactions. These were reactions of synthesizing water from hydrogen and oxygen, oxidizing carbon monoxide, decomposing the peroxide radical, and hydrogenating acetylene. The following three new concepts have

changed the qualitative results to ones that are quantitative.

(1) The requirement of a single oxidation state at the catalytic site has diminished the number of metals selected to one-half the former number. This makes differences in the reaction mechanisms with different metals clearly apparent.

(2) The number of metals and their different oxidation states that are included in the theory has been expanded (3) from 10 to 42. It is now possible not only to select the metals and oxidation states that are active in these reactions but also to show that others are not active.

(3) A relationship has been established between the chemical oxidation states of metals and the electronic states of their gaseous ions. With this relationship, the appropriate oxidation state of the metal for catalysis or the oxide most easily reduced may be specified. The method of assignment of the oxidation states of the metals in these reactions is described in a forthcoming paper (3).

In a very abbreviated summary in Table 1, the catalysts found by experiment are compared with the metals and oxidation states predicted for these reactions. The metals predicted show good agreement with experiment. However, in some examples, the oxidation state predicted is not the same as indicated by the empirical formula of the active compound. These differences will be discussed when the reactions of the individual metals are considered.

A more detailed description is presented in Table 2 of the conditions and results of the experimental investigations reported for the synthesis of water and reduction of oxides. A discussion of the predictions presented in Table 3 indicates the method of assigning the elementary reactions catalyzed by each metal. Finally, a detailed description of the calculations necessary to construct Table 3 is presented in Part B of this paper.

#### DISCUSSION. PART A

The interpretation of a catalytic reaction by means of the Intermedion Theory

involves a comparison of two somewhat independent sets of numbers. One set is generated by the simultaneous solutions of the equations of the intermedions of the two reactants. These are the equations relating vibration frequency to numbers of valence electrons. The solutions are those numbers of electrons for which the vibration frequencies of the two reactants match or differ by factors of 2. These numbers of electrons are generally nonintegral, that is, numbers composed of an integer and a fraction. The significant solutions are those for which the numbers of electrons of the pair of matching intermedions have the *same fraction*. These fractions are considered the "optimum fractions" for the reaction. It may be noted that the optimum fractions do not necessarily depend on data from chemisorption or catalysis. The equations of the intermedions can be obtained from the measured vibration frequencies of molecules and ions of the reactants when this information is available.

The other set of numbers is composed of the fractions which are characteristic of the polarization exerted on adsorbates by each metal. These fractions, called "polarization fractions," were discovered during an infrared study of chemisorbed carbon monoxide (18). The possibility that these fractions are a fundamental property of the metal is strongly supported by the discovery of a quantitative relationship between the polarization fractions determined by carbon monoxide chemisorption and the electronic energy levels of metal ions. In a forthcoming paper (3), this relationship is used to calculate the polarization fractions of many metals which have not yet been studied with infrared spectroscopy as adsorbents for carbon monoxide.

These two sets of fractions are used to explain or predict catalytic activity by comparing the optimum fractions of a reaction with the polarization fractions of specific metals. The metal (in the appropriate oxidation state), whose polarization fraction matches one of the optimum fractions of the reaction should chemisorb

TABLE 1  
A COMPARISON OF EXPERIMENTAL AND PREDICTED ACTIVITIES OF METALS AND OXIDES  
*Experimental*

	H <sub>2</sub> O synthesis Heterogeneous	H <sub>2</sub> O synthesis Homogeneous <sup>a</sup>	Oxide reduction
<i>Experimental</i>			
Active	Co <sub>3</sub> O <sub>4</sub> , CuO, MnO <sub>2</sub> , Mn <sup>3+</sup> , <sup>4+</sup> , NiO Pt, Pd, Ir, & Ru metals	Cu (ic) salts Ag salts	Co <sub>3</sub> O <sub>4</sub> , CoO, CuO, Cu <sub>2</sub> O, NiO, Mn <sub>2</sub> O <sub>3</sub> , Cr <sup>(4?)</sup> , <sup>5+</sup> , <sup>6+</sup> Fe <sub>2</sub> O <sub>3</sub> , MnO <sub>2</sub> , Ag oxide
Inactive	TiO, V <sub>2</sub> O <sub>5</sub> , Cr <sub>2</sub> O <sub>3</sub> ZnO, Fe, Co, and Ni Metals	Salts of Fe, Mn, V, Ti, Ni, Co, Pt, Pd, Ir, Rh and Ru	V <sub>2</sub> O <sub>5</sub> , ZnO, Mn <sub>3</sub> O <sub>4</sub> Cr <sub>2</sub> O <sub>3</sub> , MnO, FeO
<i>Predicted</i>			
Active	Co <sup>4+</sup> , Cu, <sup>b</sup> Mn <sup>3+</sup> , <sup>4+</sup> , Ni <sup>3+</sup> , Pt <sup>b</sup> , Pd <sup>b</sup> , Ir <sup>b</sup> , Ru <sup>2+</sup> , <sup>3+</sup> Fe <sup>4+</sup> , Cr <sup>4+</sup> , Ag <sup>b</sup>	Cu <sup>b</sup> (ic) salts Ag <sup>b</sup> salts Cr <sup>4+</sup> , Fe <sup>4+</sup> , Co <sup>4+</sup> , Ni <sup>3+</sup>	Co <sup>4+</sup> , Cu <sup>b</sup> (ic) Ni <sup>3+</sup> , Mn <sup>3+</sup> , <sup>4+</sup> , Cr <sup>4+</sup> Fe <sup>4+</sup> , Ag <sup>b</sup>
Inactive	Ti <sup>3+</sup> , <sup>4+</sup> , V <sup>3+</sup> , <sup>4+</sup> , <sup>5+</sup> Cr <sup>2+</sup> , <sup>3+</sup> , Zn <sup>b</sup> , Fe <sup>1+</sup> , <sup>2+</sup> , <sup>3+</sup> Co <sup>1+</sup> , <sup>2+</sup> , <sup>3+</sup> , Ni <sup>1+</sup> , <sup>2+</sup>	Fe <sup>1+</sup> , <sup>2+</sup> , <sup>3+</sup> All Mn, V, Ti, Pt, Pd Ir, and Ru salts Ni <sup>1+</sup> , <sup>2+</sup> , Co <sup>1+</sup> , <sup>2+</sup> , <sup>3+</sup>	V <sup>3+</sup> , <sup>4+</sup> , <sup>5+</sup> , Zn <sup>b</sup> , Mn <sup>2+</sup> , <sup>3+</sup> Cr <sup>2+</sup> , <sup>3+</sup> , Fe <sup>2+</sup> , <sup>3+</sup>

<sup>a</sup> Assume single-step mechanism and maintenance of oxidation state.

<sup>b</sup> Data necessary to assign oxidation state are not available.

the two reactants, forming intermediions with matching vibration frequencies. The metals listed in Table 3 satisfy this criterion for catalysis of these reactions.

The reactions shown in Table 3 may be grouped into the following three mechanisms for the formation of water: The single-step mechanism combines a hydrogen molecule intermedion with an oxygen atom intermedion, that is,  $H_2 + O \rightleftharpoons H_2O$ . (It is assumed that some dissociation of chemisorbed  $H_2$  and  $O_2$  intermedions takes place so that H and O atom intermedions are present.) The two-step mechanism involves the formation of OH radicals by  $H + O \rightleftharpoons OH$  and the addition of a second H by  $H + OH \rightleftharpoons H_2O$ . The three-step mechanism forms OH, adds  $H_2$  by  $H_2 + OH \rightleftharpoons H_3O^+ + e^-$ , then dissociates the hydronium ion by  $H_3O^+ + e^- \rightleftharpoons H + H_2O$ . Thus the particular elementary reactions whose optimum fractions are matched by the polarization fraction of a metal and/or its compounds indicate the reaction mechanism when the synthesis of water is catalyzed by that metal.

All of the metals in Table 3 are among the efficient catalysts or readily reducible oxidants in Table 2. Since the polarization fractions of Hg, Pb, Cd, and Sn are not known at this time, predictions can not be made of their activity. The more subtle aspects of these reactions are indicated by the oxidation states of the metals in the tables. Experiments reported in Table 2, No. 5 show that a very high temperature is necessary to reduce  $Cr_2O_3$ . This observation is consistent with the first reaction indicated for chromium in Table 3. This reaction, catalyzed by  $Cr^{3+}$ , would reduce a hydroxide but would not reduce  $Cr_2O_3$ . In contrast, the second reaction for chromium will lead from chemisorbed  $H_2$  and O intermedions to water. Oxygen atom intermedions may be formed by the dissociative chemisorption of oxygen molecules in the catalytic reaction. They may come from the lattice of the metal oxide in the case of reduction by hydrogen.) Higher oxides of chromium which contain  $Cr^{4+}$  at any point in the lattice should be readily reduced by hydrogen. Depletive reduction will stop at

TABLE 2  
EXPERIMENTAL RESULTS ON THE SYNTHESIS OF WATER AND REDUCTION  
OF OXIDES REPORTED BY OTHER INVESTIGATORS

1.	Oxidation of hydrogen at 150°C $\text{Co}_3\text{O}_4 > \text{CuO} > \text{MnO}_2 > \text{Fe}_2\text{O}_3 > \text{Cr}_2\text{O}_3 > \text{V}_2\text{O}_5 > \text{ZnO} > \text{TiO}_2$ $\times 10^7$ ———relative activity——— $\times 10$	(4)
2.	Initiation temp. for reduction of oxides by hydrogen CuO, 138°C; Cu <sub>2</sub> O, 144°; Co <sub>3</sub> O <sub>4</sub> , 197°; CoO, 222°; HgO, 258°; NiO, 298°; PbO, 319°; Mn <sub>2</sub> O <sub>3</sub> , 319°; CdO, 340°; Fe <sub>2</sub> O <sub>3</sub> , 309°; Fe <sub>3</sub> O <sub>4</sub> , 362°; FeO, 348°; SnO, 400°; Mn <sub>3</sub> O <sub>4</sub> , 409°; GeO <sub>2</sub> , 480°; V <sub>2</sub> O <sub>5</sub> , 492°; ZnO, 568°.	(5)
3.	Recombination of H <sub>2</sub> + O <sub>2</sub> in aqueous solution Cupric salts—only effective catalysts Silver salts—slight activity but precipitated Pt, Pd, Os, Ir, Ph, and Ru compounds—reduced to metal, then catalyzed explosions Fe, Tl, Ca, Sn, Mn, V, and Ti compounds with UO <sub>2</sub> SO <sub>4</sub> —very slight Ni, Co, Zn, Cd, Pb, As, Li, Rb, K, and Mg—no activity	(6)
4.	Synthesis of water at room temp. by metals Os, Rh, Ir, Pd, and Pt—active Fe, Co, and Ni—inactive	(7)
5.	Cr <sub>2</sub> O <sub>3</sub> reduced by hydrogen in temp. range at 1400°C Cr <sup>4+</sup> to Cr <sup>3+</sup> oxides reduction initiated at 140°C	(8, 9) (10)
6.	MnO not reduced by H <sub>2</sub> at 1100°C Oxidation of hydrogen catalyzed by oxygen-deficient MnO <sub>2</sub> at 25°C, requires both Mn <sup>3+</sup> and Mn <sup>4+</sup> Depletive reduction of MnO <sub>2</sub> at relatively low temp. stops at Mn <sub>2</sub> O <sub>3</sub>	(9) (11)
7.	FeO requires high temp. for reduction Higher oxides may be reduced at 265°C	(9) (12)
8.	Copper oxide reduced at 75°C In high H <sub>2</sub> concn. activity of copper oxide diminishes above 300°C	(13) (4)
9.	In high H <sub>2</sub> concn. activity of nickel oxide diminishes above 200°C	(4)
10.	Silver oxide reduced at 90°C Silver precipitated from silver nitrate solns. by H <sub>2</sub>	(14)
11.	WO <sub>3</sub> reduction by H <sub>2</sub> accelerated by Pt and H <sub>2</sub> O	(15, 16, 17)

Cr<sub>2</sub>O<sub>3</sub> since Cr<sup>4+</sup> is necessary for the reaction, H<sub>2</sub> + O  $\rightleftharpoons$  H<sub>2</sub>O. In addition, the difficulty of reducing Cr<sub>2</sub>O<sub>3</sub> suggests that Cr<sup>4+</sup> sites for intermedions are not available in Cr<sub>2</sub>O<sub>3</sub>.

The elementary reactions predicted in Table 3 for manganese fit exactly the experimental observations reported by Brooks (11), indicated in Table 2, No. 6. He found that an oxygen-deficient, nonstoichiometric manganese dioxide was a very efficient catalyst for the synthesis of water from hydrogen and oxygen. He concluded that both Mn<sup>3+</sup> and Mn<sup>4+</sup> were necessary for catalytic reaction. Further he observed that depletive reduction of MnO<sub>2</sub> at relatively mild conditions stops at Mn<sub>2</sub>O<sub>3</sub>. The first three reactions predicted for manganese in Table 3 form the three-step mechanism for the synthesis of water starting with H and

O intermedions. The 3+ oxidation state is required for the first and third reactions while the 4+ state is required for the second reaction. Thus reduction will stop when the Mn<sup>4+</sup> is exhausted. As in the example of chromium oxides, it is concluded that Mn<sup>4+</sup> sites for intermedions are not in equilibrium with lower oxidation states in Mn<sub>2</sub>O<sub>3</sub>.

The oxidation states which are present in compounds are not always indicated by the empirical formulas. This is well illustrated by the oxides of cobalt. Kuznetsov and Kulish (19) propose that CoO is thermodynamically unstable below 291°C, disproportionating to Co and Co<sub>2</sub>O<sub>4</sub>. Even Co<sub>3</sub>O<sub>4</sub> is a compound containing cobalt in more than one oxidation state. The high activity of Co<sub>3</sub>O<sub>4</sub> as a catalyst or oxidant in these reactions is indicated by its early

TABLE 3  
METALS AND OXIDATION STATES PREDICTED FOR ELEMENTARY REACTIONS

Reaction	Optimum fractions	Metal	Polarization fraction	Chemical oxidation state
$H + OH \rightleftharpoons H_2O$	0.098	Cr	0.09 <sub>9</sub>	3+
$H_2 + O \rightleftharpoons H_2O$	0.199	Cr	0.20 <sub>5</sub>	4+
$H + H_2O \rightleftharpoons H_3O^+ + e^-$	0.365	Cr	0.36 <sub>8</sub>	6+
$H + O \rightleftharpoons OH$	0.158	Mn	0.15 <sub>3</sub>	3+
$H_2 + OH \rightleftharpoons H_3O^+ + e^-$	0.151	Mn	0.15 <sub>3</sub>	4+
$H + H_2O \rightleftharpoons H_3O^+ + e^-$	0.146	Mn	0.15 <sub>3</sub>	3+
$H + O \rightleftharpoons OH$	0.284	Mn	0.28 <sub>0</sub>	6+
$H_2 + OH \rightleftharpoons H_3O^+ + e^-$	0.281	Mn	0.28 <sub>0</sub>	6+
$H + H_2O \rightleftharpoons H_3O^+ + e^-$	0.529	Mn	0.53 <sub>4</sub>	7+
$H + O \rightleftharpoons OH$	0.257	Fe	0.25 <sub>7</sub>	1+
$H + H_2O \rightleftharpoons H_3O^+ + e^-$	0.253	Fe	0.25 <sub>7</sub>	1+
$H_2 + O \rightleftharpoons H_2O$	0.315	Fe	0.30 <sub>8</sub>	4+
$H_2 + O \rightleftharpoons H_2O$	0.315	Cu	0.32	*
$H_2 + O \rightleftharpoons H_2O$	0.544	Ag	0.54	*
$H_2 + OH \rightleftharpoons H_3O^+ + e^-$	0.534	Ag	0.54	*
$H + H_2O \rightleftharpoons H_3O^+ + e^-$	0.529	Ag	0.54	*
$H_2 + O \rightleftharpoons H_2O$	0.544	Co	0.54 <sub>2</sub>	4+
$H + O \rightleftharpoons OH$	0.798	Ir	0.80	*
$H + OH \rightleftharpoons H_2O$	0.797	Ir	0.80	*
$H + O \rightleftharpoons OH$	0.817	Pd	0.81	*
$H_2 + OH \rightleftharpoons H_3O^+ + e^-$	0.815	Pd	0.81	*
$H + H_2O \rightleftharpoons H_3O^+ + e^-$	0.811	Pd	0.81	*
$H + O \rightleftharpoons OH$	0.817	Pt	0.81 <sub>7</sub>	*
$H_2 + OH \rightleftharpoons H_3O^+ + e^-$	0.816	Pt	0.81 <sub>7</sub>	*
$H + H_2O \rightleftharpoons H_3O^+ + e^-$	0.812	Pt	0.81 <sub>7</sub>	*
$H_2 + O \rightleftharpoons H_2O$	0.856	Ni	0.85 <sub>7</sub>	3+
$H + O \rightleftharpoons OH$	0.857	Ni	0.85 <sub>7</sub>	2+
$H + O \rightleftharpoons OH$	0.750	Ru	0.74 <sub>5</sub>	3+
$H + OH \rightleftharpoons H_2O$	0.944	Ru	0.94 <sub>2</sub>	2+
$H + OH \rightleftharpoons H_3O^+ + e^-$	0.945	Ru	0.94 <sub>2</sub>	2+
$H + H_2O \rightleftharpoons H_3O^+ + e^-$	0.944	Ru	0.94 <sub>2</sub>	1+

TABLE 4  
MECHANISMS AND OXIDATION STATES PREDICTED FOR SYNTHESIS OF WATER

<i>Single Step</i> $H_2 + O \rightleftharpoons H_2O$	<i>Two Step</i> $H + O \rightleftharpoons OH$ $H + OH \rightleftharpoons H_2O$	<i>Three Step</i> $H + O \rightleftharpoons OH$ $H_2 + OH \rightleftharpoons H_3O^+ + e^-$ $H_3O^+ \rightleftharpoons H^+ + H_2O$
Cr <sup>4+</sup>	Ir	Mn <sup>3+, 4+, 6+</sup>
Fe <sup>4+</sup>	Ru <sup>2+, 3+</sup>	Pd
Cu		Pt
Ag		Ru <sup>1+, 2+, 3+</sup>
Co <sup>4+</sup>		
Ni <sup>3+</sup>		

position in the series reported in Table 2, Nos. 1 and 2. This activity is consistent with the close match of the optimum fraction of 0.544 in Table 3 to the polarization fraction of 0.54<sub>3</sub> for Co<sup>4+</sup>. Thus Co<sup>4+</sup> may be in equilibrium with lower oxidation

leads to water by the single-step mechanism. The higher temperatures for reduction of FeO may be required to generate some Fe<sup>4+</sup> sites for intermediates.

Popovskii and Boreskov (4) report that the catalytic activity of nickel oxide for the

TABLE 5  
 $\nu(\text{H-H}) = 2080.57 E(\text{H}_2)$  (1)  
 $\nu(\text{O}) = 778.19 [8 - E(\text{O})]$  (2)  
 $\text{O}^6 + \text{H}_2^2 \rightleftharpoons \text{H}_2\text{O}^8$  (3)

Apparent electron transfers electron exchanges		Optimum fractions	Corresponding gaseous ions	Metal	Polarization fractions	Chemical oxidation state
O	H <sub>2</sub>					
2 - e	2 - e	0.003	—	—	—	—
e	2 - e	0.003	—	—	—	—
2 - e	2 - e	0.006	—	—	—	—
e	2 - e	0.006	—	—	—	—
2 - e	2 - e	0.012	—	—	—	—
e	2 - e	0.012	—	—	—	—
2 - e	2 - e	0.023	—	—	—	—
e	2 - e	0.023	—	—	—	—
2 - e	2 - e	0.046	II	V	0.04 <sub>2</sub>	ic 2+
e	2 - e	0.046	II	V	0.04 <sub>2</sub>	ic 2+
1 - e	1 - e	0.089	II	Sc	0.08 <sub>8</sub>	ous 1+
e	2 - e	0.089	II	Sc	0.08 <sub>8</sub>	ic 2+
2 - e	2 - e	0.091	II	Sc	0.08 <sub>8</sub>	ic 2+
e	2 - e	0.171	—	—	—	—
2 - e	2 - e	0.179	—	—	—	—
1 + e	1 - e	0.199	IV	Cr	0.20 <sub>5</sub>	ous 4+
e	2 - e	0.315	—	Cu	0.32	ic
2 - e	2 - e	0.342	III	Fe	0.30 <sub>8</sub>	ic 4+
1 + e	1 - e	0.499	—	—	—	—
e	2 - e	0.544	—	Ag	0.54	ic
e	2 - e	0.544	III	Co	0.54 <sub>3</sub>	ic 4+
2 - e	2 - e	0.630	—	—	—	—
1 - e	1 - e	0.712	II	Ta	0.71 <sub>2</sub>	ous 1+
1 + e	1 - e	0.714	II	Ta	0.71 <sub>2</sub>	ous 1+
1 + e	1 - e	0.846	—	—	—	—
e	2 - e	0.856	III	Ni	0.85 <sub>7</sub>	ic 3+
1 + e	1 - e	0.920	—	—	—	—
1 + e	1 - e	0.959	—	—	—	—
1 + e	1 - e	0.979	—	—	—	—
1 + e	1 - e	0.990	—	—	—	—

states in oxides which have the empirical formula of CoO and Co<sub>3</sub>O<sub>4</sub>.

The equilibria between oxidation states in iron oxides may be similar to the equilibria suggested for cobalt oxides. As with cobalt, it is the 4+ oxidation state which is predicted in the third reaction shown for iron in Table 3. This reaction

oxidation of hydrogen actually decreases at temperatures above 200°C at the higher hydrogen concentrations. The 3+ oxidation state is required in the first reaction for nickel in Table 3. This is the single-step mechanism to form water. Thus reaction conditions which cause the reduction of Ni<sup>3+</sup> to Ni<sup>2+</sup>, if only on the surface, should

diminish the activity of nickel oxides for this reaction.

Nickelous salts were found to be inactive as homogeneous catalysts for the recombination of hydrogen and oxygen gas, Table II, No. 3. The inactivity of the lower oxidation states of nickel is also

The oxidation states of copper, silver, iridium, palladium, and platinum which are active in these reactions can not be determined by the method used for the other metals in Table 3. The data are not available to assign the numerical oxidation states from the electronic energy levels of

TABLE 6  
 $\nu(\text{H}) = 4161.14 E(\text{H})$  (4)  
 $\nu(\text{O}) = 778.19 [8 - E(\text{O})]$  (2)  
 $\text{O}^6 + \text{H}^1 \rightleftharpoons (\text{OH})^7$  (5)

Apparent electron transfers electron exchanges		$\epsilon$ Optimum fractions	Corresponding gaseous ions	Metal	Polarization fractions	Chemical oxidation state
O	H					
1 + e	1 - e	0.003	—	—	—	—
1 + e	1 - e	0.006	—	—	—	—
1 - e	1 - e	0.009	—	—	—	—
1 + e	1 - e	0.012	—	—	—	—
1 - e	1 - e	0.017	—	—	—	—
1 + e	1 - e	0.023	—	—	—	—
1 - e	1 - e	0.035	—	—	—	—
1 + e	1 - e	0.045	II	V	0.04 <sub>2</sub>	ous 1+
1 - e	1 - e	0.069	II	Ti	0.06 <sub>4</sub>	ous 1+
1 + e	1 - e	0.086	II	Sc	0.08 <sub>8</sub>	ous 1+
1 - e	1 - e	0.134	—	—	—	—
1 + e	1 - e	0.158	IV	Mn	0.15 <sub>3</sub>	ous 3+
1 - e	1 - e	0.257	II	Fe	0.25 <sub>7</sub>	ous 1+
1 + e	1 - e	0.272	—	—	—	—
e	e	0.284	V	Mn	0.28 <sub>0</sub>	ic 6+
[2 - e]	[e]	[0.361]	—	—	—	—
1 + e	1 - e	0.428	—	—	—	—
1 - e	1 - e	0.473	III	Zr	0.46 <sub>3</sub>	ous 3+
1 + e	1 - e	0.599	II	Y	0.59 <sub>7</sub>	ous 1+
1 + e	1 - e	0.750	III	Ru	0.74 <sub>5</sub>	ous 3+
e	e	0.798	—	(Ir)	(0.80)	ic
1 - e	1 - e	0.817	—	(Pd)	(0.81)	ous
1 - e	1 - e	0.817	—	Pt	0.81 <sub>7</sub>	ous
1 + e	1 - e	0.857	III	Ni	0.85 <sub>7</sub>	ous 2+
1 + e	1 - e	0.923	—	—	—	—
1 + e	1 - e	0.960	—	—	—	—
1 + e	1 - e	0.980	—	—	—	—
1 + e	1 - e	0.990	—	—	—	—
1 + e	1 - e	0.995	—	—	—	—

indicated by the data shown in Table 2. Remy and Gonningen (7) reported that metallic nickel did not catalyze the synthesis of water at room temperature. These observations are not inconsistent with the possibility that some  $\text{Ni}^{3+}$  may be present when  $\text{NiO}$  participates in these reactions as a catalyst or oxidant.

gaseous ions of Cu, Ag, Ir, Pd, and Pt. However, the activity of these metals in reactions of hydrogen and oxygen is very well known. The catalytic activity of the metallic state of Ir, Pd, and Pt, shown in Table 2, No. 4, suggests that species corresponding to the 1+ or even 2+ oxidation states may occur at the surfaces of metals.

However, in the case of a reaction such as the synthesis of water, a single-layer epitaxial oxide film might form. This would oxidize some of the metal atoms at the surface and the catalytic activity might be due to higher oxidation states.

The reactions of aqueous solutions of Ag, Pd, and Pt salts more clearly indicate the catalytic activity of their higher oxidation states. These are "noble" metals since they can be precipitated by hydrogen from aqueous solutions of their salts at room

by the following activity of platinum in a heterogeneous reaction.

Khoobiar (15), Kohn and Boudart (16), and Benson *et al.* (17), have shown that  $WO_3$  is reduced by hydrogen at room temperature in the presence of platinum and water. The reactions in Table 3 show that platinum should catalyze the reaction of H and  $H_2O$  intermediates, forming  $H_3O^+$  and an electron. The marked effect of platinum and water on the reduction of  $WO_3$  suggests that the reducing agent may

TABLE 7  
 $\nu(H) = 4161.14 E(H)$  (4)  
 $[\nu(-OH) + 2189.69][E(OH) - 0.1862] = 17109.7 \text{ cm}^{-1}$  (6)  
 $-OH^7 + H^1 \rightleftharpoons H_2O^8$  (7)

Apparent electron transfers electron exchanges		Optimum fractions	Corresponding gaseous ions	Metal	Polarization fractions	Chemical oxidation state
OH	H					
1 + e	1 - e	0.0	—	—	—	—
1 - e	1 - e	0.011	—	—	—	—
1 - e	1 - e	0.022	—	—	—	—
1 - e	1 - e	0.044	II	V	0.04 <sub>2</sub>	ous 1+
1 - e	1 - e	0.085	II	Sc	0.08 <sub>8</sub>	ous 1+
e	e	0.098	III	Cr	0.09 <sub>9</sub>	ic 3+
1 - e	1 - e	0.162	—	—	—	—
[2 - e]	[e]	[0.185]	—	—	—	—
1 - e	1 - e	0.294	—	—	—	—
e	e	0.400	—	—	—	—
1 - e	1 - e	0.500	—	—	—	—
e	e	0.638	—	—	—	—
[2 - e]	[e]	[0.727]	—	—	—	—
1 - e	1 - e	0.779	—	(Rh)	(0.78)	ous
e	e	0.797	—	(Ir)	(0.80)	ic
e	e	0.892	—	—	—	—
e	e	0.944	II	Ru	0.94 <sub>2</sub>	ic 2+
e	e	0.971	—	—	—	—

temperature. These three metals are predicted in Table 3 to catalyze the following reaction which should lead to reduction of the metallic component in solution. The combination of a hydrogen molecule with an OH radical would form an  $H_3O$  species with nine outershell electrons. Since an oxygen atom can accommodate no more than eight outershell or valence electrons, and remain in the electronic ground state, the extra electron would be released and available for reduction of the metallic component. This reaction is also suggested

be these electrons. The removal of these electrons by  $WO_3$  should drive this reaction to the right. Other metals in Table 3 which catalyze this reaction may also facilitate the reduction of  $WO_3$ , provided they are not reduced to an inactive oxidation state.

The activity of copper as a catalyst for the oxidation of hydrogen is very well known. The polarization fraction of copper matches one of the optimum fractions in Table 3 for the single-step synthesis of matter. The decrease in catalytic activity of copper oxide above 300°C with a high



hydrogen concentration may be due to a reduction of the copper from a higher oxidation state which is required for this reaction. The homogeneous catalysis by aqueous solutions of salts of the recombination of gaseous hydrogen and oxygen also suggests that some oxidation state higher than the metallic state is active in this reaction. While it is not possible to assign the numerical oxidation state of the copper

The mechanisms and oxidation states predicted for these metals in the synthesis of water and reduction of their oxides are summarized in Table 4.

### Conclusion

There does not seem to be any fundamental difference between the catalytic reaction of the synthesis of water from hydrogen and oxygen gases and the chem-

TABLE 8

$$\begin{aligned} \nu(\text{H}_2) &= 2080.57 E(\text{H}_2) & (1) \\ [\nu(-\text{OH}) + 2189.69][E(\text{OH}) - 0.1862] &= 17109.7 & (6) \\ -\text{OH}^{\cdot} + \text{H}_2^{\cdot} &\rightleftharpoons \text{H}_3\text{O}^{\cdot} + \text{e}^- & (8) \end{aligned}$$

Apparent electron transfers electron exchanges		Optimum fractions	Corresponding gaseous ions	Metal	Polarization fractions	Chemical oxidation state
OH	H <sub>2</sub>					
2 - e	2 - e	0.005	—	—	—	—
2 - e	2 - e	0.010	—	—	—	—
e	2 - e	0.019	—	—	—	—
2 - e	2 - e	0.020	—	—	—	—
e	2 - e	0.037	—	—	—	—
2 - e	2 - e	0.040	II	V	0.04 <sub>2</sub>	ic 2+
e	2 - e	0.071	—	—	—	—
2 - e	2 - e	0.079	—	—	—	—
e	2 - e	0.132	—	—	—	—
2 - e	2 - e	0.151	IV	Mn	0.15 <sub>3</sub>	ic 4+
e	2 - e	0.230	—	—	—	—
1 - e	1 - e	0.232	—	—	—	—
2 - e	2 - e	0.281	V	Mn	0.28 <sub>6</sub>	ic 6+
e	2 - e	0.369	—	—	—	—
2 - e	2 - e	0.496	—	—	—	—
e	2 - e	0.534	—	Ag	0.54	ic
e	2 - e	0.534	VI	Mn	0.53 <sub>4</sub>	ic 8+
1 - e	1 - e	0.692	—	—	—	—
e	2 - e	0.692	—	—	—	—
e	2 - e	0.815	—	(Pd)	(0.81)	ic
2 - e	2 - e	0.816	—	Pt	0.81 <sub>7</sub>	ic
e	2 - e	0.897	—	—	—	—
e	2 - e	0.945	II	Ru	0.94 <sub>2</sub>	ic 2+
e	2 - e	0.972	—	—	—	—
e	2 - e	0.986	—	—	—	—

species which catalyze the single-step synthesis of water, the pair of matching H<sub>2</sub> and O intermediations shown in Part B correspond to the "ic" oxidation state of copper. This is in good agreement with the experimental observation that cupric salts are the effective catalysts for this homogeneous reaction.

ical reaction of the reduction of metal oxides by hydrogen. In the case of the catalytic reaction both reactants must be supplied to the metal compound. This is different from the chemical reaction in which the oxygen of the metal compound is consumed. The chemical reaction generally requires the higher temperature. The

TABLE 9 A

$$\begin{aligned} \nu(\text{H}) &= 4161.14 E(\text{H}) && (4) \\ [\nu_1(-\text{OH}_2) + 2153.49][E(\text{H}_2\text{O}) - 0.0552] &= 17109.7 && (9) \\ \nu_1(-\text{OH}_2)^8 + \text{H}^1 &\rightleftharpoons \text{H}_3\text{O}^8 + \text{e}^- && (10) \end{aligned}$$

Apparent electron transfers electron exchanges		Optimum fractions	Corresponding gaseous ions	Metal	Polarization fractions	Chemical oxidation state
H <sub>2</sub> O	H					
1 - e	1 - e	0.009	—	—	—	—
1 - e	1 - e	0.018	—	—	—	—
1 - e	1 - e	0.036	II	V	0.04 <sub>2</sub>	ous 1+
1 - e	1 - e	0.069	II	Ti	0.06 <sub>4</sub>	ous 1+
1 - e	1 - e	0.128	—	—	—	—
[2 - e]	[e]	[0.207]	—	—	—	—
1 - e	1 - e	0.224	II	Nb	0.22 <sub>0</sub>	ous 1+
1 - e	1 - e	0.362	—	—	—	—
1 - e	1 - e	0.526	—	—	—	—
[2 - e]	[e]	[0.668]	—	—	—	—
1 - e	1 - e	0.685	—	—	—	—
1 - e	1 - e	0.811	—	(Pd)	(0.81)	ous
1 - e	1 - e	0.811	—	Pt	0.81 <sub>7</sub>	ous
1 - e	1 - e	0.894	—	—	—	—
1 - e	1 - e	0.944	II	Ru	0.94 <sub>2</sub>	ous 1+
1 - e	1 - e	0.971	—	—	—	—
1 - e	1 - e	0.986	—	—	—	—

TABLE 9 B

$$\begin{aligned} \nu(\text{H}) &= 4161.14 E(\text{H}) && (4) \\ [\nu_2(-\text{OH}_2) + 1671.05][E(\text{H}_2\text{O}) + 2.2390] &= 17109.7 && (11) \\ \nu_2(-\text{OH}_2)^8 + \text{H}^1 &\rightleftharpoons \text{H}_3\text{O}^8 + \text{e}^- && (12) \end{aligned}$$

Apparent electron transfers electron exchanges		Optimum fractions	Corresponding gaseous ions	Metal	Polarization fractions	Chemical oxidation state
H <sub>2</sub> O	H					
1 - e	1 - e	0.011	—	—	—	—
1 - e	1 - e	0.021	—	—	—	—
1 - e	1 - e	0.041	II	V	0.04 <sub>2</sub>	ous 1+
1 - e	1 - e	0.079	—	—	—	—
1 - e	1 - e	0.146	III	Ti	0.14 <sub>7</sub>	ous 1+
1 - e	1 - e	0.146	IV	Mn	0.15 <sub>3</sub>	ous 3+
1 - e	1 - e	0.253	II	Fe	0.25 <sub>7</sub>	ous 1+
[2 - e]	[e]	[0.289]	—	—	—	—
1 - e	1 - e	0.400	—	—	—	—
1 - e	1 - e	0.567	—	—	—	—
1 - e	1 - e	0.721	—	—	—	—
[2 - e]	[e]	[0.764]	—	—	—	—
1 - e	1 - e	0.836	—	—	—	—
1 - e	1 - e	0.910	—	—	—	—
1 - e	1 - e	0.953	—	—	—	—
1 - e	1 - e	0.976	—	—	—	—

TABLE 9 C

$$\nu(\text{H}) = 4161.14 E(\text{H}) \quad (4)$$

$$[\nu_3(-\text{OH}_2) + 2169.24][E(\text{H}_2\text{O}) - 0.1123] = 17109.7 \quad (13)$$

$$\nu_3(-\text{OH}_2)^8 + \text{H}^1 \rightleftharpoons \text{H}_3\text{O}^8 + \text{e}^- \quad (14)$$

Apparent electron transfers electron exchanges		Optimum fractions $\epsilon$	Corresponding gaseous ions	Metal	Polarization fractions	Chemical oxidation state
H <sub>2</sub> O	H					
1 - e	1 - e	0.009	—	—	—	—
1 - e	1 - e	0.019	—	—	—	—
1 - e	1 - e	0.036	II	V	0.04 <sub>2</sub>	ous 1+
1 - e	1 - e	0.070	—	—	—	—
1 - e	1 - e	0.129	—	—	—	—
[2 - e]	[e]	[0.217]	—	—	—	—
1 - e	1 - e	0.227	—	—	—	—
1 - e	1 - e	0.365	V	Cr	0.36 <sub>8</sub>	ous 6+
1 - e	1 - e	0.529	—	Ag	0.54	ous
1 - e	1 - e	0.529	VI	Mn	0.53 <sub>4</sub>	ous 7+
[2 - e]	[e]	[0.678]	—	—	—	—
1 - e	1 - e	0.688	—	—	—	—
1 - e	1 - e	0.812	—	(Pd)	(0.81)	ous
1 - e	1 - e	0.812	—	Pt	0.81 <sub>7</sub>	ous
1 - e	1 - e	0.895	—	—	—	—
1 - e	1 - e	0.944	II	Ru	0.94 <sub>2</sub>	ous 1+
1 - e	1 - e	0.971	—	—	—	—
1 - e	1 - e	0.985	—	—	—	—

oxygen removed as water from the catalytic site may have to be replenished by diffusion of oxygen from other parts of the metal oxide lattice. Constant regeneration of a particular lattice face and oxidation state may be necessary to continue reduction of the oxide.

Heterogeneous and homogeneous reactions are also shown to be interpreted by the same group of elementary reactions. The role of intermedions as the long sought activated species in catalytic reactions is supported by these correlations between experiment and theory.

#### DISCUSSION. PART B

This section presents the calculations and tables which produce the data in Tables 1 and 3 of Part A. The requirement of a single oxidation state at the catalytic site seems to be the last general restriction to be applied to the optimum fractions. Therefore, for each of the reactions, all of the optimum fractions are listed so that they will be available when polarization fractions are determined for additional

metals. The numerical oxidation states of the metals predicted are included in the tables. However, the method of assignment of these oxidation states is described in the forthcoming paper (3). The oxidation states are derived from the polarization fraction. Thus they are more easily discussed in the paper which describes the calculation of polarization fractions.

In contrast with the previous paper (2), the Tables 5-9 are arranged to emphasize the oxidation states of the metals. As noted in the previous paper, there appear to be two species of the metallic component of the adsorbent. If the polarization fraction is designated by  $\epsilon$ , these two species appear to have partially filled orbitals containing  $\epsilon$  and  $1 + \epsilon$  electrons. On the basis that the effect of the apparent electron transfer is to fill or empty the partially filled orbital, the electron transfers shown in the drawing below appear to take place. The adsorbate may *donate*  $2 - \epsilon$  electrons to fill the orbital or *accept*  $\epsilon$  electrons to empty the orbital in contact with a metal species containing  $\epsilon$  in its partially filled

orbital. Correspondingly, the adsorbate may appear to *donate*  $1 - \epsilon$  or *accept*  $1 + \epsilon$  in contact with a metal species containing  $1 + \epsilon$  electrons in this orbital. Two species of a metal differing by 1 electron seem to fit the conventional designations of the "ic" and "ous" oxidation states. Thus, in columns 1 and 2 of the tables, the "ic" state of the metal corresponds to apparent electron transfers which are indicated by  $2 - \epsilon$  and/or  $\epsilon$ . The "ous" state of the metal corresponds to apparent electron transfers indicated by  $1 - \epsilon$  and/or  $1 + \epsilon$ . The designations "ic" and "ous" derived in this manner are observed to agree in many cases with the chemical name of the metal compound.

The Optimum Fractions in column 3 of Tables 5-9 are found by the simultaneous solutions of the equations at the top of the table. These are the fractions (of electrons) for which the vibration frequencies of the two intermedions match. Those metals are noted in column 5 that have polarization fractions close to or equal to the optimum fractions. The oxidation states of the metals are identified in column 4 by the ionization state of the corresponding gaseous ions (using the physicists' notation where the atom is designated by "I") and by the "ic" or "ous"

designation in the last column. The forthcoming paper (3) lists the polarization fractions of the various metals and explains the relationship of the gaseous metal ion and the "ic" or "ous" designation to the chemical oxidation state in the last column. In the equations at the top of each table, the symbol  $\nu$  refers to the vibration frequency and the symbol  $E$  refers to the total number of valence electrons which are assigned to the reactant. This number of electrons may be written as a post-superscript to the symbol of the reactant.

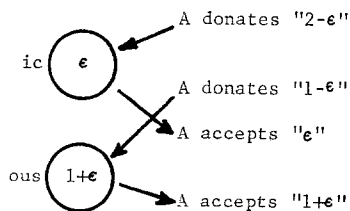
The optimum fraction, 0.856, in Table 5 may be used to further illustrate this type of analysis of a catalytic reaction. An oxygen atom intermedion which has accepted  $\epsilon$  electrons matches a hydrogen molecule intermedion which has donated  $2 - \epsilon$  electrons when  $\epsilon$  equals 0.856. The neutral oxygen atom has six valence electrons; the acceptance of 0.856 makes  $E(O) = 6.856$ . Substituting this value for  $E(O)$  in Eq. (2), in Table 1,  $\nu(O^{6.856}) = 890.25 \text{ cm}^{-1}$ . The neutral  $H_2$  molecule has two valence electrons. The loss of  $(2 - \epsilon)$ ,  $[2 - (2 - \epsilon) = 2 - 2 + 0.856]$ , makes  $E(H_2) = 0.856$ . From Eq. (1), in Table 5,  $\nu(H_2^{0.856}) = 1780.97 \text{ cm}^{-1}$ . The two frequencies differ by a factor of 2. The fraction 0.856 is, therefore, an optimum

Example:

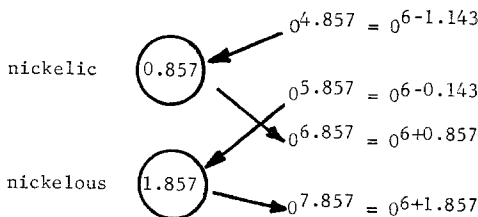
Oxygen atom intermedions on nickel compounds  
 Neutral oxygen atom has 6 valence electrons  
 Polarization fraction of nickel is 0.857

Therefore:  $\epsilon = 0.857$   
 $1+\epsilon = 1.857$   
 $1-\epsilon = 0.143$   
 $2-\epsilon = 1.143$

Partially Filled  
 Metal Orbitals



Partially Filled  
 Nickel Orbitals



"A" = adsorbate

fraction for the reaction of a hydrogen molecule intermedion with an oxygen atom intermedion to form water. The polarization fraction of nickel, namely, 0.85<sub>7</sub>, is certainly close enough to the optimum fraction, 0.856, to satisfy this criterion to catalyze this reaction. The matching pair of intermedions, donating 2 -  $\epsilon$  and accepting  $\epsilon$  correspond to the "ic" state of nickel. The last column notes that the 3+ chemical oxidation state corresponds to the "ic" state of the nickel species whose polarization fraction of 0.85<sub>7</sub> corresponds to the gaseous III Ni ion.

Table 5 presents the data for the reaction of a hydrogen molecule intermedion with an oxygen atom intermedion to form water in the single step mechanism. Table 6 presents the initial step in the other mechanisms, that is, the reaction of atomic H and O intermedions to form an OH radical. Although the optimum fraction, 0.361, is shown in Table 6, it is in brackets. The pair of intermedions for this fraction requires that the O atom corresponds to an electron donor, donating 2 -  $\epsilon$  electrons while the H atom accepts  $\epsilon$ . Since an O atom is more electronegative than an H atom, a site which accepts electrons from an O atom would not donate to an H atom. Thus this is a pair of intermedions which cannot coexist at the same site. This situation is also encountered in Table 7 and 9. Tables 7 and 8 present the reactions of H atom and H<sub>2</sub> molecule intermedions with OH radical intermedions. Tables 9A, B, and C present reactions of H atom intermedions with water intermedions to form a hydronium molecule, H<sub>3</sub>O<sup>+</sup>, and an electron. Since water has three normal vibrations, there are three tables. In Part A, it is indicated that this reaction proceeds as written in Tables 9 during the platinum-catalyzed reduction of tungstic oxide with hydrogen and water. This reaction goes to the left in the three-step mechanism for the formation of water, shown in Tables 3 and 4 of Part A. All reactions are considered to be reversible, at least microscopically reversible. The direction depends on the thermodynamics of the system.

The formation of water by any of the

three reaction mechanisms requires the initial combination of H or H<sub>2</sub> with O. Therefore all metals active in these reactions should be in Tables 5 and/or 6. In addition to the active metals several others which are inactive in these reactions are found in these two tables. These are V 1+ and 2+, Ti 1+, Sc 1+ and 2+, Fe 1+, and Zr 3+. The 1+ and 2+ oxidation states may correspond to the metallic state or the lower oxidation state compounds. No experimental data were found concerning any activity of these oxidation states of these metals for the synthesis of water. The occurrence of Zr 3+ in Table 6 does not lead to water since Zr does not appear on any of the other tables.

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#### REFERENCES

1. MYERS, R. R., *Ann. N. Y. Acad. Sci.* **72**, 341 (1958).
2. GARDNER, R. A., *J. Catalysis* **3**, 7 (1964).
3. GARDNER, R. A., to be published.
4. POPOVSKII, V. V., AND BORESKOV, G. K., *Probl. Kinetiki i Kataliz, Akad. Nauk SSSR* (No. 10), pp. 67-72 (1960).
5. OATES, W. A., AND TODD, D. D., *J. Australian Inst. Metals* **7**, 109 (1962).
6. McDUFFIE, H. F., COMPERE, E. L., STONE, H. H., WOO, L. F., AND SECOY, C. H., *J. Phys. Chem.* **62**, 1030 (1958).
7. REMY, H., AND GONNINGEN, H., *Z. Anorg. Allgem. Chem.* **148**, 279-292 (1925).
8. STRATER, K., AND MANTELL, C. L., *Trans. AIME* **230**(5), 1141-1150 (1964).
9. MANCHINSKII, V. G., LYUBAN, A. P., AND SEMENOV, A. M., *Nauchn. Tekhn. Inform. Buyl. Leningr. Politekhni. Inst.* (10), pp. 92-95 (1961) (Russ).
10. MIYAKI, R., *J. Pharm. Soc. Japan* **68**, 1-4 (1948).
11. BROOKS, C. S., *J. Catalysis* **4**, 535-545 (1965).
12. MORIYAMA, A., *Kogyo Kagaku Zasshi* **66**(9), 1289-1295 (1963).

13. HAASE, G., ROYEN, P., KORINTH, E., AND LOUIS, R., *Angew Chem.* **69**, 778 (1957).
14. ERMOLAEV, A. V., *Tr. Tomsk. Gos. Univ., Ser. Khim.* **157**, 205-216 (1963).
15. KHOBIAR, S., *J. Phys. Chem.* **68**, 411 (1964).
16. KOHN, H. W., AND BOUDART, M., *Science* **145**, 149 (1964).
17. BENSON, J. E., KOHN, H. W., AND BOUDART, M., *J. Catalysis* **5**, 307 (1966).
18. GARDNER, R. A., AND PETRUCCI, R. H., *J. Am. Chem. Soc.* **82**, 5051 (1960).
19. KUZNETSOV, A. N., AND KULISH, N. F., *Izv. Akad. Nauk. SSSR, Otd. Tekhn. Nauk. Met. i Toplivo* (No. 4), pp. 52-58 (1959).