general feature of the catalytic activity of semi-conductors, it yields no definite information as to the catalytic mechanism. It is anticipated, however, that through the introduction of the concept of a "virtual atmosphere", one will in time succeed in gaining a deeper insight into the catalytic mechanism at least in some cases. One of the best examples for such a case is found in the oxydation of carbon monoxide, as will be discussed in Part II of the present work.

The Ionic Adsorption of Gases on Semi-Conductors and Their Catalytic Activities
Part II. The Law of the Virtual Atmosphere and Its Applications

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In Part I of the present work the theory of ionic adsorption was developed. In the present paper, the theory of the catalytic activity of semi-conductors is extended on the basis of the previous conclusions as to the ionic adsorption of gases. By introducing the concept of a "virtual atmosphere", a guiding principle for the selection of catalysts is obtained. The law of the virtual atmosphere here derived is applied to the oxidation of carbon monoxide on a semi-conductor, and provides the reasons the Rideal mechanism in this reaction is observed not on n-type but on p-type semi-conductor catalysts. Moreover, the relation between the catalytic activity and the history of a sample is reasonably interpreted in terms of the virtual atmosphere. Other reactions such as the decomposition of nitrous oxide and the synthesis of methanol are discussed qualitatively.

In Part I of the present work[1], the author developed a theory of ionic adsorption on semi-conductors with due regard to the space charge induced near the surface of a crystal, and discussed the catalytic activities of semi-conductors with special consideration for the types of semi-conductors and the signs of the electric charge on the adsorbed molecules. The results obtained, contradict the prediction made by Dowden[2] that p-type (or n-type) semi-conductors will in general be good catalysts for reactions in which the amount of negatively (or positively) charged adsorbates plays a decisive role in the rate of reaction concerned, and that the greater electronic conductivity, the more active the semi-conductor will be. In the previous theory the effect due to the migration of the constituent ions of a semi-conductor was not taken into consideration and the mechanism of catalytic reactions could not be discussed in detail.

It is now desirable, at least qualitatively, to take into account the migration of ions and the changes in the properties of a catalyst with the surrounding atmosphere. For this purpose it is convenient to introduce the concept of "the virtual atmosphere" which specifies the external conditions acting on the working catalyst.

1. The Law of the Virtual Atmosphere

The theory developed is based on the previous theory of adsorption in which the plane model of adsorption sites has been adopted for the sake of mathematical simplicity, but the essential results remain unaltered if the problem is treated from the standpoint of an active-center model; since the energy of the electric double layer which plays a primary role in the present theory is almost independent of the model of the adsorption sites.

If an n-type semi-conductor catalyst is placed in an oxidizing atmosphere, it will be gradually oxidized, approach a stoichiometric composition and consequently become less active owing to the decrease in the concentration of electronic carriers or in its ability for adsorption, as was shown in Part I. In the case of p-type semi-conductors, further oxidation brings about an increase of positive holes, and re-

[1] T. Takaishi, Z. Naturforschg. 11 a, 286 [1956].

[2] D. A. Dowden, J. Chem. Soc., Lond. 1950, 242.

sults in the elevation of catalytic powers, unless a different crystal phase developes. Thus, in an oxidizing atmosphere, p-type semi-conductors may in general be considered better catalysts than n-type semi-conductors, in so far as the ionic adsorption plays an important role in the reaction process. The reverse is the case with a reducing atmosphere, i. e., n-type semi-conductors act as better catalysts.

In general, the molecules adsorbed on working catalysts are not in equilibrium with the respective molecules in the gaseous phase, i. e., there is a difference in their chemical potentials. It is not, however, the chemical potential of the gaseous molecules but that of the adsorbed molecules that determines the oxidizing or reducing power. In order to distinguish between the two atmospheres resulting from gaseous and adsorbed molecules, it is convenient to introduce the concept of the virtual atmosphere defined as follows.

Imagine the partial pressure of a gas which is virtually in equilibrium with the respective adsorbate. The partial pressure thus conceived is commonly called "the virtual pressure". Among the virtual pressures in an atmosphere composed of various species, the virtual pressure that determines the composition of a semi-conductor is that of the constituent species of the semi-conductor. The atmosphere represented by this virtual pressure is called the virtual atmosphere. In the case of an oxide catalyst for example, the virtual atmosphere is represented by the partial pressure of oxygen which is virtually in equilibrium with the adsorbed oxygen.

Using the concept of the virtual atmosphere, one can express the above conclusion as to the catalytic activities of semi-conductors in the following simple form: *n-type and p-type semi-conductors act as good catalysts only in reducing and oxidizing virtual atmospheres, respectively,* in so far as the amount of adsorbates with an induced charge plays an important role in the reaction processes. This may be called the law of the virtual atmosphere, and is not only useful to select catalysts for a specified reaction but also gives a good insight into the catalytic mechanism and into the change of catalytic activities with time.

In the above considerations, the effect of impurities was not considered. So it might seem that the conclusion is valid only for pure semi-conductors whose conductivities are easily affected by the surrounding atmosphere, but the same conclusion is valid also for the semi-conductor doped with impurities and which has high conductivity unaffected by small changes of atmosphere, because the law of controlled conductivity in doped semi-conductors ceases to hold when a semi-conductor is put in an atmosphere which acts as a powerful agent in keeping the semi-conductor in stoichiometry. Then the controlled imperfection may predominate and may result in the diminution of electronic carriers, as shown earlier by WAGNER [3] and more thoroughly by KRÖGER and his coworkers in their recent works [4].

In this connection, a few remarks may be made on the problem of determining experimentally the virtual atmosphere of a working catalyst. A primitive method consists in determining the concentration of adsorbed particles on the working catalyst by chemical analysis after an abrupt interruption of the reaction, but this method is applicable only in restricted cases [5]. In the case of semi-conductor catalysts more convenient methods have been used, one of which is based on measurements of the electronic conductivities of catalysts under various conditions. Use is made of the sensitivity of the conductivity to the surrounding atmosphere; that is, one can obtain information on the amount and the chemical potential of adsorbed particles with an induced charge by comparing the electronic conductivity of a semi-conductor acting as a catalyst with that of the semi-conductor in an atmosphere of the component reactants or products, and consequently can determine the virtual atmosphere and the reaction mechanism [6,7]. Another method is to observe the colour of a semi-conductor which undergoes a sensitive colour-change with the surrounding atmosphere. The procedure to determine the virtual atmosphere in this case [8] is the same as in the case of conductivity measurements.

The applications of the law of the virtual atmosphere to various reactions will be discussed in subsequent sections.

[3] C. WAGNER, J. Chem. Phys. **18**, 62 [1950].
[4] F. A. KRÖGER, H. J. VINK and J. VAN DEN BOOMGAARD, Z. phys. Chem. **203**, 1 [1954]; J. BLOEM, F. A. KRÖGER and H. J. VINK, Defects in Crystalline Solids, 1955, p. 273.
[5] W. E. GARNER, T. J. GRAY and F. S. STONE, Proc. Roy. Soc., Lond. A **197**, 294 [1949].
[6] C. WAGNER and K. HAUFFE, Z. Elektrochem. **44**, 172 [1938].
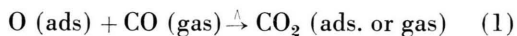[7] W. E. GARNER, F. S. STONE and P. F. TILEY, Proc. Roy. Soc., Lond. A **211**, 472 [1952].
[8] T. SATO, Read at the 8th Annual Meeting of the Chem. Soc. Japan, 1955 (will be published shortly).

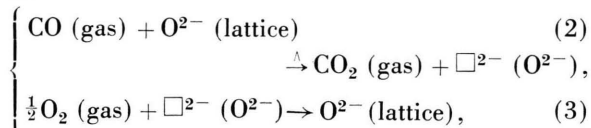## 2. The Oxidation of Carbon Monoxide on Metallic Oxides

The catalytic oxidation of carbon monoxide on metallic oxides has been investigated by many authors from both practical[9] and theoretical[10] points of view. As this reaction is very simple and one of the most suitable for a theoretical treatment of catalysis, the present author has analysed the existing data concerning this reaction in terms of the law of the virtual atmosphere, with the intention thus to obtain an insight into a variety of reaction mechanisms. It is convenient first to discuss the catalyst which has been most widely investigated, viz., nickel oxide.

a) NiO Catalyst (p-type Semi-Conductor)

WAGNER and HAUFFE[6] measured the electronic conductivities of NiO acting as a catalyst in the oxidation of carbon monoxide and the electronic conductivities of NiO in pure oxygen and in mixtures of carbon monoxide and dioxide at temperatures near $700°$ C, and found that the conductivity under working condition was very close to that in pure oxygen at the same partial pressure, that is, that the adsorbed oxygen was almost in equilibrium with gaseous oxygen and the rate-determining step consisted of the reaction between adsorbed oxygen and gaseous carbon monoxide. Recently SCHWAB and BLOCK[10] observed that the overall rate of reaction was proportional to the partial pressure of carbon monoxide, P_{CO}, was independent of the partial pressure of oxygen, P_{O_2}, and has an activation energy of 16 kcal/mol at temperatures between $250°$ C and $400°$ C. In view of these results, the following two reaction mechanisms may be assumed for the temperature region above $250°$ C:

$$O \text{ (ads)} + CO \text{ (gas)} \xrightarrow{\wedge} CO_2 \text{ (ads. or gas)} \quad (1)$$

or

$$\begin{cases} CO \text{ (gas)} + O^{2-} \text{ (lattice)} & (2) \\ \quad \xrightarrow{\wedge} CO_2 \text{ (gas)} + \square^{2-} (O^{2-}), \\ \tfrac{1}{2} O_2 \text{ (gas)} + \square^{2-} (O^{2-}) \rightarrow O^{2-} \text{ (lattice)}, & (3) \end{cases}$$

where O^{2-} (lattice) and $\square^{2-} (O^{2-})$ denote respectively the oxygen ion constituting the crystal lattice

and the oxygen ion vacancy trapping two electrons. The reaction (1) is well known as the RIDEAL mechanism, while the mechanism expressed by (2) and (3), which will hereafter be referred to as reduction-oxydation mechanism, was first proposed by BENTON[11] in 1923 and extensively investigated with respect to CuO by SCHWAB and DRIKOS[12]. In our present state of knowledge, no rigorous choice can be made between the two alternatives, but the former seems to be more probable in the present case, since the initial heat of adsorption of oxygen, 54 kcal/mol[13], is far greater than that of carbon monoxide, 26 kcal/mol, and the amount of adsorbed oxygen may be expected to be considerably large even at higher temperatures. Moreover, the adsorbed oxygen reacts more easily than the lattice oxygen, as has been observed in some cases[6]. Accordingly, the RIDEAL mechanism is assumed to be valid in the following discussion. It is to be remarked, however, that the conclusion to be attained remains the same even when the reduction-oxidation mechanism is presumed.

PARRAVANO[14] investigated this reaction on nickel oxide at lower temperatures, with the result that the rate of reaction was found to be proportional to $P_{O_2}^{0,5} P_{CO}^{0,5}$ and to have an activation energy of 2.2 kcal/mol at temperatures between $106°$ C and $174°$ C, but to be proportional to $P_{O_2}^{0,2} P_{CO}$ and to have an activation energy of 13 kcal/mol at temperatures between $205°$ C and $222°$ C. These results may be interpreted in such a way that the rate-determining step of the reaction at temperatures below $174°$ C is

$$O \text{ (ads)} + CO \text{ (ads)} \xrightarrow{\wedge} CO_2 \text{ (ads)} . \quad (4)$$

In other words, the LANGMUIR-HINSHELWOOD (abbreviated to L-H) mechanism takes place, and that the temperature range between $205°$ C and $222°$ C should be regarded as the transition region from the L-H mechanism to the RIDEAL mechanism.

DELL and STONE[13] studied the adsorption of CO, O_2 and CO_2 on nickel oxide and the reaction between CO and O_2 at room temperature. The observed that the activation energy of the reaction was about 2 kcal/mol in the temperature range between $20°$ C and $160°$ C, in general in accord with

[9] M. KATZ, Adv. in Catalysis, Vol. V, 1953, p. 177; cf. also the references cited in it.

[10] G. M. SCHWAB and J. BLOCK, Z. phys. Chem. N. F. 1, 42 [1954]; cf. also the references cited in it.

[11] A. F. BENTON, J. Amer. Chem. Soc. 45, 887, 900 [1923].

[12] G. M. SCHWAB and G. DRIKOS, Z. phys. Chem. B 52, 234 [1942].

[13] R. M. DELL and F. S. STONE, Trans. Faraday Soc. 50, 501 [1954].

[14] G. PARRAVANO, J. Amer. Chem. Soc. 75, 1448 [1953].

Parravano's results, and the heat of adsorption of carbon dioxide had the value of 28 kcal/mol. They therefore concluded that the adsorbed carbon dioxide, the reaction product, might retard the reaction at and below room temperature, as was actually shown by Roginsky and Tselinskaya [15].

Although the results obtained by the abovementioned authors show some divergence, e. g., with respect to the effect of foreign ions in nickel oxide on catalytic activities [16], one may reasonably build up the general feature of reaction processes by arranging the common aspects of their results as illustrated in Fig. 1. Curve E in this figure represents the experimental results constructed from the data given by these authors [6, 10, 13, 14, 15]. If lines R and L-H in Fig. 1 are assumed to indicate different steps of the same reaction path, the observed results should be given by dotted curve E′. This is not observed and, therefore, these lines must represent different reaction paths. This fact justifies the preceding interpretations that curves R and L-H refer respectively to the Rideal and Langmuir-Hinshelwood mechanisms. Line D, which indicates the desorption of the reaction products from the surface of the nickel oxide, is not so well-defined as the other lines, and so the lower-temperature portion of curve E is shown by a broken curve.
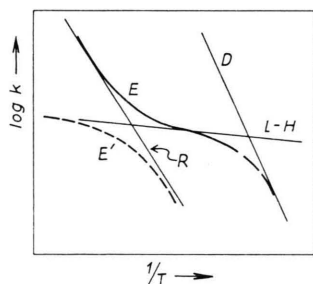

Fig. 1. The schematic representation of the rate constant for oxidation of CO on NiO.

These conclusions are also justified from energy and entropy considerations. The activation energy of the reaction is in general reduced by a deformation of the electron cloud of reactants due to adsorption. In the case of the L-H mechanism both reactants are in adsorbed states so that the activation energy of the reaction is considerably lower than in the homogeneous reaction but at the same time the activation entropy is small, inasmuch as the constraints due to the adsorptive force will create serious steric hindrances in the freedom of

reactants. On the other hand, in the Rideal mechanism only one of the partners is in the adsorbed state, hence both the activation energy and entropy are large due to relatively smaller constraints. Thus the L-H mechanism may predominate in the lower temperature region on account of its low activation energy, while the Rideal mechanism may become predominant at higher temperatures on account of its large activation entropy. These situations are in perfect harmony with the scheme represented in Fig. 1.

The above-mentioned results will now be considered from the viewpoint of the virtual atmosphere. In the case of the L-H mechanism the surface of the working catalyst is covered with both adsorbates, oxygen and carbon monoxide, whose concentrations vary widely with external conditions. The oxidizing or reducing action of the virtual atmosphere will, therefore, vary according to their concentrations. In the Rideal mechanism, on the other hand, the adsorbed oxygen is nearly in equilibrium with gaseous oxygen, so that the virtual atmosphere will be highly oxidizing. Fig. 2 represents schematically these situations along with the law of the virtual atmosphere. From this figure it may be inferred that the Rideal mechanism can be observed on p-type semi-conductor catalysts but not on n-type semi-conductors. In the case of nickel oxide, a p-type semi-conductor, there is no discrepancy between the above theoretical conclusion and the experimental results, but this by itself can hardly be regarded as a sufficient evidence in favour of the present theory. More positive verification of the theory will be given by analysing the
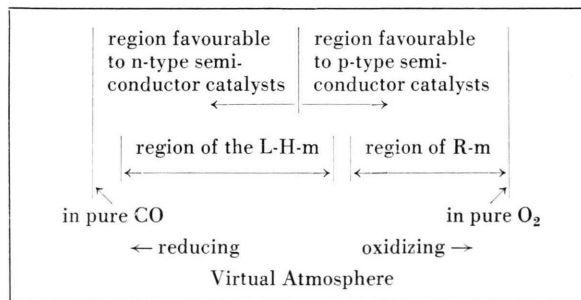

Fig. 2. The schematic representation of the law of the virtual atmosphere and the relation between the reaction mechanism and the virtual atmosphere in the oxidation of CO. L-H-m and R-m are respectively the abbreviations for the Langmuir-Hinshelwood mechanism and the Rideal mechanism.

[15] S. Roginsky and Tselinskaya, J. Phys. Chem. USSR **21**, 919 [1947]; **22**, 1360 [1948] through Chem. Abstr.

[16] G. M. Schwab and J. Block, J. Chim. Phys. **51**, 664 [1954]; cf. the discussion at the end of their paper.

data with respect to n-type semi-conductors, as shown in Subsection c).

Here it may be worth discussing about the change in catalytic activities with time and the effects of histories of samples. PARRAVANO [14] observed that freshly prepared NiO, while it was initially a very active catalyst, rapidly diminished in activity until it finally approached a stationary value, and moreover that this effect manifested itself most remarkably at lower temperature. Such an effect, however, could not be found with the catalyst preheated in carbon monoxide. These results may be understood from the following considerations. The fresh NiO prepared by heating in dry air is in a more oxidized state and hence more active than that at work as catalyst. But the difference in degree of oxidation and accordingly in catalytic activity between the above two states is to be remarkable only at low temperatures where the L-H mechanism predominates (cf. Fig. 2). These trends of change in catalytic activity are shown in Fig. 3.
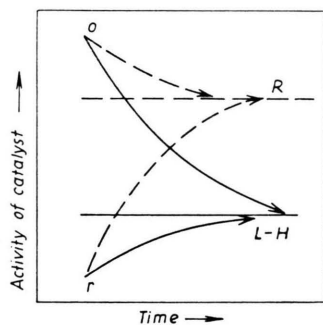

Fig. 3. The change in the catalytic activity of p-type semiconductors for the oxidation of CO and the effect of pretreatment in an oxidizing or a reducing atmosphere. The solid and broken curves indicate respectively the cases of lower and higher temperatures. The letters, o and r, refer to the catalysts preheated in O_2 (or freshly prepared) and in CO, respectively. R and L-H denote the stationary value of the catalytic activity attained respectively at higher and lower temperatures.

b) CU_2O (p-type Semi-Conductor)

The physical properties of cuprous oxide have been studied by a number of authors because of its practical importance as a rectifier, but its nature as a catalyst has not yet been fully investigated. The oxidation of carbon monoxide on cuprous oxide at room temperature was extensively investigated by GARNER and his coworkers [6], but its feature at higher temperatures has only been inferred from several experimental results concerning

adsorption. The conclusion that at room temperature the rate-determining step consists of the reaction,

$$O_2(gas) \rightarrow 2\,O(ads) + 55\,kcal/mol\,,$$
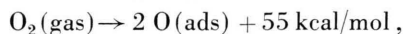
was drawn by them not only from the kinematical data which indicate that the overall rate was proportional to the first order of P_{O_2}, but also from the fact that the surface of the working catalyst was nearly saturated with adsorbed carbon monoxide as if it were in the atmosphere of pure carbon monoxide.

On the other hand, they supposed it is the reduction-oxidation mechanism that becomes important at higher temperatures, on the basis of the fact that the heat of adsorption of oxygen (55 kcal/mol) is far greater than that of carbon monoxyde (20 kcal/mol), so that the adsorption of oxygen will predominate at higher temperatures. This view must be corrected in some respects, since the dissociation pressure of oxygen at equilibrium in the reaction,

$$2\,CuO\;(black) \rightleftharpoons Cu_2O\;(red) + \tfrac{1}{2}O_2\,,$$

is so small ($10^{-18.9}$ atm. at $25°$ C [17] and $10^{-16.1}$ atm. even at $250°$ C) that Cu_2O cannot be stable in the oxidizing virtual atmosphere attributed to the RIDEAL or reduction-oxidation mechanisms. Moreover, the oxidation of Cu_2O to CuO proceeds at such a considerable rate at $250°$ C that the working catalyst Cu_2O must change into CuO at that temperature in so far as the virtual atmosphere is oxidizing. Hence the RIDEAL mechanism cannot be observed when Cu_2O is in a stationary catalytic state, but it might be able to be observed when the catalyst is in a transient state while heated from room temperature to $250°$ C.

With this in view, the present author has investigated the transient change of Cu_2O catalyst during oxidation of CO in a flow system. The preliminary experiment showed that the catalyst became black, i.e., turned into CuO at temperatures near $200°$ C even in the flowing gas with excess carbon monoxide (CO : O_2 = 10 : 3 in volume). (Such is the case also with $ZnCr_2O_4$ catalyst, as will be described later.) If the reaction mechanism at room temperature had been maintained up to such a high temperature, the virtual atmosphere would have been reducing and the oxidation of the catalyst should not have taken place. The above

[17] National Bureau of Standards, Selected Values of Chemical Thermodynamic Properties.

results indicate, therefore, that at higher temperatures the transient state of the catalyst is realized and another reaction mechanism occurs e.g. the RIDEAL type with an oxidizing virtual atmosphere. Thus the general feature of the catalytic reaction of Cu_2O is similar to that of the nickel oxide catalyst; namely, the reaction mechanism at higher temperatures is of RIDEAL type in both cases. This is in excellent agreement with the theory developed in Subsection a).

c) The n-type Semi-Conductors: ZnO, Fe_2O_3 and V_2O_5

In spite of a large number of studies concerning the oxidation of carbon monoxide on n-type semiconductor catalysts, only a portion of the data can be used for the analysis of the mechanism. Such data have been given by SCHWAB and BLOCK [10] on ZnO, by ECKELL [18] on Fe_2O_3, and by TARAMA, TERANISHI and YASUI [19] on V_2O_5.

The rate of reaction on ZnO was found to be so small that it was necessary for SCHWAB and BLOCK to perform measurements at a temperature as high as $500°$ C in order to obtain reliable data. The overall rate was proportional to $P_{O_2}{}^m P_{CO}{}^n$ where m and n are positive and m is slightly less than unity. Hence they concluded that the reaction mechanism belongs to the L-H type. Since they could observe no signs of the RIDEAL mechanism even at $550°$ C, one may safely conclude that the RIDEAL mechanism does not take place in the oxidation process of carbon monoxide on ZnO. This result tends to verify the predication of the foregoing theory in Subsection a) that the RIDEAL mechanism cannot be observed in the case of n-type semi-conductor catalysts.

They also investigated the relations between the history and the activity of the catalysts. The catalytic activity of ZnO preheated in pure carbon monoxide was initially very high, but diminished rapidly to the normal value. On the contrary, ZnO preheated in air was initially less active, recovering gradually its normal activity. These effects of pretreatment can also be understood from the viewpoint of the virtual atmosphere. ZnO preheated in air is in a more oxidized state and hence less active than ZnO working as a catalyst, for the n-type

semi-conductor acts as a good catalyst only in a reduced state according to the present theory. Conversely, the catalyst preheated in carbon monoxide is in a more reduced state and therefore more or less highly active according to its degree of reduction. Fig. 4 summarizes these tendencies together with those of the p-type semi-conductors discussed in Subsection a).
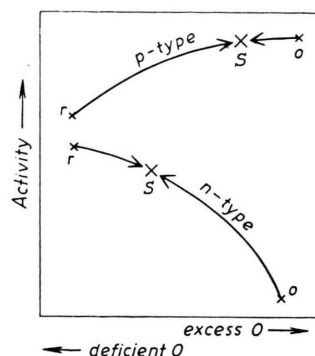

Fig. 4. The catalytic activities and histories of catalysts. o, r and s designate oxidized, reduced and stationary state, respectively.

ECKELL studied ferric oxide as a catalyst for the oxidation of carbon monoxide at temperatures between $160°$ C and $250°$ C, and concluded that the overall rate of reaction was proportional to P_{CO} and independent of P_{O_2}. But, as he pointed out, the individual rate constants determined in several series of experiments with different initial compositions of gas mixtures had not the same value. Nevertheless he assumed the reduction-oxidation mechanism without careful analysis of the dependency of the rate constant on the initial composition. The present author has reanalysed his data and arrived at the conclusion that the overall rate is proportional to $P_{O_2}{}^{-m} P_{CO}{}^n$ where m and n are positive numbers, though no precise values can be assigned for m and n due to the scarcity of the available data. It may well be assumed tentatively that the L-H mechanism is more probable to occur in the temperature range in question, because such a pressure dependency is characteristic of this mechanism. At any rate, it may be asserted, in accord with the present theory, that the RIDEAL mechanism has not been observed in the case of the n-type semi-conductor catalyst Fe_2O_3.

[18] J. ECKELL, Z. Elektrochem. **39**, 807 [1933].
[19] K. TARAMA, S. TERANISHI and A. YASUI, Read at 8th Annual

Meeting of Chem. Soc. Japan, 1955 (will be published shortly).

HUGHES and HILL [20] investigated the V_2O_5 catalyst at temperatures between 370° C and 430° C by a flow method, with the results that the catalyst was reduced by the reactant gases at a concentration of CO higher than 10 volume per cent, and that the overall rate of reaction was proportional to P_{CO} and independent of P_{O_2}. The first result shows that the rate of adsorption of O_2 is slow in comparison with that of CO, or, in other words, the virtual atmosphere is reducing, while the second result seems to show that the surface is saturated with adsorbed oxygen and the RIDEAL mechanism takes place, i. e., the virtual atmosphere is oxidizing. The first result must, however, be regarded as more reliable, since it is not easy to determine the pressure dependency with certainty by the flow method, especially to determine the dependency on the major component of reactant gases in the case where the concentration of the minor component is as small as in their investigations.

Recently TARAMA and his coworkers obtained essentially different results. The rate of reaction was found to depend both on P_{O_2} and P_{CO} at temperatures between 400° C and 450° C, a fact which shows that the reaction mechanism prevailing at such high temperatures is of L-H type. Thus, it may safely be concluded that the RIDEAL mechanism takes place neither on V_2O_5 nor ZnO catalyst, as predicted in Subsection a).

d) Miscellaneous Catalysts: $ZnCr_2O_4$ (p-type) [21], $Ba_8Fe_8O_{21}$ (p-type?) and Others.

SATO [8] in this laboratory investigated the oxidation of carbon monoxide on $ZnCr_2O_4$ catalyst at temperatures near 400° C by a flow method. Owing to some experimental difficulties, he did not study the kinetics of the reaction by the usual procedures, but observed the colour change in this catalyst. The colour of $ZnCr_2O_4$ is greenish-blue in a reduced state (stoichiometric composition) and brownish-black in an oxidized state (with excess oxygen). On contact with the reactant gases with a large excess of carbon monoxide (including $0.1 \sim 10$ mol per cent of O_2), the green catalyst changes colour instantaneously to black. This means that the virtual atmosphere acting on the catalyst becomes strongly oxidizing in spite of small concentration of oxygen. He

thus concluded that the mechanism of the reaction is similar to the case of WAGNER and HAUFFE [6], namely the RIDEAL mechanism becomes predominant on the p-type semi-conductor catalyst $ZnCr_2O_4$ in this temperature range.

ERCHAK and WARD [22] discovered a highly active catalyst $Ba_8Fe_8O_{21}$ for the oxidation of carbon monoxide. This has a modified perovskite structure; that is, its lattice constant is twice as large as that of the perovskite structure of $BaFeO_3$ and three oxygen atoms are missing from the unit cell which consists of eight cubes of $BaFeO_3$; hence the resultant composition $Ba_8Fe_8O_{21}$. They maintain that these vacant lattice points of oxygen in $Ba_8Fe_8O_{21}$ easily absorb and then release excess oxygen, which is supplied from the gaseous oxygen and consumed in the oxidation of carbon monoxide. Although such a detailed but as yet unestablished model for the reaction process is left out of the present consideration, it is worthy of notice in connection with the high catalytic activity of $Ba_8Fe_8O_{21}$ that the excess oxygen might occupy the normally vacant sites to form a p-type semi-conductor.

The important catalysts from a practical point of view are manganese dioxide and its mixture with cupric oxide, i. e., hopcalite which has been studied extensively by FRAZER and his coworkers. According to the results of structural investigations by X-rays [23], the most active MnO_2 is almost amorphous or composed of exceedingly minute crystals, so that it is open to question whether one may apply the band structure of a very large crystal to the case of such a small crystal or amorphous solid. Moreover, since, as far as the present author is aware, the semi-conducting properties of MnO_2 are uncertain, further discussion of this interesting catalyst is impossible.

e) Summary of the Discussion of the Oxidation of CO

The important results from the above theoretical considerations may be briefly summarized in the following three points:

[1]   The p-type semi-conductor is generally superior to the n-type semi-conductor in catalytic action for the oxidation of CO;

[20] M. F. HUGHES and G. R. HILL, J. Phys. Chem. 59, 388 [1955].

[21] D. J. M. BEVAN, J. P. SHELTON and J. S. ANDERSON, J. Chem. Soc., Lond. 1948, 1729.

[22] M. ERCHAK and R. WARD, J. Amer. Chem. Soc. 68, 2093 [1946].

[23] E. C. PITZER and J. C. W. FRAZER, J. Phys. Chem. 45, 761 [1941].

[2] The RIDEAL mechanism never takes place on n-type semi-conductors even at higher temperatures;

[3] The effect of pretreatment of the catalyst is such as schematically represented in Fig. 4.

The comparison of the present theory with existing experimental results shows, as can be seen from Table 1, that all the available data are in substantial agreement with the theory. This gives some tangible evidence for the utility of the law of the virtual atmosphere developed in Section 1. In particular, [2] is to be regarded as an interesting result in that it gives one an insight into the nature of heterogeneous catalysis, since one has hitherto only analysed the mechanism of reaction without obtaining any knowledge as to the reason why such a mechanism takes place in favour of some other reaction mechanisms.

3. Other Reactions

There are several interesting reactions which take place on semi-conductor catalysts, such as the decomposition of nitrous oxide, synthesis of methanol, oxidation of sulphur dioxide, and oxidation of ammonia. One can discuss only the outlines of some of reactions from the viewpoint of a virtual atmosphere, since they have not been as extensively studied as the oxidation of carbon monoxide.

First, the decomposition of nitrous oxide is to be considered. The virtual atmosphere for working catalysts is always more or less intensely oxidizing in this reaction, since the adsorbed oxygen, the product of decomposition, may be either in equilibrium with or at a higher chemical potential than the gaseous oxygen. Hence, it may be inferred from the theory developed in Section 1 that p-type semi-con-

Temp. °C	Catalyst	Type of Semi-conductor	Occurence of the RIDEAL Mechanism	Effect of Pretreatment	Reference
below 50°	$Ba_8Fe_8O_{21}$	p ?	—	—	22
50° ~ 150°	MnO_2	?	—	—	
	Co_2O_3	?	—	—	
	NiO	p	above 250° C	good	10, 14
	Cu_2O	p	probably above 200° C	—	preliminary experiment
	CuO	i	above 280° C	—	12
	$ZnCr_2O_4$	p	occure	—	8
150° ~ 250°	Fe_2O_3	n	not (to 250° C)	—	18
	ZnO	n	not	good	10
	TiO_2	n	—	—	
	ZrO_2	?	—	—	
	CeO_2	n	—	—	
	Cr_2O_3	i. i.	—	—	
	V_2O_5	n	not	—	19
above 250°	BeO	n		—	
	ThO_2	n		—	
	WO_3	n		—	
	Al_2O_3	n		—	

Table 1. The Activities, Mechanism of Reaction, and Types of Semi-Conductor Catalysts for Oxidation of CO.

Temp. °C in the 1st column denotes the temperature at which the reaction is first detectable, according to the SCHWAB and BLOCK's table[10]; i. i. denotes the intrinsic impurity type[24] semi-conductor; "good" in the 5th column means "in good agreement with the tendency shown in Fig. 4." As for the lines without reference number, see ref.[10].

Though, in the foregoing discussion, it has been taken for granted that the RIDEAL mechanism is more probable than the reduction-oxidation mechanism, the conclusion will not be altered if the reduction-oxidation mechanism is postulated, because the virtual atmosphere is in both cases always oxidizing.

ductors ought to be better catalysts than n-type semi-conductors. Such is actually the case, as shown by DELL, STONE and TILEY[25], who on the basis of available data arranged the semi-conductors in order of their catalytic activities in this reaction:

$$CoO(p) > Cu_2O(p) > NiO(p) > MgO(n)$$
$$> CeO_2(n) > CaO(n) > BeO(n) > Al_2O_3(n)$$
$$> ZnO(n) > TiO_2(n) > Fe_2O_3(n) .$$
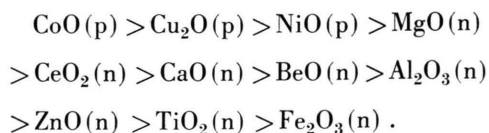
[24] K. HAUFFE and J. BLOCK, Z. phys. Chem. **198**, 232 [1951].
[25] R. M. DELL, F. S. STONE and P. F. TILEY, Trans. Faraday Soc. **49**, 201 [1953].

Furthermore, using granular copper coated with cuprous oxide as catalyst, they observed a large increase in the catalytic activity of a sample which had previously sorbed a small amount of oxygen at $60°$ C, in spite of the usual retarding effect of gaseous oxygen. This effect may be interpreted in such a way that at a temperature as low as $60°$ C the sorbed oxygen is not all consumed in oxydizing the underlying metallic copper but some remains in the form of excess oxygen in the cuprous oxide. This catalyst may then become active as it has a larger number of electronic carriers than in vacuum. In contrast to this, they considered that the reaction was accelerated by the pre-adsorbed oxygen through the process:

$$O \text{ (ads)} + N_2O \text{ (gas)} \rightarrow N_2 \text{ (gas)} + O_2 \text{ (ads)} .$$

This explanation is inconsistent with the retarding effect of gaseous oxygen observed in the usual case.

Recently AMPHLETT[26] found an interesting feature concerning the decomposition of nitrous oxide as shown in Table 2; namely, there are two temperature regions with different activation energies of overall reaction. In the higher temperature region both the activation energy and entropy are larger than those in the lower temperature region. This bears a close parallel to the oxidation of carbon monoxide. The direct experimental investigation of the virtual atmosphere, however, has not yet been performed to such an extent that the detailed mechanism of the decomposition of nitrous oxide can be thoroughly discussed.

Catalyst	Activation Energy in kcal/mol	
	at higher temp.	at lower temp.
CoO	—	17 (below $500°$ C)
CuO	37 (above $350°$ C)	19 (below $350°$ C)
NiO	24 (above $370°$ C)	14 (below $370°$ C)
Cu_2O on Cu-film	—	20 ($195° \sim 245°$ C)

Table 2. The Activation Energy for Decomposition of N_2O on Various Oxide Catalysts (according to AMPHLETT).

Finally, the synthesis of methanol will be considered briefly. Since in this reaction both reactants, hydrogen and carbon monoxide, are reducing agents, it is evident that a good catalyst may be found in n-type semi-conductors, such as ZnO, CdO,

Fe_2O_3, Al_2O_3 and V_2O_5. It is outside the scope of the present theory to predict which of these is the best catalyst, since this is a problem to be attacked on the basis of more advanced studies on the wave functions of catalysts and molecules.

4. Conclusion

In the present work, the theory has been developed, taking into account only the energy levels and level densities of electrons in semi-conductors; nothing of the form of the wave functions has been considered. Notwithstanding such crude treatments, the theory has been able to explain the reason why in the oxidation process of carbon monoxide the RIDEAL mechanism takes place not on n-type semi-conductor catalysts but on the p-type or intrinsic catalysts. This may prove the utility of the law of the virtual atmosphere in semi-conductor catalysts. The most important point of the present results lies not in the fact that the law on virtual atmosphere is correct and infallible, but rather that the concept of the virtual atmosphere has been shown to be useful in visualizing the physical situations in heterogeneous catalysis, the case not only with semi-conductor but also with metal catalysts.

As early as in 1939, WAGNER and HAUFFE[27] studied the hydrogenation of ethylene on palladium which is a good absorber of hydrogen. Making use of the change in the conductivity of palladium with absorption of hydrogen, they succeeded in obtaining some knowledge on the mechanism of the hydrogenation, similar to the case of the oxidation of carbon monoxide on nickel oxide. This result may be clearly visualized by means of the concept of the virtual atmosphere; that is, a virtual hydrogenizing atmosphere on palladium. Another important example is the synthesis and decomposition of ammonia on an iron catalyst. Iron is a good absorber of nitrogen and in some cases becomes the nitride. The absorption of nitrogen by iron or the phase change into iron nitride may be accompanied by an essential change in physical and catalytic properties of the solid phase. This situation may be conveniently represented by aid of the concept of a virtual nitrogenizing atmosphere. The virtual atmosphere will be in general different in character in synthetic

[26] C. B. AMPHLETT, Trans. Faraday Soc. 50, 273 [1954].

[27] C. WAGNER and K. HAUFFE, Z. Elektrochem., 45, 409 [1939].

and decomposing reactions; hence it is difficult to deduce the feature of the synthetic reaction from the results pertaining to the decomposition reaction of ammonia. In order to gain correct knowledge, it is necessary to determine the virtual nitrogenizing atmosphere directly by experiments. In other words, one may obtain more substantial clues for analys-

ing heterogeneous catalysis by measuring the virtual atmosphere.

Über die Dunkel- und Photoleitfähigkeit des Anthracens

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Herrn Prof. P r i n g s h e i m zum 75. Geburtstag

Photo- und Dunkelstrom von Anthracen-Einkristallen wurden bei Verwendung von aufgedampften und angepreßten Elektroden untersucht. Das Verhalten der Kristalle wird durch die Elektrodenanordnung wesentlich beeinflußt. Eingebautes Tetracen erhöht den Dunkelstrom und vermindert den Photostrom. Durch Bestrahlung mit α-Teilchen wird die Photoleitfähigkeit verringert.

Über die Photo- und Dunkel-Leitfähigkeit organischer Substanzen ist noch relativ wenig bekannt, weil sie in der Regel sehr hohe Widerstände besitzen und Meßanordnungen für Ströme bis herunter zu 10^{-16} Amp. benötigen. Am besten untersucht sind Anthracen-Einkristalle. Sie besitzen einen spezifischen Widerstand in der Größenordnung von $10^{15}\,\Omega/\text{cm}$, so daß bei geeigneter Anordnung der Elektroden und bei hinreichend hohen Spannungen Dunkelströme von einigen 10^{-13} Amp. erzeugt werden können.

Vartanjan[1] und Bayliss[2] stellten fest, daß Anthracen schon bei Einstrahlung in die Hauptabsorptionsbande (um 3650 Å) neben der Lumineszenz lichtelektrische Leitung zeigt. Carswell[3] fand, daß bei Anthracen der Logarithmus des Absorptionskoeffizienten und der Photostrom in gleicher Weise von der Wellenlänge des eingestrahlten Lichtes abhängt. Auf Grund dieser und eigener Messungen entwickelte Lyons[4] eine Theorie der Photoleitfähigkeit in Anthracen- und Tetracenkristallen, die deren Photostrom als Oberflächeneffekt beschreibt. Pick und Mette[5] untersuchten die Dunkelleitfähigkeit des Anthracens. Sie fanden, daß die Erzeugung freier Ladungsträger eine thermische Energie von 1,65 eV benötigt.

I. Apparatives

1. Die Meßanordnung

Der Kristall befand sich in einer geerdeten Metallkammer, die auf einige 10^{-3} Torr evakuiert wurde. Sie besaß ein Quarzfenster zum Einlaß des Erregerlichtes. Der Photostrom erzeugte über einem mit dem Kristall in Reihe liegenden Widerstand einen Spannungsabfall, der mit Hilfe eines Meßverstärkers FH 408 der Firma F r i e s e k e & H o e p f n e r gemessen wurde (Abb. 1). Der *RC*-Wert am Eingang war kleiner als 0,1 sec, die Zeitkonstante des Meßverstärkers kleiner als 0,5 sec. Zur Vermeidung elektrischer Nachwirkungen konnte der Meßverstärker erst eine Sekunde nach dem Anlegen der Spannung eingeschaltet werden. Meßverstärker, Meßkammer, Batterie und Spannungsteiler befanden sich zur Abschirmung gegen kapazitive Einflüsse in einem Faraday-Käfig.
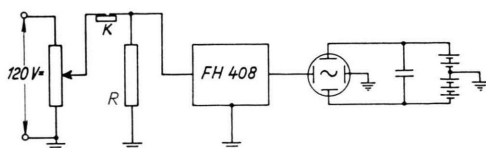

Abb. 1. Prinzipschaltbild der Meßanordnung. K=Kristall, $R=10^{10}\,\Omega$.

Abb. 2 zeigt eine Skizze der Kristallhalterung. In die Bohrungen eines Kupferblockes war ein U-förmig gebogenes Kupferrohr eingelötet, durch welches das Wasser eines Thermostaten floß. Zur elektrischen Iso-

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[2] N. S. Bayliss, Rev. Pure Appl. Chem. **1**, 64 [1951].
[3] D. J. Carswell, J. Chem. Phys. **21**, 1890 [1953].
[4] L. E. Lyons, J. Chem. Phys. **23**, 220 [1955].
[5] Pick u. Mette, Z. Phys. **134**, 571 [1952/53].