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The Decomposition of Hydrogen Peroxide on Silver–Gold Alloys

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The decomposition of hydrogen peroxide was studied on silver–gold alloys in the concentration range from 5 to 0.05 M H_2O_2 and in the temperature range from 10 to 60°C at pH 8 on oxide-free contacts.

The reaction order for the alloys proceeds continuously from second order with the silver (above 0.3 M H_2O_2) to first order with gold. The experimental activation energies and preexponential factors increase from silver to gold at first less and later more strongly.

In silver and gold we have basically different reaction mechanisms which are not only different limiting cases of one mechanism. From pertinent computations and considerations it could be concluded that for the alloys not a superposition but rather a transition of the two mechanisms occurs.

The catalyst behavior is primarily determined by the oxygen affinity of the catalyst, in respect of which gold and silver differ substantially although otherwise they have largely similar properties.

INTRODUCTION

For the homologues silver and gold a similar catalytic behavior might be expected in heterogeneous catalysis on account of the close correspondence of their structure and properties. However, an examination of H_2O_2 decomposition on the two metals showed fundamental differences (*1*). In particular, the reaction proceeds according to quite different mechanisms, and silver has a specially high activity in comparison to other metals. These circumstances are explained in that the two metals differ essentially in one property, namely their affinity for oxygen, and that that property is especially a catalytically determining factor for an oxygen-transferring process such as the H_2O_2 decomposition.

These differences prompted us to study the behavior on the homogeneous alloy system silver–gold. There is a need to clarify, among other things, whether a simple overlapping of the two mechanisms occurs on the alloys or whether there is an exchange of elementary steps.

Moreover, from the catalytic correlations one may proceed to make a contribution to the complex of questions pertaining to the alterations of properties within the alloys of homologues.

On silver and silver alloys surface oxides (AgO_x) appear during treatment with H_2O_2 under certain conditions (*2*). Such oxide formations were therefore currently examined by means of electron diffraction and the conditions were investigated under which an oxidizing attack on the alloys does not occur. The catalytic experiments were then carried out under those conditions.

EXPERIMENTAL METHODS

The investigations were carried out in the same manner as described in our preceding paper (*1*). The catalysts were mechanically polished and cathodically reduced prior to the experiments. The examinations concerned 11 different catalysts (produced by Degussa, purity 99.99%): pure silver, pure gold, and alloys of the two metals in steps of 10 at. % which are marked in the following by I–IX in accordance with their increasing gold contents.

Results

1. Electron Diffraction

During the kinetic measurements, silver dissolution should not take place (in order to maintain the alloy composition) nor should oxide formation occur on the catalyst. Since silver dissolution occurs only in acid solutions (*3*), we used reaction solutions of pH 8. The alloy series was checked for oxide formation after treatment with 5–0.1 *M* solutions at pH 8. After treatment with 5 *M* solutions, a very thin AgO_x layer was found on all silver-containing catalysts. After treatment with solutions whose concentrations were between 4 and 5 *M* H_2O_2, some additional lines were established in the electron diffraction patterns besides the Ag lines or Au lines. These lines were, however, so weak that it was impossible to measure and identify them. At concentrations $\leqslant 4\,M$ no oxide layer could be established. In no case was an oxide layer detected on pure gold.

2. Reaction Orders and Rate Constants

Measurements of kinetics were carried out at pH 8 with 4–0.35 *M* hydrogen peroxide solutions.

The reaction orders measured for the alloy series are shown in Fig. 1 and Table 1. In the examined temperature range between 10 and 60°C the reaction orders proved to be independent of the reaction temperature.

The reproducibility of the measurements on the pure metals proved to be excellent. On pure silver and pure gold we always obtained the orders 2.0 and 1.0, respectively. For the alloys, on the other hand, the experimental points were scattered (Fig. 1). Sometimes the points were scattered during one and the same experiment, so that the plotting of straight lines and thereby the unequivocal determination of a reaction order was not possible; in other experiments the points were situated on a straight line, but different examinations furnished different reaction orders.

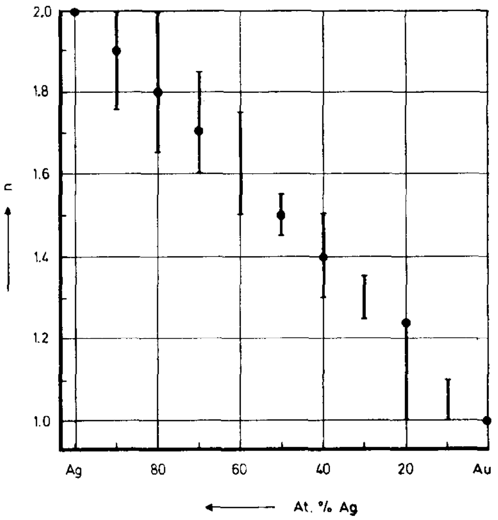

FIG. 1. Order of reaction *n* as a function of the composition of the alloys (with scattering bars shown).

The rate constants k_n of the alloy series were determined at 15, 30, 35, 45 and 55°C. For each catalyst the *k*-value corresponding to the experimentally found reaction order was calculated (Fig. 2 and Table 1). The rate constants refer to 1 cm² geometrical surface of catalyst.

TABLE 1

REACTION CHARACTERISTICS FOR THE H_2O_2 DECOMPOSITION ON Ag–Au ALLOYS (AT pH 8)

Catalyst	Reaction order *n*	Rate constant $k \times 10^3$ (45°C) (1^n/ $mole^{n-1}$ min cm^2)	Activation energy *q* (kcal/ mole)	Pre-exponential factor A (units as for *k*)
Ag	2.0	5.0	8.2	2.5×10^3
I	1.9	4.1	8.6	3.0×10^3
II	1.8	3.2	9.0	5.0×10^3
III	1.7	2.6	9.2	6.0×10^3
IV	1.6	2.1	9.7	8.4×10^3
V	1.5	1.7	9.9	9.2×10^3
VI	1.4	1.3	10.5	3.0×10^4
VII	1.3	1.1	11.1	6.4×10^4
VIII	1.2	0.9	12.0	9.0×10^5
IX	1.1	0.7	12.9	7.1×10^6
Au	1.0	0.55	14.1	8.5×10^7

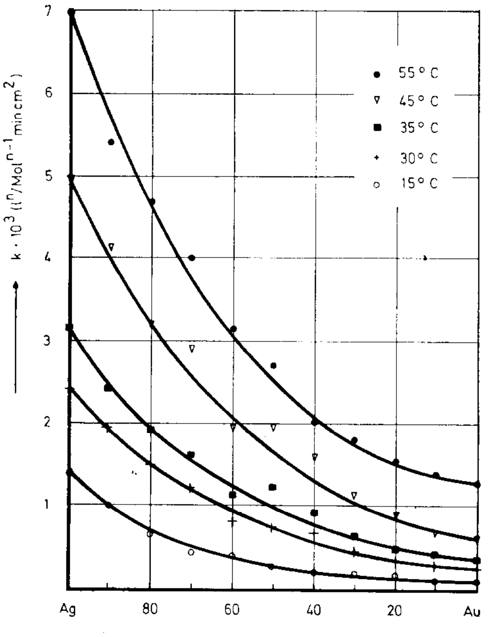

FIG. 2. Rate constants k at various reaction temperatures.

3. Dependence on Stirring

For gold it was established that in the concentration range below 2 M H_2O_2 the reaction rate varies with the stirring velocity below certain temperatures depending on the pH of the solution; for silver the course of the reaction was not influenced by an alteration of the stirring velocity in the whole temperature range (10–60°C), concentration range (5–0.05 M H_2O_2) and pH range (pH 5.5–9) investigated (*1*).

For alloys containing less than 50% of silver, there exists a dependence on stirring in 1 M solutions. In solutions with $c >$ 2.5 M H_2O_2 there is no dependence on stirring in the range examined.

4. Dependence on Temperature

For establishing the experimental activation energies q and the experimental preexponential factors A, the H_2O_2 decomposition was examined in the temperature range between 10 and 60°C.

The experimental points all gave good Arrhenius lines (Fig. 3). These were determined from 4 to 5 measurements at pH 8 in the concentration range from 4 to 3 M H_2O_2. In this range there is no dependence on stirring.

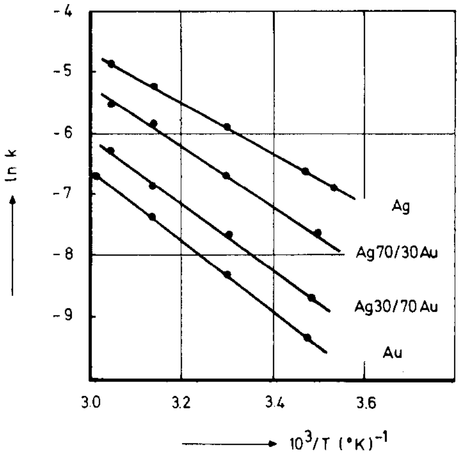

FIG. 3. Examples of Arrhenius plots.

The various temperatures were usually adjusted during a single experiment by gradual heating or cooling of the thermostatic bath. Points from separately set up experiments yielded Arrhenius lines of the same quality. The activation energies and preexponential factors computed from the Arrhenius lines,

$$\ln k = \ln A - q/RT,$$

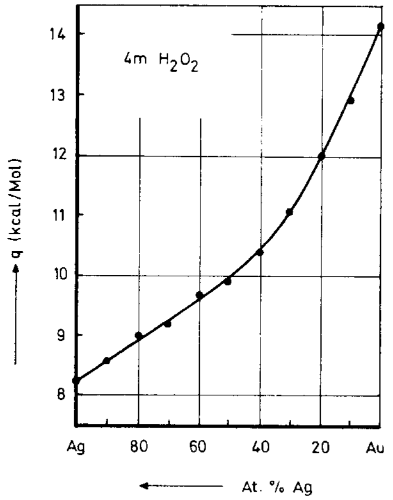

FIG. 4. Dependence of the activation energies q on the composition of the alloys.

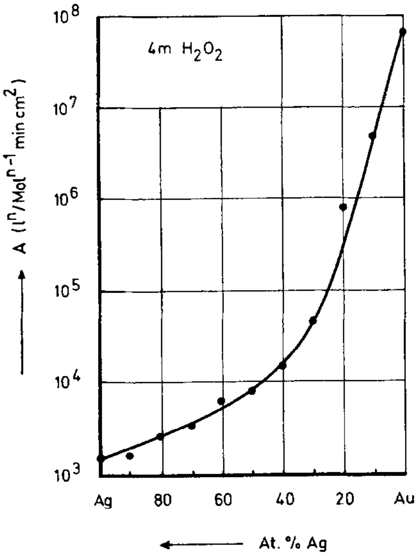

FIG. 5. Dependence of the preexponential factors A on the composition of the alloys.

are represented in Figs. 4 and 5 (see also Table 1).

DISCUSSION

1. Pattern of the Reaction Data

Over the transition from silver to gold, all the investigated reaction data change monotonously. Individually there are certain differences in the forms of the pattern.

The reaction rate (v) for silver is higher by about a factor 5 than for gold. In the alloy series it decreases at first more strongly, then less from ca. 50% Au.

The reaction orders (n) change more uniformly, probably even linearly, with the alloy composition from $n = 2$ for Ag to $n = 1$ for Au.

The second order (in the concentration range $c > 0.3\,M$) for the reaction on silver was secured in several earlier investigations (*1, 3–5*). The first order for the H_2O_2 decomposition on gold (*1*) corresponds with the literature data known to us (*6, 7*). Both values for the pure metals are genuine integral reaction orders whose values are obtained very exactly by experiment.

The temperature dependence of the reaction accords in all cases with the Arrhenius equation. The activation energies (q) and preexponential factors (A) increase monotonously on going from silver to gold. But the changes proceed neither linearly (as those of the reaction orders) nor in the same sense with those of the reaction velocity. On the contrary, both the activation energies and the preexponential factors increase at first slightly, up to approximately 50% Au, and then more strongly up to gold.

Compensation effect (theta rule). The pairs of values of ln A and q for all alloys, and the pure metals, may be coordinated to one single compensation line,

$$\ln A = (1/R\theta) \cdot q + \ln k_\theta$$

(Fig. 6), with

$$\theta = 485°\text{K} \mathrel{\widehat{=}} 212°\text{C} \quad \text{and} \quad \ln k_\theta = -1.05.$$

On account of the differing reaction mechanisms for the various catalysts this is only a formal correlation, but one for which obviously a real basis seems to exist.

2. Reaction Orders

It is conspicuous that the values of the reaction orders for the alloys are scattered whereas those for the pure metals are exactly reproducible. This is probably due to the influence of differing kinetic conditions.

The integral concentration exponents for gold ($n = 1$) and silver ($n = 2$) are gen-

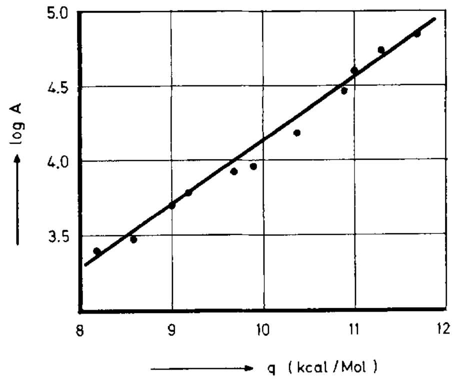

FIG. 6. Plot showing the compensation effect (theta rule).

uine reaction orders, i.e., the defined constants for the kinetic limit laws ($v = k c^n$). On the other hand, fractional exponents cannot be genuine reaction orders of exactly valid limit kinetics, with the exception of certain root values such as 0.5, etc. They are only apparent reaction orders, i.e., approximations of compounded rate equations for sections of kinetic transitional regions. Such approximations are affected by an increased arbitrariness of evaluation and scattering. So the scattering of the n-values for the alloys is in unison with the fact that a transition from the defined limit kinetics of the silver to that of the gold occurs within the alloy series.

The possibility that the scatterings are caused by differences of the composition of various test specimens (alloy inhomogeneities, surface alterations due to surface treatment) seems to be improbable.

3. The Kinetic Transition

There are various possibilities to be checked.

A. Pure additivity of the component catalyses, i.e., maintenance of the individual actions of silver and gold also in the alloy combination. Although basically a modification of the properties of the components (i.e., loss of their individuality) is to be expected in the alloy, we think it worthwhile to check whether in the case of two homologues with very similar atomic properties this modification would not be, by any chance, negligibly small. In such a case the rate law for the reaction in an alloy (i) should be the simple sum for the reactions on the components,

$$v_i = \gamma_i k_S c^2 + (1 - \gamma_i) k_G c,$$

corresponding to their proportionality (γ_i = atomic fraction of silver).

The computations show not only quantitative but also qualitative deviations from the experimental findings; the computed apparent reaction orders change inversely (Fig. 7) to the course of the experimental ones (Fig. 1). The case of a simple additivity may therefore be excluded.

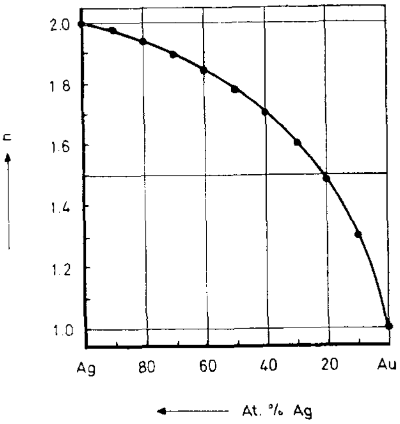

FIG. 7. Computed reaction orders n for undisturbed additive overlapping.

For the properties and catalytic activity of alloys three cases may be considered:

i. The properties of the individual atoms of the components of an alloy surface remain unchanged by alloying: *Pure additivity.*

ii. The individual character of one metal is preserved though modified by the influence of the neighboring atoms of the other component: *Modification.*

iii. The properties of the individual components are lost, such that it is not possible to distinguish furthermore the atoms A and B, the alloy becoming a new individuality: *Collective model.*

The case of simple additivity could be maintained if we introduced the further assumption of special surface compositions, i.e., different compositions for the bulk and surface layers of the alloys, respectively. Particular surface phases or compositions are becoming increasingly known, but in the present case we have no experimental evidence for them, and it also seems improbable in view of the good consistencies for the mechanistic and oxygen affinity correlations discussed here and found independently.

For pure additivity a surface enrichment of *gold* would be demanded in order to match the experimental results (compare Fig. 1 with Fig. 7).

Between the "modification" and "collective model" a distinction appears to be difficult (if not even artificial). For both cases, however, there exist two *kinetic* possibilities which are to be checked:

a. The reaction mechanism, i.e., the sequence of elementary steps, remains the same for all Ag–Au alloys and there are only changes between different limiting kinetics (rate determining steps).

b. The reaction mechanisms vary, i.e., the elementary steps are different for different catalysts.

In case (a) a Rideal-Eley kinetics scheme fits for the limiting orders $n = 2$ and $n = 1$, respectively.

B. Rideal-Eley kinetics. For such kinetics the general velocity law is

$$v = kKc^2/(1 + Kc),$$

where K means the adsorption coefficient of a reactant. For $Kc \gg 1$ and $v\ Kc \ll 1$ there result the limiting cases of a reaction of first order and a reaction of second order; fractional apparent reaction orders can be stated for intermediate values. Transitions result here from a change of the determining reaction step (as a consequence of alteration of the K value) of a single reaction mechanism remaining otherwise unchanged. However, we have found fundamentally different reaction mechanisms for silver and gold. The case of a Rideal-Eley kinetics scheme comprising all catalysts must therefore also be ruled out.

C. Transition between various mechanisms. We can neglect the pH-independent reaction* in our considerations because it contributes only slightly to the overall reaction at pH 8, at which the alloy examinations were carried out.

For the pH-dependent reactions we have indicated the following mechanisms (*1, 8*):

Silver:

$$2\,H_2O_2 \rightleftharpoons 2\,OOH^- + 2\,H^+, \qquad (1)$$

$$OOH^- + * \rightleftharpoons *OOH^-, \qquad (2)$$

$$*OOH^- \rightleftharpoons *O + OH^-, \qquad (3)$$

$$*O + OOH^- \rightarrow O_2 + OH^- + *, \qquad (4)$$

$*$ = adsorption site.

Gold:

$$H_2O_2 + e + * \rightleftharpoons *OH + OH^-, \qquad (5)$$

$$OH^- + * \rightleftharpoons *OH^-, \qquad (6)$$

$$(3x)\ *OH^- + H_2O_2 \rightarrow *OOH^- + H_2O, \qquad (7)$$

$$2\,*OOH^- \rightarrow 2\,OH^- + O_2 + 2\,*, \qquad (8)$$

$$*\,OOH^- + *\,OH \rightarrow O_2 + H_2O + 2* + e. \qquad (9)$$

On comparison an essential difference is found only in the formation of adsorbed OOH^-. Since OOH^- ions are present also during the reaction on gold as a consequence of the dissociation of H_2O_2, it must be assumed that OOH^- ions are adsorbed according to Eq. (2) also on gold. An estimate shows, however, that the formation of $*OOH^-$ according to this equation is negligible in composition with the formation according to Eq. (7) on gold. The partial reaction (5) occurs both on gold and on silver (on silver in the pH-independent mechanism) (*8, 9*). The transition between the mechanisms therefore consists mainly of a transition in the nature of the adsorption of OOH^-

$$\begin{array}{ll} \rightarrow \{OOH^- + * \rightleftharpoons *OOH^-\}(Ag) & (2) \\ \rightarrow \left\{\begin{array}{c} OH^- + * \rightleftharpoons *OH^- \\ *OH^- + H_2O_2 \rightarrow *OOH^- + H_2O \end{array}\right\}(Au) & \begin{array}{c}(6)\\(7)\end{array} \end{array}$$

and in the mode of the subsequent reaction of OOH^-.

$$\begin{array}{ll} \rightarrow \{*OOH^- \rightleftharpoons *O + OH^-\}(Ag) & (3 \\ \rightarrow \left\{\begin{array}{c} 2*OOH^- \rightarrow 2\,OH^- + O_2 + 2* \\ *OOH^- + *OH \rightarrow H_2O + O_2 + 2* + e \end{array}\right\}(Au) & \begin{array}{c}(8\\(9\end{array} \end{array}$$

That is, in traversing the alloy series from silver to gold, Eqs. (6), (7), and (8), (9) replace Eqs. (2) and (3) in the mechanism.

On the alloys, therefore, mechanisms will occur which are combined from Eqs. (1) through (9). Exact reaction mechanisms for each individual alloy cannot be given, nor can more precise statements concerning the transitions be made.

Measurements of the pH-dependence for the alloys (particularly in the range pH 4 to pH 8) which perhaps could furnish some clues concerning the transition were not carried out for the reasons already mentioned (see Results, paragraph 1). A computation of the reaction mechanisms [as made for gold (*8*)] which correspond to the measured rate formula, did not lead to

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[*] For the pH-independent reaction on silver several mechanisms have been discussed: they are reviewed by Bischof (*9*).

the desired goal, since on account of the high number of possible equations a plurality of approximations would have to be made, the reliability of which could no longer be checked.

4. Contact-Chemical Comparison

a. The experiments were made on oxide-free catalysts, so differences in oxide layer formation cannot be responsible for the activity changes on going from silver to gold.† The activity variation must be due to the change of catalytically determining properties of the metals and their alloys themselves.

Silver has a particularly high catalytic activity for H_2O_2 decomposition compared with other metals. The activity-reducing effect of gold additions is probably to be attributed to the lack of affinity between oxygen and gold, as indicated by the following analysis.

b. Silver and gold, being homologues (IB metals), coincide nearly quantitatively in many properties, especially also in properties which are often considered determining for catalytic behavior.

The crystal structure of the two metals and their alloys is in all cases the same and the pure metals have equal lattice dimensions. The detail of the electronic structure is largely unknown, especially for the alloys.

The work functions of the two metals have different values (Ag, 4.30 eV; Au, 4.78 eV) according to the most recent work on single crystals (*10*); for polycrystalline material they are possibly nearly equal, according to older papers. For alloys there are no data available as far as we know. It is common knowledge that there are differences in the *d–s* promotion energies; that of silver (4.0 eV) is higher than that of gold (3.2 eV).

We shall not try to give an interpretation on the basis of these insufficiently known characteristics but will restrict ourselves to the comparison of the catalytic properties with properties known for the alloys and determinable directly by measurements.

c. The comparison in Fig. 8 (el. resistance, hardness, lattice constant, Hall constant, magnet susceptibility, thermal expansion, oxidation, oxygen solubility) shows that only the oxidation and the oxygen solubility coincide qualitatively with the course of the reaction rate. In this respect it should be stated that the oxygen solubility in silver–gold alloys decreases with increasing gold content at first strongly, later more weakly (*11*). We therefore assume that the oxygen affinity of the metals is primarily determining for the catalytic behavior. This property, with a substantial difference between silver and gold, is expressed also in the reaction mechanisms found by us and it is observed to be determining now also by the findings with alloys.

d. According to our measurements the activation energy increases with increasing gold contents at first slowly, but then begins to increase more strongly with a gold

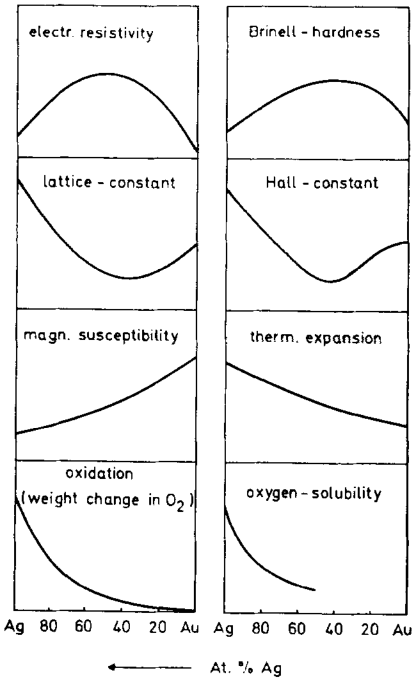

FIG. 8. Qualitative course of some properties of the alloy system Ag–Au (schematic).

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† With increasing gold contents, by the way, the formation of (inactive) oxide layers should decrease.

content of 50 at. %. This corresponds to the course of the reaction rate,‡ so that also the course of the activation energy seems to be connected with the oxygen affinity as the determining property.

The change occurring at a gold content of 50 at. % corresponds with the results of oxidation-resistance in the alloy series. Silver–gold alloys which contain less than 50 at. % of silver are completely resistant to strong oxidizing agents. According to Masing and Glaubatz (*12*), the resistance is removed by the incorporation of oxygen into the lattice or by its adsorption. The important role to be attributed to the oxygen in the H_2O_2 decomposition is further underlined by the work of Bliznakov and Peschev (*13*), according to which the presence of chemisorbed oxygen is a condition for the catalytic efficiency of silver.

5. Dependence on Stirring

For the reaction on pure gold and on alloys with a content of more than 50 at. % of gold the reaction velocity depends on the velocity of stirring under certain conditions. This stirring-dependence is probably the consequence of a surface blocking due to oxygen bubbles adhering to the catalyst. This problem has been discussed in detail in an earlier paper (*1*).

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‡ With regard to the compensation effect it should be mentioned that the compared rate values are sufficiently distant in the same direction from the compensation point to render unequivocal statements possible.