

rates on two different electrode sites. This situation should, however, be differentiated from the case (of polyelectrodes) in which two or more different reactions occur simultaneously on the same electrode surface. For the latter, a term like polyreaction seems to be more suitable.

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## On the Variation of the Activation Energy of a Catalytic Reaction as a Consequence of the Doping of Semiconductor Catalysts

The search for correlations between the catalytic activity of a semiconductor and its electronic structure, which can be modified by doping, leads one to regard as an argument in favor of the electronic theory of catalysis the fact that *the measured activation energy* of a reaction varies with the introduction of dopes. In this way, for example, the introduction of lithium or gallium into oxides such as ZnO or NiO leads to catalysts for which the activation energy for a catalytic reaction is either decreased or increased with respect to the activation energy observed for the undoped oxide. Since at the same time the Fermi level of these solids is modified by the doping, and also the concentration of charge carriers is decreased or increased, often with a variation of the activation energy of the electrical conductivity, a correlation seems to be found between the electronic structure of the catalyst and its catalytic activity.

The explanation of numerous experimental data relative to the modification of

the apparent activation energy for the reaction when dopes are introduced into the catalyst can equally be sought in considering the *variation of coverage of the surface* of the catalyst by the reactants and the products and its effect on the apparent activation energy of the reaction.

### I. VARIABLE ORDER OF REACTION

**a. Pure catalyst.** It is easy to establish (1), assuming that the adsorption of the reactant follows a Langmuir isotherm, that for a unimolecular heterogeneous reaction the apparent activation energy,  $E_a$  (measured), is the "true" activation energy decreased by the heat of adsorption,  $Q$ , of the reactant when this last covers only a small fraction of the catalyst surface

$$E_a = E - Q$$

When on the other hand, the surface is almost completely covered, the apparent activation energy for the reaction is no

longer affected by the heat of adsorption of the reactant

$$E_a = E$$

An additional complication is encountered when the product of the reaction is itself strongly adsorbed and inhibits the reaction. Under these conditions the apparent activation energy of the reaction reflects, in addition, the heat of adsorption,  $Q_p$ , of the inhibitor, which is added to the "true" activation energy

$$E_a = E - Q + Q_p$$

In the case of bimolecular reactions, which are examined below in more detail, following a Langmuir-Hinshelwood mechanism, the apparent activation energy of the reaction similarly reflects the heats of adsorption,  $Q_A$  and  $Q_B$ , of the reactants when these are weakly adsorbed

$$E_a = E - Q_A - Q_B$$

Assuming that the two reactants are adsorbed on different sites, without competition in adsorption, their heats of adsorption no longer appear in the apparent activation energy when the coverage is high

$$E_a = E$$

If, in addition, the product of the reaction is an inhibitor which is strongly adsorbed on one type of sites, the apparent activation energy is similarly increased by the heat of adsorption,  $Q_p$ , of the inhibitor

$$E_a = E - Q_A - Q_B + Q_p$$

In the determination of apparent activation energies of catalytic reactions an Arrhenius diagram is obtained for a certain temperature range. If this range (Fig. 1) is not wide (I, II, or III), a single value of the activation energy can be found corresponding to the fact that throughout this temperature range the coverage of the surface by the reactants or the effects of the inhibitor are not modified.

But if the investigations are made in a wider range of temperature (I plus II, for example), two values of the activation energy can be observed, the second of which, in the example of Fig. 1, results from the fact that the surface of the catalyst is no longer saturated by one of the reactants (passing from the region of a maximum of the adsorption isobar for this

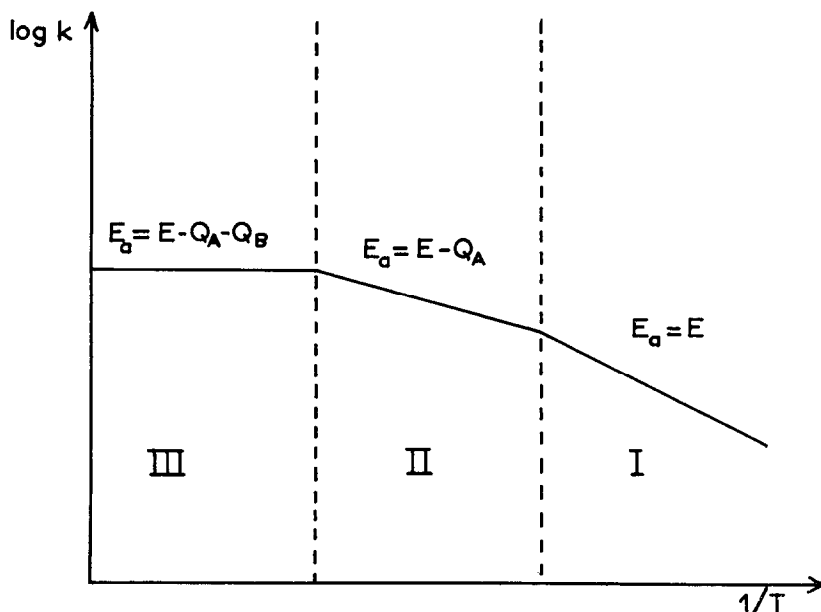


FIG. 1. The variation of the activation energy with coverage for pure catalyst (variable order of reaction).

reactant to the region of a minimum). Finally, in region III a new decrease of the apparent activation energy can be observed, with it becoming even zero or negative and corresponding in the example of Fig. 1 to the desorption of the second reactant.

**b. Doped catalysts.** Doping of a catalyst changes the position of the maxima and minima of the adsorption isobars of the reactants (2). In other words when the temperature increases, the coverage, at first complete and afterwards incomplete, of the surface of a doped catalyst by a reactant can be observed in different temperature ranges from those for an undoped catalyst, in Fig. 1.

In this way, for example, the determination of the apparent activation energy in a narrow range (II) of temperatures for three catalysts, e.g., a lithium-doped oxide (No. 1), the pure oxide (No. 2), and the gallium-doped oxide (No. 3), could give three different values. However, these three values could result not only from the modification of the Fermi level but also from the fact that in a given temperature range (II) the modification by the dope of the

nature of the surface of catalyst No. 1 may be such that the two reactants are strongly adsorbed; for catalyst No. 2, undoped, one of the reactants is not strongly adsorbed in this range (II) of temperature; and finally the modification by the other dope of the surface of catalyst No. 3 results in this same temperature range by a low surface coverage by both reactants A and B (Fig. 2).

It is, in fact logical to assume that the addition of a dope to a pure solid modifies the electronic structure of the solid and equally, by accumulation of the dopes at the surface, changes the number of active surface sites and their affinity with respect to particular reactants, displacing in one sense or the other, along the temperature axis, the extremes of the adsorption isobars.

But in the preceding examples the overall order of the reaction for the pure catalyst (Fig. 1) changes from zero in region I, to first in region II, and then to second in region III. In the same manner, the overall order of the reaction in region II (Fig. 2) is equal to zero for catalyst No. 1, to first for catalyst No. 2, and to second for

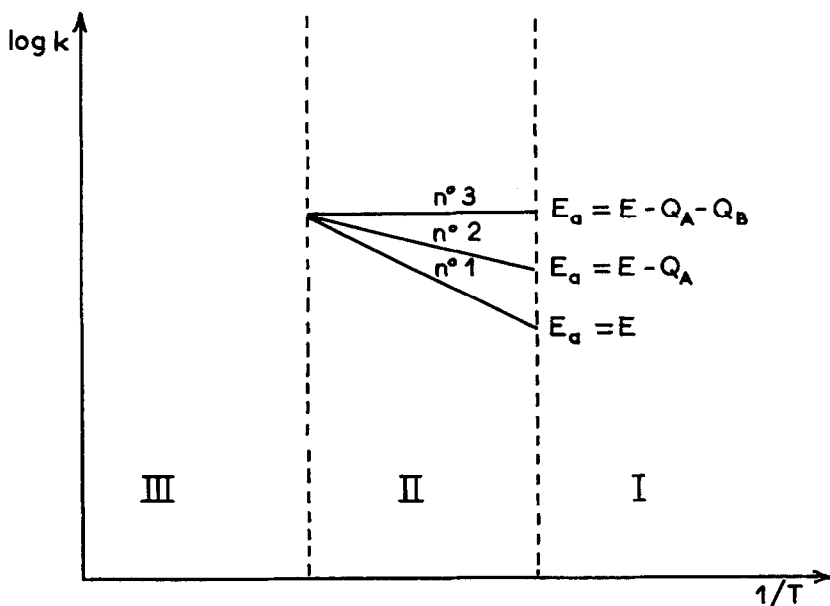


FIG. 2. The variation of the activation energy with coverage for pure and doped catalysts (variable order of reaction).

catalyst No. 3. Table 1 summarizes the behavior of the undoped catalyst.

TABLE 1  
THE VARIATION OF THE ORDER OF REACTION AND OF THE ACTIVATION ENERGY WITH COVERAGE

Temperature range <sup>a</sup>	I	II	III
$\theta_A$	1	$\epsilon$	$\epsilon$
$\theta_B$	1	1	$\epsilon$
Over-all order	0	1	2
$E_A$	$E$	$E - Q_A$	$E - Q_A - Q_B$

<sup>a</sup> Small coverage,  $\theta = \epsilon$ ; high coverage,  $\theta = 1$ .

**c. Conclusions.** It is evident that when in the Arrhenius diagram one plots the rate constant,  $k$ , of the reaction, knowledge of this implies a prior determination of the order; and the experimenter is warned of a change of mechanism in the three domains of temperature for the undoped catalyst (Fig. 1). Similarly, he is warned of a change of mechanism in domain II (Fig. 2) according as he considers the undoped catalyst No. 2 (first order), the doped catalyst No. 1 (zero order), or the doped catalyst No. 3 (second order).

It is, however, possible for this change of the mechanism to escape the observer if he is content to determine the reaction order for the undoped catalyst No. 2 exclusively and then to plot on the Arrhenius diagram no longer the logarithms of the rate constants which he has not determined but, as is very often done, the logarithms of the half-life times of reaction, for example, or the logarithms of the experimental initial rates. It is evident that conclusions drawn from values of activation energies obtained under these conditions are of little value.

## II. CONSTANT ORDER OF REACTION

**a. Pure catalyst.** It is, however, possible to conceive that the over-all order, e.g., unity, remains sensibly constant for an undoped catalyst in the three regions of temperature and that the differences in the values of activation energy are explained in terms of another phenomenon.

Assume, for example, that the coverage of the undoped catalyst by reactant A is

small in region I, moderate in region II, and high in region III while coverage of the catalyst by reactant B follows exactly the reverse order, this being summarized in Table 2. This is the behavior of pure zinc oxide with respect to hydrogen and ethylene (3).

TABLE 2  
THE VARIATION OF THE COVERAGE AND OF THE ACTIVATION ENERGY FOR A CONSTANT ORDER OF REACTION (PURE CATALYST)

Temperature range	I	II <sup>a</sup>	III
$\theta_A$	$\epsilon$	0.5	1
$\theta_B$	1	0.5	$\epsilon$
Over-all order	1	1	1
$E_A$	$E - Q_A$	$E - \lambda(Q_A + Q_B)$	$E - Q_B$

<sup>a</sup>  $\lambda$  is the appropriate coefficient, less than unity, resulting from the partial desorption of A and B, together.

If, for example,  $Q_A < Q_B$ , it is again easy to conceive that the general shape of the Arrhenius curve for the undoped catalyst will be that represented by Fig. 3, analogous to that of Fig. 1, this time without a change of the over-all order, which permits considering equivalently the rate constant, the half-time of reaction or the experimental initial rate (except for inhibition of the catalyst in the course of reaction).

**b. Doped catalysts.** Assume as a first hypothesis that the values of  $Q_A$  and  $Q_B$  are unchanged for the doped catalysts but that the temperature range in which the phenomena listed in Table 2 occur are displaced one step to the right for the doped catalyst No. 3 and one step to the left for the doped catalyst No. 1 with respect to the undoped catalyst No. 2. Table 3 summarizes the situation for the three catalysts, the arrows indicating the sense of the displacement of the temperature regions.

Thus, in region II the three catalysts exhibit three different apparent activation energies. But the difference is due not to the true activation energy, which here is supposed constant, but to the difference of coverage of the three catalysts by the

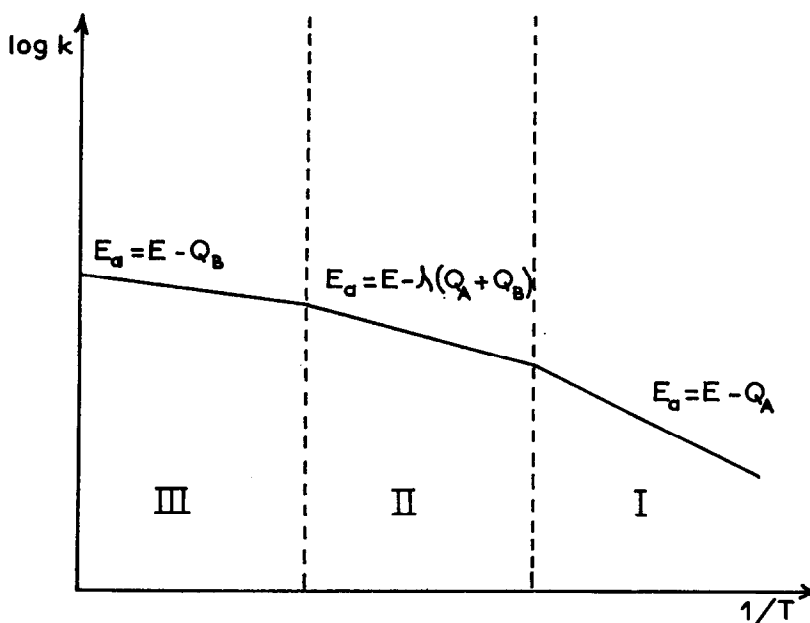


Fig. 3. The variation of the activation energy with coverage for pure catalyst (constant order of reaction).

TABLE 3  
THE VARIATION OF THE COVERAGE AND OF THE ACTIVATION ENERGY FOR A CONSTANT ORDER OF REACTION (PURE AND DOPED CATALYSTS)

Temperature range	I	II	III
Oxide (Li), No. 1	$[E (?)]$	$E - Q_A$	$E - \lambda(Q_A + Q_B)$
Pure oxide, No. 2	$E - Q_A$	$E - \lambda(Q_A + Q_B)$	$E - Q_B$
Oxide (Ga), No. 3	$E - \lambda(Q_A + Q_B)$	$E - Q_B$	$[E - Q_A - Q_B (?)]$

reactants, without change of the over-all order.

A second hypothesis which also permits retaining the over-all order of unity for the three catalysts, while conferring on them different apparent activation energies, consists in assuming that the values of  $Q_A$  and  $Q_B$  are not identical for the undoped catalyst No. 2 and the doped catalysts No. 1 and 3. This variation of the heats of adsorption with doping is, for example, observed with nickel oxide (4).

If the over-all order of the reaction remains equal to unity in the three temperature ranges, while the coverage by the reactants of the doped and pure catalysts are those of Table 2 and thus no longer

depend, in each region, on the nature of the dope, the heats of adsorption of the reactants, which differ according to the nature of the catalyst, can modify the apparent activation energies.

These characteristics are summarized in Table 4.

Let us assume for simplification that

$$Q'_A < Q''_A < Q'''_A \text{ and } Q'_B > Q''_B > Q'''_B, \\ Q'_A \approx Q'''_B \quad Q''_A \approx Q''_B \text{ and } Q'''_A \approx Q'_B$$

According to this hypothesis, doping by one type of dope increases the affinity of the doped catalyst for one of the reactants and weakens it for the other, while the other type of dope has the opposite effect

TABLE 4  
THE VARIATION OF THE COVERAGE AND OF THE ACTIVATION ENERGY FOR A CONSTANT ORDER OF REACTION WHEN THE HEATS OF ADSORPTION ARE DIFFERENT FOR PURE AND DOPED CATALYSTS

Ranges	Oxide (Li), No. 1			Pure oxide, No. 2			Oxide (Ga), No. 3		
	I	II	III	I	II	III	I	II	III
$\theta_A$	$\epsilon$	0.5	1	$\epsilon$	0.5	1	$\epsilon$	0.5	1
$\theta_B$	1	0.5	$\epsilon$	1	0.5	$\epsilon$	1	0.5	$\epsilon$
Order	1	1	1	1	1	1	1	1	1
$E_a$	$E - Q'_A$	$E - \lambda(Q'_A + Q'_B)$	$E - Q'_B$	$E - Q''_A$	$E - \lambda(Q''_A + Q''_B)$	$E - Q''_B$	$E - Q'''_A$	$E - \lambda(Q'''_A + Q'''_B)$	$E - Q'''_B$

(4). This is obviously an extreme case because if, for example,  $Q'_A$  is too small, reactant A will not be able to saturate the surface of catalyst No. 1 in temperature region III. Inversely, if  $Q'''_B$  is too small, reactant B will not be able to saturate the surface of catalyst No. 3 in temperature region I. Thus, it is probable that the three temperature ranges are less well delimited than is shown in Fig. 4, which summarizes the situation.

**Conclusions.** It is obvious after these observations that better correlations between catalytic activity and a property of the catalysts should be based on the true activation energies and not on apparent ac-

tivation energies, unless operating under conditions of constant saturation of the surface by the reactants, an objective which is not always easy to achieve, even in the case of a unimolecular reaction.

Finally, it is not suggested that all the experimental data cited in the literature, relative to the variation of the experimental activation energy of a reaction with the nature and quantity of doping, find their explanation in the hypotheses advanced above. Various phenomena have been neglected such as, for example, inhibition by the products of the reaction or the competitive adsorption of two reactants on the same sites or finally the compensation ef-

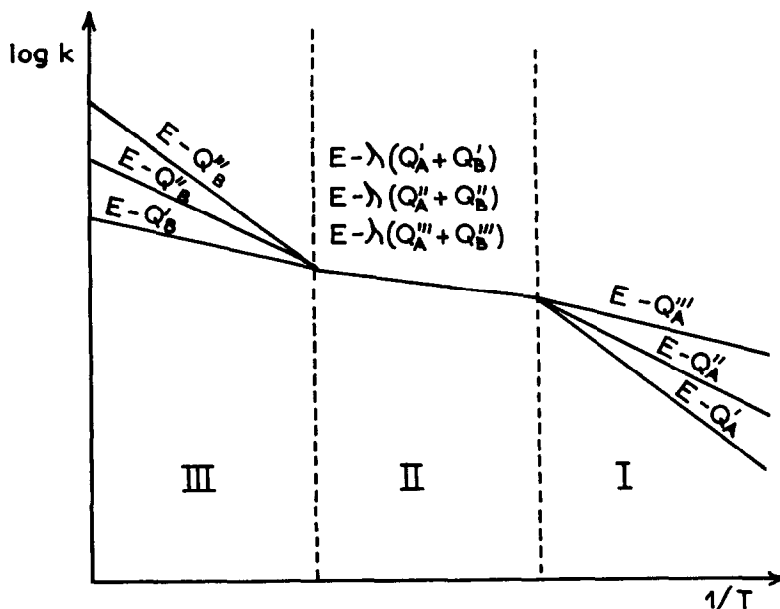


FIG. 4. The variation of the activation energy with coverage when the heat of adsorption varies for pure and doped catalysts (constant order of reaction).

fect of the pre-exponential factor. It seems, however, that the next to the last scheme (Table 3) is, for example, that which explains the behavior of zinc oxide, pure and doped with lithium or with gallium, in the hydrogenation of ethylene (3).

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