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The Hedvall Effect in the Decomposition of Hydrogen Peroxide on Single Crystals of α-Cr_2O_3

The kinetic parameters of certain catalyzed reactions depend on the magnetic state of the ferromagnetic (*1, 2*) and antiferromagnetic (*3–5*) solids catalyzing them (the Hedvall effect).* Since the magnetic phase transitions, at least with the catalysts investigated in the papers cited above, do not change substantially the basic physical properties (excluding, of course, the magnetic ones) or the chemical properties of the solids, the Hedvall effect can be used as a sensitive instrument for studying the nature of catalytic action. There is evidence that nonmagnetic phase transitions of second order can also be used for that purpose (*6*). However, the conditions under which the Hedvall effect can be observed in its pure form are not clear enough and this is the reason why there is not any definite opinion on its general features. Furthermore, some authors have observed no influence of the magnetic phase transitions on the course of the catalytic reactions investigated [e.g., with CO-oxidation, Ref. (*7*)]. Hence, it is clear that studies of some other catalyst-reaction systems near the magnetic transition points of the catalyzing solids could be of interest.

The present paper contains results obtained in the investigation of the catalytic decomposition of hydrogen peroxide on α-Cr_2O_3 single crystals. This system is very appropriate for the investigation of the Hedvall effect for the following reasons: (a) α-Cr_2O_3 passes from the antiferromagnetic into the paramagnetic state at about 307°K (the Néel temperature, T_N) (*8*); (b) this temperature lies within the range which is convenient for investigating the kinetics (*9*); (c) the use of single crystals enables one to study the problem under very pure conditions, i.e., with a small and clean surface, a sharp phase transition, etc., and (d) the decomposition of hydrogen peroxide is a model reaction of redox type which is relatively well studied (*10*).

A convenient method for the investigation of the catalytic properties of single crystals during the decomposition of hydrogen peroxide has been proposed by Bliznakov *et al.* (*11, 12*). The oxygen bubbles formed at different sites of the single crystal faces during the H_2O_2 decomposition are observed by means of a microscope with small magnification (Fig. 1) and the bubble diameters as well as their increase with time are measured. The surface area of the crystal face giving oxygen to a bubble has a diameter of about 5 μm. The single crystals used by us were prepared by the method of chemical transport (*13*). Electron probe microanalysis (with a diameter of the electron beam of about 10 μm) showed that the surface is homogeneous and that no other

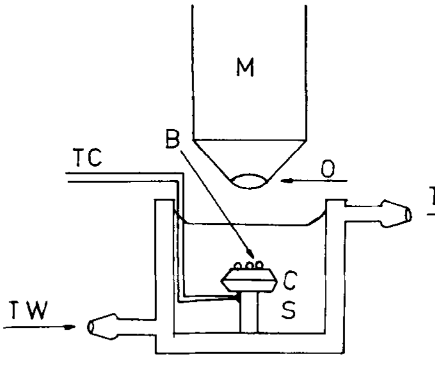

FIG. 1. Experimental conditions: (M) microscope; (O) objective; (B) bubble; (C) crystal; (S) solution; (TC) thermocouple; (TW) water from the thermostat.

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* It is interesting to note that all the reactions investigated have been redox reactions.

phases are present *(14)*. The solutions of hydrogen peroxide were prepared by diluting preliminary distilled perhydrol in redistilled water. Concentrations ranging from 0.5–4 wt% were used.

We investigated the reaction both at constant temperatures and under continuous heating or cooling of the system at a constant rate (Å/min). The processing of the kinetic data in both cases is described in detail elsewhere *(11, 12)*. In determining the exact volume of the oxygen bubbles, the pressure of water vapor at each temperature was taken into consideration. In experiments with continuous heating (cooling), the quantity d^3/T was plotted against t, d being the diameter of the bubble; T, the absolute temperature; and t, the time. By graphical differentiation of these curves the quantities proportional to the rate constants (k) were obtained for each temperature. This is obvious if we write down the dependence of the oxygen evolved on time bearing in mind that the reaction is of zero order:

$$\text{const.}\,\frac{d^3}{T} = C_{\mathrm{H_2O_2}} \int_0^t k(\tau)d\tau + \text{const.}\,\frac{d_0^3}{T}$$

where

$$T = at + T_0.$$

The temperature was measured with a copper–constantan thermocouple touching the crystal and was recorded by an electronic balance-type potentiometer. The accuracy of temperature measurements within the range 283–335°K was about ±0.15°. The same "thermometer" was used in determining the Néel temperature of the single crystals from the temperature dependence of the EPR line width *(15)*.

Investigations of hydrogen peroxide decomposition at fixed temperatures below and above the temperature of the phase transition showed: (a) as in many other cases of H_2O_2 decomposition *(11)*, the reaction is of first order with respect to the peroxide concentration but, as only a small amount of the peroxide is used up during the experiment, the reaction is practically of zero order; (b) the surface is energetically inhomogeneous, i.e., for bubbles formed at different sites of the surface, different activation energies ranging from 10 to 30 kcal/mole are obtained, and (c) treatment of the crystals with hydrogen peroxide for several hours leads, especially at temperatures above 313°K, to a decrease in activity and even to deviations from the zero order. For these reasons, we carried out the experiments with continuous heating or cooling (about 1°/min). This enabled us to investigate the rate constant over the whole temperature range for a bubble located at a definite site of the surface in the course of 20 min during which the crystal activity showed no substantial change. After 2–3 successive experiments, the crystals were reactivated by heating at 673°K in a stream of dry hydrogen for 3 hr. These conditions favor the restoration of the normal stoichiometry of the surface *(16)*, which is obviously disturbed under the effect of a medium of active oxygen and hydroxyl groups.

Figure 2 shows data on the activity of the crystals in the case when no anomalies are observed in curves of log k vs $1/T$. Curve a represents the kinetics within the range 288–305°K, and curve b, in the interval between 309 and 324°K, i.e., in intervals which do not include the transition temperature. Curve c which covers the whole temperature interval (291–326°K) and also shows no peculiarities, is more interesting. Such Arrhenius straight lines are obtained when the kinetics are investigated on crystals which have been kept in peroxide a sufficient time but have not yet become passive (i.e., the reaction is still a zero order reaction). It could be assumed that in this case the surface is modified by the hydroxyl groups and active oxygen to such an extent that it becomes insensitive towards the changes in volume. (Probably analogous circumstances obscure the Hedvall effect with other systems as well.) This assumption is confirmed by the behavior of freshly activated crystals. In this case, on reaching the temperature of the phase transition by means of continuous heating or cooling, the increase in the bubble volume stops (Fig. 3). The

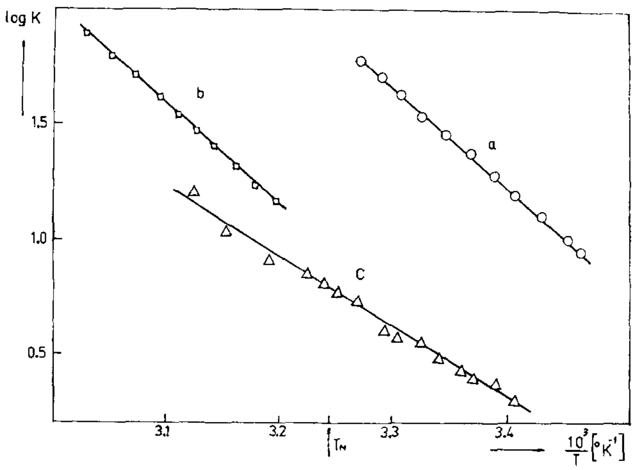

FIG. 2. Dependence of the rate constant (arbitrary units) of the H_2O_2 decomposition on the reciprocal temperature: (a) freshly activated single crystal in the range 288–305°K; (b) freshly activated single crystal in the range 309–327°K; (c) a single crystal treated at 313.2°K for 60 min in H_2O_2.

dependence of the rate constant on temperature in this case is shown in Fig. 4 in the usual Arrhenius coordinates. As is evident, here both the Hedvall effect I (a discontinuity of the Arrhenius straight line) and the Hedvall effect II (a change in the slope of the line) are observed. A comparison with the investigations cited above (*1–4*) in which the Hedvall effect II is established shows an interesting peculiarity in all cases: irrespective of the catalyst nature (metal or semiconducting) and of the different magnetic ordering (ferro- or antiferromagnetic), the temperature dependence of the rate constant becomes steeper with the transition into the paramagnetic state (i.e., an increase in the activation energy is observed).

It is usually assumed that the effect of the phase transition on the kinetic parameters of redox reactions may be determined on the basis of the change in structure of the electron energy spectrum of the catalyst (*1, 17–19*). However, for a concrete model of this effect in each separate case it is necessary to know in detail the rate determining step of the corresponding reaction in order to find a relationship between the kinetic parameters and the

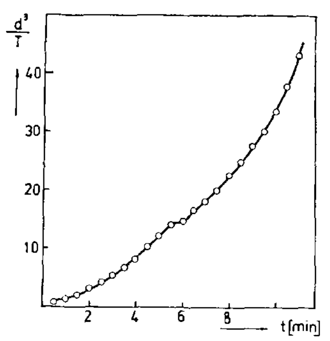

FIG. 3. Dependence of the reduced volume of an oxygen bubble (d^3/T) on time during continuous heating of a freshly activated single crystal.

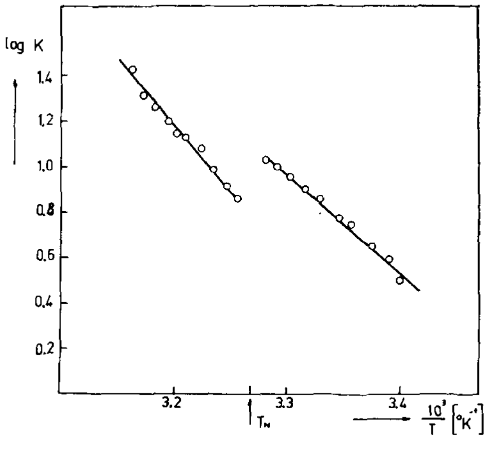

FIG. 4. The data of Fig. 3 in Arrhenius coordinates [the arrow points to the T_N determined in (*15*)].

parameters of the electron energy spectrum. The more general peculiarity of the Hedvall effect II mentioned above could, perhaps, lead to a simpler solution without using concrete data.

Another interesting and, probably, general feature of the phenomenon under consideration is the "discontinuity" of the Arrhenius straight line within a temperature range around the transition point (Hedvall effect I). This in our case corresponds to a pronounced minimum in the rate constant in the vicinity of the Néel point. It is well known that in this region many physical quantities of the magnetic materials have anomalous temperature dependences. These anomalies (maxima or minima) are due to the critical fluctuations of the magnetization (*20*). It can be surmised that these fluctuations affect in some manner also the normal course of the H_2O_2-decomposition.

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G. BLIZNAKOV
S. ANGELOV
S. MANEV

Institute of General and Inorganic Chemistry
Bulgarian Academy of Sciences
Sofia 13, Bulgaria
and
Department of Chemistry
University of Sofia
Sofia, Bulgaria

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