

## A Theoretical Model for the Deactivation of a Neodymium Sulfide Catalyst During the Reaction Between Hydrogen and Oxygen

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The reaction between hydrogen and oxygen, catalyzed by neodymium sulfide, does not go to completion; the reaction stops when unreacted hydrogen and oxygen are still present in the system. The results have been explained using the assumptions that the true overall order for the reaction is zero, and that the catalyst is being deactivated during the course of the reaction. Good agreement is obtained between experimental and theoretical results by assuming that the deactivation process is first order in concentration of remaining active sites.

### INTRODUCTION

#### *Deactivation*

Many catalysts show a change in activity with time due to a change in the number of active sites on the surface. This change can be caused by the formation of a different crystalline structure (1), by sintering (2), or by a surface reaction in which thermodynamically stable, inactive sites are formed from less stable, active sites (3). Poisoning by impurities (4), reactants (5), or products (6) can also lead to a decrease in the number of active sites.

Quantitative studies on the relationship between activity and amount of added poison have been carried out by several workers (4, 7-9). Nonselective poisoning leads to a linear relationship between activity and amount of added poison, whereas selective poisoning, caused by heterogeneous surfaces or poisons blocking pores, leads to more complex relationships.

Deactivation occurring during a catalytic run can lead to anomalous kinetic results

and, therefore, factors must be included in the general kinetic equation to account for the change in available surface. The rate constant must be multiplied by a term  $(1 - \theta_I)$ , where  $\theta_I$  represents the fraction of the initial active surface that has been deactivated (6, 10-12). In some cases, particularly in flow systems, an equilibrium is soon established and  $\theta_I$  remains effectively constant. In other cases, there is a slow rate of deactivation, and the fraction of the surface remaining catalytically active changes while the reaction is in progress. This can be caused by a continuous change in surface area or by a change in the rate of poisoning by reactants or products as their concentration in the gas phase changes.

Various relationships have been suggested to express the rate of deactivation. Rozovskii (3) has proposed that, in a closed system where the regeneration of active sites is negligible, the loss of activity follows a first order equation in concentration of remaining active sites. Herrmann *et al.* (2) have shown that, for hydrogen, the rate of decrease in chemisorptive capacity of platinum because of sintering

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is second order with respect to the remaining chemisorptive capacity. This result has been verified by Butt and Rohan (13). Wojciechowski (14) considers that the order of the deactivation equation depends on the number of sites removed per deactivating event.

### The Hydrogen-Oxygen Reaction

The catalyzed reaction between hydrogen and oxygen has been extensively studied [for example (15)], including two studies using lanthanide oxides (12, 16). The overall order of the reaction depends on the catalyst used and the pressure of the reactants. An overall order of zero has been noticed by Gray and Darby (17) with excess oxygen over nickel oxide, and by Rudham and Read (12), particularly during the initial stages of the reaction, over neodymium oxide, dysprosium oxide and erbium oxide.

It was the purpose of the present study to show that, during the reaction between a stoichiometric mixture of hydrogen and oxygen catalyzed by neodymium sulfide, the anomalous kinetic results, and the complete deactivation of the catalyst, can be explained using the assumptions that the deactivation process is first order in concentration of active sites and that the reaction between hydrogen and oxygen is zero order in total pressure of hydrogen plus oxygen.

### NOMENCLATURE

$k$	pseudo-rate constant for the reaction between hydrogen and oxygen (Torr <sup>1-n</sup> min <sup>-1</sup> )
$k_2$	pseudo-rate constant for the deactivation process (min <sup>-1</sup> )
$n$	overall order with respect to total pressure of hydrogen plus oxygen
$n_0$	initial number of active sites per unit surface area (m <sup>-2</sup> )
$P_T$	total pressure of hydrogen plus oxygen (Torr)
$P_0$	total initial pressure of hydrogen plus oxygen (Torr)
$P_\infty$	total final pressure of hydrogen plus oxygen when the reaction has stopped (Torr)

$S$	total surface area (m <sup>2</sup> )
$t$	time (min)
$\theta_A$	fraction of the initial active surface that is still active
$\theta_I$	fraction of the initial active surface that has been deactivated (= 1 - $\theta_A$ )

### THEORY

#### Deactivation

The rate of the reaction between hydrogen and oxygen can be expressed as:

$$-\frac{dP_T}{dt} = k[Sn_0\theta_A]P_T^n \quad (1)$$

If the overall order with respect to the total pressure of hydrogen plus oxygen is zero the equation reduces to:

$$-\frac{dP_T}{dt} = k_1\theta_A, \quad (2)$$

where  $k_1 = kSn_0$ .

If the deactivation process is first order in concentration of active sites, an equation can be written thus:

$$-\frac{d\theta_A}{dt} = k_2\theta_A \quad (3)$$

For both Eqs. (2) and (3) to be obeyed, the relationship between  $P_T$  and  $\theta_A$  should be of the type

$$\theta_A = \frac{k_2}{k_1} [P_T + k_3], \quad (4)$$

where  $k_3$  is constant during the course of the reaction. In a closed system,

when

$$P_T = P_0, \quad \theta_A = 1,$$

and, when

$$P_T = P_\infty \quad \theta_A = 0.$$

Substitution of these conditions into Eq. (4) gives

$$\frac{k_2}{k_1} = \frac{1}{[P_0 - P_\infty]}, \quad (5)$$

and

$$k_3 = -P_\infty \quad (6)$$

Substitution of Eqs. (5) and (6) into Eq. (4) gives:

$$\theta_{\Lambda} = \left[ \frac{P_T - P_{\infty}}{P_0 - P_{\infty}} \right], \quad (7)$$

and substitution of Eq. (7) into Eq. (2) gives:

$$-\frac{dP_T}{dt} = k_1 \left[ \frac{P_T - P_{\infty}}{P_0 - P_{\infty}} \right] \quad (8)$$

Integration of Eq. (8) gives:

$$\log_e (P_T - P_{\infty}) = -k_2 t + \log_e (P_0 - P_{\infty}) \quad (9)$$

### Analysis of Results

The analysis of the results according to Eq. (9) can only be achieved when the value for  $P_{\infty}$  is known. Since this value is not always available, a computer program was written to estimate an appropriate value for  $P_{\infty}$  which would fit Eq. (9).

A computer program was written to solve the general equation

$$y = Ax^2 + Bx + C \quad (10)$$

where  $y$  represents  $\log_e(P_T - P_{\infty})$ ;  $x$  represents  $t$ ;  $B$  represents  $-k_2$ ; and  $C$  represents  $\log_e(P_0 - P_{\infty})$ .

An estimate of  $P_{\infty}$ , together with values for  $P_T$  and  $t$ , were fed into the computer. The value for  $P_{\infty}$  was changed by increments of 0.001 Torr to obtain a value for the  $A$  coefficient closest to zero. The corrected value for  $P_{\infty}$ , together with values for  $P_0$  and  $k_2$  were obtained.

## EXPERIMENTAL METHODS

### Catalyst

The catalyst used in the experiments was powdered  $\gamma$ -Nd<sub>2</sub>S<sub>3</sub>, supplied by Cerac, Incorporated. X-Ray analysis showed that it had a cubic structure of the thorium phosphide type (18). The structure showed no change with use. The total weight used was 0.4853 g.

The catalyst was conditioned by heating for 7 days at 500°C and  $<10^{-6}$  Torr pressure. Between runs, the catalyst was heated for 6 hr at the temperature of the next run and at  $<10^{-6}$  Torr.

### Apparatus and Measurement Procedure

The apparatus comprised a conventional high-vacuum system. Stoichiometric mixtures of hydrogen and oxygen (assayed grade, supplied by The Matheson Company, Incorporated) were prepared, and allowed onto the catalyst. The reaction was followed by measuring the total pressure in the closed reaction chamber every 3 min, using a McLeod gauge. Variations in the measuring procedure and in the apparatus assured that the pressure readings were valid. Most runs were followed for about 90 min. A trap, surrounded by liquid nitrogen, protected the catalyst from contamination and allowed the water produced in the reaction to be condensed.

The reaction was studied over the temperature range 250 to 412°C at initial pressures in the range 0.40 to 0.65 Torr.

An IBM 1130 computer was used for the calculations.

## RESULTS

The results, plotted as total pressure of hydrogen plus oxygen versus time, gave smooth curves, leveling off before the reaction was complete. The overall orders with respect to time, determined from the pressure versus time plots, were high (in the region of six) during the initial stages of the reaction, and decreased as the reaction proceeded.

The catalyst activity was quickly regenerated by evacuating the system. Consistent results were obtained using an evacuation time of 6 hr between runs. Evacuation for a considerably longer period of time resulted in increased activity. For example, at 280°C evacuation for 6, 18, and 45 hr, resulted in initial rates of 0.0012, 0.0013, and 0.0053 Torr min<sup>-1</sup>, respectively.

### Analysis of Results

In view of the deactivation occurring during the reaction, and the anomalously high order with respect to time, the results were analyzed according to Eq. (9).

In Table 1 the values obtained for  $P_0$  and  $P_{\infty}$  from Eq. (9) are compared with the value for  $P_0$  obtained by extrapolating

TABLE I  
SUMMARY OF RESULTS FOR THE HYDROGEN-OXYGEN REACTION ON NEODYMIUM SULFIDE

Run	Temp (°C)	$P_0$ (Torr); value from		$P_\infty$ (Torr); value from		$k_2$ (min <sup>-1</sup> ); value from Eq. (9)
		Eq. (9)	Extrapolation	Eq. (9)	Expts.	
1	280	0.568	0.569	0.515		0.023
2	278	0.549	0.550	0.497		0.022
3	339	0.473	0.491	0.337		0.028
4	319	0.549	0.561	0.422		0.017
5	380	0.466	0.478	0.350	0.351	0.108
6	400	0.393	0.434	0.325	0.326	0.220
7	412	0.585	0.636	0.461	0.460	0.235
8	389	0.605	0.604	0.464	0.467	0.171
9	370	0.408	0.413	0.314	0.315	0.146
10	350	0.630	0.650	0.429		0.017
11	330	0.579	0.593	0.458		0.018
12	310	0.628	0.585	0.448		0.016
13	300	0.633	0.636	0.440		0.008
14	292	0.633	0.636	0.469		0.009
15	269	0.613	0.613	0.334		0.005
16	250	0.545	0.544	0.123		0.002

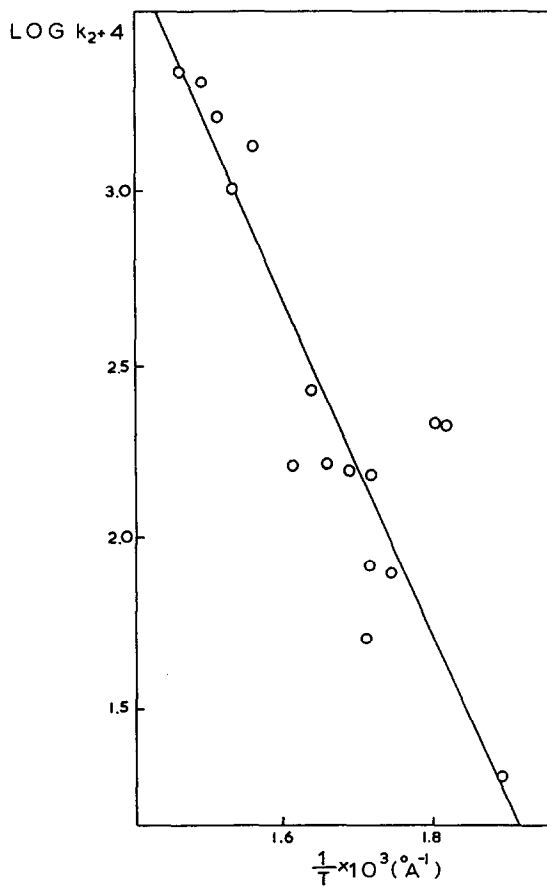


FIG. 1. Arrhenius plot using the rate constant for the deactivation process.

the  $P_T$  versus  $t$  graph back to  $t = 0$ , and with the value for  $P_\infty$  obtained from the runs which went to completion. An Arrhenius plot, using the calculated values for  $k_2$ , is shown in Fig. 1. The best straight line through the points, together with the lines giving maximum and minimum slopes, were determined using an IBM least squares polynomial curve fitting program. The activation energy for the deactivation process is  $18 \pm 3$  kcal mole<sup>-1</sup>.

#### Evaluation of the Constant, $k_1$

From Eq. (2),

$$k_1 = - \left[ \frac{dP_T}{dt} \right]_{t \rightarrow 0}, \quad (11)$$

whereas, by rearranging Eq. (5)

$$k_1 = k_2 (P_0 - P_\infty). \quad (12)$$

Table 2 compares the values obtained for  $k_1$  by measuring initial rates [Eq. (11)] and by using calculated values for  $k_2$ ,  $P_0$  and  $P_\infty$  [Eq. (12)]. The values from Eq. (11) are quoted to two significant figures, the error being approximately 20%.

The two values for  $k_1$  are compared in the Arrhenius plots shown in Fig. 2. The

TABLE 2  
VALUES FOR  $k_1$  OBTAINED FROM INITIAL RATES [Eq. (11)] AND FROM CALCULATED VALUES FOR  $k_2$ ,  $P_0$ , AND  $P_\infty$  [Eq. (12)]

Run	$P_0 - P_\infty$ (Torr); value from Eq. (9)	$k_1$ (Torr min <sup>-1</sup> ); value from	
		Eq. (11)	Eq. (12)
1	0.053	0.0012	0.0012
2	0.052	0.0014	0.0011
3	0.136	0.011	0.0038
4	0.127	0.0057	0.0022
5	0.116	0.014	0.0125
6	0.068	0.020	0.0150
7	0.124	0.036	0.0291
8	0.141	0.018	0.0241
9	0.094	0.013	0.0137
10	0.201	0.010	0.0034
11	0.121	0.0082	0.0022
12	0.180	0.0045	0.0029
13	0.193	0.0029	0.0015
14	0.164	0.0020	0.0015
15	0.279	0.0014	0.0014
16	0.422	0.0010	0.0008

slopes were drawn as before giving activation energies using  $k_1$  values calculated according to Eqs. (11) and (12) of  $16 \pm 3$  and  $18 \pm 3$  kcal mole<sup>-1</sup>, respectively.

## DISCUSSION

### Validity of the Model

The validity of the theoretical model can be assessed on the basis of the correspondence between theoretically calculated and experimentally measured quantities.

There is close agreement in all cases between the experimentally measured and theoretically calculated values for  $P_\infty$ , and, in most cases, between the extrapolated and theoretically calculated values for  $P_0$  (Table 1). The extrapolated values for  $P_0$  are particularly inaccurate at high temperatures.

The values for  $k_1$ , calculated according to Eqs. (11) and (12), are in fairly good agreement and give similar Arrhenius plots (Fig. 2) and activation energies. The inaccuracy in measuring the initial rates, particularly at high temperatures, where the absolute error is high, may account for the difference between lines 1 and 2.

The Arrhenius plot using  $k_2$  is tolerably linear (Fig. 1). The values for  $k_2$  from the first two runs appear to be high, indicating that the deactivation process is more pronounced during these runs than during the later runs. This is also shown in Table 2 where the values for  $(P_0 - P_\infty)$  are low. Conversely, the values for  $(P_0 - P_\infty)$  seem high for the last two runs, although there is no indication that  $k_2$  is abnormally low.

### Order of the Reaction Between Hydrogen and Oxygen

In the preceding presentation, it has been assumed that the true overall order for the reaction is zero. This assumption is based on rather limited experimental and literature (12, 17) evidence. However, preliminary studies have shown that there is less agreement between calculated and measured values for  $P_0$  and  $P_\infty$  when orders other than zero are used.

Attempts have been made to determine the overall order with respect to concentration (the true order) from initial rate data.

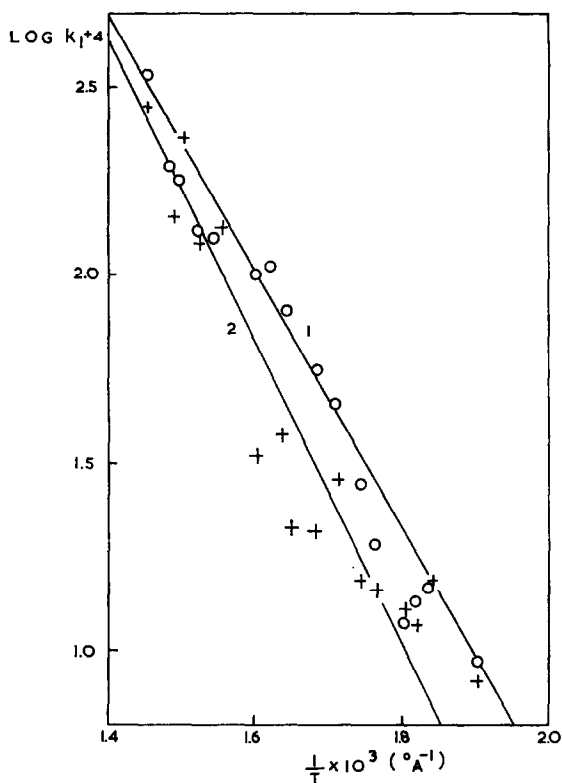


FIG. 2. Arrhenius plots using the rate constant for the hydrogen-oxygen reaction: The results from Eq. (11) (○ line 1); and the results from Eq. (12) (+, line 2).

However, due to the small range of initial pressures studied at any one temperature, and due to the difficulties involved in measuring the initial rates accurately, these results, though suggesting a zero order dependence, were inconclusive.

#### *Causes of Deactivation*

It would seem unlikely that deactivation is caused by diffusion of active sites from the surface, or diffusion of impurities to the surface, although there is some evidence that nonstoichiometric mobile sulfur can be very active (19).

The most likely cause of deactivation is a surface reaction leading to irreversibly adsorbed products, probably water. The similarity in the values obtained for the activation energies from  $k_1$  and  $k_2$  indicate that a similar step could be involved in the hydrogen-oxygen reaction and the deactivation process.

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