Rate of reaction of nitric oxide by calcium sulfide on high surface area supports
by John Carl McIntyre

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemical Engineering
Montana State University

Abstract:
Oxides of nitrogen are one of the major air pollutants in the United States today. Because of the kinetics, most of the oxides of nitrogen are emitted in the form NO, which is converted into NO2 at equilibrium.

NO and NO2 are both harmful in themselves, and have been linked to other harmful constituents of smog.

Previous work has shown that calcium sulfide is a good reducing agent for NO. Therefore this research, was performed to study the rate of the following reaction; (Formula not captured by OCR) where CaS was adsorbed on some high surface area support.

In runs using 2.5% NO, 97.5% He at .15 to .20 standard cm 3 per second reacting with 8.6% CaS impregnated on a high alumina, high surface area pellet, the average global rates of reaction increased with increasing temperature. At 390°C the rate was .25 x 10-4 moles CaSO4 formed per hour per gram of pellet. At 493°C the average rate was .45 x 10-4 moles per hour per gram.

At each temperature and flow rate, a molecular sieve support gave greater average rates than the alumina pellets. At 392°C the rate was .32 x 10-4, at 410°C the rate was .64 x 10-4, and at 438°C the rate was .47 x 10-4 moles CaSO4 formed per hour per gram. Some difficulty was encountered with oxidation of the pellets in air during storage.

The average global rate of reaction was lower using five pellets in a bed than using one pellet. The average rate at 442°C for five alumina pellets was .05 x 10-4 moles per hour per gram using a 2.5% NO, 97.5% He feed at .16 standard cm3 per second. This corresponds to .31 to .34 x 10-4 moles per hour per gram at about the same conditions using one pellet. The apparent cause of this lower rate is an added diffusional resistance.

It was found that, for the flow rates in this experiment, external film diffusion was probably not important. At 440°C and 3.48 standard cm3 per second the average global rate was .25 x 10-4 moles per hour per gram. At 444°C and .12 standard cm3 per second the average global rate was .22 x 10-4 moles per hour per gram. This difference in rate is within the experimental error for the test.

Oxygen was found to react with CaS faster than nitric oxide under the same conditions for an alumina pellet. In a 2.5% O2, 97.5% He stream at .12 standard cm3 per second and at a temperature of 444°C, the average global rate of reaction was .41 x 10—4 moles CaSO4 formed per hour per gram of pellet. In a 2,5% NO, 97.5% He stream at .12 standard cm3 per second reacting with a pellet from the same batch, the average rate was .22 x 10-4 moles per hour per gram. Thus it is probably desirable to remove oxygen from the feed gas since oxygen apparently reacts faster than NO at the same concentration and would therefore reduce pellet life.

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JOHN CARL MCINTYRE

A thesis submitted in partial fulfillment
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ABSTRACT

Oxides of nitrogen are one of the major air pollutants in the United States today. Because of the kinetics, most of the oxides of nitrogen are emitted in the form NO, which is converted into NO_2 at equilibrium. NO and NO_2 are both harmful in themselves, and have been linked to other harmful constituents of smog.

Previous work has shown that calcium sulfide is a good reducing agent for NO. Therefore this research was performed to study the rate of the following reaction:

$$CaS_{(s)} + 4NO_{(g)} \rightarrow CaSO_{4(s)} + 2N_{2(g)}$$

where CaS was adsorbed on some high surface area support.

In runs using 2.5% NO, 97.5% He at .15 to .20 standard cm^3 per second reacting with 8.6% CaS impregnated on a high alumina, high surface area pellet, the average global rates of reaction increased with increasing temperature. At 390°C the rate was $.25 \times 10^{-4}$ moles $CaSO_4$ formed per hour per gram of pellet. At 493°C the average rate was $.45 \times 10^{-4}$ moles per hour per gram.

At each temperature and flow rate, a molecular sieve support gave greater average rates than the alumina pellets. At 392°C the rate was $.32 \times 10^{-4}$, at 410°C the rate was $.64 \times 10^{-4}$, and at 438°C the rate was $.47 \times 10^{-4}$ moles $CaSO_4$ formed per hour per gram. Some difficulty was encountered with oxidation of the pellets in air during storage.

The average global rate of reaction was lower using five pellets in a bed than using one pellet. The average rate at 442°C for five alumina pellets was $.05 \times 10^{-4}$ moles per hour per gram using a 2.5% NO, 97.5% He feed at .16 standard cm^3 per second. This corresponds to $.31$ to $.34 \times 10^{-4}$ moles per hour per gram at about the same conditions using one pellet. The apparent cause of this lower rate is an added diffusional resistance.

It was found that, for the flow rates in this experiment, external film diffusion was probably not important. At 440°C and 3.48 standard cm^3 per second the average global rate was $.25 \times 10^{-4}$ moles per hour per gram. At 444°C and .12 standard cm^3 per second the average global rate was $.22 \times 10^{-4}$ moles per hour per gram. This difference in rate is within the experimental error for the test.

Oxygen was found to react with CaS faster than nitric oxide under the same conditions for an alumina pellet. In a 2.5% O_2, 97.5% He stream at .12 standard cm^3 per second and at a temperature of 444°C, the average global rate of reaction was $.41 \times 10^{-4}$ moles $CaSO_4$ formed per hour per gram of pellet. In a 2.5% NO, 97.5% He stream at .12 standard cm^3 per second reacting with a pellet from the same batch, the average rate was $.22 \times 10^{-4}$ moles per hour per gram. Thus it is probably desirable to remove oxygen from the feed gas since oxygen apparently reacts faster than NO at the same concentration and would therefore reduce pellet life.

INTRODUCTION

Oxides of nitrogen (NO_x) are among the major pollutants in the United States today. In 1968 alone, 16 million tons of NO_x (calculated as NO_2) were released into the atmosphere (1). By comparison, in 1967 30.8 million tons of SO_2 were released (2). The principal sources of the oxides of nitrogen are stationary fossil fuel power generation plants. Stationary sources are accredited with 60% of the total NO_x released to the air (1).

Oxides of nitrogen are present in many forms, though by far the most common are nitrogen dioxide (NO_2), nitric oxide (NO), and nitrous oxide (N_2O). NO_2 and NO are poisonous irritants while N_2O, commonly called laughing gas, is a relatively harmless anesthetic. NO_2 is reddish-brown and this is what gives the air over Los Angeles its distinctive color. NO and N_2O are both colorless. Although N_2O is a narcotic and can be harmful at high concentrations, it is harmless at ordinary low concentrations and can be dismissed as a serious pollutant. However, NO_2 and NO must be removed from the air because of their toxicity at high concentrations and irritating qualities at low concentrations.

Oxides of nitrogen are formed in many ways. For instance, the action of bacteria in the soil causes the concentration of N_2O to reach about .3 ppm in the air. NO is produced by the oxidation of nitrogen (N_2) by oxygen (O_2) at high temperatures. For instance, the equilibrium concentration of NO with N_2 and O_2 is about 25,000 ppm at 4400°F (the approximate combustion temperature in a car engine). By comparison, the

equilibrium concentration is only .001 ppm at 70°F (3).

NO_2 is formed in a somewhat different manner. At 4400°F the kinetics of the N_2, O_2, NO_2, and NO reactions are such that only 5 to 10% of the NO_x formed is NO_2 with most of the rest being NO (1). However at 70°F the equilibrium between NO_2, O_2 and NO highly favors NO_2. Thus in car engine exhausts, for example, most of the excess oxygen in the exhaust gases leaves the engine as NO, while at equilibrium most of these gases are converted to NO_2.

Kinetics plays a very important role in NO_x formation. At 4400°F the formation of NO from N_2 and O_2 is very fast, while at 70°F the decomposition of NO to N_2 and O_2 is very slow. In fact, the decomposition is so slow that in one experiment several containers of NO were sealed with various catalysts at ordinary temperatures in 1917. Upon opening the containers in 1958 there was no detectable N_2 (1). Thus, though thermodynamically unstable at ordinary temperatures, oxides of nitrogen can be particularly long lived.

PREVIOUS WORK

NO_2 has been linked to various photochemical oxidation products of hydrocarbons which are irritating to the eyes and harmful to plant life (3). Because of this it is necessary to control NO_x emissions. Research into abatement of oxides of nitrogen generally falls into one of four categories: a) process modification; b) chemical or physical adsorption; c) thermal or catalytic reduction of NO to O_2 and N_2 or

N_2O; or d) chemical reduction of NO with N_2 or N_2O as a product.

Process modification is specific to each NO_x source. Generally it involves adjustment of flame temperatures, recycle of exhaust streams, and changes in fuel/air ratio (1).

Chemical adsorption was studied by Bartok, et. al (1) who concluded that common adsorbents such as silica gel, alumina, molecular sieves, char, and ion exchange resins all had insufficient capacities necessitating very large contactors and frequent regeneration. Aqueous absorption systems of alkaline solutions or sulfuric acid looked promising but these require equimolar NO and NO_2 in the gas, since the soluble product is probably N_2O_3. Most promising of the alkaline solutions were lime-water and magnesium hydroxide (1).

Thermal decomposition of NO is thermodynamically favored below about 1000°K as noted previously. However, the rate of decomposition is extremely low which agrees with the experimentally observed high activation energy. Catalysts have been developed which lower this activation energy by as much as a factor of 4 but the decomposition rate remained low. This has been linked to an exceptionally low pre-exponential factor in the rate constant. Rates for heterogeneous catalytic decompositions fell within the range 9×10^{-8} to 6×10^{-6} $\frac{\text{moles NO removed}}{m^2\ hr}$ which was considered too slow to be commercially practical (4).

None of the methods mentioned so far has proven entirely satisfactory so that considerable effort has been turned to the use of chemical reducing agents. Shelef and Kummer (4) studied carbon monoxide,

hydrogen, and methane which all proved successful in reducing NO at temperatures between 110 and 800°C depending on the catalyst and support used. Catalysts showing the most promise were supported precious metals and supported copper oxides or copper chromite. Ammonia was another excellent reducing agent over precious metal catalysts and transition metal oxides at temperatures around 250°C. Activated carbon was found to be a slow reducing agent (4).

In all these tests of reducing agents, it was found that oxygen was selectively reduced before NO. Thus the reduction of NO was slowed by the presence of O_2. Ammonia was the only exception and it was found that the presence of oxygen actually enhanced the rate. Water vapor was found to have no effect or, in the case of CO and H_2O, the rates were improved (4).

Urea has also been tried as a reducing agent. Optimum temperatures for this reaction were between 40 and 100°C. Oxygen was necessary for the reaction but at 16% O_2 the catalyst became poisoned after 16 hours. The main disadvantage stems from the fact that urea decomposes at 110°C so that temperatures, and therefore rates, were limited. The greatest observed rate was 3.4×10^{-4} mole NO removed/g-hr, which the author felt would be too slow for practical catalyst bed sizes (5).

Ault and Ayen studied the hydrocarbon series C_1 to C_8 as reducing agents over a barium-promoted copper chromite catalyst. They found appreciable reduction of NO at temperatures between 300 and 500°C. They found that an increase in number of carbon atoms per molecule decreased

the temperature required for a given conversion. Also, for a given number of carbon atoms per molecule a decrease in saturation led to a decrease in temperature required for a given conversion. They used a constant feed rate of 1×10^{-2} mole NO/g-hr, and obtained 20 to 80% conversions for various hydrocarbons at 500°C. They observed that CO_2 and H_2O had a deactivating influence on the catalyst (6).

REDUCTION WITH METAL SULFIDES

White (7) showed that metal sulfides could be used to reduce NO at temperatures between 400 and 800°C. He showed that addition of various chemicals lowered the needed temperature for conversion of NO to N_2. He also showed that the solid products of the reaction of calcium sulfide (CaS) with NO were at least 80% calcium sulfate ($CaSO_4$). CaS was found to be one of the best metal sulfides because of its low cost and stability of the sulfate.

Erickson (8) studied the effects of different support materials for CaS and different contaminants in the feed. He discovered that a high alumina high surface area support, the Harshaw 1602-T, was very favorable for reduction of NO with no H_2S or SO_2 released. Some H_2S was observed in the exhaust gases from a high silica support, the Nalco 2910-A. A molecular sieve, the 1/8 inch Linde TM-Q-1114, gave good reduction of NO but also released some SO_2. In the contaminants tests he found that neither oxygen nor carbon dioxide have a detrimental effect on the reduction. Water gave H_2S and decreased reduction. Natural gas,

acetylene, and hydrogen each gave some H_2S (8).

If calcium sulfide could be regenerated from the sulfate the process could become economically more attractive. Zadick found that calcium sulfide could be generated from the sulfate at temperatures between 600 and 760°C by using various catalysts and reducing agents. He was able to get up to 95% conversion on some runs so that it is possible to regenerate the sulfide from the sulfate (9).

This research is closely related to the work of Erickson and White. The main reaction to be studied is:

$$CaS_{(s)} + 4NO_{(g)} \rightarrow CaSO_{4(s)} + 2N_{2(g)}$$

As can be seen, four nitric oxide molecules are removed per molecule of calcium sulfate formed. The solid will increase in weight from 72 g/mole to 136 g/mole so that by continuously weighing the solid the rate of reaction vs time can be easily determined.

For this reaction $\Delta H^{\circ}_{298°K} = -313.5$ kcal/mole and $\Delta F^{\circ}_{1000°K} = -215.7$ kcal/mole so that the reaction is thermodynamically very favorable and highly exothermic. Because of the favorable thermodynamics, the ease of measuring global rates, the possibility of regeneration of the sulfide, and the lowering of the temperature required for reduction of NO by the use of high surface area supports, the study of global rates using different high surface area supports seems justified for this reaction.

OBJECTIVES

The primary objective of this research was to find the global rate of reaction of NO with CaS adsorbed on various high surface area supports at different ambient temperatures. Another purpose of this research was to determine the relative rate of reaction of oxygen with calcium sulfide to find out if oxygen contamination of the feed could be a problem.

APPARATUS

Figure 1 is a schematic diagram of the apparatus used to study the reaction. The balance mechanism is a Cahn R-100 Electrobalance. This device is used to measure the weight of a sample continuously as it hangs suspended into the reactor. The R-100 Electrobalance has a 100 gram capacity for sample weight and container. Tare capacity is 100 g mechanically and 50 mg with the coarse zero. The electrobalance has three electrical weight suppression ranges capable of electronically taring as little as 10 μg or as much as 10 g.

The readability of the electrobalance is .5μg and it has six weight ranges: 10 g, 1 g, 100 mg, 10 mg, 1 mg, and 100 μg full chart scale. An automatic range expander automatically brings the chart pen back to zero up to ten times when a weight change takes the weight outside of the recorder weight range. The precision of the instrument is $\pm 10^{-3}$ of meter and recorder range and $\pm 10^{-6}$ of load and the accuracy is $\pm 5 \times 10^{-4}$ of mass suppression range for absolute weighings. The maximum weight change is 10 g increase or decrease.

The system shown in Figure 1 normally operates with feed gas passing through a rotameter and entering the bottom of the reactor. Exhaust gases leave just above the reactor and are vented to a hood. A helium line is run into the glass bell housing the balance mechanism to keep the bell purged of exhaust gases. During startup the valve arrangement makes it possible to pass helium through the reactor as well as over the balance mechanism.

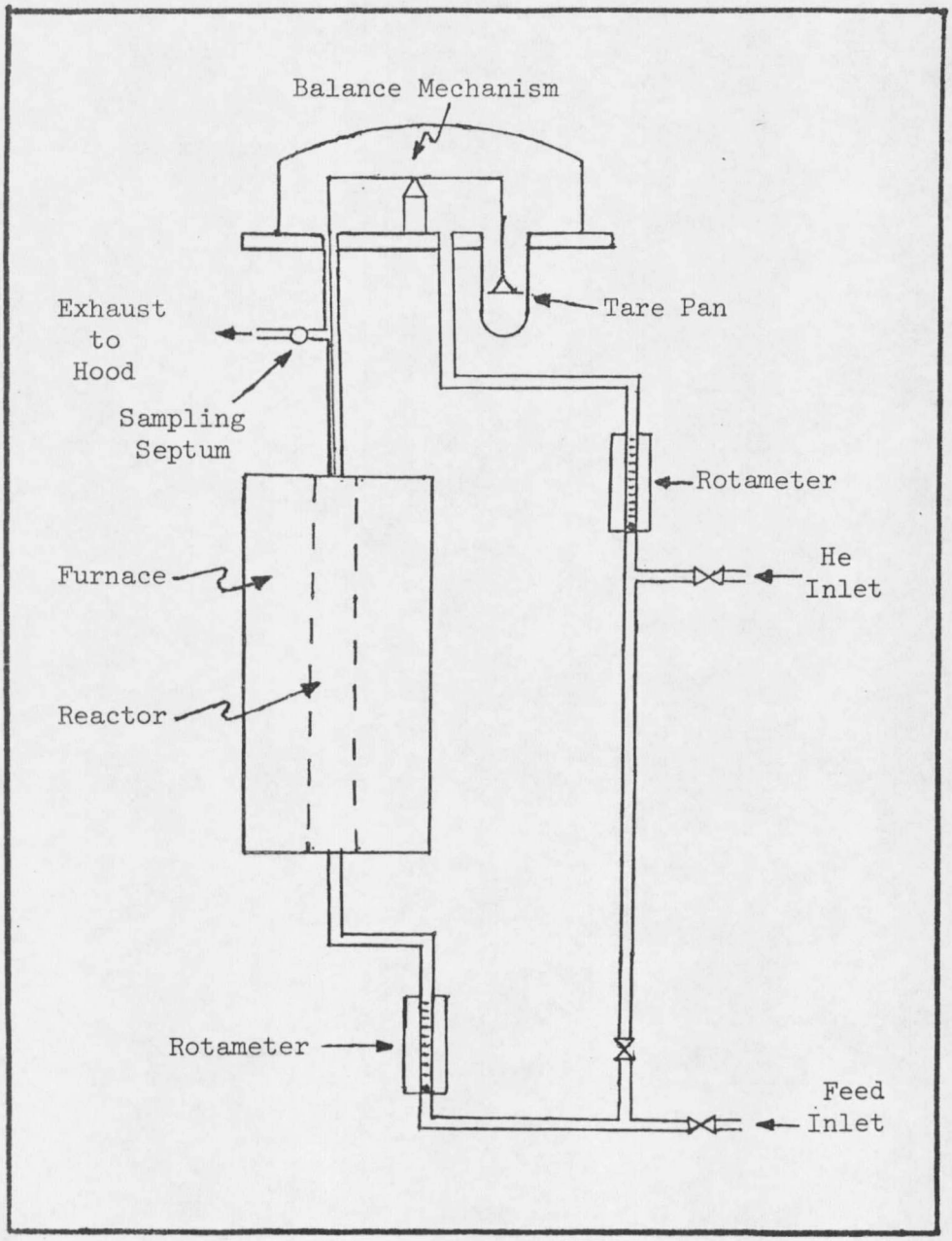

Figure 1. Flow diagram of apparatus for measuring rate of reduction of NO

The reactor is enclosed in a Lindberg 54031 hinged tube furnace during normal operation. It can be removed to allow access to the reactor tube before and after a run. It is controlled by a Teco TC-1000 proportional temperature controller (not shown).

The reactor cross-section is shown in Figure 2. The catalyst support pellet rests on a 9mm diameter, 200-mesh stainless steel screen suspended by a .1 mm nickel wire from the balance arm. The reactor is a 16 mm diameter, 78 cm long ATM Mullite tube with a ground glass joint at the bottom and a ground glass ball joint at the top.

Attached to the bottom joint of the reactor is a glass connector, and in this connector is mounted a porous glass plate. Two thermocouples are cemented with epoxy into a hole in the side of the glass connector and extend up the Mullite tube to a point just below the support pan. One thermocouple wire is attached to a proportional temperature controller and the other is attached to a temperature recorder. The Mullite tube is filled with 40-mesh Ottawa sand to preheat the feed gas. The gas is fed into the bottom of the reactor, passes over the pellet and is exhausted out the top.

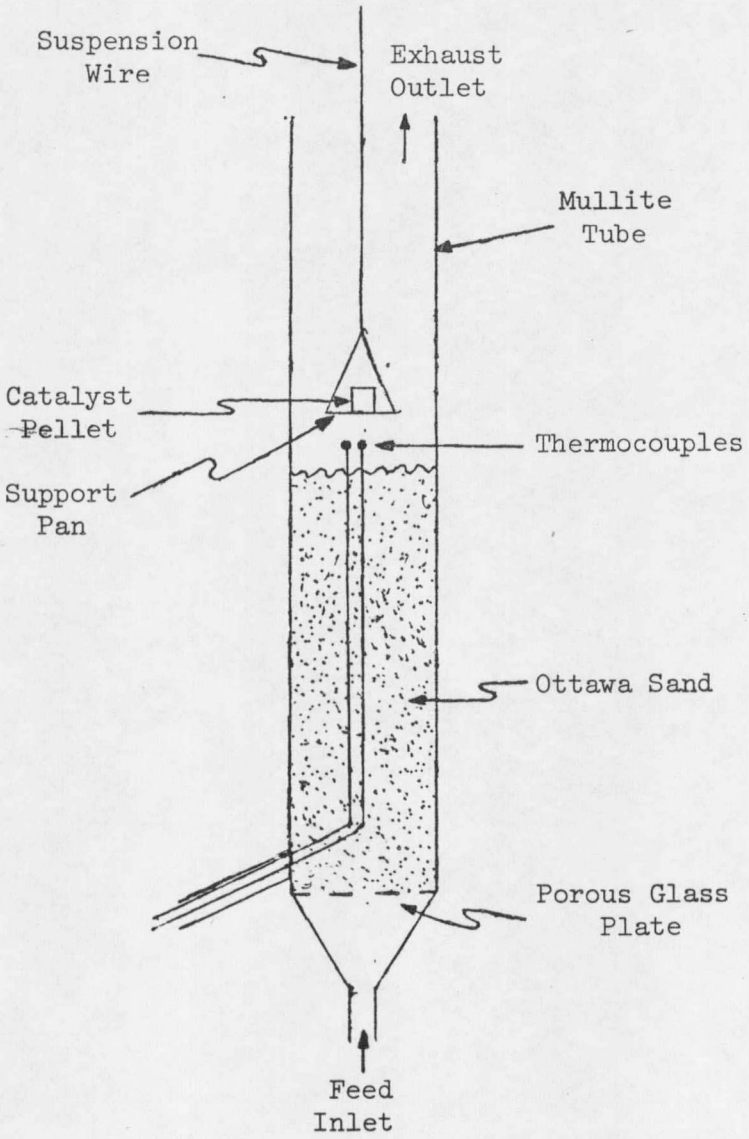

Figure 2. Reactor cross-section

PROCEDURE

For testing the support materials, an amount of the support material was put into a muffle oven at 400°C for 24 hours, then placed in a desiccator to cool. This drives off any adsorbed gases or H_2O that may have been picked up by the support. A few pellets were weighed and soaked in water overnight to determine the amount of solution that could be absorbed. Then a solution of calcium nitrate (as $Ca(NO_3)_2 \cdot 4H_2O$) and water was prepared so that the pellets would be about 5% CaS by weight. The weighed support material was then soaked in this solution for 24 hours. The excess solution was stripped off and the support material was put into the muffle oven at 400°C for 24 hours. This evaporated the water and converted the calcium nitrate to calcium oxide. Finally the pellets were placed in a reactor in a stream of pure H_2S at 400°C for a day to convert the calcium oxide to CaS, then they were cooled in a desiccator and weighed. The weight increase was the amount of CaS precipitated on the pellets. It was discovered that prolonged exposure to air in an ordinary desiccator gradually oxidizes the CaS to $CaSO_4$, so the impregnated support materials were stored under pure nitrogen gas until needed.

A prepared pellet was reacted by placing it on the weighing pan of the Cahn electrobalance. A stream of pure helium was passed through the purge line in the bell and another stream of pure helium (He) was passed through the reactor until the weight remained constant. Next a 2.5% NO, 97.5% He mixture was fed into the reactor at an upstream pressure of 15 psig and the temperature was simultaneously brought to operating

levels where it was maintained for the run. When the pellet no longer showed a weight gain or loss the run was stopped.

RESULTS AND DISCUSSION

Table I gives the properties of the various supports used. The Harshaw 1602-T support is a 1/8 inch pellet primarily composed of alumina. The Linde molecular sieves are high surface area alumino-silicates containing sodium metal in the crystal structure. No specific details of composition were available for the sieves though they were originally designed to absorb SO_2 at low temperatures. No specific properties were available for the Nalco pellets though it is known that they are a high silica, high surface area catalyst support.

The reaction conditions are shown in Table II. The feed gas mixture was 2.5% NO and 97.5% He for all runs except the run indicated, which had a 2.5% O_2, 97.5% He feed. Flow rates of the feed gas were generally around .18 standard cm^3 per second with the helium purge rate about .045 standard cm^3 per second.

All of the pellets underwent a color change upon reaction. The Harshaw pellets were initially light blue and became light brown or beige when impregnated with CaS. Upon reaction with NO they became bright white. The Linde molecular sieves were initially brown and turned black when impregnated with CaS. After reaction with NO they again became brown.

The weight vs time and rate vs time curves for the Harshaw pellet at 390°C are shown in Figure 3. The rates were obtained by evaluating the slopes of the weight curve by the least squares technique over small intervals. The weight of the pellet increased over the entire run from about 31.0 mg to about 31.5 mg in about seven hours. The rates varied

TABLE I. Support Material Properties

Manufacture and Type Support Material	COMPOSITION Al_2O_3 (%)	SiO_2 (%)	Fe_2O_3 (%)	Na_2O (%)	Surface Area (m^2/g)	Pore Volume (ml/g)	Form
Harshaw 1602-T	91	6.0	-	.03	225	.48	1/8" pellets
Linde TM-0-1114	(Synthetic crystalline metal alumino-silicate containing Na)				-	.53	1/16" extrusions

TABLE II. Reaction Conditions

Run No.	Type of Support	Temperature °C	CaS (Wt %)	Flow Rate (Std cm^3/ sec)	He Purge (Std cm^3/ sec)	Total Run Time (hr)	No. of Pellets
1	Harshaw	390	8.6	.18	.046	7	1
2	Harshaw	410	8.6	.15	.045	9-1/2	1
3	Harshaw	437	8.6	.16	.045	8	1
4	Harshaw	438	8.6	.18	.045	9	1
5	Harshaw	468	8.6	.20	.032	5	1
6	Harshaw	493	8.6	.18	.045	4	1
7	Harshaw	442	8.6	.16	.045	18	5
8	Harshaw	440	.9*	3.48	.052	4	1
9	Harshaw	444	.9*	.12	.052	3-1/2	1
10**	Harshaw	444	.9*	.12	.063	4-1/2	1
11	Linde	392	6.6	.14	.043	12	1
12	Linde	410	11.4	.14	.043	4	1
13	Linde	438	6.6	.17	.043	18-1/2	1

* Pellets were pre-oxidized by contact with air

** Feed gas composition was 2.5% O_2, 97.5% He

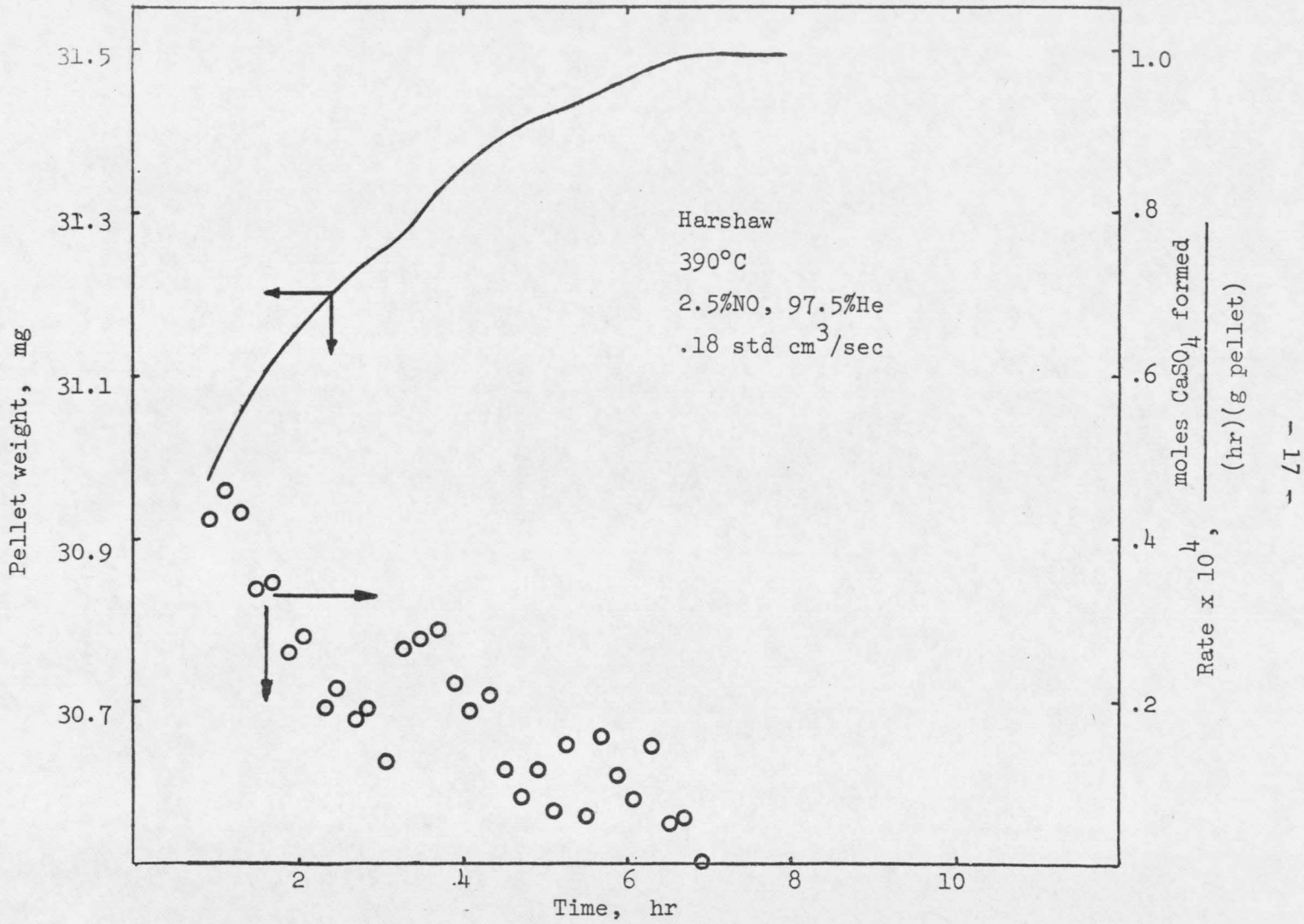

Figure 3. Reaction data for a Harshaw pellet at 390°C

between zero and $.46 \times 10^{-4}$ mol $CaSO_4$ formed per hour per gram of pellet.

The rates generally decreased with time for this run with a few exceptions. However, at this time it appears that the scatter in the data could easily account for these deviations. The cause of the scatter can be traced to the magnitude of the weight changes. If a smooth curve were drawn through the weight data the deviations would be around 2 or 3%. However, by taking slopes of the weight curve, the magnitude of the error in the weight data increases the scatter in the rate data by as much as 30 to 50%. The relatively small weight deviations which produce these apparent rate changes could be due to several things. The ambient temperature is held to $\pm$ 1°C, but temperature increases within the pellet due to the highly exothermic reaction cannot be controlled.

Another cause of small weight changes could be from external vibrations. Sometimes vibrations caused as much as a 10% change in absolute weight over a few seconds. Occasionally these large vibrations leave a permanent offset of a few tenths of a milligram in one direction, probably because of a shift of the position of the balance arm. These large offsets were corrected for but the effects of smaller vibrations which did not leave a significant offset are unknown.

Figure 4 shows the weight vs time and rate vs time curves for a Harshaw pellet at 410°C. The weight of the pellet increased from about 31.7 to about 32.5 mg over about nine and a half hours. The rates dropped with time from about $.5 \times 10^{-4}$ to about $.3 \times 10^{-5}$ mole $CaSO_4$

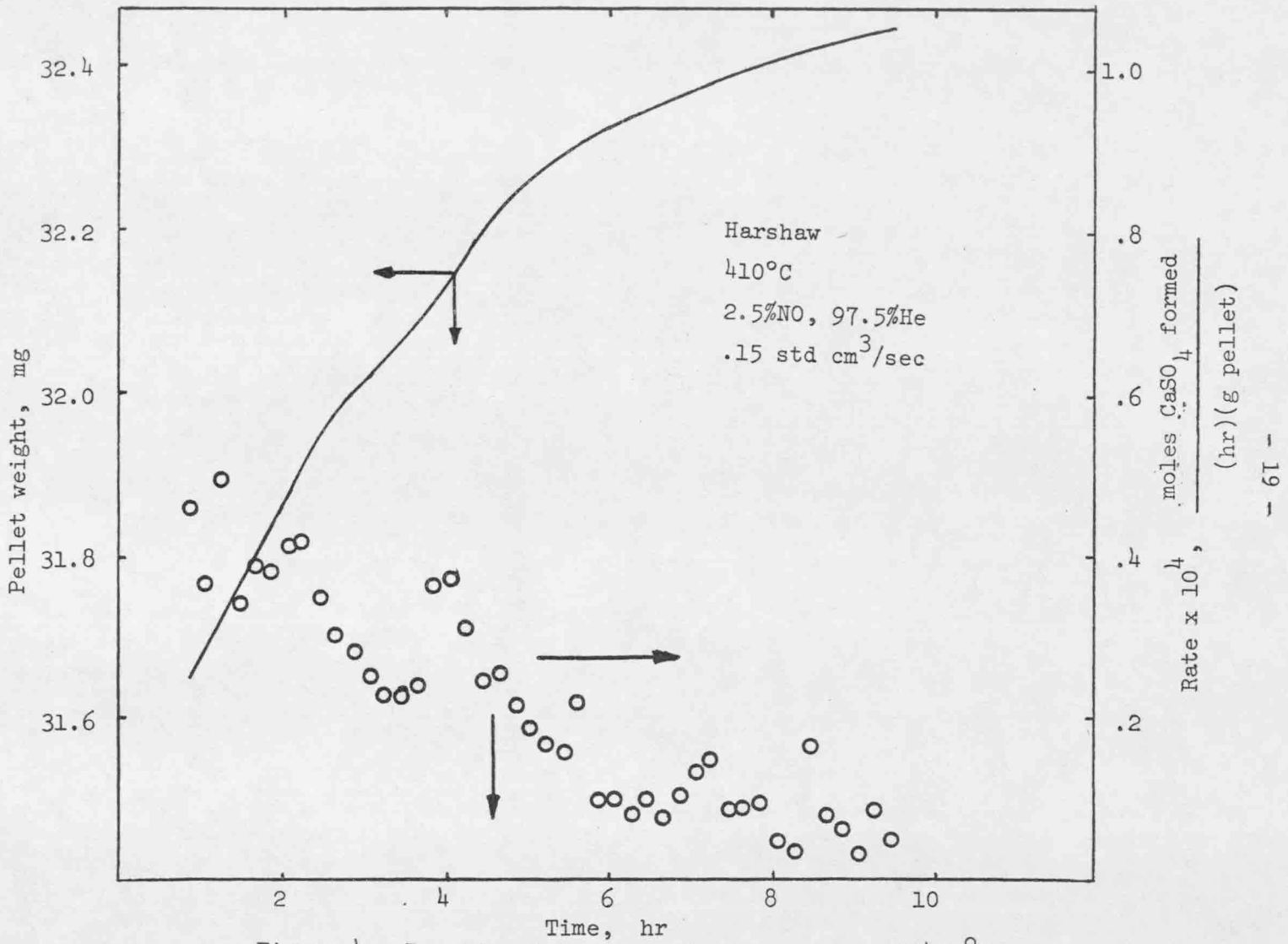

Figure 4. Reaction data for a Harshaw pellet at 410°C

formed per hour per gram.

Figure 5 shows the data for the run at 437°C. The weight increased from 31.9 to 32.9 mg in about eight hours. The rates generally decreased from $.52 \times 10^{-4}$ to $.62 \times 10^{-5}$ moles per hour per gram. Figure 6 shows the weights and rates at 438°C. The weight increased with time from 29.2 to 30.1 mg over about nine hours. The rates decreased from $.44 \times 10^{-4}$ to $.11 \times 10^{-5}$ moles per hour per gram.

The run at 438°C was made to verify the previous run at 437°C. The results show that the two runs are in fair agreement given the experimental scatter, as can be seen by comparing rates at any given time. Also some trends can be seen by comparing rates for these two runs. Between hours one and three the rates are approximately constant at about $.45 \times 10^{-4}$ moles per hour per gram. Then the rates gradually drop to zero by about the ninth hour. This may be an indication that the rate remains high as long as easily accessible CaS remains on the surfaces throughout the pellet. Then, after about three hours reaction may be controlled by a slower diffusion of NO through reacted layers of sulfate. This run shows that a relatively high constant rate can be maintained by these pellets at 437°C and suggests an optimum pellet life of about three hours at the given feed concentrations.

Figure 7 gives the weight and rate vs time curves for the run at 468°C. The weight constantly increased from 33.8 to 34.4 mg in about five hours. The rate decreased with time from about $.60 \times 10^{-4}$ to about $.52 \times 10^{-5}$ moles per hour per gram.

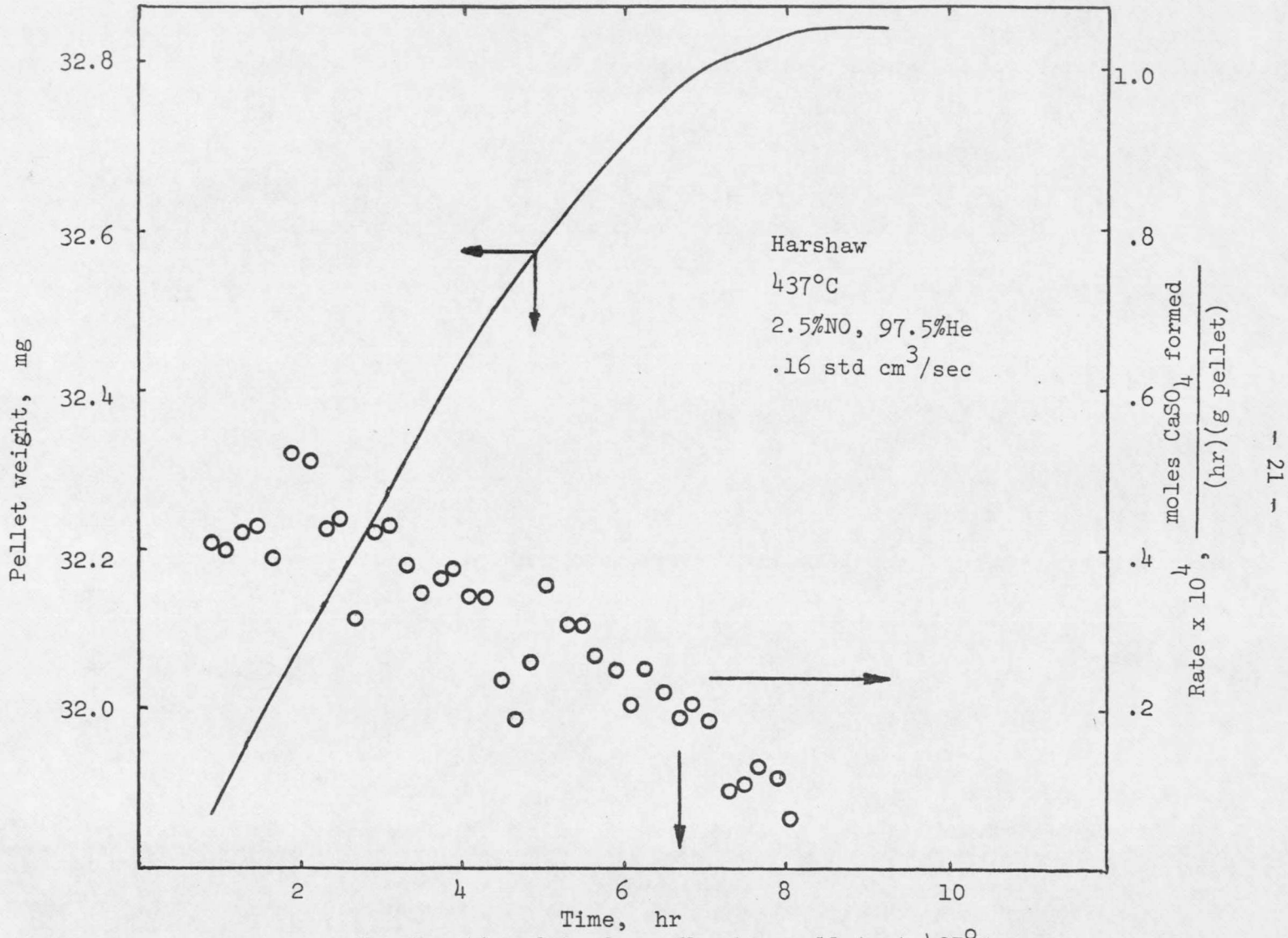

Figure 5. Reaction data for a Harshaw pellet at 437°C

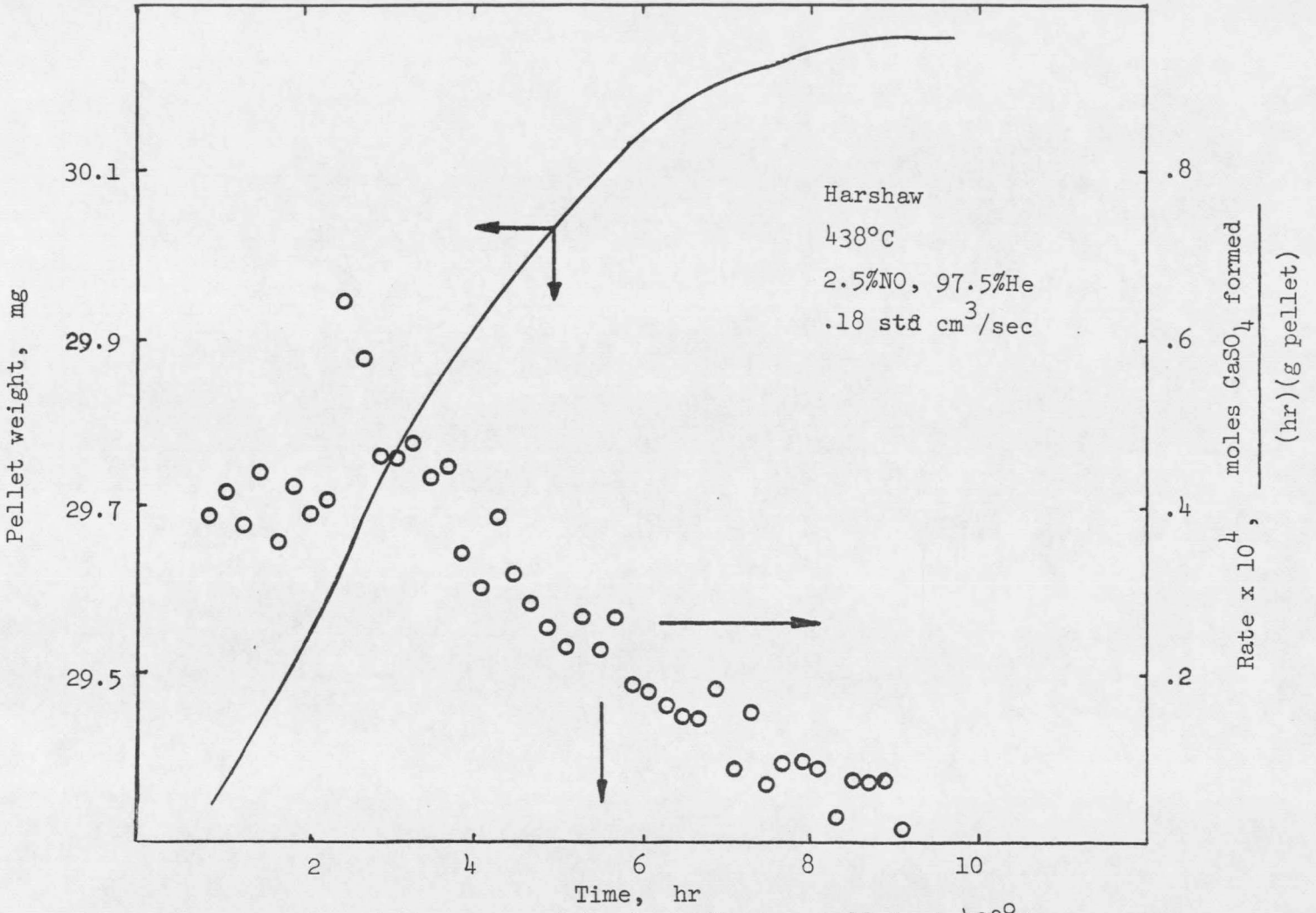

Figure 6. Reaction data for a Harshaw pellet at 438°C

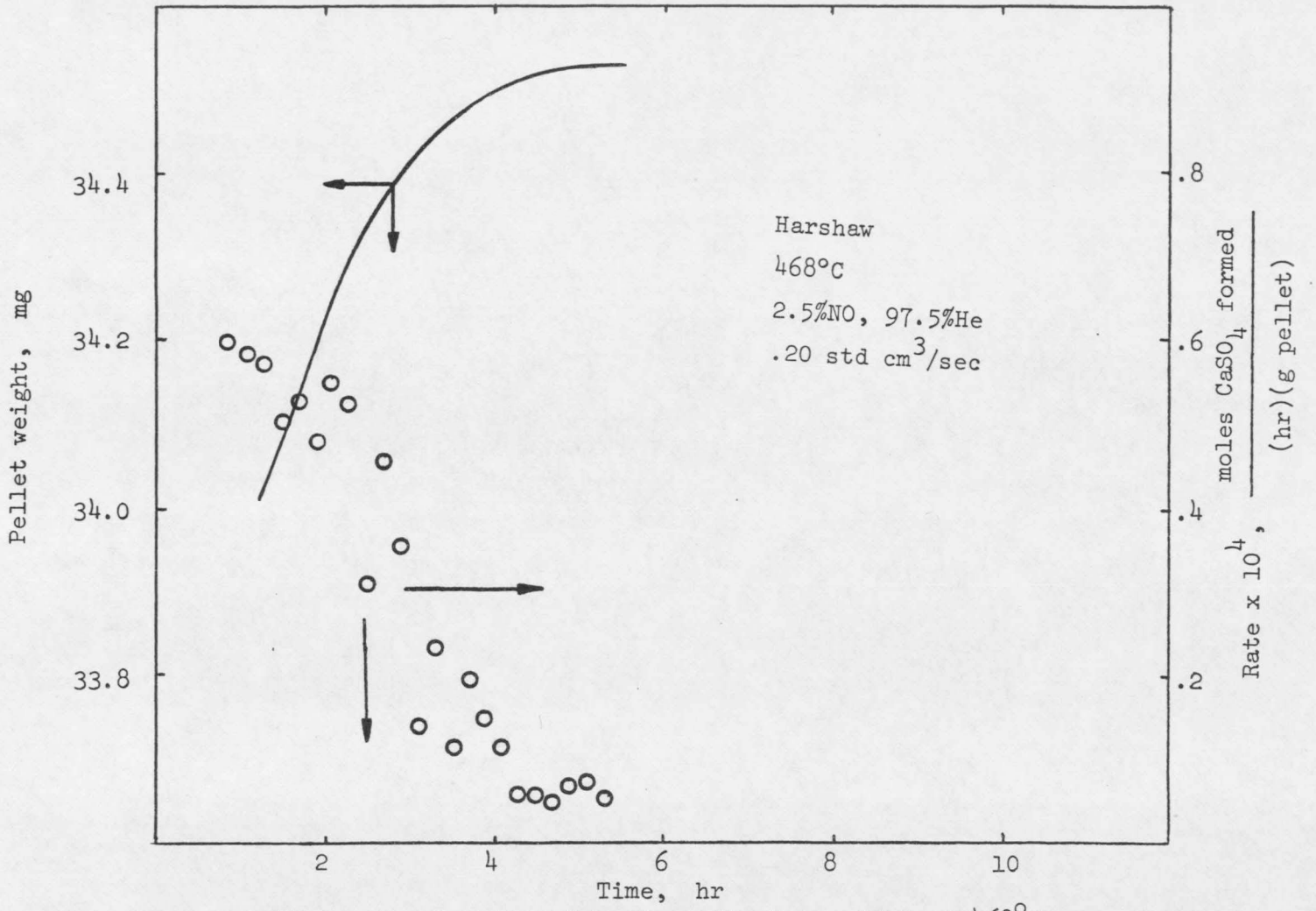

Figure 7. Reaction data for a Harshaw pellet at 468°C

Figure 8 shows the weight and rate data for the reaction at 493°C. The weight increased from 31.3 to 31.8 mg in about four hours. The rate first increased for about a half hour from about $.39 \times 10^{-4}$ to about $.63 \times 10^{-4}$ moles per hour per gram and then decreased to zero. The period of increase is probably due to initial unsteady state within the pellet. At time zero and at the end of the run the rates must be zero while somewhere in between the rate would be some positive value. In the other runs the weights in the unsteady state portion of the curve were not read.

It was decided to test the effect of having several pellets at once on a pan. Figure 9 gives the weight vs time and rate vs time curves for a random assortment of five pellets heaped on a pan. The sample weight increased from 261.6 to 264.0 mg over about 18 hours. The rate data shows an interesting triangle shape corresponding to the S-shaped weight curve. The rates begin at very close to zero at time zero and steadily increase to a maximum at about eight and one half hours. The maximum rate is about $.90 \times 10^{-5}$ moles per hour per gram. From the maximum the rates steadily drop to zero at about nineteen hours.

Several things should be noted about this rate curve. First it has an unusual shape. For fully half of the run the rates increase. Previously, as shown in Figure 8, the period of unsteady state was less than 40% of the total reaction time (assuming one and one half out of four hours). This could be caused by several things. The reaction is highly exothermic and it is possible that with all of the

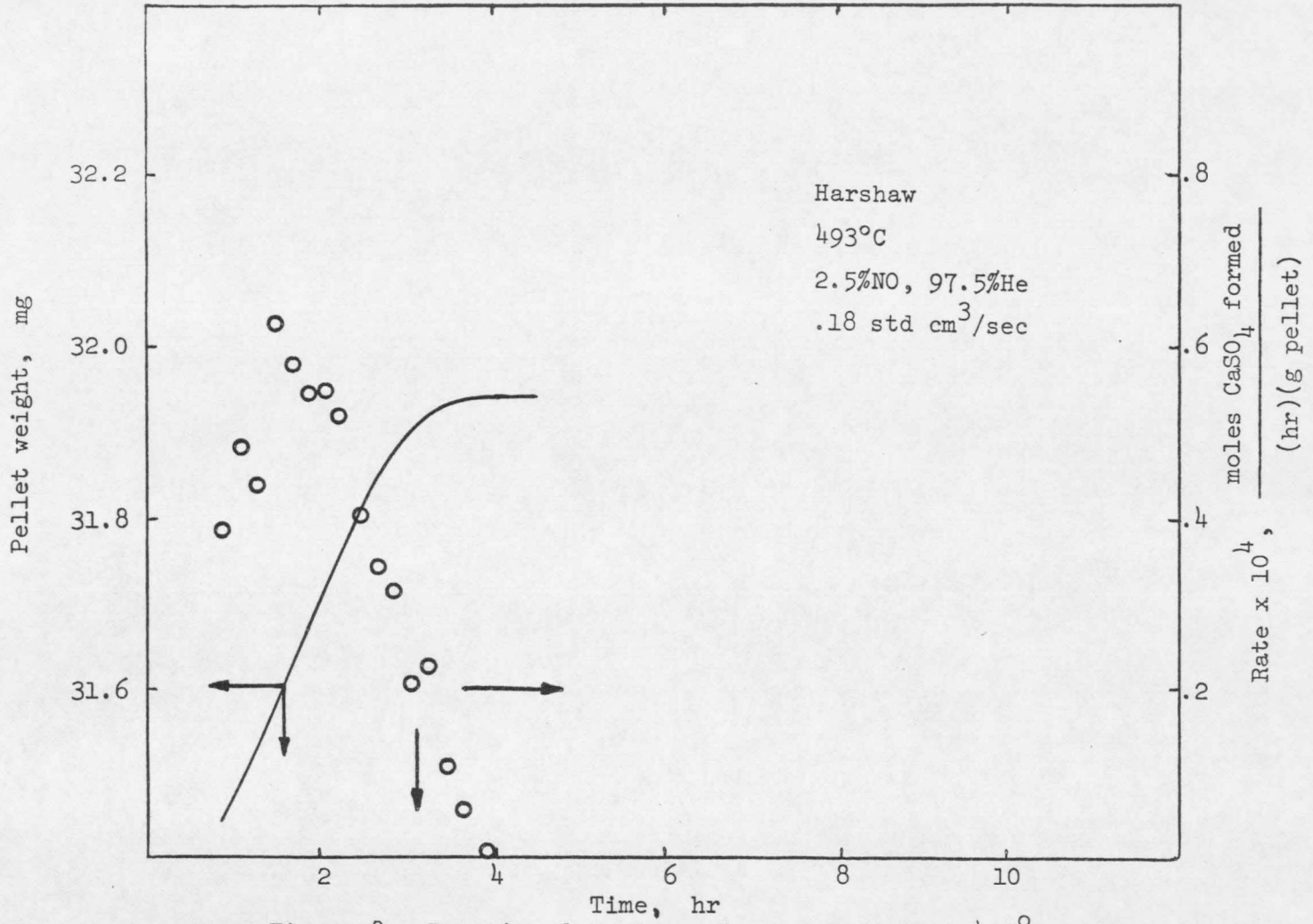

Figure 8. Reaction data for a Harshaw pellet at 493°C

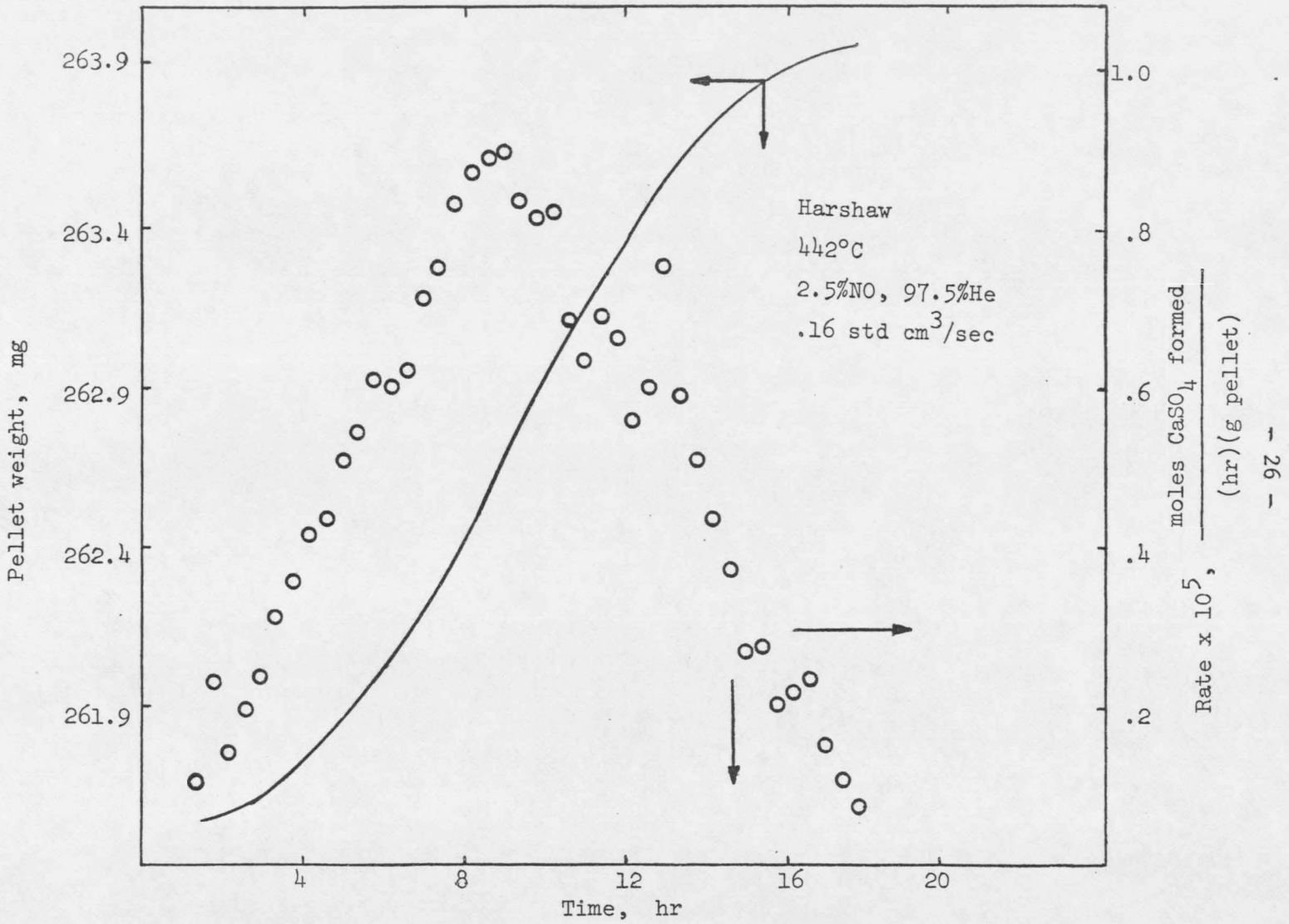

Figure 9. Reaction data for five Harshaw pellets at 442°C

pellets in contact and with stagnant pockets of gas insulating the pellet pile, the temperature, and therefore the rate, could slowly build up. Also, with the increased diffusional resistance of these stagnant gas pockets the time required to reach a steady concentration gradient would be increased. Opposed to these two effects is one which would make the rate decrease with time. As the easily accessible surface CaS is used up, diffusion through the reacted layer of $CaSO_4$ could cause the reaction to slow down. These two effects could combine to increase the unsteady state portion of the reaction.

Another unusal thing about the run is that the scatter of the rate data is small. The probable reason is that the sample for this run was five times the sample weight of the previous runs. Vibrations would tend to have the same magnitude regardless of total sample weight so that the scatter for this run would not be as bad.

The last noteworthy thing about this run is the relative rate of reaction. The maximum rate (and, as will be seen later, the average rate) is very low. The maximum rate is slightly over one sixth of the maximum rate for a single pellet. This seems to reinforce the theory of strong surface diffusion control for the five pellets.

In order to determine the effect of surface diffusion control for a single pellet, a run was made at a high flow rate. The reaction conditions are given in Table II and the results are plotted in Figure 10. The pellet increased in weight from about 25.5 to about 25.7 mg over about four hours. The rate of reaction decreased from about $.33 \times 10^{-4}$

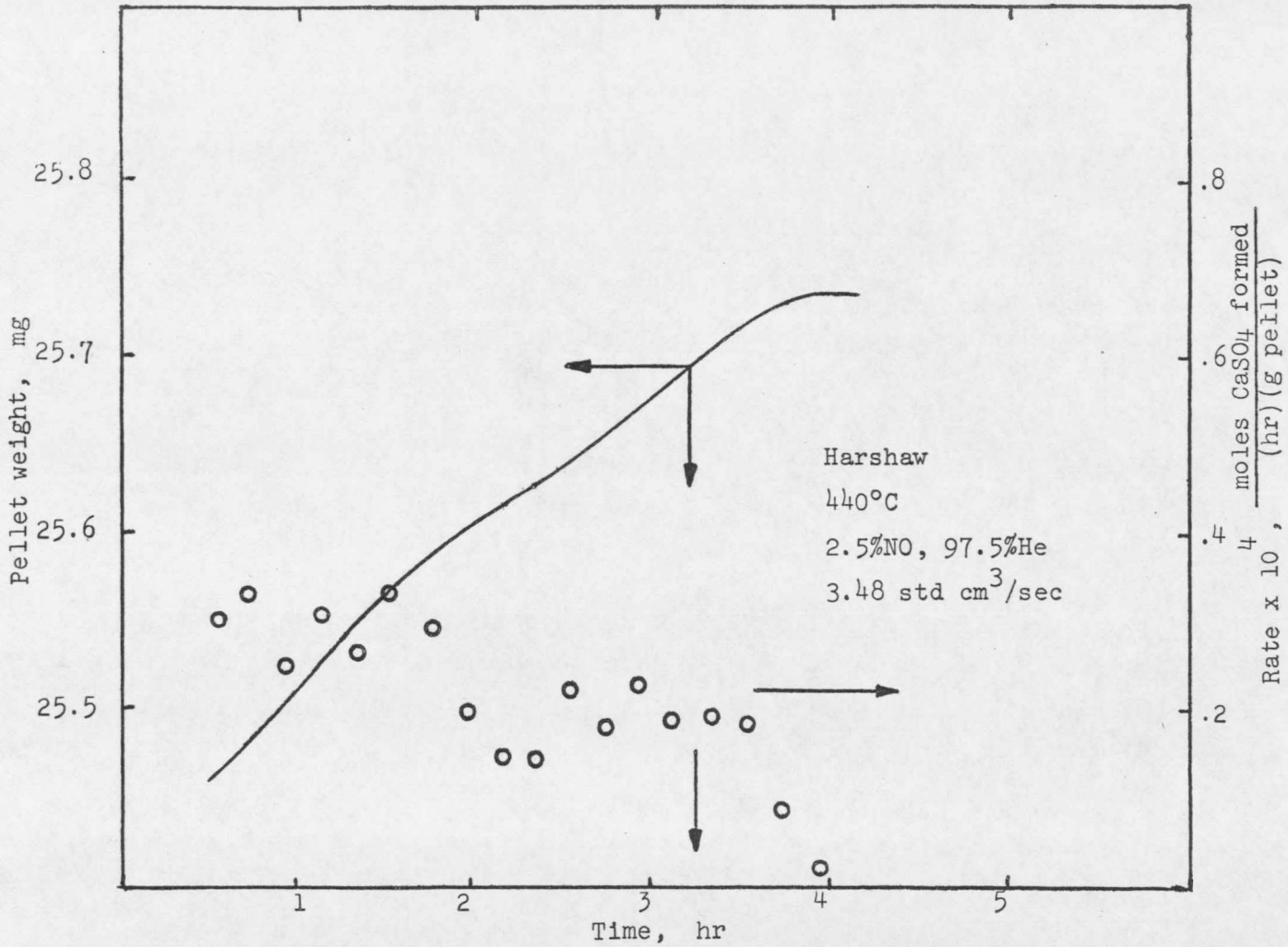

Figure 10. Reaction data for a Harshaw pellet at high flow rates

to about .26 x 10^{-5} moles per hour per gram.

The run shown in Figure 10 indicates a low conversion, and it was discovered that the pellets used for this run had become oxidized in the air prior to the run. This has the effect of lowering the apparent rates for the run since the NO must diffuse through an existing layer of sulfate to react. In order to be able to compare reaction rates for high and low flow rates, another pellet from the same batch was run at a low flow rate and the same temperature. The reaction conditions are shown in Table II and the results are plotted in Figure 11. Percent CaS in Table II is based on total weight gain assuming 100% conversion of CaS to $CaSO_4$. Conversion was again low with the weight increasing from 25.4 to 25.6 mg in about three and a half hours. Rates decreased from about .45 x 10^{-4} moles $CaSO_4$ formed per hour per gram of pellet to about zero.

Comparing Figures 10 and 11 it can be seen that the rate curves have a somewhat different shape. The rate of reaction for the low flow rate run attains a high value then rapidly drops to zero. The high flow rate reaction never reaches as high a maximum rate, but it maintains a moderate rate longer than the low flow rate reaction. This surprising result indicates that, for the conditions given in Table II, for higher flow rates the pellets last longer than for lower flow rates. In order to compare overall rates it is necessary to find an integrated average rate of reaction. But first the results of other runs will be presented.

The secondary purpose of this research was to determine whether

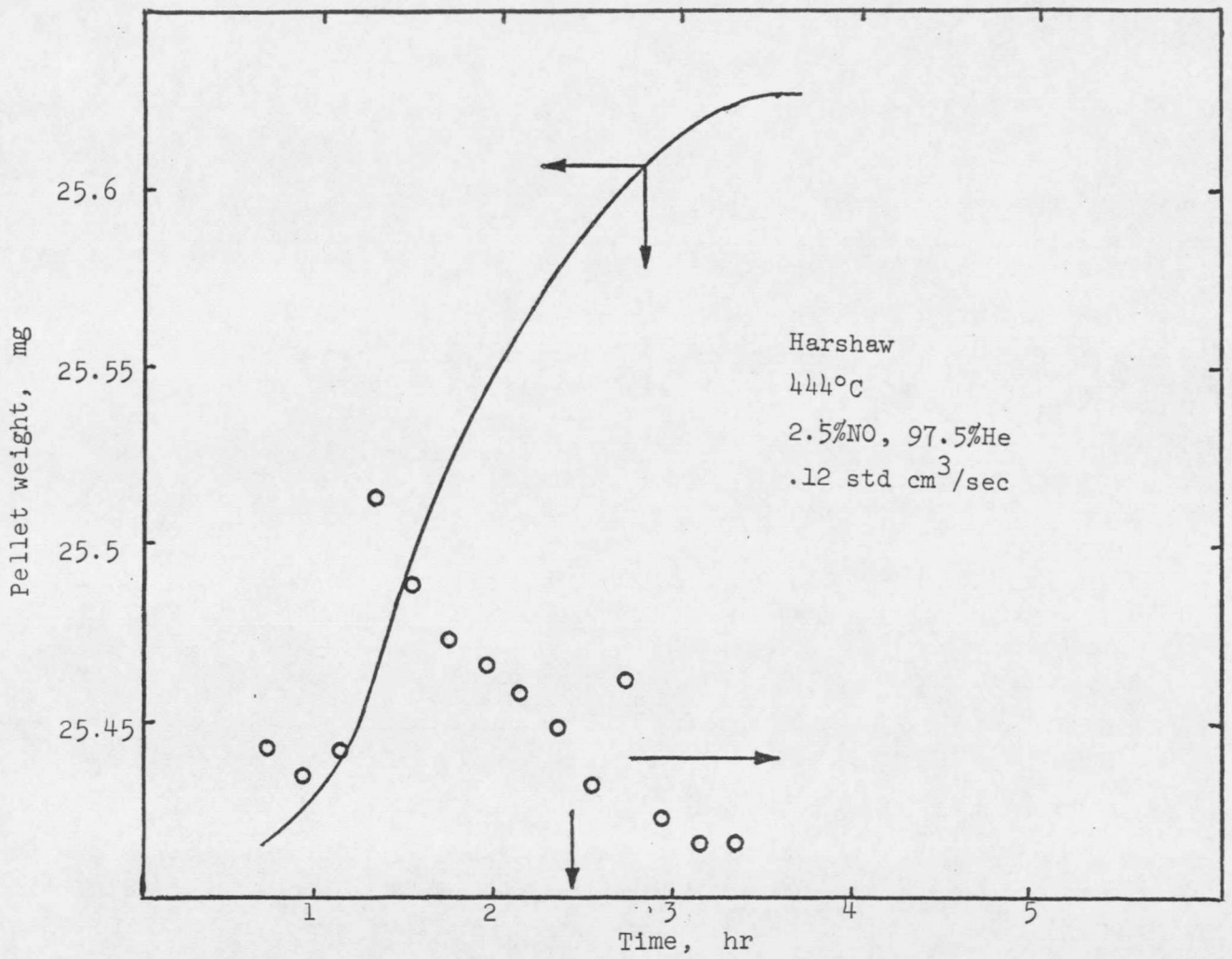

Figure 11. Reaction data for a Harshaw pellet at low flow rates

oxygen would react with CaS and if so how fast. Run number 10 was performed for this purpose under the reaction conditions given in Table II. The results are shown in Figure 12. As can be seen, a 2.5% O_2, 97.5% He stream caused a pellet to gain weight from 27.2 to 27.5 mg in about four and a half hours. Not only was there a reaction, but the maximum rate reached 2.42×10^{-4} moles per hour per gram which is about six times the maximum rate for NO. However, the reaction quickly slowed down, probably because the surface CaS was quickly oxidized and a diffusion mechanism through reacted sulfate became controlling. This run demonstrates that CaS does react with O_2 so that it would probably compete with NO for free CaS.

The first ten runs were all made using Harshaw pellets. The last three were made using Linde molecular sieves. The properties of the sieves are given in Table I and the details of the run conditions are given in Table II. The feed gas was again 2.5% NO, 97.5% He and the flow rates were generally around .14 to .17 standard cm^3 per second. Each run was made using one pellet and temperatures varied between 392° and 438°C.

Figure 13 shows the weight vs time and rate vs time curves for the reaction at 392°C. The weight increased from 24.6 to 25.6 mg over about 12 hours. The rate data has some scatter but generally decreases from about $.84 \times 10^{-4}$ to about $.45 \times 10^{-5}$ moles $CaSO_4$ formed per hour per gram of pellet. Figure 14 shows that at 410°C the weight increased from 25.6 to about 26.5 mg in about four hours. The rates for this run

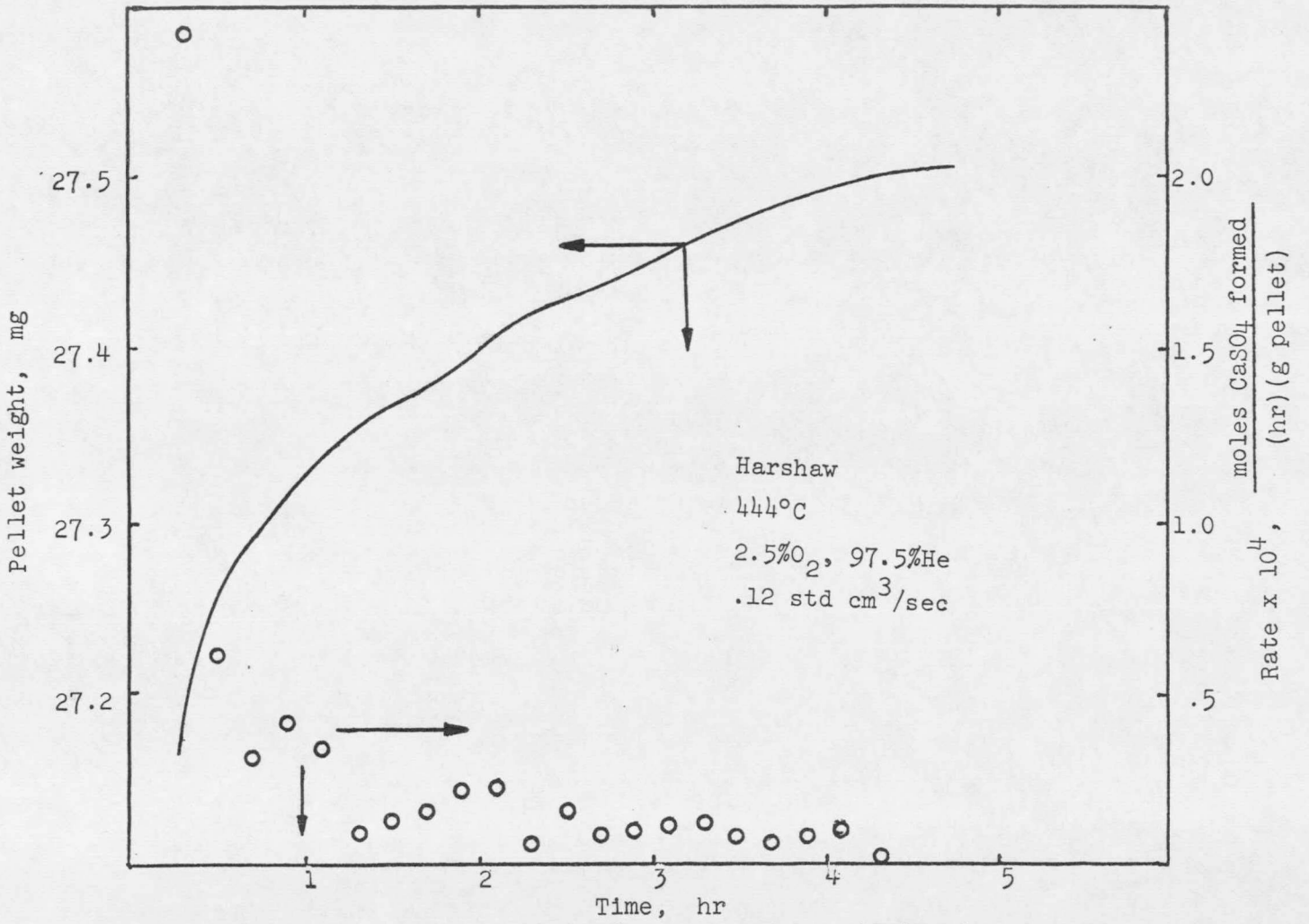

Figure 12. Reaction data for a Harshaw pellet using oxygen

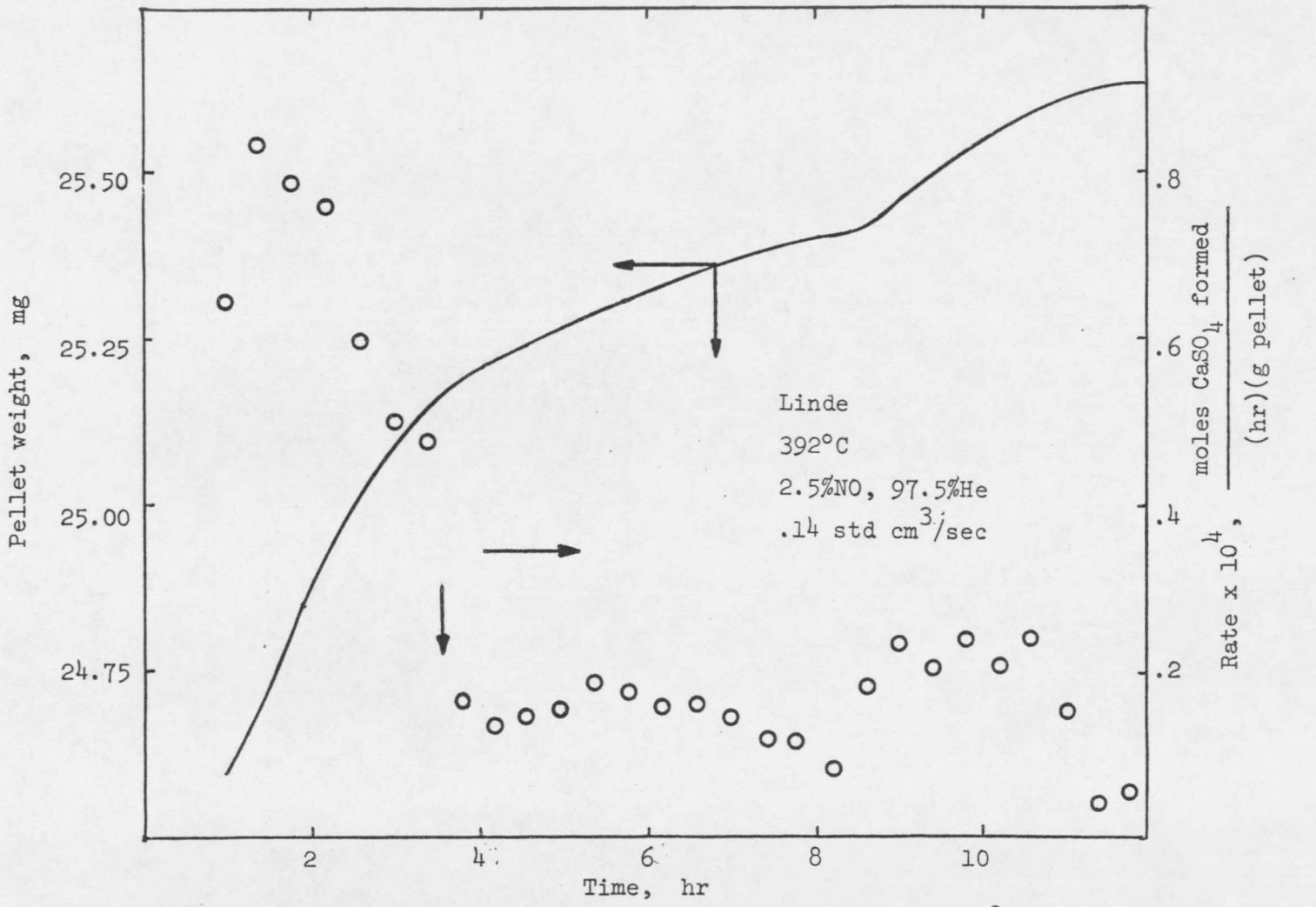

Figure 13. Reaction data for a Linde sieve at 392°C

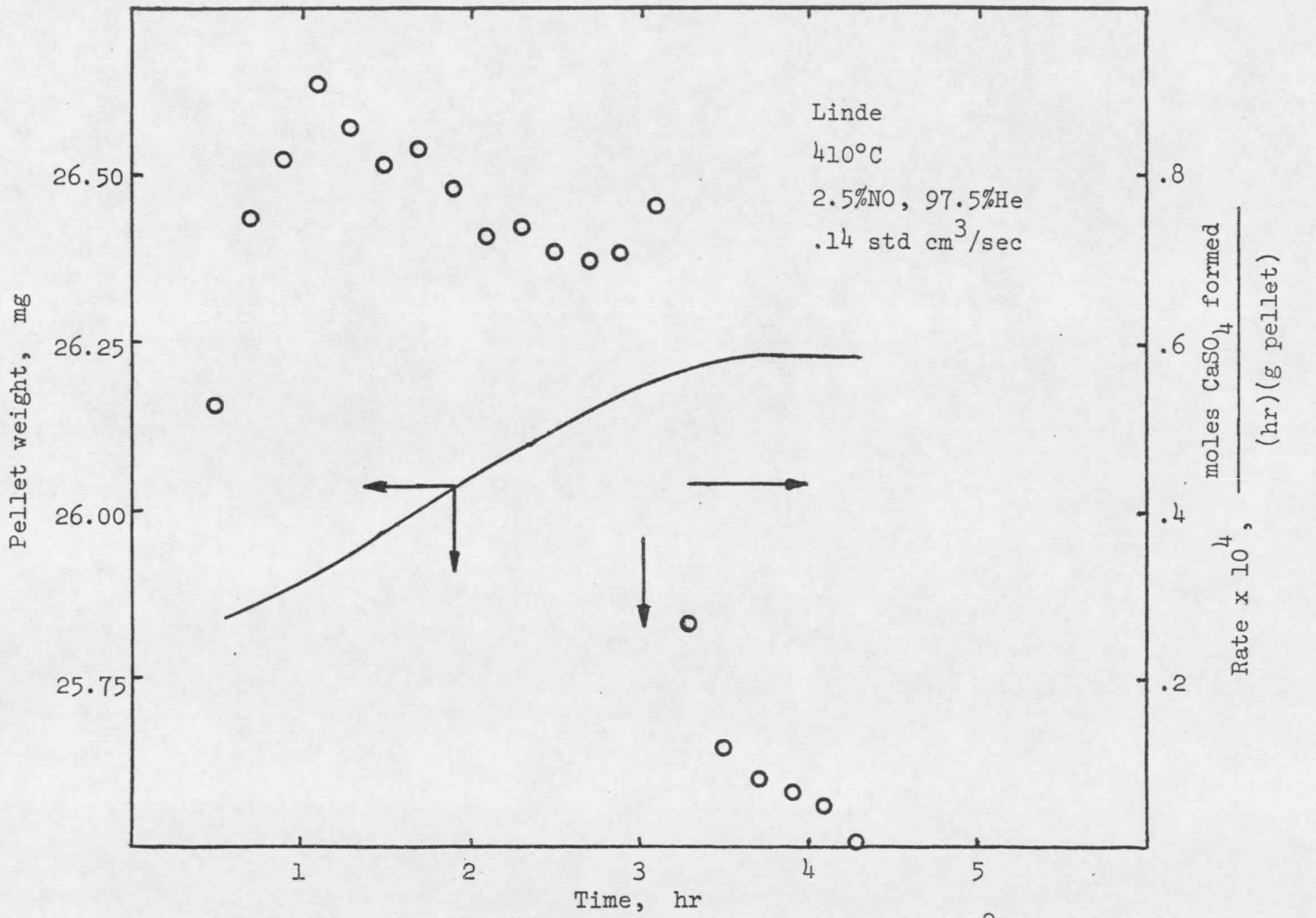

Figure 14. Reaction data for a Linde sieve at 410°C

generally decreased from a high of about $.91 \times 10^{-4}$ to a low of about $.65 \times 10^{-6}$ moles per hour per gram. Figure 15 shows a Linde molecular sieve reacted at 438°C. The weight increased from 20.1 to 22.5 mg in about 18-1/2 hours. The rates decreased from about $.13 \times 10^{-3}$ to $.22 \times 10^{-4}$ moles per hour per gram.

The rate data for the Harshaw pellets have a different shape from the data for the sieves. Both types of supports show an overall decline in rate vs time. However the Harshaw pellets show a gradual decrease with time while the Linde molecular sieves show a sudden drop in rate. The sudden drop occurs for all three runs at around three or four hours.

The explanation for the sudden drop in rate followed by a long period of slow reaction is probably the same as noted previously. If pore diffusion is relatively fast and diffusion through reacted sulfate is slow with fast chemical reaction then the behavior of the rate data can be explained. For the first three or four hours reaction is with surface CaS with the rate being controlled by pore diffusion or chemical reaction. When all of the surface CaS is reacted, reaction proceeds at the slow rate of diffusion of NO through $CaSO_4$.

This model could also be used to explain the relative rates of the Harshaw and Linde pellets. No data is available on the surface area of the Linde molecular sieves but it is assumed that they have greater surface area than the Harshaws. This seems to be born out by the fact that the molecular sieves gain more weight per pellet weight than the Harshaw pellets when soaked in calcium nitrate solution. In order for

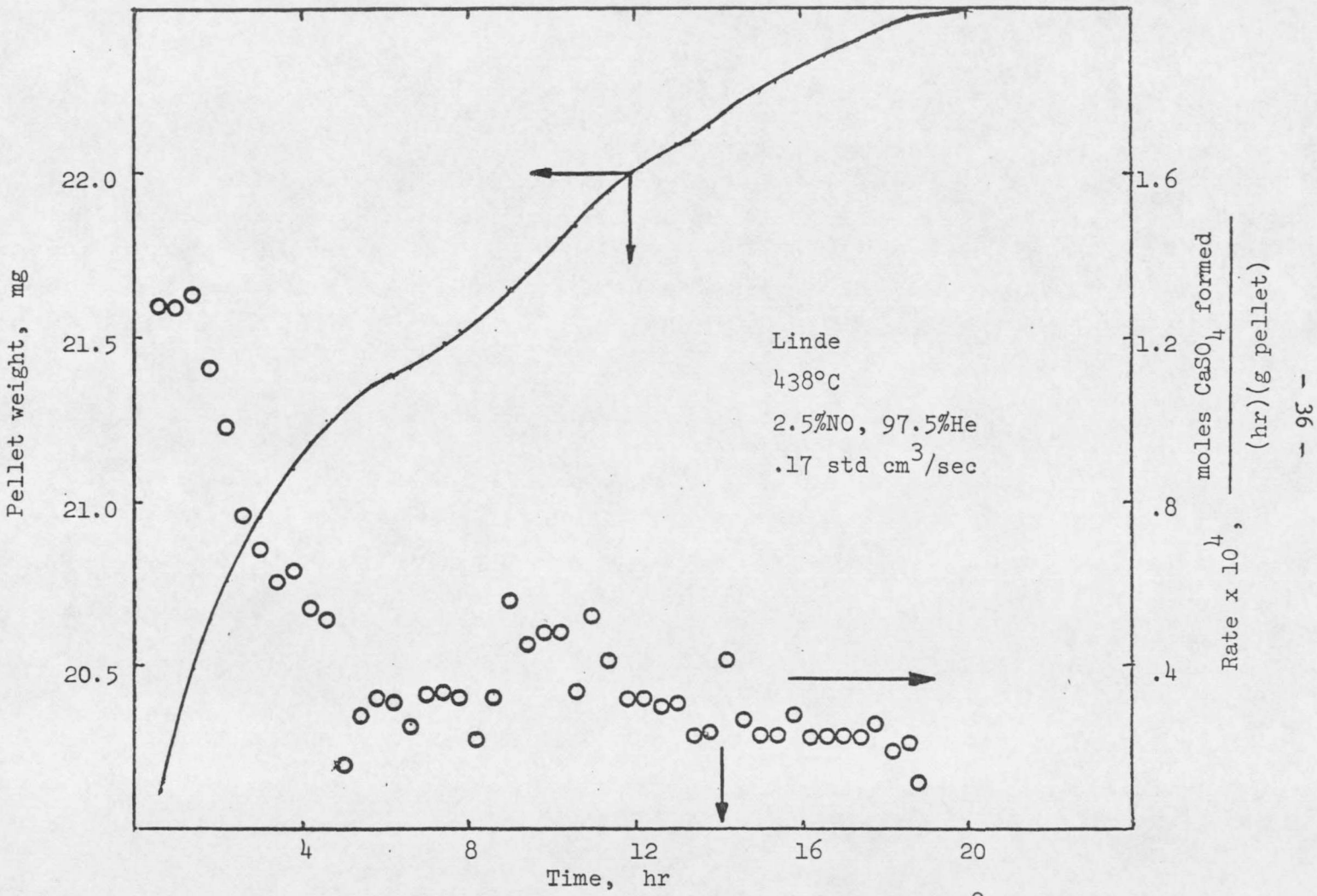

Figure 15. Reaction data for a Linde sieve at 438°C

the Harshaw pellets to have the same overall CaS composition as the sieves, the CaS must form thicker layers on the Harshaws than on the molecular sieves. For the sieves much of the reaction would be with surface CaS at a relatively fast rate. The Harshaw pellets probably have such small surfaces that a layer of sulfate is formed over the entire surface before a steady state concentration gradient is formed. Thus the only reaction observed for the Harshaw pellets is the slow sulfate diffusion rate. The Linde sieves would therefore be expected to react much faster than the Harshaw pellets initially.

Because of the difficulties in comparing maximum rates, average rates for each run were computed. Table III gives the integrated average global rates at each reaction temperature. Also the rate of NO removal is given. Because of differences between individual pellets the time ranges for the integration are given. Though total reaction times vary without much pattern, the overall rates consistently increase with temperature.

For the single Harshaw pellets the rates increased consistently with temperature from $.25 \times 10^{-4}$ to $.45 \times 10^{-4}$ moles $CaSO_4$ formed per hour per gram of pellet. This is a twofold increase in rate over 100°C. Kinetically, this means that some form of diffusion is probably controlling. If the chemical reaction had been controlling, the rate would probably do much more than double. This is because chemical reaction rates usually obey some sort of Arrhenius-type relation with temperature and can be expected to double in approximately 10°C. For

TABLE III. Average Rates of Reaction vs. Temperature

Run No.	Type of Support	Temperature °C	Rate x 10^4 $\frac{\text{mol } CaSO_4 \text{ formed}}{(hr)(g \text{ pellet})}$	Rate x 10^4 $\frac{\text{mol NO removed}}{(hr)(g \text{ pellet})}$	Time Range Hr.
1	Harshaw	390	.25	1.00	.9 to 6.9
2	Harshaw	410	.25	1.00	.9 to 9.5
3	Harshaw	437	.34	1.36	.9 to 8.1
4	Harshaw	438	.31	1.24	.9 to 9.1
5	Harshaw	468	.40	1.60	.9 to 5.3
6	Harshaw	493	.45	1.80	.9 to 3.9
7*	Harshaw	442	.05	.20	1.4 to 17.8
8**	Harshaw	440	.25	1.00	.50 to 3.9
9**	Harshaw	444	.22	.90	.7 to 3.3
10***	Harshaw	444	.41	1.84	.3 to 4.3
11	Linde	392	.32	1.28	1.0 to 12.2
12	Linde	410	.64	2.56	.5 to 4.3
13	Linde	438	.47	1.88	.6 to 18.6

* 5 pellets

** pellets partially oxidized before run

*** 2.5% O_2, 97.5% He feed

design purposes, this means that for the Harshaw pellets not much advantage is obtained by raising the temperature.

The run using five Harshaw pellets at 442°C shows an overall rate of about $.05 \times 10^{-4}$ moles per hour per gram. This is approximately one sixth of the rate for the runs at 437° and 438°C. As mentioned earlier, this is probably due to some surface diffusion effect. It should be noted, however, that this run does not simulate real catalyst bed conditions very well. The problem is that the weighing pan must be free of the sides of the reactor for accurate weighing. Thus the majority of the diffusion occurs at the sides and top of the pellet heap rather than at the bottom. For an actual catalyst bed the concentration of NO could be expected to decrease with increasing height in the bed while for the conditions of this experiment the composition is almost uniform around the bed. Furthermore, there is no flow through the heap so that thermal conditions are probably considerably different for this experiment than for a real bed. For these reasons it was decided that a single pellet would be more meaningful in spite of the greater scatter.

As for external film diffusion, the rate of reaction at the high flow rate (#8) is only barely greater than the rate of reaction at the low flow rate (#9). In fact, the difference in rates could be due to experimental error. The absolute deviation between supposedly identical runs (3 and 4) is the same as the absolute deviation between runs 8 and 9. Therefore, film diffusion is probably not significant for this experiment.

The runs with the sieves show an interesting result. The run at 410°C is twice the rate at 392°C while the rate at 438°C is only slightly greater than the rate at 392°C. This can be attributed to deactivation by exposure to air. Several batches of Linde molecular sieves were made before these runs and none of them showed any weight increase when contacted with NO. Sulfide and sulfate determinations (see Zadick (9) for a good description of the procedure) showed almost complete oxidation to $CaSO_4$ before the pellets ever entered the reactor. The sieves became hot to the touch after a few minutes exposure to air while the Harshaw pellets had become 50% oxidized after 17 days. The result was that the prepared supports were always kept in a pure nitrogen atmosphere. Nevertheless, the sieves were so active in air that after the runs at 392° and 438°C the entire batch had become deactivated despite extreme care. Furthermore, the batch was not used immediately but sat in the nitrogen a few days before being used and it is not certain that all of the air was purged. The pellet run at 410°C was used immediately after leaving the H_2S so that it is possible that the freshness of the pellet can account for the anomalous run at 410°C.

Run number 10 with oxygen shows that the Harshaw pellets react with oxygen faster than with NO. In fact, comparing runs 9 and 10, the average global rate of reaction with a 2.5% oxygen in helium mixture is almost twice as fast as the reaction with NO. When comparing instantaneous maximum rates, oxygen reacted as much as six times as fast

as NO. Because of this, oxygen would have to be removed from a stream of NO to maintain the life of a reactor bed. From the standpoint of ease of handling, the less active Harshaw pellets would be better than the more reactive sieves.

After four trials, no reaction could be found for CaS on the high silica Nalco pellets. The reason for this seems to be because of oxidation by the air before the pellets had a chance to react with NO. A reason for this could be indicated by the pore volume. The Nalco pellets absorbed twice as much calcium nitrate solution by weight as the Linde molecular sieves, and six times as much as the Harshaw alumina pellets. This could indicate a larger pore diameter as well as volume, and therefore less pore diffusion control. At any rate, the Nalco pellets seem more reactive than the molecular sieves. Therefore, because there was no way to avoid contact with air for less than about two minutes, and because of the reactivity of the Nalco pellets, it was impossible to determine the rate of reaction with NO.

No reaction rate expression could be determined from this research because the rate was very strongly controlled by diffusion. A rate constant could not be determined because the rates were diffusion controlled and did not increase exponentially with temperature. It is also likely that changes in concentration would have given a misleading reaction order. A diffusion model would be difficult to develop since both diffusion through reacted material and pore diffusion seemed important. Finally, because of the scatter in the instantaneous rates,

checking a mathematical model would be difficult. For these reasons, only experimental global rates are reported in this thesis.

CONCLUSIONS

1. The reaction of NO with CaS on high surface area supports was measured at several temperatures. For the high alumina Harshaw pellets, average global rates of reaction increased uniformly with increasing temperature from $.25 \times 10^{-4}$ at 390°C to $.45 \times 10^{-4}$ moles $CaSO_4$ formed per hour per gram of pellet at 493°C. All rates were measured using a 2.5% NO, 97.5% He feed over pellets containing 8.6% CaS.

2. In spite of difficulties due to air oxidation of the sulfide, the Linde molecular sieves gave greater average rates at each temperature than the Harshaw pellets. Rates varied between $.32 \times 10^{-4}$ and $.64 \times 10^{-4}$ moles $CaSO_4$ formed per hour per gram of pellet for three temperatures between 392 and 438°C.

3. The average rate of reaction was low using five pellets simultaneously. The rate at 442°C averaged $.05 \times 10^{-4}$ moles per hour per gram. A probable reason for the low rate was an added diffusional resistance within the bed of pellets.

4. External film diffusion was not important for the reaction using the Harshaw pellets. The average global rate at 440°C and 3.48 standard cm^3 per second was $.25 \times 10^{-4}$ moles per hour per gram. The average global rate at 444°C and .12 standard cm^3 per second was $.22 \times 10^{-4}$ moles per hour per gram.

5. Oxygen reacts well with CaS on high surface area supports. For Harshaw pellets using a 2.5% O_2, 97.5% He feed, the average global rate at 444°C was $.41 \times 10^{-4}$ moles per hour per gram. For a

Harshaw pellet from the same batch using a 2.5% NO, 97.5% He feed, the average rate was $.22 \times 10^{-4}$ moles per hour per gram. Thus it is desirable to remove O_2 from the feed gas since O_2 apparently reacts faster than NO at the same concentration.

6. Nalco pellets are extremely active in air so that no exact rates of reaction could be determined. Nevertheless, the Nalco pellets seem to be at least as active as the Linde molecular sieves.

RECOMMENDATIONS FOR FUTURE STUDY

Several questions concerning the reaction of calcium sulfide with nitric oxide remain unanswered. An exact rate expression for the reaction could be developed if diffusion effects could be minimized. Pure, powdered CaS should be tested as the most likely way to limit diffusion effects. Powdered CaS would have the added benefit of avoiding air oxidation which the high surface area supports seem to promote.

Average rates should be studied as a function of concentration to determine a reaction order, and rates versus temperature should be studied to determine a rate constant. Also, since four molecules of NO react to form two molecules of N_2, it would be interesting to test the effect of pressure on the reaction rate. Larger smaples should be studied so that the exhaust gases could be analyzed with particular attention to SO_2 and H_2S emission.

Work should be done to find catalysts to speed the reaction and more support materials could be tried. Further work on different metal sulfides should be done to determine the best one kinetically and economically.

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McIntyre, John C
Rate of reaction of nitric oxide by calcium sulfide on high surface area supports

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