Hydrogenolysis of quinoline-constituted synthetic shale-oil
by Robert A Damon

Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering
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Abstract:
A reaction system that consisted of a quinoline-constituted synthetic shale-oil which was undergoing hydrogenolysis in the presence of a cobalt-molybdate catalyst was studied. This study was undertaken to gain fundamental information concerning the behavior of a reaction system in which one of the typical heterocyclic nitrogen-compounds that are found in the distillates of shale oil is subjected to hydrogenolysis.

A bench scale, fixed bed, flow type, catalytic reactor was used.

The synthetic shale-oil, which contained 2 wt% nitrogen, was made up from quinoline and Penetek, a commercial mineral-oil which approximates the physical properties of cetane. Integral conversion data was gathered at 830°F for reaction pressures of 250, 500, and 1,000 psig. A hydrogen flow-rate of 7500 SCF/bbl was used. The catalyst was Peter Spence cobalt-molybdate which contained 2.5% CoO and 14.0% Mo03.

Information that pertained to the chemisorptive behavior of heterocyclic nitrogen-compounds and that concerned the reaction products of the hydrogenolysis of quinoline was presented. A framework or outline for the reaction mechanism was developed from this information. The surface-rate-equation theory was used in conjunction with the framework of the reaction mechanism to postulate several mechanisms or models which would represent the behavior of the reaction system. Overall rate-equations were derived for the possible rate-controlling steps of these mechanisms. Conversion data and initial-rate data for the reaction system at 830°F were analyzed via these rate equations. Other data from Ryffel's thesis (31) which was gathered for this reaction at the temperature range of 725-775°F, was also analyzed. These analyses indicated that a complex-series reaction mechanism involving the series reactions of quinoline to dihydro-quinoline to tetrahydro-quinoline to alkyl-aniline to alkyl-benzene and ammonia, and involving dual-site reactions of quinoline and the intermediates with molecular hydrogen could be used to represent the behavior of the reaction system. They also indicated that a transition temperature existed between 775°F and 830°F where the rate-controlling step of the reaction mechanism changed. At 725-775°F, the rate-controlling step was the dual-site reaction of o-propyl aniline with molecular hydrogen. At 850°F, the rate-controlling step was the adsorption of quinoline. The rate expression for the reaction at 830°F was utilized to obtain an empirical equation which would represent the reaction system. The constants in this equation were determined from the data at 830°F and 500 psig. The close conformity of the resulting equation to the experimental data at 830°F and 500 psig supported the above mentioned mechanism indications for the 830°F reaction.

HYDROGENOLYSIS OF QUINOLINE-CONSTITUTED SYNTHETIC SHALE-OIL

by

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ABSTRACT

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A bench scale, fixed bed, flow type, catalytic reactor was used. The synthetic shale-oil, which contained 2 wt% nitrogen, was made up from quinoline and Penetek, a commercial mineral-oil which approximates the physical properties of cetane. Integral conversion data was gathered at 830°F for reaction pressures of 250, 500, and 1,000 psig. A hydrogen flow-rate of 7500 SCF/bbl was used. The catalyst was Peter Spence cobalt-molybdate which contained 2.5% CoO and 14.0% MoO_3.

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I. INTRODUCTION

Natural-resource conservationists have voiced alarm over the rising annual consumption of petroleum-based fuels. However, world petroleum reserves appear to be maintained despite increasing annual consumption, but it is important to note that the producing cost for crude-oil is continually increasing. In due time, when petroleum supplies become inadequate or when the costs of crude-oil production warrant it, synthetic fuels based on coal and probably to a lesser extent on shale oil will become sources of liquid fuels (15).

Prior to and during the second world war, the lack of petroleum sources in European countries led to the development of full-scale processes for the production of synthetic fuels by coal hydrogenation and by the Fischer-Tropsch synthesis. Work was also directed toward the development of a process for producing liquid fuels from oil shale (15).

Here in the United States, a great deal of interest was shown in the possibilities of producing liquid fuels from oil shale because of the extensive deposits of oil shale in the Pichance Creek Basin of Northwestern Colorado. The United States Bureau of Mines has expended considerable research effort in the investigation of this problem (4, 5, 36, 37).

The distillates obtained from these oil shales by various retorting processes are rich in heterocyclic nitrogen-compounds similar to

those found in the distillates of coal tars (28, 39). Consequently, interest has also been shown in the Colorado oil-shale deposits as a source of these chemicals.

The Pichance Creek Basin extends over an area of approximately 1,000 square miles. In this area, the oil-shale deposits contain a potential 350 billion barrels of shale oil. This is approximately 4/5 of the total shale-oil reserves known to exist in the United States at the present time. This quantity of shale oil is significant in that it is three times as large as the world's known reserve of petroleum (4).

The exploitation of these oil-shale deposits can be classified according to the following three considerations:

1. Mining of the oil shale.
2. Retorting of the mined oil-shale.
3. Refining and upgrading of the crude shale-oil obtained from the retorting process.

At the present time, satisfactory methods for mining and retorting have been developed, and considerable progress has been made in the refining and upgrading of the crude shale-oil obtained from the retorts (4, 5).

The mining methods that are now used for mining the oil shale enable a recovery of only 75 per cent of the oil-shale deposit. Twenty-five per cent of the deposit must be left in the mine as supporting pillars.

The mined oil-shale is crushed and then subjected to a retorting operation. Ninety-two per cent of the crude shale-oil which is present in the oil shale can be recovered by this retorting operation.

The crude shale-oil from the retorting process is usually subjected to a coking operation to adjust the boiling range to a value which is consistent with fuels which are currently in volume demand. Approximately 79.6 per cent of the crude shale-oil that is fed to the coking operation can be recovered as a 700°F end-point distillate.

The mining-retort-coking sequence that is now in use will permit a recovery of about 55 per cent of the shale oil that is present in the mine as oil-shale deposits. Efforts to boost this recovery-figure have not been successful. It is therefore imperative that any process for upgrading the coker distillate should be of such a nature that nearly all of the coker distillate can be converted to usable products. (28).

The coker distillate contains heterocyclic nitrogen, sulfur, and oxygen, and a large percentage of olefinic compounds. The sulfur and nitrogen contents of the distillate are approximately one and two per cent by weight, respectively.

Any upgrading process for the distillate would require removal of the organically-combined sulfur, nitrogen, and oxygen. It should also accomplish saturation of the olefinic compounds.

Upgrading could be achieved by conventional petroleum-processing, but the nitrogen compounds which are present in the coker distillate cause rapid deactivation of cracking catalysts (27). Gum removal and desulfurization processes, exclusive of hydrofining processes, lead to a significant volume loss from the feed to the product (5). This would be objectionable since a loss in the recovery of usable products from the shale-oil should be avoided.

The most promising method of upgrading the coker distillate appears to be catalytic hydrogenation in the presence of a cobalt-molybdate catalyst. This method enables the breaking of carbon-nitrogen, carbon-sulfur, and carbon-oxygen bonds, yielding H_2S, NH_3, and H_2O, respectively. Also, olefins are saturated in this process. The advantage of this hydrofining process is that nitrogen, sulfur, and oxygen removal and saturation of the olefinic bonds are all accomplished in one step (4). The cobalt-molybdate catalyst is selective in that it does not promote hydrogenation of aromatic compounds. This renders the hydrogen consumption less than it would be for other hydrofining catalysts (15). Eighty-five per cent of the coker distillate can be recovered as premium fuels by this process (5).

The cobalt-molybdate, hydrofining method for upgrading coker distillates has been investigated by the Chemical Engineering Department at Montana State College (6, 19, 21, 24). In these studies, four catalysts were found to be effective: HF-activated cobalt-molybdate,

Peter Spence cobalt-molybdate, palladium-promoted Harshaw molybdenum-oxide, and Harshaw cobalt-molybdate.

The optimum operating conditions were found to be:

catalyst-bed temperature: 825-875°F

treat-gas flow rate: 2000-7500 SCF/bbl

operating pressure: 1000 psig

space velocity: 1.0 gm oil/(gm catalyst)(hr)

In the hydrofining of coker distillates with cobalt-molybdate catalysts, sulfur and oxygen are easily removed. The removal of nitrogen is not achieved as easily as the removal of sulfur and oxygen is achieved. For this reason, a kinetic study which was based on the conversion of the nitrogen content of coker distillates to ammonia was undertaken by Benson at Montana State College (6).

The nitrogen compounds which are present in the shale-oil coker-distillates appear chiefly as pyridine, quinoline, acridine, and similar type compounds (23). Investigations by Clyde Berg of the Union Oil Company have indicated that a typical reaction for the removal of nitrogen from a nitrogen-containing compound in the coker distillate is as follows (4):

$$C_5H_5N + 5H_2 \longrightarrow C_5H_{12} + NH_3$$

Pyridine — Pentane Isomers

In Benson's kinetic study of shale-oil hydrogenation at Montana State College, the hydrogen feed-rate was held in excess at 50 mols of hydrogen per mol of nitrogen, so that the reaction would be dependent only upon the concentration of nitrogen in the coker-distillate charge stock. By using this method, the effects of the various process variables on the reaction were obtained. Benson's study determined that the transfer of the reactants to the catalyst's surface by external diffusion did not control the rate of nitrogen removal.

Professor L. G. Mayfield of the Chemical Engineering Department at Montana State College suggested that more insight into the process of nitrogen removal from shale oil might be obtained if a synthetic shale-oil which contained only one nitrogen compound were to be studied (23). On the basis of this suggestion, a decision was made to undertake such an investigation. This thesis is a report of that study by the author.

The synthetic shale-oil used in this study was a mixture of "Penetek", and the nitrogen-containing compound, quinoline. "Penetek" is a commercial mineral oil which closely approximates the properties of cetane.

The synthetic shale-oil contained two weight-per-cent of nitrogen. This approximates the nitrogen content of shale-oil coker-distillate.

II. OBJECTIVES AND MODE OF INVESTIGATIONS

As mentioned in the introduction of this report, a kinetic study was undertaken by Benson at Montana State College to obtain fundamental kinetic information concerning the reaction which led to the conversion of the nitrogen compounds contained in shale-oil coker-distillate to ammonia and aromatic hydrocarbons when these nitrogen compounds were destructively hydrogenated with the aid of a cobalt-molybdate catalyst. By holding the hydrogen feed-rate at approximately 50 mols of hydrogen per mol of nitrogen compounds in the initial charge stock, Benson was able to fit an empirical, pseudo-first-order rate-equation to the conversion data which he obtained. He was also able to determine whether diffusion of the reactants to the catalyst surface or diffusion of the products from the catalyst surface were controlling the rate of the conversion of the shale-oil's nitrogen compounds to ammonia.

Use of the order-of-reaction concept for fitting empirical equations to rate data or to integral data has proven very useful in many situations where a rate equation was needed for designing a reactor. However, this concept often does not provide an empirical rate-equation which fits the kinetic data well for some types of vapor-phase reactions which are catalyzed by solid catalysts. Another disadvantage of applying this concept to the analysis of kinetic data obtained from solid-catalyzed, vapor-phase reactions is that this concept does not give much insight into the reaction mechanism.

The surface-rate-equation theory does, however, enable an investigator to obtain a fair amount of information about the reaction mechanisms of solid-catalyzed vapor-phase reactions. This theory has been successfully applied in recent years and numerous examples of its application appear in the literature. In this theory it is postulated that the reaction mechanism consists of a series of integrated steps in which the reactants diffuse to the catalyst and into the pores of the catalyst, become adsorbed on the surface of the catalyst, react on the catalyst surface, desorb from the surface of the catalyst, and finally diffuse from the pores of the catalyst and from the catalyst to the main gas stream.

Application of this theory to the study of a given reaction involves the postulation of various feasible mechanisms which follow the above pattern, the derivation of overall rate-equations based on the assumption that one of the steps of the mechanism is the rate controlling step, and the correlation of kinetic data to these equations. A detailed explanation of this theory and its applications is given in the discussion section of this report.

It was decided that it would be desirable to apply the surface-rate-equation theory to the reaction for removing nitrogen from shale oil by destructive hydrogenation with a cobalt-molybdate catalyst. However, this study would be extremely complex and difficult because of the variety of heterocyclic nitrogen-compounds contained in shale-oil coker-

distillate. Many mechanisms would be possible for each of the heterocyclic nitrogen-compounds, and to distinguish what is happening with each one when all of them are reacting together from the same feed stock would be a defeating task. It was for this reason that Benson was unable to apply the surface-rate-equation theory to his study with shale-oil-coker-distillate.

If, however, a synthetic shale-oil were to be studied which contained only a single heterocyclic nitrogen-compound, insight into the mechanism for this single compound could be gained without the complications which would be involved with the coker distillate. Studies of a number of synthetic shale-oils each based on a different heterocyclic nitrogen-compound found in shale oil could be made. These could then be correlated to give an understanding of the shale-oil, coker-distillate reaction.

The objective of this particular investigation was to gain information about the mechanism of the catalytic, destructive hydrogenation (hydrogenolysis) of a quinoline-constituted, synthetic shale-oil. It was hoped that any information gained in this study would be useful in helping to understand the removal of nitrogen from shale-oil coker-distillate by catalytic, destructive hydrogenation.

The overall plan of this investigation was to apply the surface-rate-equation theory to postulated, feasible mechanisms. This was to be done by gathering experimental initial-rate data and using these in

conjunction with the above theory to determine which of the postulated mechanisms would be the most probable.

The reactor to be used in this study was a tubular, fixed bed, flow type, catalytic reactor. It was designed to produce integral reaction data. The initial-rate data was to be obtained from conversion vs. reciprocal-space-velocity curves. These curves were to be obtained at operating pressures of 250, 500, and 1000 psig, each curve yielding an initial rate value at this pressure. Each curve was to be determined by measuring the conversion of the nitrogen in quinoline to ammonia for the series of space velocities: 10.0, 7.5, 5.0, 1.0, and 0.5 (gm oil)/(gm catalyst)/(hr).

The other variables, as far as possible, were chosen as those values of these variables which gave optimum conversion of the nitrogen compounds in shale-oil coker-distillate to ammonia. These variables were held fixed for determining the conversion vs. reciprocal-space-velocity curves at the three above-mentioned pressures. These fixed variables were:

charge stock: Penetek and quinoline, 2 wt% nitrogen

hydrogen flow rate: 7500 SCF/bbl oil

temperature: 830°F (443°C)

catalyst: Peter Spence graphite-base cobalt-molybdate, 1/8" pellets, R.D. 3718, 2.5% CoO, 14.0% MoO_3

treat gas: 100% hydrogen

Prior to the actual gathering of the main body of experimental data, it was necessary to do some work toward redesigning the bench-scale reactor that was to be used in this study. It was planned to use the same reactor for this study that was used in Benson's shale-oil study. During the shale-oil studies, however, difficulty with maintaining isothermal conditions in the reaction zone was experienced. This was due to the necessity for both adding and removing heat energy in different zones of the same reactor. It was necessary, especially for high space-velocity runs, to provide a large preheat-load for the reaction stream. The exothermic nature of the hydrogenation reactions which were involved meant that the reactor must be capable of dissipating a large amount of the heat-of-reaction from the reaction zone of the reactor.

To alleviate this difficulty, a number of runs were made prior to the main body of experimental runs in which various locations of the heating coils were tried, various distributions for the insulation were examined, and various preheater arrangements were tested. A satisfactory system for all but the extremely high space-velocities was found. This system is described in the section of this report on equipment. A method for dissipating the heat-of-reaction at high space-velocities, in which the catalyst was distributed evenly among the catalyst supports in the reaction zone, was suggested by Dr. R. L. Nickelson. This method was successfully used and it solved the problem of runaway reaction- temperatures at high space-velocity runs at high pressures.

III. EQUIPMENT

A. The Hydrotreating Unit

The experimental runs were carried out in an integral type reactor which was designed for continuous flow over a fixed-bed catalyst. The feed oil was pumped into a radiant preheater and from there to the top of the reactor. Hydrogen flow was adjusted by a needle valve. The hydrogen was passed through a deoxygenating unit, a drying unit, a rotameter, and then it entered the reactor top.

A pressure regulator valve controlled the operating pressure and enabled operating at constant pressures ranging from 200 psig to 1200 psig.

The reactor was heated by means of nichrome-wire heating coils. These heating coils were connected to Powerstats which made possible a wide range of temperature control.

After the oil had passed through the reactor and had been condensed, it was collected in a receiving flask. Gaseous material which left the reactor was given a caustic scrub and then vented into the atmosphere.

A schematic flow diagram of the catalytic hydrotreating unit is shown in Figure 1.

B. The Reactor

The reactor was made from a 30-inch length of nominal 1-inch O.D., seamless, Type 18-8 stainless steel pipe. It was equipped with a flanged union at each end. The reactor was covered with a layer of asbestos tape, and the nichrome heating coils were wrapped on the reactor over this tape. A three-inch layer of 85 per cent magnesia insulation was placed over the heating coils and the insulation was covered with sheet aluminum-foil.

The lower 20-inch length of the reactor was covered with a single heating coil and another heating coil was overlaid on the bottom four inches of the first coil. The catalyst zone started at the top of the first heating coil and extended down the reactor for a length of ten inches when 100 grams of catalyst were used and five inches when fifty grams of catalyst were used.

A third coil was wrapped around the top eight inches of the reactor. Thus, a length of two inches in which there were no heating coils was allowed above the top of the catalyst zone.

A length of 3/16-inch O.D. stainless steel tubing, brazed shut at the lower end, was inserted down the center of the reactor and contained the thermocouples which were used to measure the temperature in the reactor. Thermocouples were located at the top, center, and bottom of the catalyst zone and one was located in the preheat zone.

C. The Preheater

The preheater consisted of a 3" x 11" cylinder formed from sheet stainless-steel and closed at either end. The cylinder was wrapped with asbestos tape and a heating coil and was covered with a two-inch layer of magnesia insulation. Six feet of 1/8-inch O.D. stainless steel tubing was coiled to a length of 10 inches and a diameter of one inch. This coil was placed in the center of the preheater and the oil was pumped through the coil before it entered the reactor.

IV. MATERIALS, METHODS, AND ANALYSES

A. Materials

1. The Charge Stock

The quinoline used for preparing the charge stock was purified by fractionation from a commercial type quinoline containing 90 per cent quinoline and 10 per cent quinaldine and isoquinoline. The purity of the distillate was determined by its refractive index. To keep the quinoline isolated from oxygen, the distillate was collected under an atmosphere of natural gas.

The charge stock was prepared by mixing quinoline with a pure mineral oil such that the resulting mixture was two weight per cent nitrogen.

The mineral oil used was purchased from the Penn-Drake Company and is commercially known as "Penetek". This oil very closely approximates the physical properties of cetane. It has a specific gravity of 0.797 and has a boiling range of 250-270°C.

The mixture of quinoline and Penetek was stored in a 50-liter container and kept under an atmosphere of natural gas. It was then siphoned from the container to the holding vessel of the charge-stock pump whenever it was needed for a run.

2. The Catalyst, Catalyst Supports, and Treat Gas

The catalyst used for the study was a cobalt molybdate catalyst. It was in the form of 1/8-inch pellets and it was manufactured by Peter Spence and Sons, Ltd. The catalyst was a graphite-base catalyst and was 2.5% CoO and 14.0% MoO_3.

Catalyst supports used in the reactor were 1/8-inch alundum pellets which were obtained from the Norton Abrasive Company.

The hydrotreating gas was 100 per cent hydrogen and was supplied by Whitmore Oxygen Company. There was sufficient cause to believe that this hydrogen contained small amounts of oxygen and for this reason, the hydrogen was treated in a "deoxo" unit to remove the oxygen before being sent to the reactor. The "deoxo" unit contained a palladium catalyst and removed the oxygen by catalytically promoting the reaction of oxygen with enough hydrogen to form water. The water was then removed by passing the hydrogen through a tube packed with "Drierite".

B. Methods

1. Control and Measurement of Process Operating Variables

The reactor temperature was controlled by adjusting the voltage to the heating coils by means of Powerstats. Constant voltage was supplied to the Powerstats by a constant voltage transformer. Temperatures were measured at 15-minute intervals with iron-

constantan thermocouples used in conjunction with a Leeds and Northrup indicating potentiometer.

The reactor pressure was measured with a pressure gage which was tapped into the system at the lower end of the reactor. A Fisher-Wizard controller and a Mason-Neilan air-to-close regulator valve were used to maintain the reactor at a given pressure.

The flow rate of hydrogen to the reactor was controlled manually with a gas flow-meter and a needle valve. The type used was the Brooks calibrated rotameter. A constant pressure drop across the meter was maintained by the pressure regulator valve and the needle valve on the flow meter. During the course of a run, the flow reading was checked and corrected, if necessary, every fifteen minutes.

2. Preparation of the Reactor

The reactor was designed so that it could be removed from the hydrotreating system by disconnecting the charge-stock and hydrogen feed-lines, the thermocouple connections, the blow-out line, and by separating the union at the lower end of the reactor. When the reactor was removed from the system it was inverted and charged with catalyst supports. The reaction zone was then charged with catalyst, and the remainder of the reactor was filled with catalyst supports. At 3- to 4-inch reactor-length intervals during the charging of the reactor, the reactor was tapped sharply with a

hammer until the material present in the reactor indicated no further tendency to settle. This was done to insure that there would be no shifting of the catalyst when the reactor was re-inverted and placed back in the hydrotreating system. After the reactor had been charged, the catalyst and supports were kept in place with a piece of stainless-steel screen.

3. The Time-Length of Individual Runs

During the investigations with shale oil, it was found that during the first four hours of a run the conversion of the nitrogen content of the charge stock to ammonia rose sharply to a maximum conversion and then decreased. Shortly after this first four-hour period, the conversion leveled to a reasonably constant value. Furthermore, this constant conversion was found to be maintained in runs with a duration of up to 16 hours. The time at which the maximum conversion occurred was found to vary with the space velocity (6).

This characteristic type of behavior was also found to exist in the runs made with quinoline. Figure 2 shows this behavior for runs at various space velocities.

Thus, it was decided to run for a minimum of five hours until the first sample was collected, provided that isothermal conditions were maintained in the reactor during this period. If isothermal conditions were not maintained, the time for collecting the first

sample was extended until isothermal conditions had been maintained for at least one hour. Samples of the processed oil were then collected during the last four hours of a run.

4. Operating Procedure

The same operating procedure was used for each run.

After being charged with catalyst, the reactor was heated to the operating temperature of 830°F. During the heating period, hydrogen was allowed to flow through the reactor at a low flow rate. Approximately three hours were required to heat the reactor to the operating temperature.

When the reactor had reached the operating temperature and indicated a tendency to remain at this temperature, the charge stock was pumped into the reactor at a rate determined by the space velocity. The time at which this took place was considered to be the start of the run. Periodically, during the course of the run, the flow rate of charge stock was checked and the pump was adjusted, if necessary.

The processed oil was collected in a Jerguson sight glass and allowed to drain off at a steady rate in order to avoid any sudden pressure drops in the system which would be caused by draining large amounts of product in a short time interval.

The length of the run was determined in the manner mentioned in the above section.

At 15-minute intervals the temperatures in the reactor were recorded and the hydrogen-flow rate was checked. Also, periodic checks were made to see whether or not the correct space velocity was being maintained and if isothermal conditions were being maintained in the reactor. The latter check was made by moving the thermocouples to various positions in the reactor such that a temperature profile of the catalyst zone was obtained.

C. Analyses

The conversion of the nitrogen in the charge stock to ammonia was determined by analyzing the product for nitrogen content. The samples were collected and placed in a flask where nitrogen gas was bubbled through the sample for a period of 15 minutes in order to remove any ammonia which might have been absorbed by the product oil. They were then dried with calcium chloride and filtered.

The nitrogen content of each sample was determined by the Kjeldahl method.

The product was also subjected to infrared analysis and analysis by fractionation. This was done in order to obtain a qualitative picture of the product.

V. DISCUSSION

A. Introductory Remarks

As stated in Section II of this report, the objective of this particular investigation was to gain information about the catalytic, destructive hydrogenation of a quinoline-constituted, synthetic shale-oil. This reaction was studied at a temperature of 830°F; at pressures of 250, 500, and 1000 psig; with a hydrogen flow-rate of 7500 SCF/bbl oil; and with a cobalt-molybdate catalyst of 2.5% CoO, 14.0% MoO_3.

In this discussion, known information which is pertinent to the above reaction will be presented first. This information will then be used to develop a framework for the reaction mechanism. This will be followed by a presentation of kinetic techniques which are used for tubular flow-reactors and heterogeneous reactions, and then by a presentation of rate-equation theory for fluid-phase reactions catalyzed by solids.

An example derivation of a rate equation by the surface-rate-equation method will be given. Possible mechanisms for the catalytic hydrogenolysis of quinoline will be discussed and a series of rate equations will be derived based on the surface-rate-equation theory. These rate equations will be analyzed through the application of experimental data to obtain information about the mechanism of the reaction.

B. Nitrogen Compounds and Chemisorption

Nitrogen compounds found in various crude oils have long been troublesome to the petroleum industry because of their effect of deactivating cracking catalysts (39, 2). This deactivating effect is especially pronounced when shale oils are subjected to catalytic cracking. Evidence indicated that the degree of deactivation was directly proportional to the amount of nitrogen-containing compounds present in the feed to the cracking unit. Up until the early 1950's, there was some difference of opinion as to what exactly caused this deactivation. The general concensus of opinion was that the deactivation was caused by a laydown of carbonaceous residue on the catalyst. While this was to some extent true, as evidenced by the cracking of feedstocks which were devoid of nitrogen content, there was no experimentally-backed explanation of the specific role of nitrogen compounds in the deactivation.

To resolve this question, the Houdry Process Laboratory undertook an investigation of the poisoning of cracking catalysts by nitrogen compounds (26, 27). Since catalytic action is highly specific, it has been concluded that specific chemical properties of catalysts are involved in catalytic action (8). The Houdry study attempted to establish the essential chemical properties or active principles of a number of catalysts. The nitrogen compounds pyridine and quinoline were investigated with both inactive silica gels and active metal-oxide catalysts at various pressures and temperatures from 250-500°C.

Both inactive silica gels and active catalysts were saturated with gaseous quinoline. It was found that the quinoline could be completely desorbed from the catalytically inactive silica gels by a stream of nitrogen gas, whereas under the same conditions only a very small part of the quinoline was desorbed from the active catalyst. On boiling a quinoline-treated catalyst with aqueous HCl solution an extract was obtained which was shown to contain quinoline. These observations indicated that quinoline is held as such by the catalyst rather than as its decomposed or polymerized product.

When the adsorption of quinoline and pyridine were compared, differences were found in the amount of quinoline and in the amount of pyridine chemisorbed under identical operating conditions. These differences were directly attributable to the differences in the strength of the two substances as bases. The two chief conclusions of this study were:

1. Nitrogen containing compounds are chemically held to active metal-oxide catalysts, and the amount chemisorbed is decreased with an increase in temperature.
2. The chemical properties exhibited by the active sites on the catalyst surface identify the active principle as an "acid".

Thus, it appears feasible that the basic nature of quinoline would allow it to react with the acidic function of the catalyst. This is probably the next step in the reaction mechanism of the hydrogenolysis

of quinoline after the quinoline has diffused through the surface film and into the pores of the catalyst (25). The work of Mills, et. al., indicates that while there is some physically adsorbed quinoline on the surface of the catalyst after the diffusional steps, the adsorbed quinoline is predominately present as chemisorbed and non-decomposed quinoline on the surface of the catalyst. At increased temperatures and pressures, the ratio of physically-held quinoline to chemically-held quinoline increases, but the amount of physically-held quinoline is still small compared to the amount of chemically-held quinoline.

The heterocyclic ring of quinoline is more amenable to reduction than the carbocyclic ring (16). It may be supposed that some vapor-phase hydrogenation of quinoline could occur, and that the resulting dihydro- and tetrahydro- quinolines would compete with quinoline for active chemisorption sites on the catalyst surface. Work by several investigators has shown that significant conversion of quinoline to tetrahydroquinoline can only be obtained through the use of various hydrogenation catalysts (16, 29, 33). Thus, the quinoline molecule is probably chemisorbed as such.

C. Reaction Products

Sugino and others have hydrogenated quinoline in the presence of copper catalysts to get up to 95% yields of tetrahydroquinoline (33, 16). Rapoport studied the hydrogenolysis of quinoline with a molybdenum catalyst, a hydrogen pressure of 80 atmospheres, and temperatures of

420-450°C. He obtained yields of 95-98% tetrahydroquinoline (29). The tetrahydroquinoline further decomposed to give o-propyl aniline, o-ethyl aniline, o-methyl aniline, aniline, and methane. These same investigators indicate that the further hydrogenation of tetrahydroquinoline to decahydroquinoline is difficult and that as a reaction is proceeds very slowly.

Ryffel also identified the above nitrogen compounds in the product oil. Through the use of gas-chromatography techniques, the following compounds were identified (31):

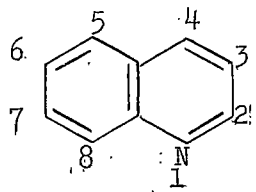
tetrahydro quinoline
o-propyl aniline
o-ethyl aniline
o-methyl aniline
aniline
ammonia
quinoline

In addition, the following pertinent compounds were also identified in the product oil:

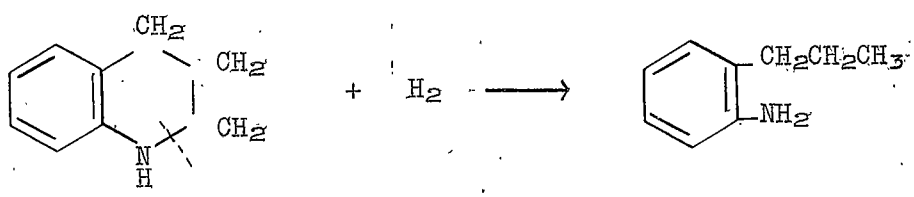
n-propyl benzene
iso-propyl benzene
ethyl benzene
toluene
benzene
o-ethyl toluene
propyl cyclohexane
ethyl cyclohexane
methyl cyclohexane
cyclohexane

D. Ring Cleavage

Atomic positions in the fused, six-membered, ring system of quinoline are, by agreement, numbered in the following manner:

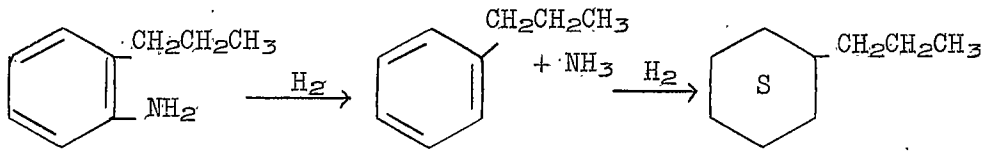


The presence of aniline and some of its homologs in the product oil probably indicates that the heterocyclic ring of tetrahydroquinoline was cleaved between the 1 and 2 positions. The absence of alkylamine substituted benzenes indicates that cleavage probably did not occur between the 1 position and the adjacent carbon in the benzene ring:



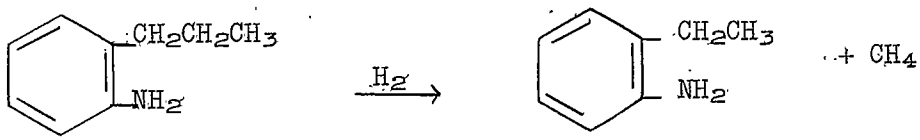
E. Order of Nitrogen Removal

The alkyl cyclohexanes present in the product oil are probably hydrogenation products of alkyl benzenes. It is also significant that no amine-substituted, alkyl cyclohexanes were found in the product oil. This would indicate that the amine group must have been removed from the aniline homologs prior to the subsequent hydrogenation which yielded the alkyl cyclohexanes:

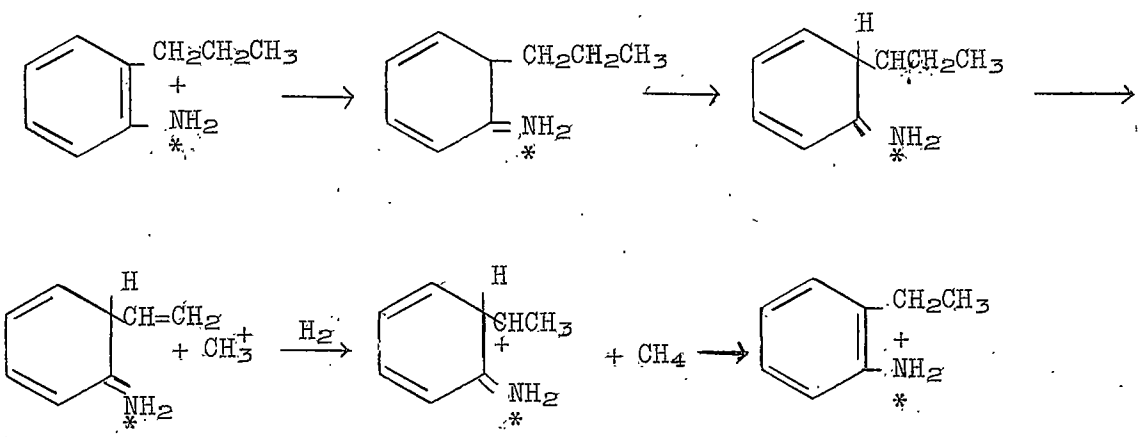


F. Cracking of the Alkyl Group

Rapoport's identification of methane, along with the aniline homologs, as a product indicated that cracking of the alkyl group occurred:



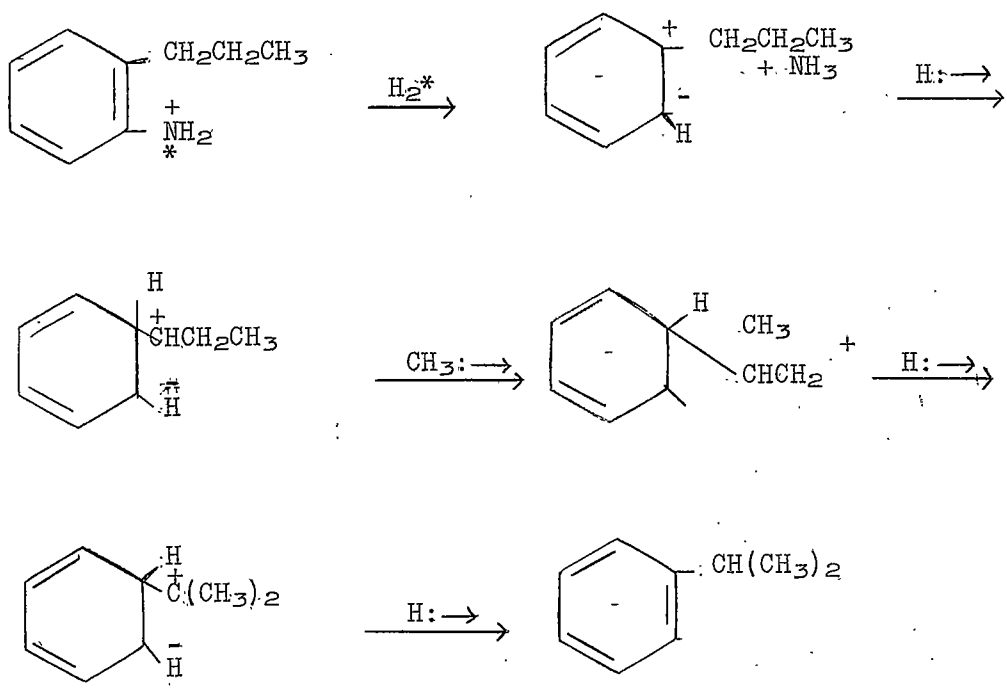
The acidic function of the catalyst probably reduces the alkyl aniline to a chemisorbed alkyl anilinium ion (30). Using this as a starting point, the cracking of the alkyl group might have occurred in the following manner:



(Where * is an active site on the surface of the catalyst.)

G. Isomerization of the Alkyl Group

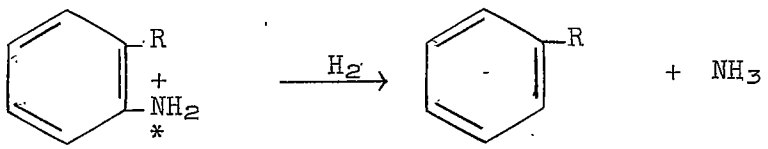
The presence of isopropyl benzene in the product oil can probably be attributed to the isomerization of o-propyl aniline. This could conceivably have occurred during the course of a dual-site reaction with adsorbed hydrogen and in a manner similar to that of the above considered cracking mechanism:



H. Removal of Nitrogen from Alkyl Aniline

The final important reaction involved in the removal of nitrogen as ammonia from the quinoline molecule is the reaction of alkyl aniline with hydrogen to give alkyl benzene and ammonia. The alkyl anilinium ion, resulting from the chemisorption of basic alkyl aniline by the acid function of the catalyst, would exert a strong inductive effect of

electron attraction and thus render the nitrogen-bonded carbon of the carbocyclic ring susceptible to electrophilic attack by hydrogen:



I. Hydrogenation of Alkyl Benzenes

Ryffel's analysis of the non-nitrogen-containing compounds in the product oil (exclusive of those in the carrier oil) revealed that 87.8% of these compounds are alkyl benzenes, the remainder being hydrogenation products of the alkyl benzenes. Those findings of the Houdry Process Laboratory which indicated that the presence of nitrogen-containing compounds poisoned or dominated the acid function of the catalyst seem to be substantiated by Ryffel's analysis. It would appear that the basic nitrogen compounds are far more able that the alkyl benzenes in the competition for active chemisorption sites and, consequently, the catalytic hydrogenation of alkyl benzenes would be retarded. The ratio of hydrogenated products of alkyl benzenes to alkyl benzenes, however, was found to increase at higher reaction pressures. This would indicate that the ability of alkyl benzenes to compete with the nitrogen-containing compounds for active chemisorption sites is increased at higher pressures. Groggins and other sources report that hydrofining processes using cobalt-molybdena catalysts have very little effect on aromatics. Cobalt-molybdena catalysts do not appear to promote the hydrogenation of aromatics (15, 18).

J. Summary of Important Indications

The preceding discussion has revealed several probable postulations which are important in the analysis of the catalytic reaction of quinoline with hydrogen to yield ammonia and hydrocarbons. These are:

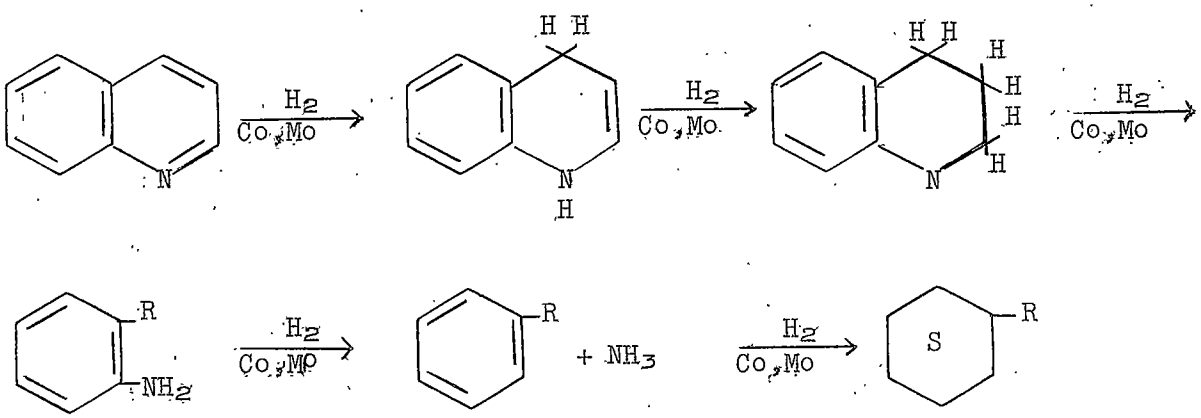
1. Although nitrogen-containing compounds are adsorbed on the catalyst surface by both physical adsorption and chemisorption, the amount held by chemisorption is far more prevalent than that held by physical adsorption.
2. Chemisorption of nitrogen compounds is effected by the interaction of the basic function of the nitrogen compound with the acid function of the catalyst.
3. The chemisorptive preference of the catalyst for a given nitrogen-containing compound is directly proportional to the relative basic strength of that compound.
4. The chemisorptive preference of acid catalysts for nitrogen-containing compounds is such that the catalyst is effectively poisoned for the reaction of other significantly less basic compounds with active centers on the surface of the catalyst.
5. The chief product involved in the initial catalytic hydrogenation of quinoline is tetrahydroquinoline.
6. Catalytic hydrogenation of tetrahydroquinoline results in cleavage of the heterocyclic ring between ring positions 1 and 2, giving alkyl anilines as products.

7. Catalytic hydrogenation of the alkyl anilines of item 6, above, gives alkyl benzenes and ammonia as products.

8. Catalytic hydrogenation of alkyl benzenes in the presence of sufficient amounts of nitrogen-containing compounds is difficult to achieve.

K. The Framework of the Reaction Mechanism

Using these important indications as a basis, it is possible to outline the framework of the reaction mechanism for the catalytic reaction of quinoline with hydrogen. This framework appears to be:



L. Tubular Flow-Reactors and Heterogeneous Reactions

An overall reaction-rate equation in terms of fractional conversion of the reactant, mass of the catalyst in the reactor, and the mass flow-rate of the feed can be developed by setting up a rate-of-flow balance for the reactant about a differential volume of the reactor with the restraint that the reactor is in steady-state operation (32, 38).

Input rate to the differential volume:

$$F(z - x')$$

Output rate from the differential volume:

$$F(z - (x' + dx'))$$

Rate of change of reactant in the differential volume:

$$r(dW)$$

Rate of accumulation of reactant in the differential volume:

zero

Where: F = total feed rate, mass/hr

z = initial mass fraction of heterocyclic nitrogen in the feed

x' = conversion, mass nitrogen converted/mass feed

W = mass catalyst

r = rate of conversion of nitrogen to ammonia, mass nitrogen/(hr)(mass catalyst)

Algebraic simplification of the balance gives:

$$F(dx') = r(dW)$$

But:

$$x' = x(m/m_t)$$

Where: m = mass of nitrogen in feed

m_t = total mass of feed

x = conversion, mass nitrogen converted/mass of nitrogen in feed

Thus, the overall rate-equation can be written as:

$$r = \frac{m}{m_t} \cdot \frac{dx}{d(W/F)} \qquad \frac{\text{(mass nitrogen)}}{\text{(hr)(mass catalyst}}$$

From the above equation it can be seen that the overall reaction-rate is the product of (m/m_t) and the slope of the x vs. (W/F) curve. Curves for x vs. (W/F) at reation pressures of 250, 500, and 1000 psig and the reaction temperature of 830°F are presented in Figures 9, 10, and 11. Corresponding curves for r vs. (W/F) are presented in Figure 12.

M. Rate-Equation Theory for Fluid-Phase Reactions Catalyzed by Solids

The order-of-reaction concept can be used to describe many homogeneous reactions. In this study, quinoline was reacted isothermally and at constant system-pressure with enough hydrogen such that the mass of hydrogen in the reactor remained essentially constant. If the reverse reaction is considered negligible, the overall reaction-rate could be described by the order-of-reaction concept with the following equation:

$$r = k(m_N)^q = (dm_N)/(dt)$$

Where: r = the reaction rate

m_N = mass of unreacted nitrogen at time t

q = the order of the reaction

k = the reaction rate-constant (including the constant hydrogen mass)

Use of the order-of-reaction concept is not recommended for representing a catalytic process (13, 18). Rate equations described by this concept fall short of truly representing a catalytic process. The chief reason is that they do not account for adsorption on the catalyst. Therefore, catalytic rate-equations based on the order-of-reaction con-

cept were not seriously considered in this study.

The mechanism of surface catalysis is very complex. Fluid-phase reactions catalyzed by solids are conceived to proceed according to at least the following seven steps (8):

1. Diffusion of the reactant molecules to the surface of the catalyst.
2. Diffusion into the pores of the catalyst.
3. Adsorption of the reactants on the catalyst surface.
4. The actual chemical reaction or series of reactions which take place in the adsorbed phase on the catalyst.
5. Desorption of the product molecules.
6. Diffusion of the products to the exterior of the catalyst pellet.
7. Diffusion from the pellet to the main gas stream.

These seven steps take place in series. It is, therefore, possible for any one of the seven steps to control the overall reaction-rate. This would occur if the rate of any one of these steps were significantly slower than the rates of the others, allowing the overall reaction-rate to adjust itself to the rate of the slow step.

N. The Diffusional Steps

Since the adsorption, desorption, and chemical reaction steps are primarily influenced by temperature and pressure, while in addition, the diffusional steps are influenced not only by temperature and pressure,

but by mass velocity or catalyst size; it is possible to determine whether or not the rate of one of the diffusional steps were slow enough such that it controlled the overall reaction-rate.

In steps 1 or 7, diffusion occurs through a stagnant layer of gases at the catalyst surface. If either steps 1 or 7 were controlling the overall reaction-rate, a series of runs made at identical conditions, with the exception that the mass velocity would be varied, would show a direct variation of the overall reaction-rate with mass velocity (8). This is illustrated in Figure 3. Increased mass velocity under the conditions of steps 1 or 7 controlling, would decrease the resistance of the stagnant gas-layer to a diffusional process and would thus increase the overall reaction-rate.

Steps 2 and 6 are known as internal diffusional steps. If either of these two steps were rate controlling, a decrease in the size of the catalyst used would lower the resistance to internal diffusion and thus increase the overall reaction-rate. There is an optimum size, however, below which a further reduction in the size of the catalyst particles would not increase the rate of internal diffusion. A series of runs made at identical conditions but with varying catalyst particle-size would indicate whether or not steps 2 or 6 were controlling the reaction rate. This is illustrated in Figure 3.

Benson and Damon, in a study of the destructive hydrogenation of coker-distillate shale-oils in the presence of a cobalt molybdate

catalyst, completed a series of runs which were designed to determine whether or not diffusion through the stagnant gas-film were rate controlling (6). These shale-oils contained heterocyclic nitrogen-compounds such as pyridine, lutidine, picoline, quinoline, and quinaldine. The resulting indication of this study was that diffusion through the stagnant gas-film was not rate controlling. This study is illustrated in Figure 4. Ryffel also completed a similar study with quinoline, using the same catalyst and a lower reaction temperature (31). His work also indicated that diffusion through the stagnant gas-film was not rate controlling.

A study of the effect of internal diffusion on the rate of nitrogen removal from quinoline by destructive hydrogenation in the presence of a cobalt molybdate catalyst was also made by Ryffel (31). His study utilized runs made with varying sizes of the catalyst. The runs strongly indicated that internal diffusion is not rate controlling in the conversion of quinoline to hydrocarbons and ammonia through the use of hydrogen and a cobalt molybdate catalyst. This is illustrated in Figure 5.

O. Example Derivation of a Rate Equation by the Surface-Rate-Equation Method

Rate equations for fluid-phase reactions catalyzed by solids can be derived by treating adsorption and desorption as chemical steps. It was shown earlier in this discussion that the assumption that the adsorption and the desorption of quinoline by the cobalt-molybdate catalyst are

probably chemical steps is a safe assumption.

For the purpose of demonstrating the derivation of rate equations, a reaction involving chemisorbed quinoline with vapor-phase hydrogen to yield dihydroquinoline will be assumed. It will also be assumed that none of the diffusional steps of the seven-step catalytic-reaction-path are rate controlling, and that the reaction takes place in the presence of gases that are inert to the reaction.

The adsorption, main-reaction, and desorption equations for this assumed reaction can be written in the following manner:

1. $Q + s \rightleftharpoons Qs$

2. $Qs + H_2 \rightleftharpoons Ds$

3. $Ds \rightleftharpoons D + s$

Where: Q = quinoline

s = an active site

Qs = quinoline chemisorbed on an active site

D = dihydroquinoline

Ds = dihydroquinoline chemisorbed on an active site

In step 1, the rate of adsorption of quinoline by the catalyst is proportional to the partial pressure of quinoline in the gas phase and the fraction of active sites left vacant. The rate of desorption from the catalyst is proportional to the fraction of active sites covered with quinoline. Thus, a rate equation can be written for step 1. In a simi-

lar manner, rate equations can be written for the two other steps. Also, since gases inert to reaction step 2 may be adsorbed by the catalyst, an additional adsorption-desorption rate-equation can be written for these inert gases. These equations, along with their corresponding equilibrium constants, are:

1. $r_1 = k_1 P_Q f_s - k_1' f_Q \qquad K_1 = \dfrac{f_Q}{P_Q f_s}$

2. $r_2 = k_2 P_{H_2} f_Q - k_2' f_D \qquad K_2 = \dfrac{f_D}{P_{H_2} f_Q}$

3. $r_3 = k_3 f_D - k_3' P_D f_s \qquad K_3 = \dfrac{P_D f_s}{f_D}$

(i). $r_i = k_i P_i f_s - k_i' f_i \qquad K_i = \dfrac{f_i}{P_i f_s}$

Where: P_Q, P_D, P_{H_2}, P_i = partial pressures of quinoline, dihydroquinoline, hydrogen, and the inert gases, respectively.

f_Q, f_D, f_i = fraction of the active sites covered by quinoline, dihydroquinoline, and the inert gases, respectively.

f_s = fraction of vacant active-sites.

k, k' = forward-reaction and reverse-reaction rate-constants, respectively.

If step 1, the adsorption step, were rate controlling, the rate equation for step 1 would represent the rate of the overall reaction. Steps 2, 3, and i would be at equilibrium, and the equilibrium expressions for these steps: K_2, K_3, and K_i could be used to evaluate the unknown quantity f_Q in the rate equation. The rate equation would then be in terms of the unknown quantity f_s. This quantity, however, can be evaluated by making use of the equilibrium expressions for steps 2, 3, and i, since the following relation holds:

$$f_s = (1 - f_Q - f_D - f_i)$$

Substituting for the unknown f's in this equation gives:

$$f_s = 1/(1 + \frac{P_D}{K_3 K_2 P_{H_2}} + K_i P_i)$$

The final form of r_1 can be developed as follows:

$$r_1 = k_1 P_Q f_s - k_1' f_Q$$

Substitution for f_Q gives:

$$r_1 = k_1 f_s (P_Q - \frac{P_D}{K_1 K_2 K_3 P_{H_2}})$$

The overall reaction, $Q + H_2 \rightleftharpoons D$, is the sum of steps 1, 2, and 3; thus: $K_1 K_2 K_3 = K$, where K is the overall equilibrium constant. Using this relationship and the definitions: $K_Q = 1/K_1$ and $K_D = 1/K_3$, the

rate equation can be simplified to the following form:

$$r_1 = \frac{k_1\left(P_Q - \frac{P_D}{KP_{H_2}}\right)}{\left(1 + \frac{K_Q P_D}{KP_{H_2}}\right) + K_D P_D + K_i P_i}$$

Yang and Hougen (40) have classified all rate expressions derived in this manner according to the following form:

$$r = \frac{(\text{kinetic term})(\text{potential term})}{(\text{adsorption term})^n}$$

For the rate equation just derived, the kinetic term would be k_1; the potential term would be the remaining portion of the numerator; the adsorption term would be the denominator.

In a manner similar to that used in deriving the overall rate-expression for the case where step 1 is controlling, overall rate expressions can be derived for the cases where step 2 or step 3 are controlling. The resulting rate expressions for all three cases are presented below:

Step	Kinetic Term	Potential Term	Adsorption Term
1	k_1	$P_Q - \frac{P_D}{KP_{H_2}}$	$1 + \frac{K_Q P_D}{KP_{H_2}} + K_D P_D + K_i P_i$
2	$k_2 K_Q$	$P_Q P_{H_2} - \frac{P_D}{K}$	$1 + K_Q P_Q + K_D P_D + K_i P_i$

Step	Kinetic Term	Potential Term	Adsorption Term
3	$k_3 K K_D$	$P_Q P_{H_2} - \frac{P_D}{K}$	$1 + K_Q P_Q + K K_D P_Q P_{H_2} + K_i P_i$

This method of deriving rate expressions will be applied in a subsequent section of this discussion to the overall reaction of quinoline with hydrogen to give ammonia and hydrocarbons.

P. The Use of Initial Rates for Mechanism Determination

Referring back to the example mechanism, a study can be made of the initial rates for the case of any one of the individual steps of the mechanism being rate controlling. This theoretical initial-rate can then be compared with the experimental initial-rate as a basis for deciding whether or not the given step under consideration is the rate controlling step.

The initial rate is the reaction rate at zero conversion. At zero conversion, the partial pressures of the products of the reaction are equal to zero. Thus, it is possible to simplify the theoretical rate-equations by setting these partial pressures equal to zero. Since the initial partial-pressures of the reactants can be expressed as the products of the initial mol-fractions and the total pressure, it is possible to express the initial rate-equations in terms of total pressure. Using these methods on the rate equation for the case of adsorption controlling, the initial rate equation would be:

$$r_{o_1} = \frac{k_1(P_Q)_o}{(1 + K_i(P_i)_o)}$$

Where: $(P_Q)_o$, $(P_i)_o$ = initial partial pressures of quinoline and the inert gases, respectively.

Putting this in terms of the total pressure gives:

$$r_{o_1} = \frac{k_1(y_Q)_o P}{(1 + K_i(y_i)_o P)}$$

Where: $(y_Q)_o$, $(y_i)_o$ = initial mol-fractions of quinoline and the inert gases, respectively.

P = total system pressure.

This can be further simplified to:

$$r_{o_1} = \frac{aP}{(1 + bP)}$$

Where: $a = k_1(y_Q)_o$

$b = K_i(y_i)_o$

In a similar manner the initial rate-equations for the cases of the other two steps being rate controlling can be found; these are presented below:

Controlling Step	Initial Rate-Equation
1	$r_o = \frac{aP}{(1 + bP)}$
2	$r_o = \frac{aP^2}{(1 + bP)}$
3	$r_o = \frac{aP^2}{(1 + bP + cP^2)}$

Examination of the initial rate equation for any given step controlling indicates that there is a typical r_o vs. P curve for each of the controlling cases. These curves for the example mechanism being presented here are represented in Figure 6. If an experimental r_o vs. P curve is obtained, its shape can be compared by visual inspection with the theoretical r_o vs. P curves. Similar theoretical and experimental curve-shapes can help decide on the rate controlling step. For difficult decisions, it may be helpful to regroup the variables of the initial rate-equations which are in doubt and make a decision on the basis of the different curve-shape obtained by regrouping the variables (13).

These methods can be extended to rates plotted against such variables as feed-composition, temperature, and conversion. But the rate vs. pressure curves are by far the most important (40).

The use of initial rates alone for determining the most plausible mechanism for a given reaction usually will not enable a definite decision as to the correct mechanism because: the initial rate equations are directed toward controlling-steps in a specific mechanism; many mechanisma are usually possible (13). It is important to note, however, that these initial-rate methods are very helpful in narrowing down the number of possible mechanisms (38). Also, it is important to remember that other information about a reaction, in conjunction with initial rate information, will often enable the buildup of a substantial case for a particular reaction-mechanism.

Q. Development of the Quinoline Hydrogenation Mechanism

1. Introductory Remarks

Earlier in this discussion, evidence was presented which enabled the author to determine the framework of the reaction mechanism. Attention will now be turned to the completion of the mechanism structure. In other words, an effort will be made to establish a more detailed picture of the reactants-to-product path than is presented by the framework of the reaction mechanism alone.

The surface-rate-equation method, which was presented in this discussion by its use in the derivation of an example rate-equation, is now widely accepted by the chemical engineering profession. Before the development of this method, it was customary to correlate catalytic reaction data on the basis of equations which were valid for homogeneous reactions only, with empirical terms sometimes being incorporated to account for the adsorption of individual components on the catalyst surface (11). Numerous attempts have been made to establish rigorous adsorption relations, but as yet there is little evidence that their use is justified in rate equations for complex reaction systems. It is believed more generally satisfactory to use the surface-rate-equation method to develop the rate equation and then to evaluate the constants in the rate equation from experimental rate measurements at conditions representing the ranges of interest of the variables (20). The surface-rate-equation method represents a compromise between those methods which

are so involved in theory as to be impractical, and those methods which are so empirical as to be unsafe for extrapolation beyond the range of experimentation (40). The author has chosen to use the surface-rate-equation method in this study.

2. Basic Assumptions in the Surface-Rate-Equation Method

In the development of a rate equation for an homogeneous, fluid-phase, catalytic reaction, the following assumptions are usually made (11, 38):

1. The resistance to the diffusional steps is so slight that only a chemical step can control the reaction.
2. Since the resistance to diffusion is slight, the partial pressure in the bulk of the gas stream is for practical purposes nearly the same as that at the interface of the catalyst with the gas stream.
3. Only one of the steps is rate controlling.
4. The adsorption steps are chemisorption steps and can be treated as chemical steps.
5. The specific rate-constants and the equilibrium adsorption-constants are independent of total pressure.
6. The rate equation for the rate-controlling step may be written as a simple-order reaction.
7. The active sites and the adsorption compounds react according to the law of mass action.

For the catalytic reaction of quinoline with hydrogen that is being considered in this report, it has been shown previously in this discussion that assumptions 1, 2, and 4 above are safe assumptions. The remaining assumptions, 3, 5, 6, and 7, are assumptions inherent to the surface-rate-equation method.

Assumption 3 may not hold if there is a shift to another rate-controlling step during the course of the reaction, or if each step of the series contributes almost equally to the resistance. These complications can be accounted for, however, in the writing of the particular rate equations concerned. The primary effect would be that the resulting overall rate-equation would be somewhat more complicated than that for the case of assumption 3 being strictly valid (11).

Enough fundamental research has not been undertaken or completed to fully establish the validity of assumptions 5, 6, and 7. But the deviations from these latter assumptions are thought to be masked by a normal amount of experimental error and they are therefore accepted without too much objection by the chemical engineering profession (40, 11).

3. Possible Reaction-Paths

In this discussion the following symbols will be taken as abbreviations for those chemical species indicated below. The conjunction of any of these symbols with the small letter 's' will

indicate that the particular compound being represented is chemisorbed on an active site.

Q = quinoline

D = dihydroquinoline

T = tetrahydroquinoline

R = alkyl aniline

B = alkyl benzene

A = ammonia

C = alkyl cyclohexane

The framework of the reaction mechanism has been shown to consist of five primary reactions:

1. $Q + H_2 \rightleftharpoons D$

2. $D + H_2 \rightleftharpoons T$

3. $T + H_2 \rightleftharpoons R$

4. $R + H_2 \rightleftharpoons B + A$

5. $B + H_2 \rightleftharpoons C$

The course of the reaction was followed by analyzing the nitrogen content of the product oil. The rate of the overall reaction was determined by using the integral-reactor rate-equation which depended on the conversion values of quinoline to non-nitrogen containing hydrocarbons. Since the alkyl benzenes are the first

non-nitrogen-containing compounds produced in the series of framework reactions, the overall reaction-rate would not be directly sensitive to the reaction involving the hydrogenation of alkyl benzenes to yield alkyl cyclohexanes. The hydrogenation products of the alkyl benzenes were considered to be a part of the inert gases along with Penetek and those gases resulting from the cracking of Penetek. In this respect, however, the hydrogenation products of the alkyl benzenes, being a part of the inert gases, will enter into the overall rate-expression since the inert gases are included in the adsorption term of the overall rate-expression. Thus, for the purpose of developing an overall rate-expression, the reaction framework will be considered to consist of the series of reactions 1, 2, 3, and 4.

Analysis of the reaction framework indicates that the overall reaction could be classified as a complex-series reaction (18). The reaction is a series reaction with respect to quinoline, and it is a parallel reaction with respect to hydrogen.

By considering the different possible mechanisms for each reaction of the reaction series, it is possible to find the total number of combinations of these individual mechanisms. This total number of combinations would constitute the total number of mechanisms possible for the overall reaction.

In each of these four framework reactions, the nitrogen-containing compounds could react in the vapor phase, or in the adsorbed phase from a single site. The hydrogen could react in the vapor phase, in the adsorbed phase from a single site as molecular hydrogen, or in the adsorbed phase from a single site as atomic hydrogen. Thus, there are (2) (3) or 6 different ways for each individual reaction of the series to proceed.

Since these four reactions proceed in series to constitute the overall reaction, the total number of possible reaction paths for the overall reaction is (6)(6)(6)(6) or 1296.

In the light of the strong chemisorption exhibited between the nitrogen-containing compounds and the cobalt-molybdate catalyst, it is very probable that these compounds react in the adsorbed phase from a single site. This would cut the total number of possible reaction-paths from 1296 to $(3)^4$, or 81.

As indicated above, an adsorbed nitrogen-containing compound may react with hydrogen in three different ways. It is quite unlikely that the manner in which an adsorbed nitrogen-containing compound reacts with hydrogen is different for each of the four reactions of the overall-reaction framework. Thus, the total number of possible reaction-paths would be reduced to $(3)^1$, or 3.

Surface-reaction mechanisms for each of these three possible ways for hydrogen to react with the adsorbed nitrogen-compounds will be presented, and rate equations based on the surface-rate-equation theory will be derived for all possible rate-controlling steps of each of these three mechanisms.

4. Surface Mechanism for Adsorbed Nitrogen-Compounds and Gaseous Hydrogen

On the basis of evidence which was presented earlier in this discussion, the complex-series reaction-mechanism for the reaction of adsorbed nitrogen-compounds with gaseous hydrogen could be postulated according to the following six steps:

1. $Q + s \rightleftharpoons Qs$

2. $Qs + H_2 \rightleftharpoons Ds$

3. $Ds + H_2 \rightleftharpoons Ts$

4. $Ts + H_2 \rightleftharpoons Rs$

5. $Rs + H_2 \rightleftharpoons B + As$

6. $As \rightleftharpoons A + s$

$Q + 4H_2 \rightleftharpoons A + B$

This reaction series is initiated by the chemisorption of a quinoline molecule by an active site on the catalyst surface. The

chemisorbed quinoline then reacts with gaseous hydrogen to give a molecule of chemisorbed dihydroquinoline. This same reaction procedure is followed in steps 3, 4, and 5. The reaction products from step 5, however, are gaseous alkyl-benzene and chemisorbed ammonia. The chemisorbed ammonia then desorbs to give gaseous ammonia and a vacant site. The sum of these six individual steps gives the overall reaction of quinoline plus four hydrogen molecules to yield ammonia and alkyl benzene.

Rate equations and corresponding equilibrium constants for each of these six chemical steps are presented in Table I. If the rate of one of these steps were slower than those of the others, this step would control the rate of the overall reaction. The cases for each of these steps being the rate-controlling step have been considered and rate equations for the overall reaction have been derived. The kinetic terms, potential terms, and adsorption terms for these derived equations are presented in Table I. These equations were derived in the same manner as those for the example mechanism in section 0 of this discussion. Table I is presented in enough detail such that these derivations can be followed without too much difficulty.

The four diffusional steps which are involved with catalytic, vapor-phase reactions were shown earlier to be non-controlling of the overall reaction-rate. It was therefore assumed that the

diffusion resistances were negligible and that bulk-fluid concentrations were the same as those at the gas-catalyst interface.

Since it was shown that the active principle of the catalyst functioned as an acid, it was assumed that the nitrogen-containing compounds were chemisorbed to active sites of the catalyst via the nitrogen atom of the molecule. This explains why the products of step 5 are gaseous alkyl-benzene and chemisorbed ammonia.

5. Surface Mechanism for Adsorbed Nitrogen-Compounds and Adsorbed Molecular Hydrogen

Evidence which has been discussed earlier enables the postulation of a mechanism for adsorbed nitrogen-compounds of the reaction framework reacting with adsorbed molecular-hydrogen. This postulated mechanism can be written according to the following eight steps:

1. $Q + s \rightleftharpoons Qs$

2. $H_2 + s \rightleftharpoons H_2s$ (4 identical equations)

3. $Qs + H_2s \rightleftharpoons Ds + s$

4. $Ds + H_2s \rightleftharpoons Ts + s$

5. $Ts + H_2s \rightleftharpoons Rs + s$

6. $Rs + H_2s \rightleftharpoons Bs + As$

7. $Bs \rightleftharpoons B + s$

8. $As \rightleftharpoons A + s$

$$Q + 4H_2 \rightleftharpoons B + A$$

The reaction series is initiated by chemisorption of quinoline and by chemisorption of hydrogen on active sites of the catalyst. Chemisorbed quinoline reacts with chemisorbed hydrogen to give chemisorbed dihydroquinoline and a vacant site. This same type of reaction procedure is followed in steps 4, 5, and 6, with the reaction products from step 6 being chemisorbed alkyl-benzene and chemisorbed ammonia. These two products then desorb to give gaseous alkyl-benzene and gaseous ammonia as products. Steps 7 and 8 also provide two regenerated active-sites.

Those assumptions necessary for the surface-rate-equation theory and the assumptions made in section 4 above, were also utilized in the postulation of this mechanism.

The rate equations for each controlling case of this mechanism were derived and are presented in detail in Table II.

6. Surface Mechanism for Adsorbed Nitrogen-Compounds and Adsorbed Atomic-Hydrogen

In a manner similar to that used in sections 4 and 5 above, a complex-series reaction-mechanism for the reaction of the adsorbed

nitrogen compounds of the reaction framework with adsorbed atomic-hydrogen can be postulated. This mechanism would consist of the following nine steps:

1. $Q + s \rightleftharpoons Qs$

2. $H_2 + s \rightleftharpoons H_2s$ (4 identical equations)

3. $H_2s + s \rightleftharpoons 2Hs$ (4 identical equations)

4. $Qs + 2Hs \rightleftharpoons Ds + 2s$

5. $Ds + 2Hs \rightleftharpoons Ts + 2s$

6. $Ts + 2Hs \rightleftharpoons Rs + 2s$

7. $Rs + 2Hs \rightleftharpoons Bs + As + s$

8. $Bs \rightleftharpoons B + s$

9. $As \rightleftharpoons A + s$

$Q + 4H_2 \rightleftharpoons B + A$

This reaction is initiated by the chemisorption of quinoline and hydrogen and by the dissociation of chemisorbed hydrogen to give chemisorbed atomic-hydrogen.

Steps 4, 5, 6, and 7 involve the reaction of an adsorbed nitrogen-compound with two adjacent, adsorbed atomic-hydrogens. This situation is similar to that of a liquid-phase or a gas-phase

reaction of tri-molecularity. The reaction theory which postulates the collision of three particles to form an activated complex for a termolecular reaction states that termolecular reactions are improbable. A collision between three particles would take place much less readily than a collision between two. The only termolecular reactions which would be likely to proceed at a measurable rate would be these which involve fairly low activation energies (22).

Reaction steps 4, 5, 6, and 7 would involve a tri-site interaction which would seem far less probable than a reaction involving a single site or dual sites. The argument here would be much the same as that with the termolecular reactions mentioned above. Furthermore, the tri-site interaction would be confined to a two-dimensional surface.

For these reasons, the mechanism for the reaction of adsorbed nitrogen-compounds with adsorbed atomic-hydrogen was considered to be less probable than the mechanisms involving adsorbed molecular-hydrogen or gaseous hydrogen, and overall rate-expressions for the assumptions of each step controlling the reaction mechanism were not derived for this mechanism.

R. Analysis of Initial-Rate Data

Equations for the initial reaction-rate (the reaction rate at $W/F = 0$) as a function of the total system-pressure can be derived for each rate-controlling case of each mechanism. The method for doing this was outlined in section P of this discussion. The equations for the initial reaction-rate as a function of pressure at constant temperature and at constant initial-composition of the reactants are presented in Tables I and II. The equations for the rate-controlling cases of the mechanism with gaseous hydrogen are presented in Table I and the equations for the rate-controlling cases of the mechanism with adsorbed molecular-hydrogen are presented in Table II.

The typical curves for the equations of initial reaction-rate vs. pressure for the mechanism involving gaseous hydrogen are presented in Figure 7. These curves fall into three main types; a type for the adsorption of quinoline, or step 1 controlling; a type for the actual surface-reactions, or steps 2, 3, 4, or 5 controlling; and a type for the desorption of ammonia, or step 6 controlling.

In the type for the adsorption of quinoline controlling, the initial rate increases with pressure to a maximum asymptotic value. In the type representing the actual-surface reaction controlling, the initial rate is proportional to the square of the pressure at low pressures and approaches proportionality to the first power of the pressure at higher pressures. In the type for the desorption of ammonia controlling, the initial rate is independent of pressure.

The initial reaction-rate vs. pressure curve for the cobalt-molybdate hydrogenolysis of quinoline-constituted, synthetic shale-oil, containing 2 wt% nitrogen, at 830°F is presented in Figure 13. If the mechanism involving gaseous hydrogen is the true mechanism for this reaction, the comparison of this curve with the curves for the six controlling cases of the mechanism which involves gaseous hydrogen indicates that the rate controlling step would be the adsorption of quinoline.

The initial rate in terms of pressure for this case is:

$$r_o = \frac{aP}{(1 + bP)}$$

This can be arranged into a linear form where r_o is a function of r_o/P:

$$r_o = -(1/b)(r_o/P) + (a/b)$$

A plot of the experimental, initial-rate data in this form should give a straight line if this data is of the form for the rate-controlling step being the adsorption of quinoline. This plot is illustrated in Figure 14. The data does conform fairly well to the straight-line form.

The initial-rate data and rate data for other values of W/F which are utilized in this report were determined by the tangentiometer method from large, accurately-drawn curves of fractional conversion of quinoline vs. W/F. While there is some error in this method, empirical equations

could not be found which would fit the experimental conversion-data accurately. Rates determined from ill-fitting empirical equations would involve more error than those determined by the tangentiometer method.

The typical curves for the equations of initial reaction-rate vs. pressure for the mechanism which involves adsorbed molecular-hydrogen are presented in Figure 8. These curves exhibit four main types: a type for the adsorption of quinoline or the adsorption of hydrogen, or steps 1 or 2 controlling; a similar type for the reaction of adsorbed quinoline with adsorbed hydrogen, or step 3 controlling; a type for the other actual surface-reactions, or steps 4, 5, or 6 controlling; and a type for the desorption of alkyl benzene or ammonia, or steps 7 or 8 controlling.

In the type for the adsorption of quinoline or of hydrogen controlling, the initial rate increases with pressure to a maximum asymptotic value. The type for the quinoline-hydrogen reaction controlling is indicated by the dashed-line deviation from the first-mentioned type in Figure 8. In this type, the initial rate is proportional to the square of the pressure at low pressures but then for higher pressures, increases with pressure to a maximum asymptotic value. With the type for the other three actual surface-reactions controlling, the rate increases with pressure to a maximum value and then diminishes with further increase in pressure to a constant asymptotic value. The initial rate, in the type for the desorption of alkyl-benzene or of ammonia

controlling, is independent of pressure.

The form of the initial rate equations for steps 1 or 2 controlling is identical with that for step 1 controlling in the mechanism involving gaseous hydrogen. Since the experimental, initial-rate data appear to fit this form fairly well, either the adsorption of quinoline or the adsorption of hydrogen could be rate controlling if the mechanism which involves adsorbed molecular-hydrogen is the true mechanism for the reaction.

It is also possible that step 3 could be rate controlling since the curve for step 3 is of the same general shape as the experimental curve, and the lack of initial-rate data at pressures lower than 250 psig might not indicate the irregularity which is exhibited by the initial portion of this curve.

Initial reaction-rate vs. pressure curves for the cobalt-molybdate hydrogenolysis of Penetek-quinoline, synthetic shale-oil, containing one wt% nitrogen, at temperatures of 725, 750, and 775°F were obtained by Ryffel (31). These curves are presented in Figure 13b. Visual inspection of these curves indicates that the initial rate is some power function of pressure for the low pressure range and that it approaches proportionality to the first power of pressure at higher pressures.

If these curves are compared with the initial-rate curves of Figures 7 and 8, certain indications involving both the gaseous hydrogen mechanism

and the adsorbed molecular-hydrogen mechanism become evident. Comparison of these lower-temperature initial-rate curves of Ryffel with those of Figure 7 indicate that the mechanism which involves gaseous hydrogen could be applicable, with step 2, 3, 4, or 5, one of the actual surface reaction steps, being rate controlling. These same initial-rate curves of Ryffel, when compared with the initial-rate curves of Figure 8, indicate that the mechanism involving adsorbed molecular-hydrogen might also be applicable to the lower temperature reaction. For this case, one of the actual surface reaction steps, 3, 4, 5, or 6, could be the rate controlling step.

The use of the experimental initial-rate curves alone did not allow either of the two mechanisms which were under consideration to be chosen as the proper representative mechanism, either for the reaction at 830°F which was studied by the author, or for the lower-temperature reactions at 725-775°F which were studied by Ryffel.

For the lower-temperature reactions, however, these initial rate curves did strongly indicate that, no matter which mechanism is applicable, steps involving the adsorption of reactants or the desorption of products are probably not rate controlling; and that one of the actual surface reaction steps is probably the rate-controlling step.

The equations which represent the initial-rate curves for the actual surface reaction steps could be rearranged into linear form, and the experimental initial-rate data for the lower-temperature reactions could

then be plotted in this form and observed. This technique could serve to further eliminate certain of these steps as rate controlling steps. These equations, however, involved up to five arbitrary constants, and sufficient experimental data was not available to thoroughly apply this technique.

For the reaction at 830°F, as stated previously, the experimental initial-rate curve did not allow a distinction between the two mechanisms which were being considered. However, it did indicate that desorption of the reaction products or that one of the actual surface reaction steps, with the possible exception of step 3, for the adsorbed molecular-hydrogen mechanism, was probably not the rate-controlling step for the reaction. It also indicated that the adsorption of quinoline for either mechanism was probably the rate-controlling step. There was an indication that the adsorption of hydrogen for the mechanism involving adsorbed molecular-hydrogen might also be the rate-controlling step. The extremely large excess of hydrogen that was used for the reaction would, however, render this later indication doubtful, since hydrogen would always be in ample supply.

S. Analysis of Conversion Data

The effect of conversion on the reaction rate could be studied by obtaining a family of curves for reaction rate vs. pressure at constant temperature and initial nitrogen-concentration, with the parameters being fractional conversion. Or it could be studied by obtaining a family

of curves for reaction rate vs. initial nitrogen-content at constant temperature and pressure, with the parameters being fractional conversion.

In addition to these, useful information about the mechanism can often be obtained by plotting the reaction rate against conversion at constant temperature and pressure (40). For a mechanism where adsorption is controlling the reaction rate, with both the reactants and the products being adsorbed, this type of curve, in general, will be concave downward. For a mechanism where the surface reaction is controlling the reaction rate, or for a mechanism where the adsorption of one reactant is controlling the reaction rate when the other reactant is not adsorbed, this type of curve, in general, will be concave upward.

Plots of reaction rate vs. conversion for the reaction at 830°F and for the reaction at 725°F are presented in Figure 15. The curves for the reaction at 830°F exhibit a downward concavity. The curve for the reaction at 725°F exhibits an upward concavity.

The downward concavity exhibited by these curves for the reaction at 830°F indicates that the mechanism for adsorbed nitrogen-compounds and adsorbed molecular-hydrogen is probably applicable at this temperature, and that the adsorption of either quinoline or hydrogen is rate controlling. This is in agreement with the indications of the initial reaction-rate data for this temperature as discussed in the previous section.

The upward concavity exhibited by the curve for the reaction at 725°F indicates that one of the actual surface-reactions is probably rate controlling at this temperature, or that a mechanism where the adsorption of one reactant is controlling the reaction rate when the other reactant is not adsorbed is applicable at this temperature. The former indication agrees with the indications of the initial reaction-rate data for this temperature.

T. The Indicated Mechanism

For the cobalt-molybdate hydrogenolysis of quinoline-constituted, synthetic shale-oil, two reaction mechanisms were considered feasible: the complex-series reaction-mechanism for adsorbed nitrogen-compounds reacting with gaseous hydrogen and the complex series reaction-mechanism for adsorbed nitrogen-compounds reacting with adsorbed molecular-hydrogen. For the two temperature levels which were considered, 830°F and 725-775°F, the important indications from the previous two sections concerning the implied mechanisms for these two temperature levels are presented in the following table:

	Indications From Initial-Rate Data	Indications From Conversion Data
830°F	Gaseous H_2 Mech., Step 1 Controlling	Gaseous H_2 Mech., No Indications
	Adsorbed H_2 Mech., Steps 1, 2, or 3 Controlling	Adsorbed H_2 Mech., Steps 1 or 2 Controlling.

	Indications From Initial-Rate Data	Indications From Conversion Data
725-775°F	Gaseous H_2 Mech., Steps 2, 3, 4, or 5 Controlling.	Gaseous H_2 Mech., Steps 1, 2, 3, 4, or 5 Controlling.
	Adsorbed H_2 Mech., Steps 3, 4, 5, or 6 Controlling.	Adsorbed H_2 Mech., Steps 3, 4, 5, or 6 Controlling.

For the reaction at 830°F, this table indicates that the mechanism which is probably applicable is the complex-series reaction-mechanism for adsorbed nitrogen-compounds and adsorbed molecular-hydrogen. It also indicates that the rate-controlling step in this mechanism is either the adsorption of quinoline or the adsorption of hydrogen. However, as mentioned previously, the hydrogen was present in great excess. Using this fact, the most probable conclusion would be that the adsorption of quinoline is the rate controlling step for this reaction at 830°F.

Ryffel, in his study of the reaction at 725-775°F (31), used a combination of data at variable initial nitrogen content and at fixed initial nitrogen content, along with information gained from a thorough analysis of the reaction products and intermediates, to show that the applicable mechanism for the reaction at this lower temperature level was a dual-site mechanism involving absorbed molecular-hydrogen and adsorbed nitrogen compounds. Furthermore, he was able to show that the rate controlling step of the reaction mechanism was an actual surface reaction involving an adsorbed alkyl-aniline and adsorbed molecular-

hydrogen.

The indications in the above table do not enable an absolute differentiation as to which of the two mechanisms is applicable to the reaction for the lower temperature level, but with no evidence to the contrary, it would seem logical to assume that the same mechanism applied here, with the exception of the controlling step, as applied at the 830°F temperature level. The indications in this table are in agreement with Ryffel's findings that a mechanism involving adsorbed molecular-hydrogen is applicable and that one of the actual surface reactions is the rate-controlling step for the reaction mechanism.

The most significant indication of this table is that the rate-controlling step of the reaction mechanism changes from one of the actual surface reactions at the lower temperature level, to the adsorption of quinoline at the higher temperature level. This will be discussed in a following section.

U. Further Testing of the Indicated Mechanism

Many people have said that the primary goal of the scientific disciplines is the understanding of Nature, or more dramatically, complete comprehension and consciousness of the universe. This involves the establishment of absolute truths. Unfortunately, absoluteness of truth is apparently not intuitive.

In the last few centuries, the development of the scientific method of hypothesis-experimentation-observation and the formulation of systems of logic have enabled men to utilize their limited range of objective senses to systematically build up a body of apparent truths concerning the universe and its constituent substances. Although many or all of these apparent truths may not be absolute, men have been able to utilize this system of apparent truths to impress their will upon Nature.

One of the basic techniques in obtaining apparent truths about some part of the universe which has been set apart for study is that of visualizing a behavior-model of the system, a model which behaves in the same manner as the actual system. This model may or may not represent absolute actuality. The important consideration is whether or not the model represents the behavior of those properties of the actual system which are of interest for predicting the behavior of the actual system or for controlling the behavior of the actual system according to will.

More than one model may represent a given system. If this is the case, the problem is that of finding the one which best represents the behavior of the system.

In this thesis, a reaction system was considered. The surface-rate-equation theory was used to postulate feasible behavior-models for this system, behavior-model being synonymous with mechanism in this case. The analysis of initial-rate data and of conversion data

indicated which model probably best represented the behavior of the system. These analyses, however, only indicated the probable model and were not sufficient to establish that the indicated model truly represented the behavior of the actual reaction-system. To do this, the model must be given mathematical expression; the arbitrary constants in this expression must be evaluated; and the resulting expression must be shown to represent the behavior of the actual system.

The overall rate-equation based on the rate-controlling step of the indicated mechanism would be a mathematical expression of the behavior of the model or mechanism which represents the reaction system. For kinetic studies which are based on the gathering of experimental data from an integral reactor, the best method for determining the arbitrary constants in the rate expression and for comparing the resulting expression with the behavior of the actual reaction-system is as follows (14):

I. From the general expression for finding W/F for an integral reactor:

$$W/F \rightleftharpoons (m/m_t)(\text{integral})_0^X (1/r)dx$$

obtain expression for W/F for the particular mechanism being considered by substituting, for r, the rate expression that is to be tested.

2. Arrange W/F into the following form after integral operation and simplification:

$$W/F = af_1 + bf_2 + cf_3 + \ldots$$

where a, b, and c are arbitrary constants.

3. Determine the values of these constants from the experimental data by an appropriate mathematical method.

4. Plot this function determined by the values of the arbitrary constants and compare it with the experimental data, including those data which were not used in the determination of the constants. The goodness of fit tells how well the mechanism or model applies to the reaction system.

Essentially, this method considers the rate expression which has been dictated by the indicated mechanism to be an empirical equation. The constants in this equation are then determined from the experimental data and the resulting relation is compared with the experimental data for the goodness of fit.

The constants in the empirical equation are actually functions of the temperature and pressure of the system and are not constant except for a reaction system at fixed temperature and pressure. The rate equations that were derived from the two mechanisms considered feasible for the reaction system studied herein, involve a considerable number

of constants. The mathematical methods which are available for the determination of the constants of the empirical equation require a considerable amount of data at each fixed temperature and pressure, for a statistically reliable relation to be determined from the experimental data. The time limitation of this study did not permit the gathering of the large quantity of data that would be required. However, the empirical equation for the reaction system at 830°F and a given reaction-pressure can be arranged to involve only three arbitrary constants.

For the reaction system at 830°F, this study indicated that the rate expression which was probably the most applicable was that rate expression for the mechanism involving adsorbed molecular-hydrogen, with the adsorption of quinoline being the rate-controlling step. If this rate expression is substituted into the general expression for W/F for an integral reactor, the following expression for W/F in terms of the fractional conversion, x, is obtained:

$$W/F/ = a(\text{integral})_0^x (1 - x)^{-1}\, dx + b(\text{integral})_0^x (x)(1 - x)^{-1}\, dx + c(\text{integral})_0^x (x^2)(1 - x)^{-1}\, dx.$$

All three terms of the right member of this equation can be evaluated directly from fractional conversion data. The factors a, b, and c are functions of temperature and pressure, but they can be considered as constants for a reaction system at constant temperature and pressure.

This empirical equation was applied to the data for the reaction system at 830°F and 500 psig. Six, W/F vs. x, data points were available. Through use of the method of averages, the constants a, b, and c were determined such that the "best fit" of this empirical equation to the data was obtained. These constants are as follows:

$$a = 0.829$$

$$b = -2.829$$

$$c = -3.491$$

The empirical equation was used, with the above constants, to obtain a set of W/F values for a series of values for fractional conversion. These are tabulated, along with the observed or experimental values for W/F, in Table XI. The empirical curve was plotted and compared with the experimental data. This is illustrated in Figure 16.

The primary problem encountered in fitting an empirical equation to experimental data is that of choosing the proper form for the empirical equation. If the improper form is used, the error in the choice of form usually becomes evident when the calculated curve of the empirical equation is plotted along with the experimental or observed values. An empirical equation of the improper form, when "fitted" to experimental data, usually will not adhere to the experimental data in a satisfactory manner (24b).

In Figure 16, the goodness of fit of the empirical curve to the experimental data indicates offhandedly that the form of the empirical equation is probably the proper form. However, to insure absolutely that this is the case, it would be desirable to have, for checking purposes, a quantity of data in excess of that which was used in the determination of the constants. It is significant to note that the hand-drawn curve of Figure 10 closely approximates the empirical curve. This would tend to support the credibility of the empirical curve.

Since the form of the empirical curve was determined by the mechanism or model of the reaction system as indicated by the initial-rate data and by the conversion data, and since the empirical equation apparently fits the experimental data in a satisfactory manner, it was assumed that this gave further support to the acceptability of the indicated mechanism. Although data was not available in sufficient quantity to firmly establish this support, there is a very strong implication that the mechanism involving adsorbed nitrogen-compounds reacting with adsorbed molecular-hydrogen, in such a manner that the adsorption of quinoline is the rate-controlling step, can be used to represent the behavior of the reaction system at 830°F.

V. Analysis of the Indicated Mechanism

The results of the mechanism analyses to this point in the discussion have indicated that a complex-series reaction mechanism which involves the interaction of adsorbed nitrogen-compounds with adsorbed

molecular-hydrogen is applicable to the reaction. It was indicated that the rate-controlling step of this reaction mechanism is dependent upon the temperature level of the reaction. For the reaction at 830°F, the rate-controlling step is the adsorption of quinoline. For the reaction at 725-775°F, the rate-controlling step is one of the actual surface reactions.

The findings of Mills (26), which were presented in Section B, and data from the literature concerning the relative basicities of the nitrogen-containing compounds which are involved in the reaction can be utilized to explain the change in the rate-controlling step with temperature level and to decide which of the actual surface reaction steps is probably the rate-controlling step for the lower temperature level.

Mills stated that at constant pressure, an increase in temperature caused a decrease in the amount of chemisorbed quinoline. In other words, at adsorptive equilibrium between quinoline and an active metal-oxide catalyst, more quinoline is chemisorbed at a lower temperature and the same pressure. Pyridine was found to behave in a similar manner to quinoline. This would indicate that this type of behavior could be extended to other basic nitrogen-containing compounds. In addition, Mills found that the amount of a nitrogen-containing compound which was chemisorbed at a given temperature and pressure was directly proportional to its strength as a base.

For the higher-temperature reaction, the amount of adsorbed quinoline would be in short supply when compared to the amount of adsorbed quinoline which would be present for the lower-temperature reaction. This implies that the rate of adsorption of quinoline by the catalyst is more rapid at the lower temperature than at the higher temperature. Along with this effect, the rates of the actual surface reactions would increase with temperature. Thus, a situation exists in which the adsorption rate of quinoline diminishes with temperature and in which the reaction rates of the actual surface reaction steps increase with temperature. With increasing reaction temperature there must be a transition temperature at which the adsorption rate of quinoline becomes and remains slower than that of the slowest surface-reaction. This apparently occurs somewhere between 775°F and 830°F. Ryffel (31) was able to show that the reaction for the lower temperature level followed pseudo first-order kinetics. He did gather a small amount of data at 800°F, and he found that this data did not conform to the first-order pattern. Hence the temperature transition point for the changeover in the rate-controlling step is probably nearer to 775°F than to 830°F.

For the lower-temperature reaction, where one of the consecutive surface-reactions would be rate-controlling, the analyses of the previous sections of this discussion did not show which of these reactions was the slowest and hence the rate-controlling reaction. Extending Mills' findings to the nitrogen-containing compounds which are involved in the surface reactions, it can be stated that the most basic of these compounds

will be the most strongly adsorbed, and hence, the greater the basicity, the greater will be the amount of a given compound found in the adsorbed state. Since the reaction rate for a given compound is directly proportional to the amount of that compound in the adsorbed state, it would follow from the previous statement that the reaction rate for that compound is also proportional to its strength as a base. Thus, the least basic of the nitrogen-containing reaction-intermediates would control the overall reaction-rate for the lower-temperature reaction.

The nitrogen-containing compounds involved here are tabulated below, along with those pK_a values which could be found in the literature (1a):

Compound	pK_a
quinoline	4.9
dihydro quinoline	?
tetrahydro quinoline	5.0
o-propyl aniline	?

From this table it can be seen that quinoline and tetrahydroquinoline have very close basic strengths, with the latter being the more basic. From structural considerations, the basic strength of dihydroquinoline can be deduced to be some value between these two values.

A pK_a value could not be found for o-propyl aniline, but the value for o-toluidine (o-methyl aniline) was found to be 4.4. If the pK_a values for quinoline and o-toluidine are converted to K_b values, they

are respectively 5.4×10^{-10} and 1.7×10^{-10}. Hence, quinoline is approximately three times as basic as o-toluidine.

In deciding whether o-propyl aniline is more or less basic than o-toluidine, the inductive and hyperconjugative effects of the methyl and propyl radicals can be considered. In this particular case, however, the latter effect would be more predominant (30). Hyperconjugation would tend to enhance the electron density of the nitrogen atom and hence would be a base-strengthening effect (1a). Since hyperconjugation would be greater with the methyl group than with the propyl group, o-propyl aniline should be a weaker base than o-toluidine. Although o-propyl aniline is probably the weaker of these two bases, the difference is probably quite small. Thus, quinoline should have approximately three times the basic strength of o-propyl aniline. This statement could also be made for the dihydro- and tetrahydro-quinolines since they are approximately of the same basic strength as quinoline. Hence, o-propyl aniline, being three times less basic than the other intermediates, should control the rate of the reaction at the lower temperature level.

This same postulation was advanced by Ryffel for the reaction at the lower temperature level (31). Through analysis of the product oil by gas chromatography, he was able to show that at 50% conversion most of the nitrogen in the product oil is present as o-propyl aniline.

VI. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

The hydrofining of shale-oil distillates appears to be the most promising method for upgrading these distillates prior to their subsequent processing into commercially satisfactory fuels. The hydrofining process involves hydrogenolysis of the distillate in the presence of a suitable catalyst, one of which has been cobalt molybdate. Hydrogenolysis of the distillate promotes the removal of organically combined oxygen, sulfur, and nitrogen from the distillate. Of these, nitrogen has proven to be the most difficult to remove. A great deal of investigative activity has been directed to this problem over the last fifteen years. Kinetic studies in the area of this problem have been limited in scope because of the large number of heterocyclic nitrogen-compounds which are present in the shale-oil distillates.

The objective of this particular investigation was to gain information about the cobalt-molybdate hydrogenolysis of a quinoline-constituted synthetic shale-oil. It was hoped that a kinetic study of a synthetic shale-oil which contained only one of the typical heterocyclic nitrogen-compounds which are found in the shale-oil distillates would lead to significant fundamental information concerning the behavior of these nitrogen-containing compounds during hydrofining treatment, and would enable the circumventing of the experimental difficulties which are encountered with the actual shale-oil distillates because of the greater number of different nitrogen-containing compounds which these distillates contain.

A bench scale, fixed bed, flow type, catalytic reactor was used for this study. The time factor (W/F) was determined by fixing the mass flow-rate of charge stock over a fixed mass of catalyst. The conversion of heterocyclic nitrogen to ammonia for a given set of operating conditions was determined through analysis of the product oil for nitrogen content by the Kjeldahl method. The flow rate of hydrogen to the reactor was maintained at 7500 SCF per barrel of charge stock. The reaction temperature for all studies was maintained at 830°F, and 1/8" Peter Spence cobalt-molybdate pellets, containing 2.5% CoO and 14.0% MoO_3, were used as the catalyst. The treat gas was 100% hydrogen. Conversion data for various values of W/F were determined at reaction pressures of 250, 500, and 1000 psig.

A number of runs were completed prior to the gathering of the main body of experimental data. These preliminary runs determined a satisfactory operating procedure and permitted the redesigning of certain aspects of the reactor system.

Information concerning the chemisorptive behavior of heterocyclic nitrogen-compounds and concerning the reaction products of the hydrogenolysis of quinoline was presented and was utilized to develop several important indications about the framework of the reaction mechanism for the cobalt-molybdate hydrogenolysis of quinoline-constituted synthetic shale-oil. With these indications, the following framework for the reaction mechanism was postulated:

1. quinoline + hydrogen $\rightleftharpoons$ dihydroquinoline
2. dihydroquinoline + hydrogen $\rightleftharpoons$ tetrahydroquinoline
3. tetrahydroquinoline + hydrogen $\rightleftharpoons$ alkyl-aniline
4. alkyl-aniline + hydrogen $\rightleftharpoons$ alkyl-benzene + ammonia

Rate-equation theories for fluid-phase reactions catalyzed by solids were presented and discussed. An example derivation of a rate equation by the surface-rate-equation method was presented, and the use of this method for determining the mechanism or model of a given reaction system was subsequently discussed.

Using the above-postulated framework for the mechanism of the reaction system as a guide, the possible reaction paths for this reaction system were analyzed. The surface-rate-equation method was applied to these, and overall rate-equations, which were based on the various rate-controlling steps for each mechanism, were derived for the most feasible of these mechanisms.

Conversion data and initial-rate data for the reaction system at 830°F and various pressures were analyzed in conjunction with the rate equations which represented the various mechanisms. The results of this analysis indicated that the following complex-series reaction-mechanism probably best represents the behavior of the reaction system at 830°F:

1. quinoline + active site $\rightleftharpoons$ adsorbed quinoline
2. hydrogen + active site $\rightleftharpoons$ adsorbed molecular-hydrogen
3. adsorbed quinoline + adsorbed molecular-hydrogen
   $\rightleftharpoons$ adsorbed dihydroquinoline + active site
4. adsorbed dihydroquinoline + adsorbed molecular-hydrogen
   $\rightleftharpoons$ adsorbed tetrahydroquinoline + active site
5. adsorbed tetrahydroquinoline + adsorbed molecular-hydrogen
   $\rightleftharpoons$ adsorbed alkyl-aniline + active site
6. adsorbed alkyl-aniline + adsorbed molecular-hydrogen
   $\rightleftharpoons$ adsorbed alkyl-benzene + adsorbed ammonia
7. adsorbed alkyl-benzene $\rightleftharpoons$ alkyl-benzene + active site
8. adsorbed ammonia $\rightleftharpoons$ ammonia + active site

The rate-controlling step of this reaction mechanism was indicated as being the adsorption of quinoline.

Whether or not this mechanism would serve as a model for the behavior of the reaction system was decided by using the rate expression for this mechanism as an empirical equation, by then determining the arbitrary constants for this equation from the experimental data at 830°F and 500 psig, and by next analyzing the goodness of fit of this equation to the experimental data at 830°F and 500 psig. The goodness of fit and the nature of the curve pointed out that the above indicated mechanism would be used to represent the behavior of the reaction system at 830°F.

Other data which had been gathered at Montana State College for this same reaction system, but at a lower temperature level of 725-775°F, were applied to the rate equations for the mechanisms which were considered in this study. Analysis of conversion data and of initial-rate data indicated that the same complex-series reaction mechanism which is applicable to the system at 830°F is also applicable to the system at this lower temperature level. However, it was found that the rate-controlling step for the lower temperature reaction system was not the adsorption of quinoline but was one of the actual surface-reaction steps. Through deductive reasoning based on facts from the literature concerning the reaction intermediates, this rate-controlling step was indicated to be the dual-site reaction of o-propyl aniline with molecular-hydrogen.

Two significant results have arisen from this investigation. First, it has been shown that a complex-series reaction mechanism involving the series reactions of quinoline to dihydro-quinoline to tetrahydro-quinoline to alkyl-aniline to alkyl-benzene and ammonia, and involving dual-site reactions of quinoline and the intermediates with molecular hydrogen, can be satisfactorily used to represent the behavior of the reaction system. Secondly, it has been shown that a transition temperature exists at which the rate-controlling step of the reaction mechanism changes from one of the actual surface reactions controlling to the adsorption of quinoline controlling. This temperature for the quinoline reaction-system lies between 775°F and 830°F.

Of engineering significance, the overall rate-equation, or the mathematical expression, for this model can be used in conjunction with the general expression for the time factor (W/F) to obtain an expression for W/F in terms of a series of functions of the fractional conversion of quinoline to ammonia. These functions have coefficients which themselves are functions of the reaction temperature and pressure. Once these coefficients have been determined the W/F equation can be used for the design of all types of reactors.

It was not the objective of this work, however, to obtain a design equation for the reaction system that was studied herein. A behavior model for a system can also be used as a basis for reasoning. That is, as a basis for prediction of the behavior of the system under various conditions of restraint. And according to the principles of similarity, the model for this system could be used as a basis for conjectural prediction of the behavior of other similar systems. It is in this respect that the results of this particular investigation could be of some use in understanding the reaction system for shale-oil distillate, which contains a variety of heterocyclic nitrogen-compounds other than quinoline.

The model which the results of this study indicated was applicable to the reaction system for the cobalt-molybdate hydrogenolysis of quinoline-constituted synthetic shale-oil may not be the only model which can be used to respresent the behavior of this reaction system.

It is possible that some approach other than that used in this study may lead to a different model for representing the behavior of the system. And it is in no way implied that the model which was obtained through the results of this study is the actual working of Nature. The only claim made is that this model or mechanism appears to be suitable for representing the behavior of the reaction system.

It is suggested that this research be continued. Other heterocyclic nitrogen-compounds which are found in the shale-oil distillates could be studied. Eventually a body of knowledge concerning the behavior of these compounds would be accumulated. This body of knowledge could then be utilized to aid in the more efficient recovery of usable products from the vast deposits of oil-shale which are predicted to become increasingly important as the production of crude oil becomes more costly.

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IX APPENDIX

APPENDIX - cont.

APPENDIX - cont.

Notation

A	ammonia
As	ammonia chemisorbed on an active site
B	alkyl benzene
Bs	alkyl benzene chemisorbed on an active site
C	alkyl cyclohexane
°C	centigrade degrees
D	dihydroquinoline
Ds	dihydroquinoline chemisorbed on an active site
F	total feed rate, mass/time
°F	Fahrenheit degrees
H_2s	molecular hydrogen chemisorbed on an active site
K	overall equilibrium constant
K_j	equilibrium constant; j defined in relation to other equilibrium constants
M_j	molecular weight, component j
P	total system pressure
P_j	equilibrium partial pressure of component j
Q	quinoline
Qs	quinoline chemisorbed on an active site
R	alkyl aniline
Rs	alkyl aniline chemisorbed on an active site
SCF	standard cubic feet
T	tetrahydroquinoline

Notation - cont.

Ts	tetrahydroquinoline chemisorbed on an active site
W	mass catalyst
W/F	time factor, (mass catalyst)(hr)/mass feed
a	a constant
atmg	atmospheres gauge
b	a constant
bbl	barrel
c	a constant
d	a constant
e	a constant
f	a constant
f_j	fraction of active sites covered by component j
f_s	fraction of vacant active sites
gm	gram
hr	hours
i	components inert to the reaction
k_j	forward-reaction rate-constant, step j
k'_j	reverse-reaction rate-constant, step j
m	mass nitrogen in feed
m_N	mass unreacted nitrogen in system
m_t	total mass of feed

Notation - cont.

psia	pounds per square inch absolute
psig	pounds per square inch gauge
r	reaction rate, mass nitrogen/(mass catalyst)(time)
r_o	initial reaction rate, mass nitrogen/(mass catalyst)(time)
s	active site
t	time
wt%	weight per cent
x	fractional conversion, mass nitrogen converted/initial mass nitrogen in feed
x'	fractional conversion, mass nitrogen converted/mass feed
z	initial mass fraction nitrogen in feed

TABLE I

COMPLEX-SERIES REACTION-MECHANISM ADSORBED NITROGEN-COMPOUNDS AND GASEOUS HYDROGEN

Mechanism	Rate Equations	Equilibrium Constants
1. $Q + s \rightleftharpoons Qs$	$r_1 = k_1 P_Q f_s - k_1' f_Q$	$K_1 = \frac{f_Q}{P_Q f_s}$
2. $Qs + H_2 \rightleftharpoons Ds$	$r_2 = k_2 P_{H_2} f_Q - k_2' f_D$	$K_2 = \frac{f_D}{P_{H_2} f_Q}$
3. $Ds + H_2 \rightleftharpoons Ts$	$r_3 = k_3 P_{H_2} f_D - k_3' f_T$	$K_3 = \frac{f_T}{P_{H_2} f_D}$
4. $Ts + H_2 \rightleftharpoons Rs$	$r_4 = k_4 P_{H_2} f_T - k_4' f_R$	$K_4 = \frac{f_R}{P_{H_2} f_T}$
5. $Rs + H_2 \rightleftharpoons B + As$	$r_5 = k_5 P_{H_2} f_R - k_5' P_B f_A$	$K_5 = \frac{P_B f_A}{P_{H_2} f_R}$
6. $As \rightleftharpoons A + s$	$r_6 = k_6 f_A - k_6' P_A f_s$	$K_6 = \frac{P_A f_s}{f_A}$
(i) $i + s \rightleftharpoons is$	$r_i = k_i P_i f_s - k_i' f_i$	$K_i = \frac{f_i}{P_i f_s}$

TABLE I - cont.

Kinetic, Potential, and Adsorption Terms of the Overall Rate-Equations for Each Controlling Case

Step	Kinetic Term	Potential Term
1	k_1	$P_Q - \frac{P_A P_B}{K(P_{H_2})^4}$
2	$KK_Q k_2$	$P_Q P_{H_2} - \frac{P_A P_B}{K(P_{H_2})^3}$
3	$KK_D k_3$	$P_Q (P_{H_2})^2 - \frac{P_A P_B}{K(P_{H_2})^2}$
4	$KK_T k_4$	$P_Q (P_{H_2})^3 - \frac{P_A P_B}{K P_{H_2}}$
5	$KK_R k_5$	$P_Q (P_{H_2})^4 - \frac{P_A P_B}{K}$
6	$K_A k_6$	$KP_Q (P_{H_2})^4 - P_A P_B$

Definitions for the K's

$K = K_1 K_2 K_3 K_4 K_5 K_6$

$K_Q = 1/(K_2 K_3 K_4 K_5 K_6)$

$K_D = 1/(K_3 K_4 K_5 K_6)$

$K_T = 1/(K_4 K_5 K_6)$

$K_R = 1/(K_5 K_6)$

$K_A = 1/K_6$

TABLE I - cont.

Step	
1	$1 + K_i P_i + K_A P_A + \frac{K_R P_A P_B}{P_{H_2}} + \frac{K_T P_A P_B}{(P_{H_2})^2} + \frac{K_D P_A P_B}{(P_{H_2})^3} + \frac{K_Q P_A P_B}{(P_{H_2})^4}$
2	$1 + K_i P_i + K_A P_A + KK_Q P_Q + \frac{K_R P_A P_B}{P_{H_2}} + \frac{K_T P_A P_B}{(P_{H_2})^2} + \frac{K_D P_A P_B}{(P_{H_2})^3}$
3	$1 + K_i P_i + K_A P_A + KK_D P_Q P_{H_2} + \frac{K_R P_A P_B}{P_{H_2}} + \frac{K_T P_A P_B}{(P_{H_2})^2}$
4	$1 + K_i P_i + KK_Q P_Q + KK_D P_Q P_{H_2} + KK_T P_Q (P_{H_2})^2 + \frac{K_R P_A P_B}{P_{H_2}}$
5	$1 + K_i P_i + K_A P_A + KK_Q P_Q + KK_D P_Q P_{H_2} + KK_T P_Q (P_{H_2})^2 + KK_R P_Q (P_{H_2})^3$
6	$P_B + K_i P_i P_B + KK_Q P_Q P_B + KK_D P_Q P_B P_{H_2} + KK_T P_Q P_B (P_{H_2})^2 + KK_R P_Q P_B (P_{H_2})^3 + KK_A P_Q (P_{H_2})^4$

Exponent of Adsorption Terms: n = 1;
steps 1, 2, 3, 4, 5, 6

TABLE I - cont.

Initial Rate-Equations for Each Controlling Case

Step	Initial Rate-Equation
1	$r_o = \frac{aP}{1 + bP}$
2	$r_o = \frac{aP^2}{1 + bP}$
3	$r_o = \frac{aP^3}{1 + bP + cP^2}$
4	$r_o = \frac{aP^4}{1 + bP + cP^2 + dP^3}$
5	$r_o = \frac{aP^5}{1 + bP + cP^2 + dP^3 + eP^4}$
6	$r_o = a$

TABLE II

COMPLEX-SERIES REACTION-MECHANISM -- ADSORBED NITROGEN-COMPOUNDS AND MOLECULARLY-ADSORBED HYDROGEN

Mechanism	Rate Equations	Equilibrium Constants
1. $Q + s \rightleftharpoons Qs$	$r_1 = k_1 P_Q f_s - k_1' f_Q$	$K_1 = \frac{f_Q}{P_Q f_s}$
2. $H_2 + s \rightleftharpoons H_2s$ (4 identical equations)	$r_2 = k_2 P_{H_2} f_s - k_2' f_{H_2}$	$K_2 = \frac{f_{H_2}}{P_{H_2} f_s}$
3. $Qs + H_2s \rightleftharpoons Ds + s$	$r_3 = k_3 f_Q f_{H_2} - k_3' f_D f_s$	$K_3 = \frac{f_D f_s}{f_Q f_{H_2}}$
4. $Ds + H_2s \rightleftharpoons Ts + s$	$r_4 = k_4 f_D f_{H_2} - k_4' f_T f_s$	$K_4 = \frac{f_T f_s}{f_D f_{H_2}}$
5. $Ts + H_2s \rightleftharpoons Rs + s$	$r_5 = k_5 f_T f_{H_2} - k_5' f_R f_s$	$K_5 = \frac{f_R f_s}{f_T f_{H_2}}$
6. $Rs + H_2s \rightleftharpoons Bs + As$	$r_6 = k_6 f_R f_{H_2} - k_6' f_B f_A$	$K_6 = \frac{f_B f_A}{f_R f_{H_2}}$

TABLE II - cont.

Mechanism	Rate Equations	Equilibrium Constants
7. $Bs \rightleftharpoons B + s$	$r_7 = k_7 f_B - k_7' P_B f_s$	$K_7 = \frac{P_B f_s}{f_B}$
8. $As \rightleftharpoons A + s$	$r_8 = k_8 f_A - k_8' P_A f_s$	$K_8 = \frac{P_A f_s}{f_A}$
(i) $i + s \rightleftharpoons is$	$r_i = k_i P_i f_s - k_i' f_i$	$K_i = \frac{f_i}{P_i f_s}$

Definitions for the K's

$K = K_1 K_2^4 K_3 K_4 K_5 K_6 K_7 K_8$

$K_R = 1/(K_2 K_6 K_7 K_8)$

$K_Q = 1/(K_2^4 K_3 K_4 K_5 K_6 K_7 K_8)$

$K_B = 1/K_7$

$K_D = 1/(K_2^3 K_4 K_5 K_6 K_7 K_8)$

$K_A = 1/K_8$

$K_T = 1/(K_2^2 K_5 K_6 K_7 K_8)$

TABLE II - cont.

Kinetic, Potential, and Adsorption Terms of the Overall Rate-Equations for Each Controlling Case

Step	Kinetic Term	Potential Term
1	k_1	$P_Q = \frac{P_A P_B}{K(P_{H_2})^4}$
2	k_2	$P_{H_2} = \frac{(P_A P_B)^{1/4}}{(KP_Q)^{1/4}}$
3	$KK_Q K_2 k_3$	$P_Q P_{H_2} = \frac{P_A P_B}{K(P_{H_2})^3}$
4	$KK_D K_2 k_4$	$P_Q (P_{H_2})^2 = \frac{P_A P_B}{K(P_{H_2})^2}$
5	$KK_T K_2 k_5$	$P_Q (P_{H_2})^3 = \frac{P_A P_B}{KP_{H_2}}$
6	$KK_R K_2 k_6$	$P_Q (P_{H_2})^4 = \frac{P_A P_B}{K}$
7	$K_B k_7$	$KP_Q (P_{H_2})^4 = P_A P_B$
8	$K_A k_8$	$KP_Q (P_{H_2})^4 = P_A P_B$

TABLE II - cont.

Step	Adsorption Term
1	$1 + K_i P_i + K_A P_A + K_B P_B + K_2 P_{H_2} + (K_R + K_T + K_D + K_Q) P_A P_B$
2	$1 + K_i P_i + K_A P_A + K_B P_B + KK_Q P_Q + \frac{(P_A P_B)^{1/4}}{(KP_Q)^{1/4}} + K_R (KP_Q)^{1/4} (P_A P_B)^{3/4} +$ $K_T (KP_Q)^{1/2} (P_A P_B)^{1/2} + K_D (KP_Q)^{3/4} (P_A P_B)^{1/4}$
3	$1 + K_i P_i + K_A P_A + K_B P_B + K_2 P_{H_2} + \frac{K_R P_A P_B}{P_{H_2}} + \frac{K_T P_A P_B}{(P_{H_2})^2} + \frac{K_D P_A P_B}{(P_{H_2})^3} + KK_Q P_Q$
4	$1 + K_i P_i + K_A P_A + K_B P_B + K_2 P_{H_2} + KK_Q P_Q + KK_D P_Q P_{H_2} + \frac{K_R P_A P_B}{P_{H_2}} + \frac{K_T P_A P_B}{(P_{H_2})^2}$
5	$1 + K_i P_i + K_A P_A + K_B P_B + K_2 P_{H_2} + KK_Q P_Q + \frac{K_R P_A P_B}{P_{H_2}} + KK_D P_Q P_{H_2} + KK_T P_Q (P_{H_2})^2$
6	$1 + K_i P_i + K_A P_A + K_B P_B + K_2 P_{H_2} + KK_Q P_Q + KK_D P_Q P_{H_2} + KK_T P_Q (P_{H_2})^2 + KK_R P_Q (P_{H_2})^3$

TABLE II - cont.

Step	Adsorption Term
7	$P_A + K_1P_iP_A + K_A(P_A)^2 + K_2P_AP_{H_2} + KK_DP_AP_QP_{H_2} + KK_QP_AP_Q + KK_TP_AP_Q(P_{H_2})^2 + KK_RP_AP_Q(P_{H_2})^3 + KK_BP_Q(P_{H_2})^4$
8	$P_B + K_1P_iP_B + K_B(P_B)^2 + K_2P_BP_{H_2} + KK_QP_BP_Q + KK_DP_BP_QP_{H_2} + KK_TP_BP_Q(P_{H_2})^2 + KK_RP_BP_Q(P_{H_2})^3 + KK_AP_Q(P_{H_2})^4$

TABLE II - cont.

Initial Rate-Equations for Each Controlling Case

Step	Initial Rate Equation
1	$r_o = \frac{aP}{1 + bP}$
2	$r_o = \frac{aP}{1 + bP}$
3	$r_o = \frac{aP^2}{(1 + bP)^2}$
4	$r_o = \frac{aP^3}{(1 + bP + cP^2)^2}$
5	$r_o = \frac{aP^4}{(1 + bP + cP^2 + dP^3)^2}$
6	$r_o = \frac{aP^5}{(1 + bP + cP^2 + dP^3 + eP^4)^2}$
7	$r_o = a$
8	$r_o = a$

Exponent of Adsorption Terms: n = 1: steps 1, 2, 7, 8

n = 2: steps 3, 4, 5, 6

TABLE III

COMPLEX-SERIES REACTION MECHANISM

ADSORBED NITROGEN-COMPOUNDS AND ADSORBED ATOMIC-HYDROGEN

1. $Q + s \rightleftharpoons Qs$

2. $H_2 + s \rightleftharpoons H_2s$
(4 identical equations)

3. $H_2s + s \rightleftharpoons 2Hs$
(4 identical equations)

4. $Qs + 2Hs \rightleftharpoons Ds + 2s$

5. $Ds + 2Hs \rightleftharpoons Ts + 2s$

6. $Ts + 2Hs \rightleftharpoons Rs + 2s$

7. $Rs + 2Hs \rightleftharpoons Bs + As + s$

8. $Bs \rightleftharpoons B + s$

9. $As \rightleftharpoons A + s$

TABLE IV

FRACTION OF NITROGEN REMOVED -- 250 PSIG RUNS

Run No.	Space Velocity gm/gm-hr.	Fractional Conversion
34	10.0	0.125
27	7.5	0.119
22	5.0	0.157
21	2.5	0.353
26	1.0	0.548
26r	1.0	0.582
25	0.5	0.824

Uniform Operating Conditions

Pressure: 250 psig

Temperature: 830°F

100% Hydrogen, Flowing at: 7500 SCF/bbl

Catalyst: Peter Spence, 2.5% CoO, 14.0% MoO_3

Charge Stock: Penetek-Quinoline, 2 wt.% Nitrogen

TABLE V

FRACTION OF NITROGEN REMOVED -- 500 PSIG RUNS

Run No.	Space Velocity gm/gm-hr.	Fractional Conversion
37	10.0	0.159
16c	7.5	0.197
16b	5.0	0.355
18r	2.5	0.654
16a	1.0	0.880
7-24	0.5	0.926

Uniform Operating Conditions

Pressure: 500 psig

Temperature: 830°F

100% Hydrogen, Flowing at: 7500 SCF/bbl

Catalyst: Peter Spence, 2.5% CoO, 14.0% MoO_3

Charge Stock: Penetek-Quinoline, 2 wt% Nitrogen

TABLE VI

FRACTION OF NITROGEN REMOVED -- 1000 PSIG RUNS

Run No.	Space Velocity gm/gm-hr.	Fractional Conversion
36	10.0	0.270
19	2.5	0.779
14	1.0	0.899
15	1.0	0.904
4	0.5	0.933
23	0.5	0.938

Uniform Operating Conditions

Pressure: 1000 psig

Temperature: 830°F

100% Hydrogen, Flowing at: 7500 SCF/bbl

Charge Stock: Penetek-Quinoline, 2 wt% Nitrogen

Catalyst: Peter Spence, 2.5% CoO, 14.0% MoO_3

TABLE VII

REACTION-RATE DATA

(W/F)	r at 250 psig	r at 500 psig	r at 1000 psig
0.0	0.0227	0.0356	0.0533
0.2	0.0178	0.0340	0.0440
0.4	0.0124	0.0225	0.0153
0.6	0.0084	0.0095	0.0050
0.8	0.0070	0.0047	0.0012
1.0	0.0065	0.0014	0.0007
1.4	0.0055	0.0012	0.0007
2.0	0.0055	0.0008	0.0007

r = (gm nitrogen)/(gm catalyst-hr)

W/F = (gm catalyst-hr)/(gm oil)

Uniform Operating Conditions

Temperature: 830°F

100% Hydrogen, Flowing at: 7500 SCF/bbl

Catalyst: Peter Spence, 2.5% CoO, 14.0% MoO_3

Charge Stock: Penetek-Quinoline, 2 wt% Nitrogen

TABLE VIII

DATA FOR REACTION RATE VS. CONVERSION AT CONSTANT TEMPERATURE AND PRESSURE

250 psig		500 psig		1000 psig	
$r \cdot 10^2$	x	$r \cdot 10^2$	x	$r \cdot 10^2$	x
2.27	0.0	3.56	0.0	5.33	0.0
1.78	0.195	3.40	0.355	4.40	0.518
1.24	0.341	2.25	0.654	1.53	0.780
0.842	0.441	0.472	0.852	0.496	0.865
0.702	0.515	0.143	0.880	0.118	0.895
0.546	0.824				

x = fractional conversion of nitrogen

r = reaction rate, $\frac{\text{(gm nitrogen)}}{\text{(gm catalyst)(hr)}}$

Uniform Operating Conditions

Temperature: 830°F

100% Hydrogen, Flowing at: 7500 SCF/bbl

Catalyst: Peter Spence,
2.5% CoO, 14.0% MoO_3

Charge Stock: Penetek-Quinoline
2 wt% Nitrogen

TABLE IX

INITIAL REACTION-RATE DATA*, LOWER TEMPERATURES

Temperature, °F	Pressure, psig	$r_o \times 10^2$, $\frac{\text{(gm nitrogen)}}{\text{(gm catalyst)(hr)}}$
725	250	0.1033
725	500	0.2925
725	1000	0.821
750	250	0.1708
750	500	0.484
750	1000	1.223
775	250	0.294
775	500	0.772
775	1000	1.747

* Data from Ryffel (31).

Uniform Operating Conditions

100% Hydrogen, Flowing at: 7500 SCF/bbl

Catalyst: Peter Spence, 2.5% CoO, 14.0% MoO_3

Charge Stock: Penetek-Quinoline, 1.095 wt% Nitrogen

TABLE X

DATA FOR r_o vs. (r_o/P)

$r_o \cdot 10^2$, $\frac{\text{(gm nitrogen)}}{\text{(gm catalyst)(hr)}}$	$(r_o/P) \cdot 10^5$, $\frac{\text{(gm nitrogen)}}{\text{(gm catalyst)(hr)(psia)}}$
5.33	5.27
3.56	6.96
2.27	8.66

Uniform Operating Conditions

Temperature: 830°F

100% Hydrogen, Flowing at: 7500 SCF/bbl

Catalyst: Peter Spence, 2.5% CoO, 14.0% MoO_3

Charge Stock: Penetek-Quinoline, 2 wt% Nitrogen

TABLE XI

W/F vs. CONVERSION -- 830°F, 500 PSIG

x	W/F (Empirical)	W/F (Experimental)
0.0	0.0	
0.159		0.100
0.197		0.133
0.200	0.130	
0.355		0.200
0.400	0.220	
0.600	0.340	
0.654		0.400
0.800	0.752	
0.880		1.000
0.900	1.424	
0.926		2.000
1.000	∞	

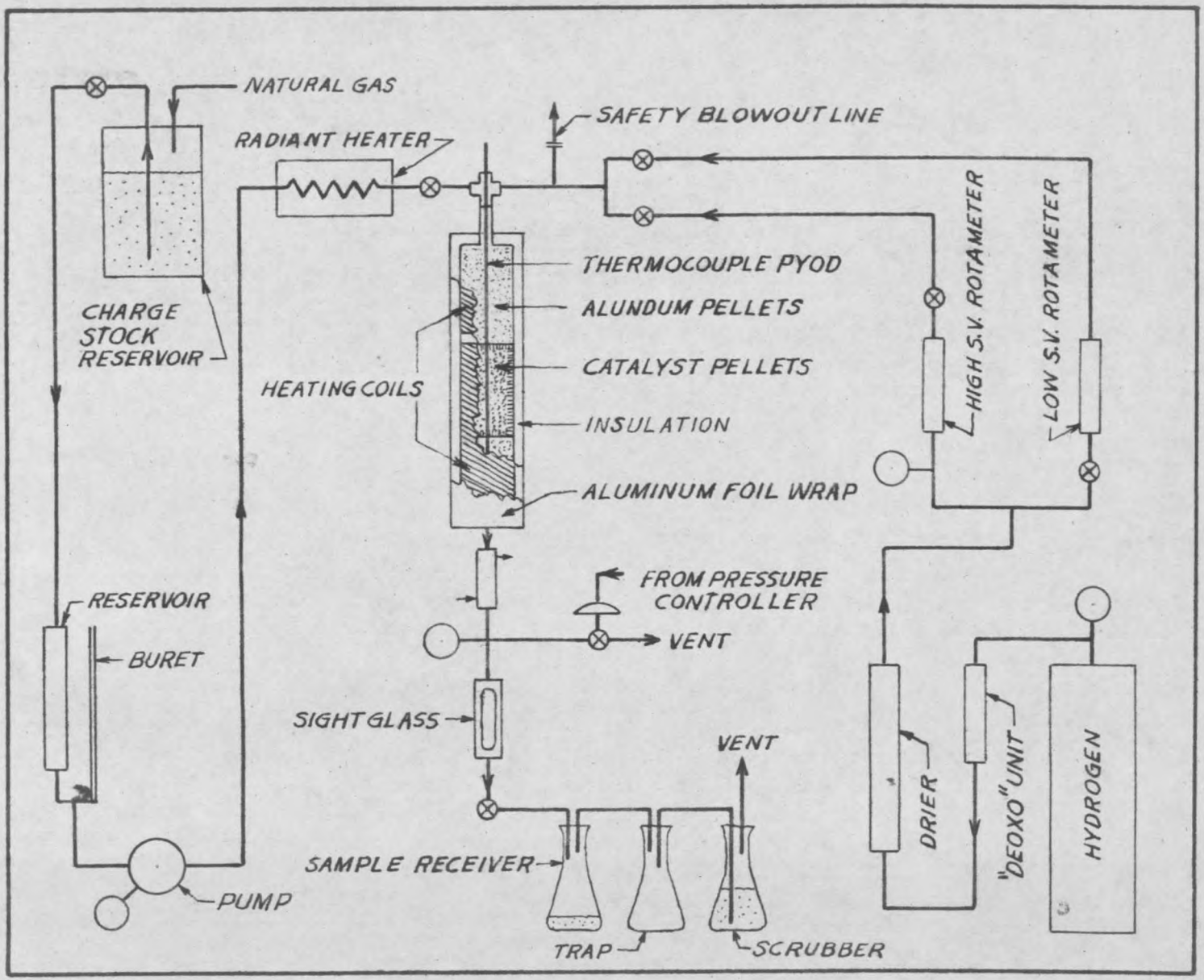


Figure 1. Schematic Diagram of the Reactor System

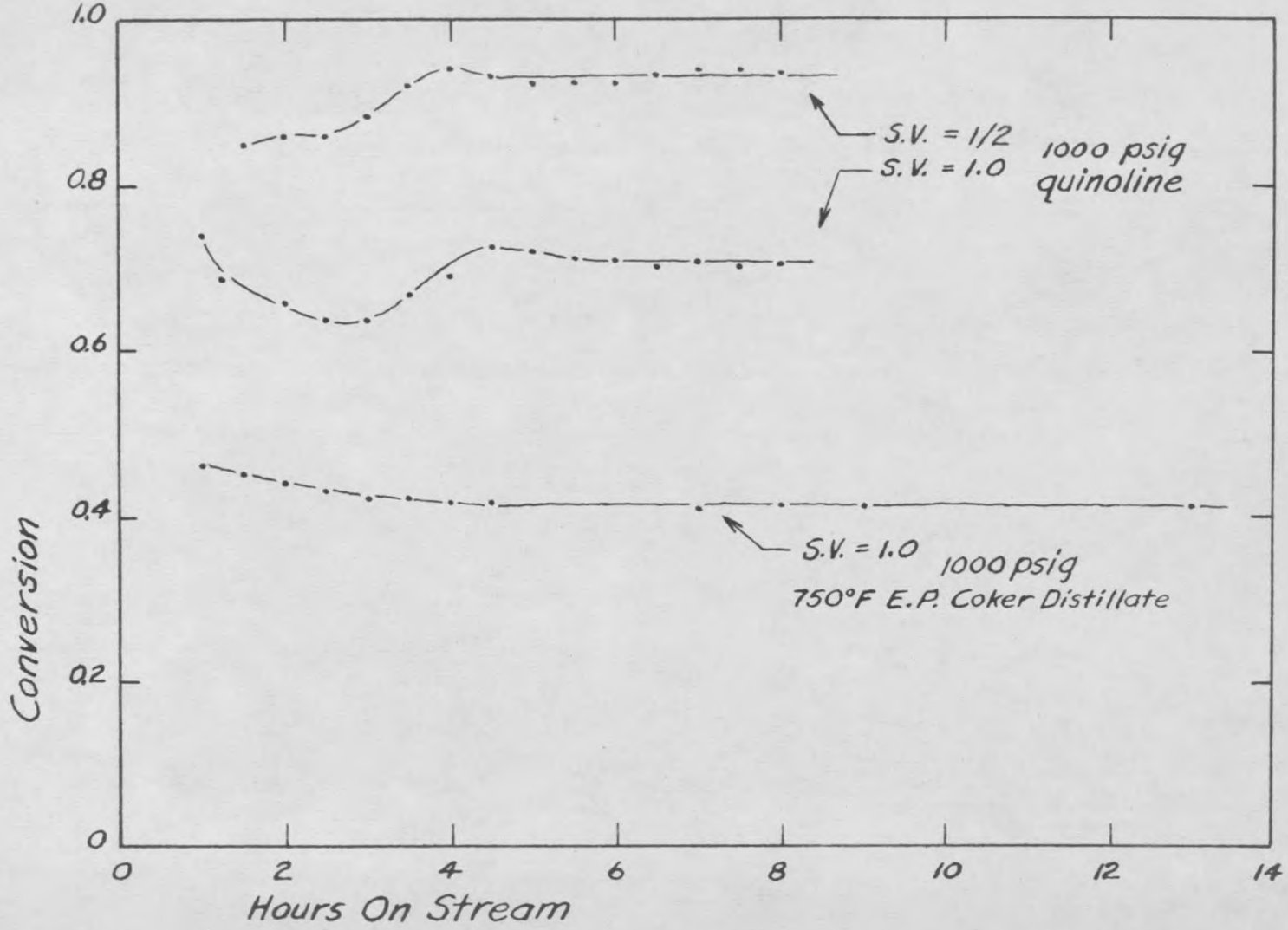


Figure 2. Graphs Illustrating Line-Out-Time with Quinoline and with Shale-Oil Coker-Distillate

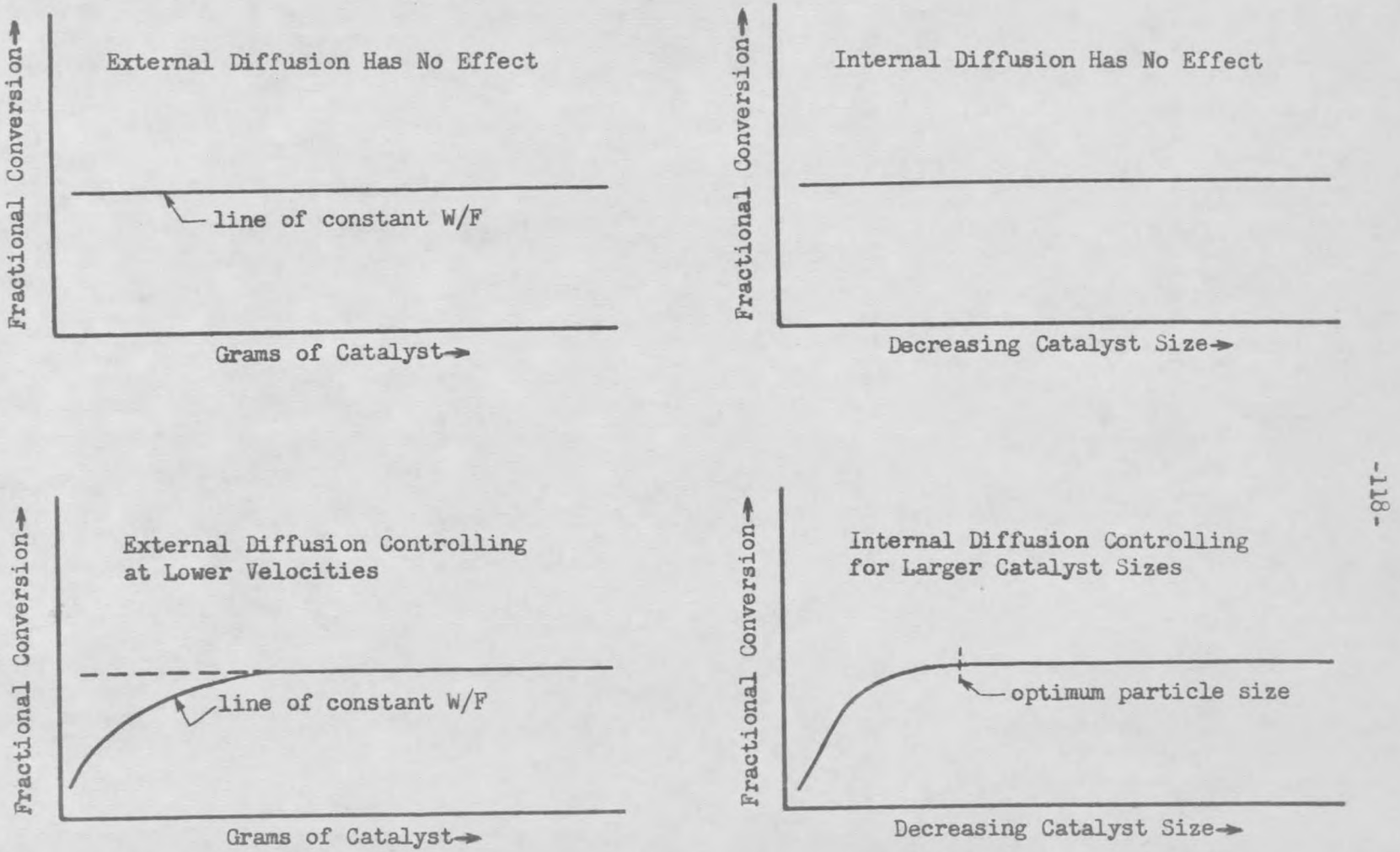


Figure 3. Illustrations of Tests For External and Internal Diffusion Controlling the Reaction Rate

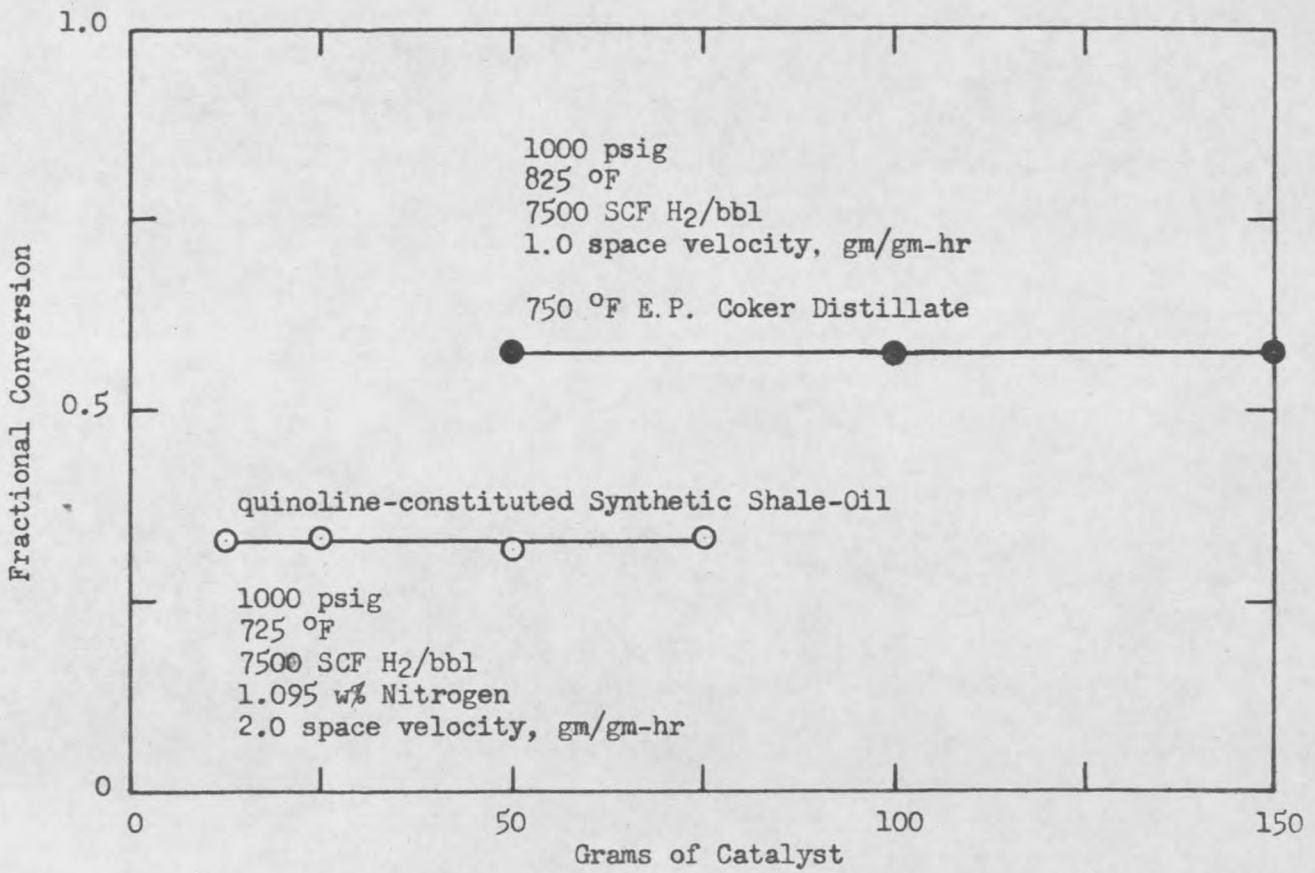


Figure 4. Conversion vs. Grams of Catalyst, Test for External Diffusion Controlling, Shale Oil and Synthetic Shale-Oil

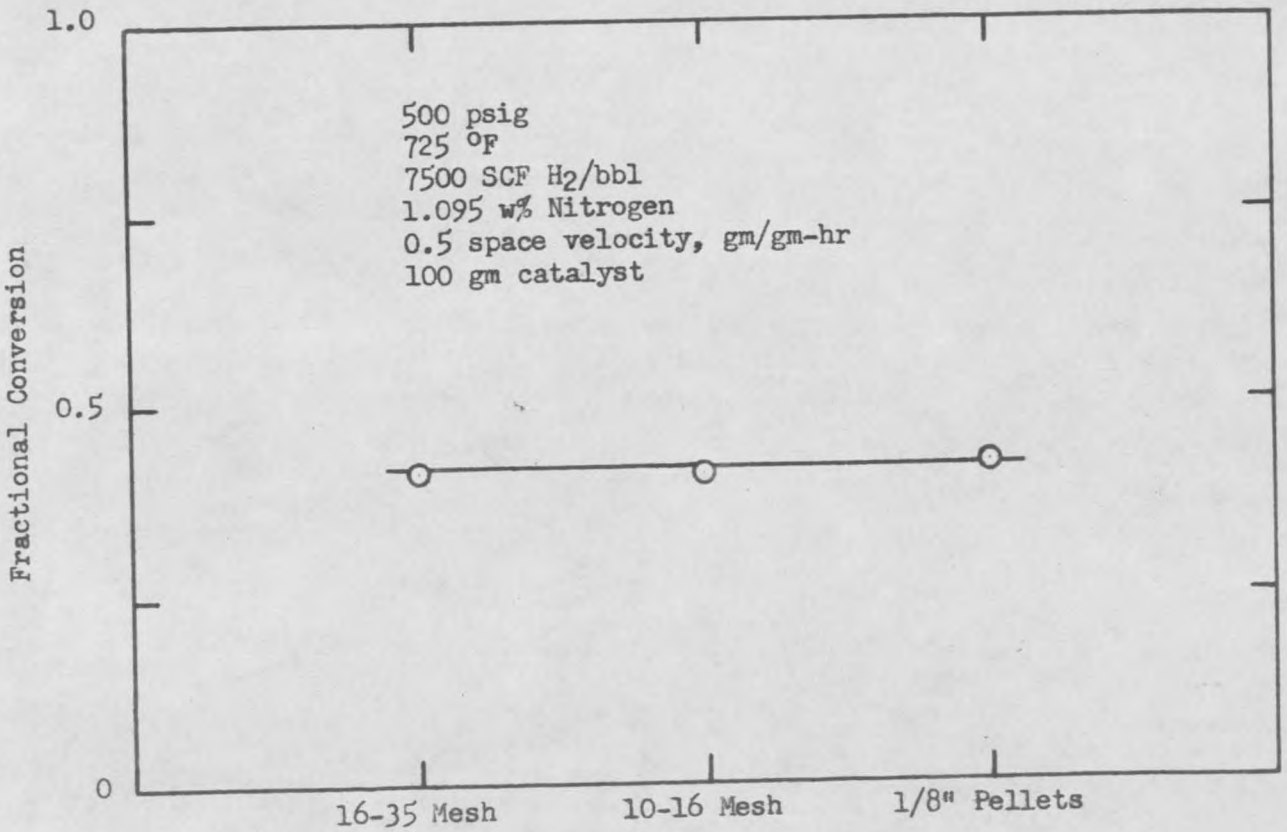
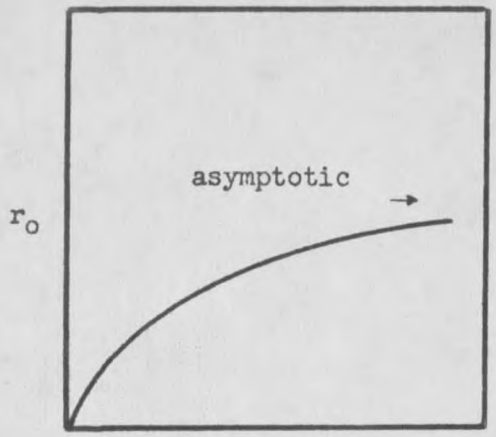
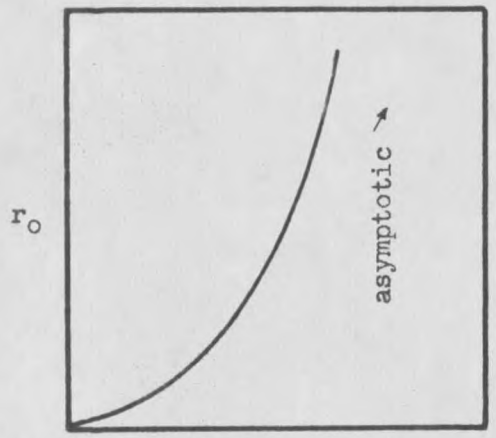


Figure 5. Conversion vs. Size of Catalyst, Test for Internal Diffusion Controlling the Reaction Rate



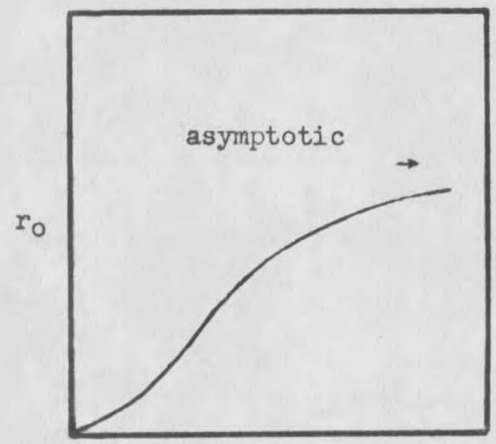
Adsorption of Q Controlling

$$r_o = \frac{aP}{(1 + bP)}$$



Surface Reaction Controlling

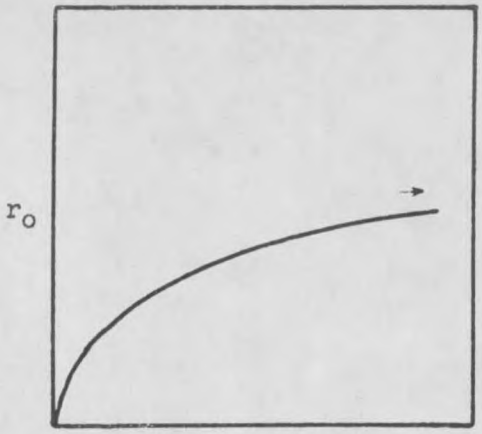
$$r_o = \frac{aP^2}{(1 + bP)}$$



Desorption of D Controlling

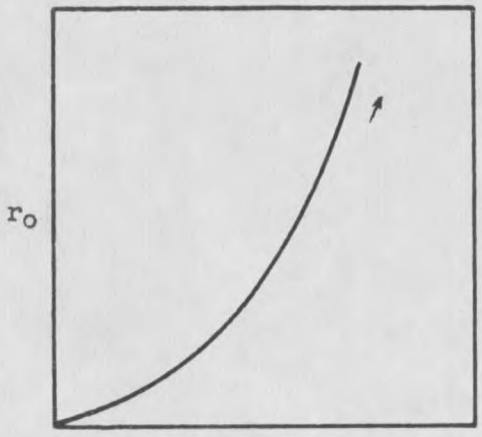
$$r_o = \frac{aP^2}{(1 + bP + cP^2)}$$

Figure 6. Characteristic Curves, r_o vs. P, Example Mechanism



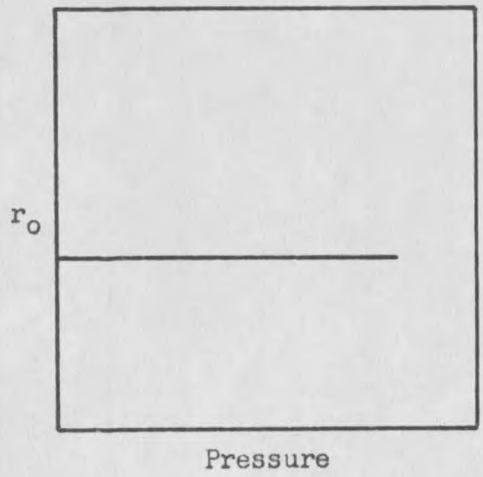
Characteristic Curve for:

Step 1 Controlling



Characteristic Curve for:

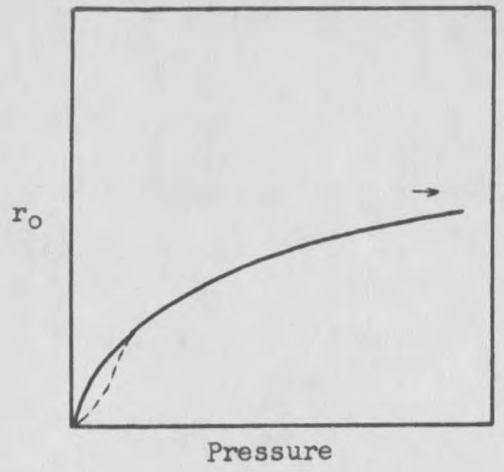
Steps 2, 3, 4, or 5 Controlling



Characteristic Curve for:

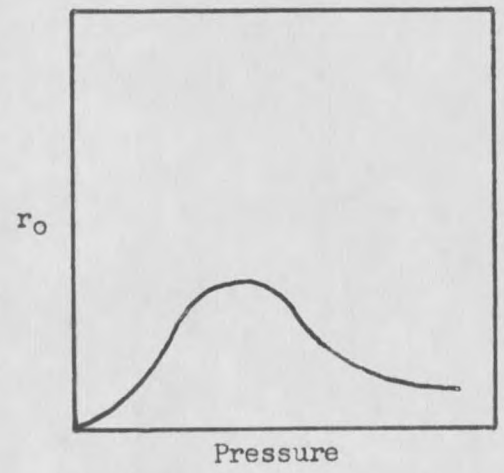
Step 6 Controlling

Figure 7. Characteristic Curves, r_o vs. P, Adsorbed Nitrogen-Compounds and Gaseous Hydrogen



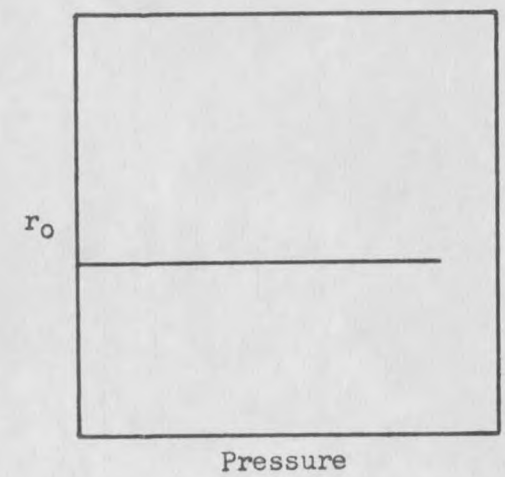
Characteristic Curve for:

Steps 1, 2, or 3 Controlling



Characteristic Curve for:

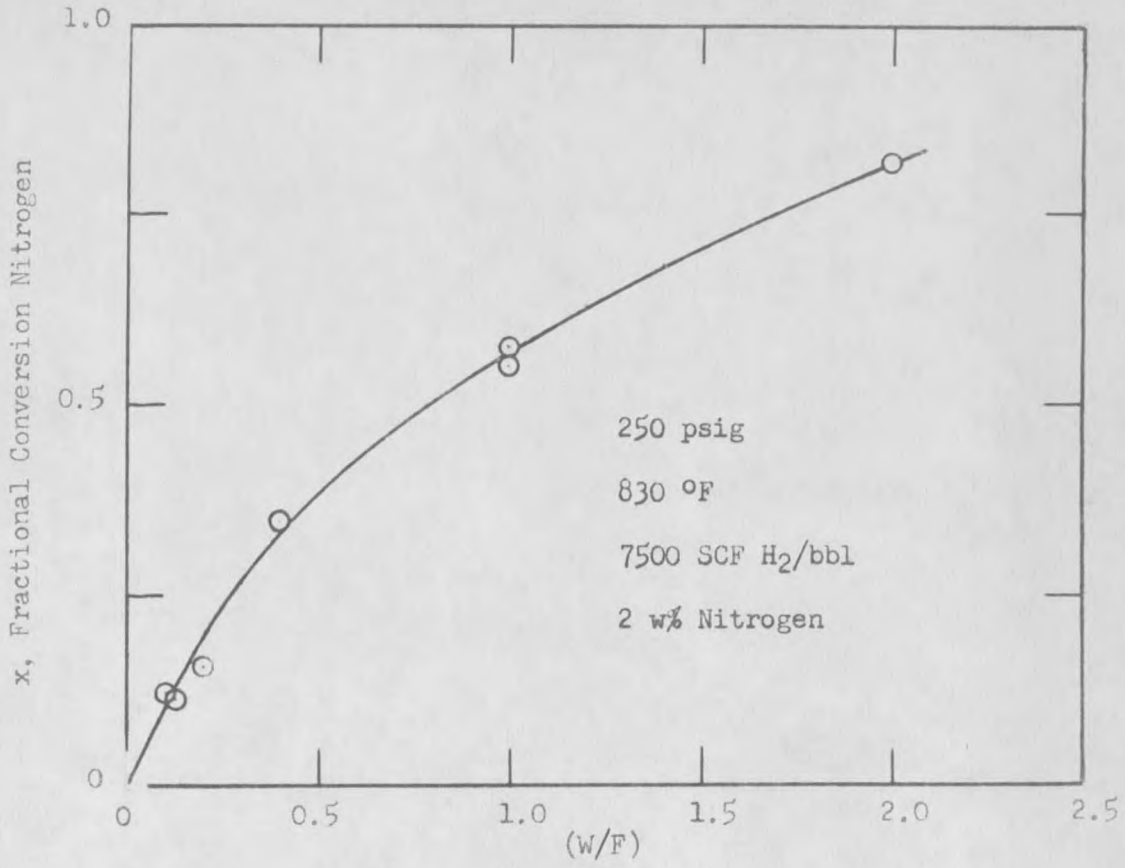
Steps 4, 5, or 6 Controlling



Characteristic Curve for:

Steps 7 or 8 Controlling

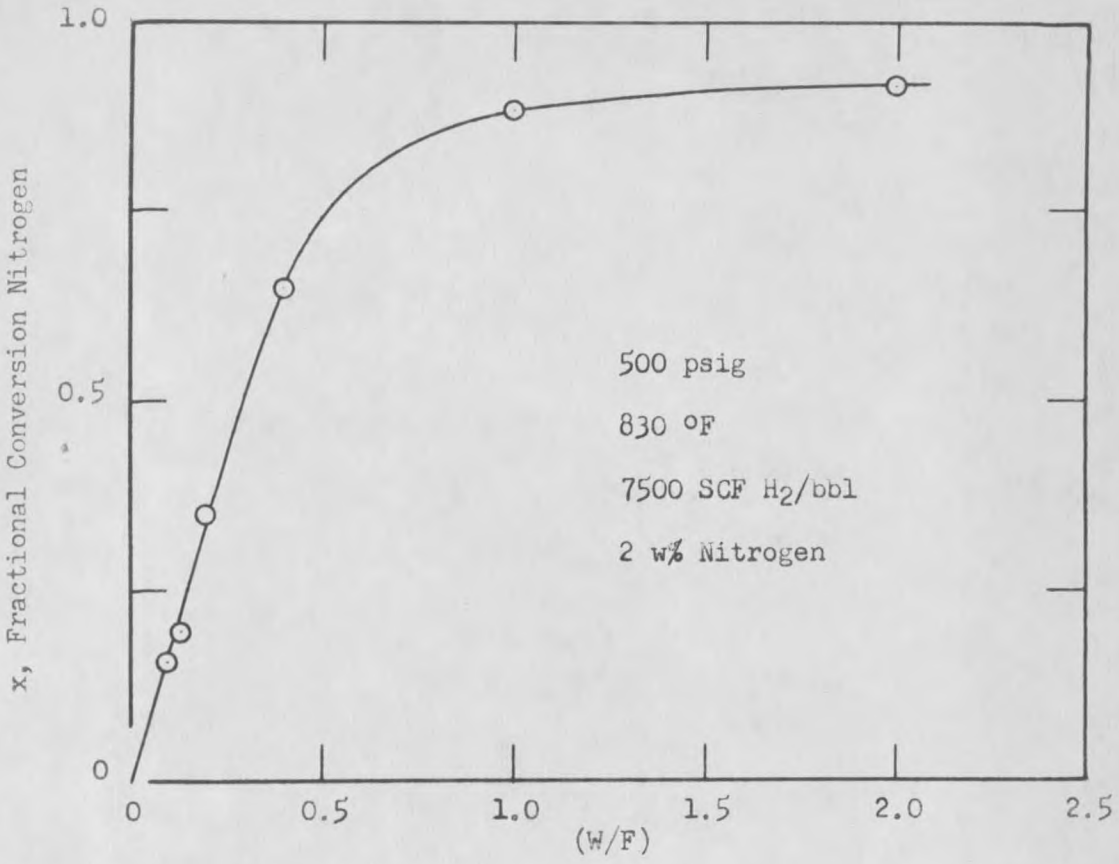
Figure 8. Characteristic Curves, r_o vs. P, Adsorbed Nitrogen-Compounds and Adsorbed Molecular-Hydrogen



x = fractional conversion of nitrogen to ammonia

W/F = reciprocal space-velocity, $\frac{\text{(gm catalyst)(hr)}}{\text{(gm oil)}}$

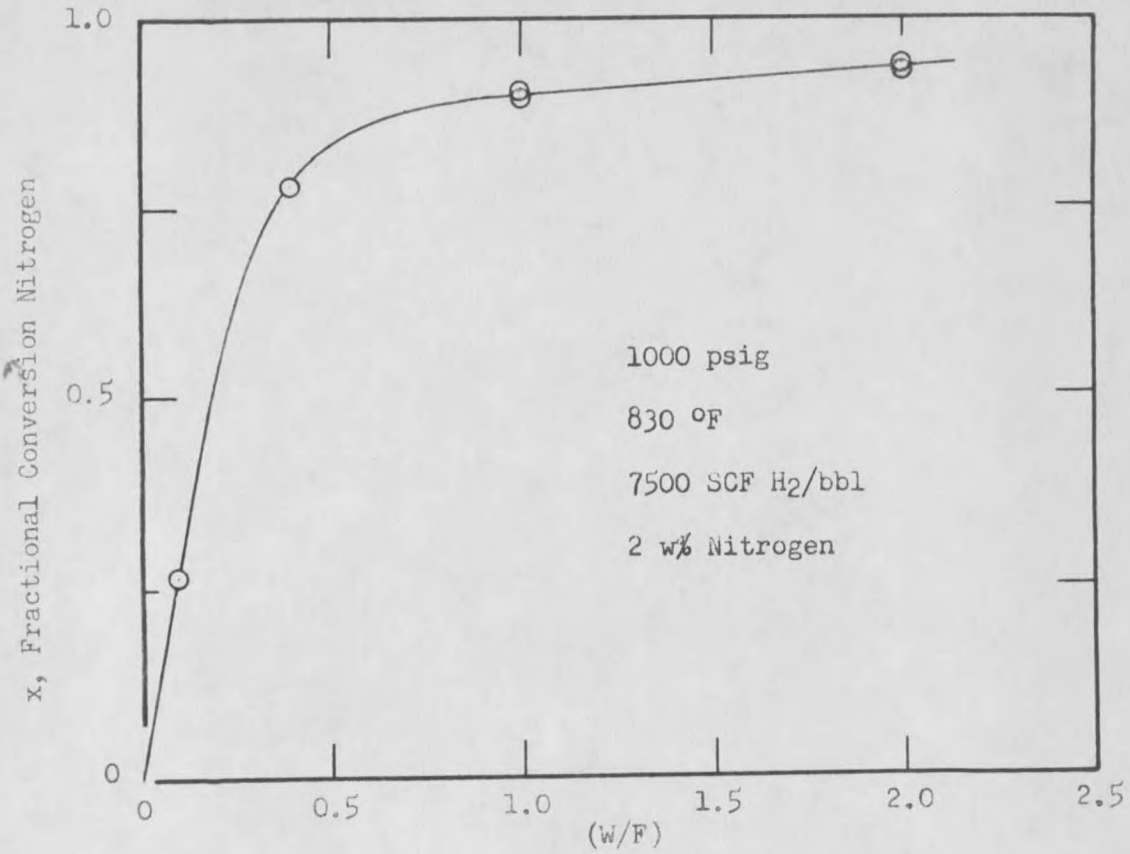
Figure 9. 250 psig Curve, x vs. W/F



x = fractional conversion of nitrogen to ammonia

W/F = reciprocal space-velocity, $\frac{\text{(gm catalyst)(hr)}}{\text{(gm oil)}}$

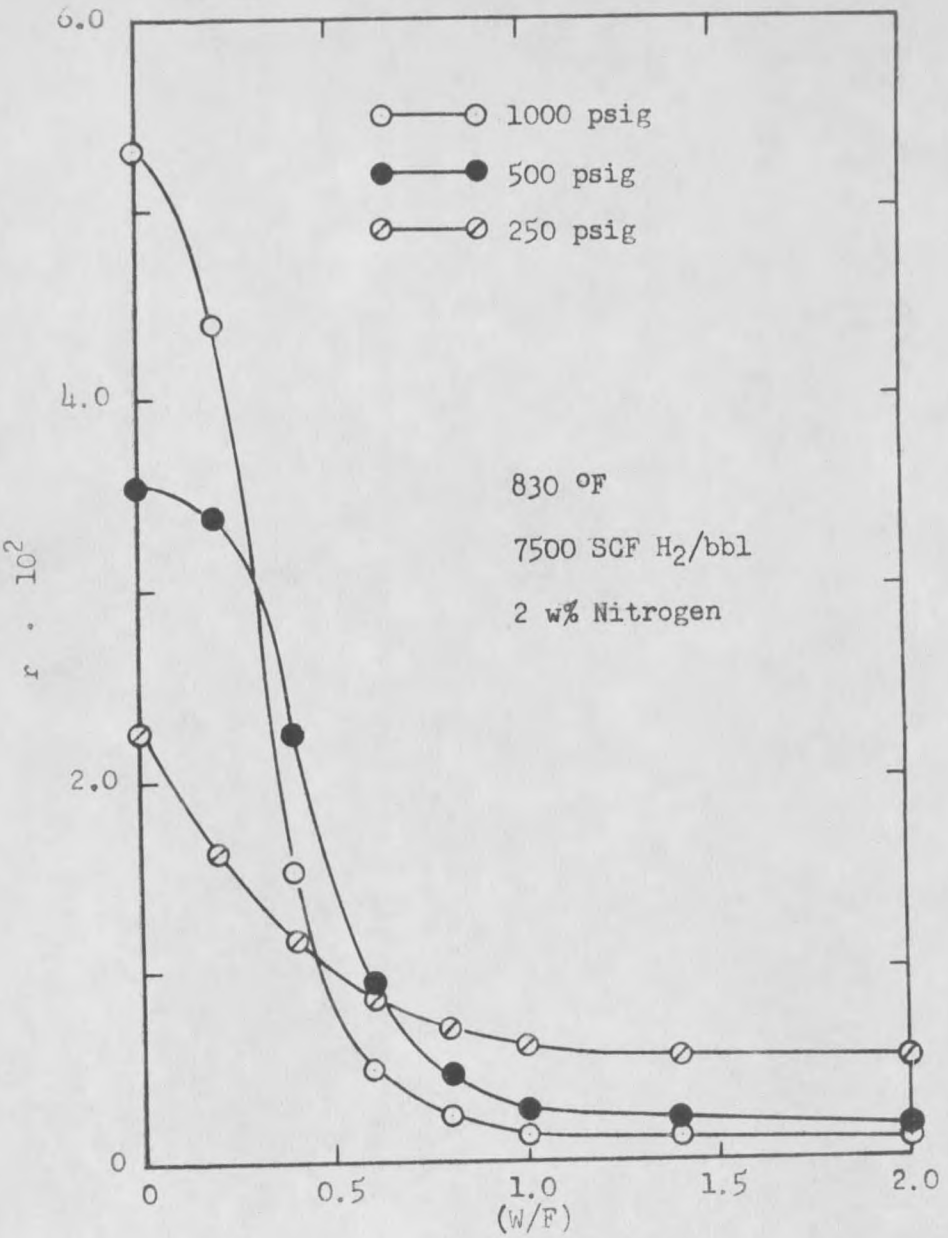
Figure 10. 500 psig Curve, x vs. W/F



x = fractional conversion of nitrogen to ammonia

W/F = reciprocal space-velocity, $\frac{(\text{gm catalyst})(\text{hr})}{(\text{gm oil})}$

Figure 11. 1000 psig Curve, x vs. W/F



r = reaction rate, $\frac{\text{(gm nitrogen)}}{\text{(gm catalyst)(hr)}}$

(W/F) = reciprocal space-velocity, $\frac{\text{(gm catalyst)(hr)}}{\text{(gm oil)}}$

Figure 12. Reaction Rate vs. Reciprocal Space-Velocity, Penetek-Quinoline Hydrogenolysis

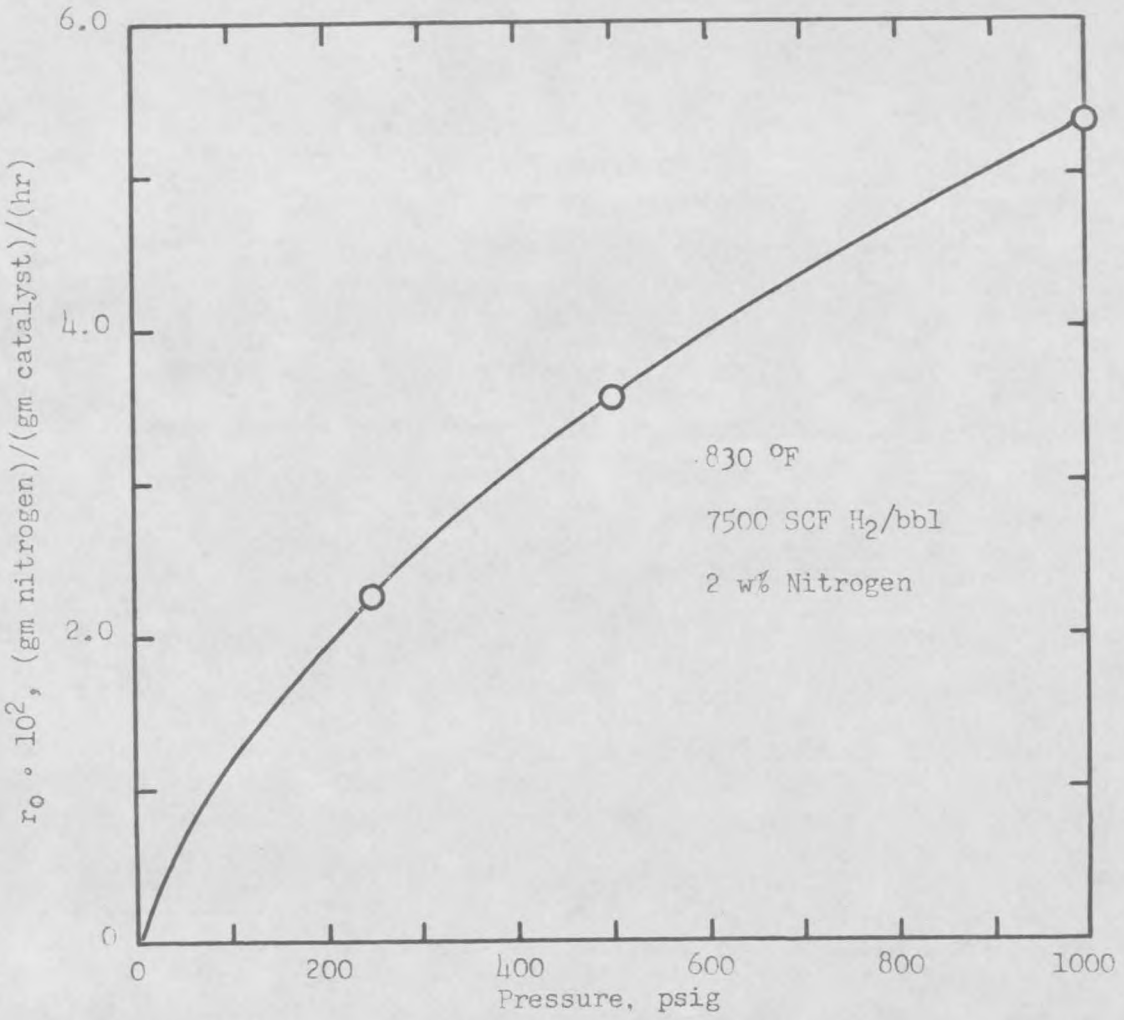


Figure 13. Initial Reaction-Rate vs. Pressure, Penetek-Quinoline Hydrogenolysis

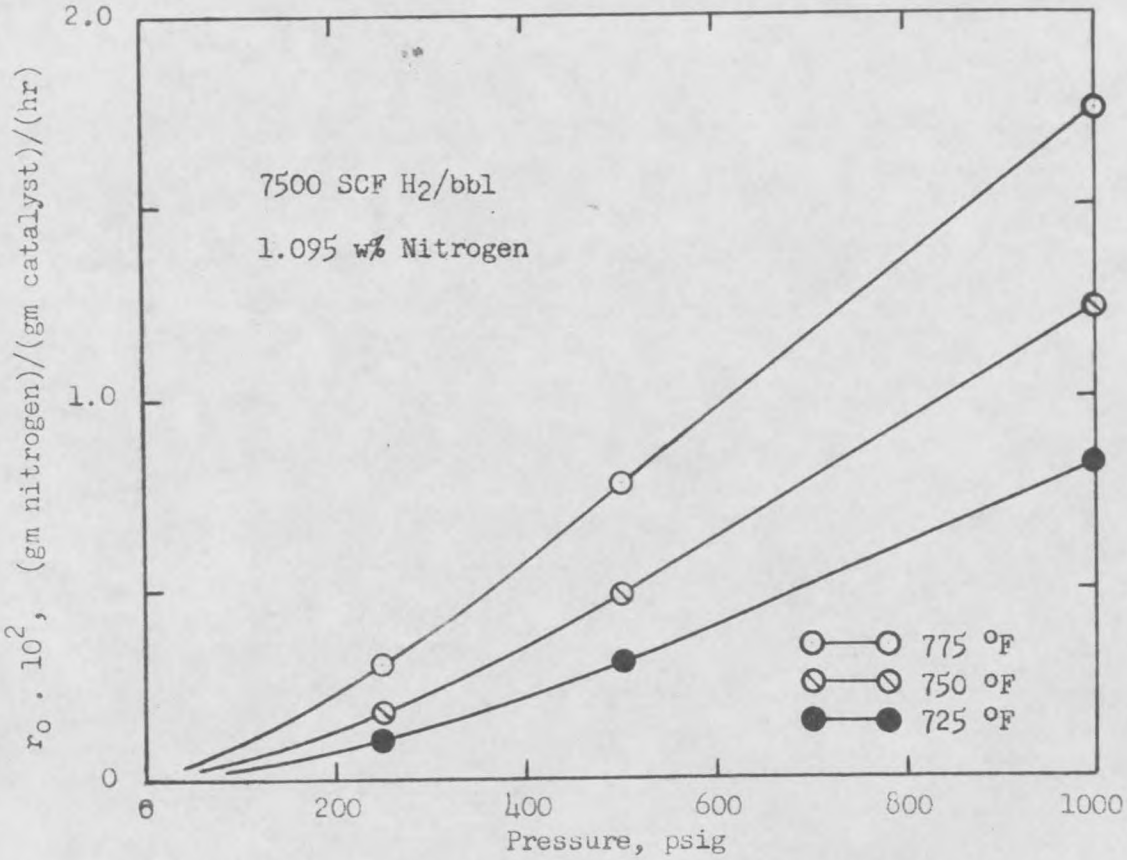
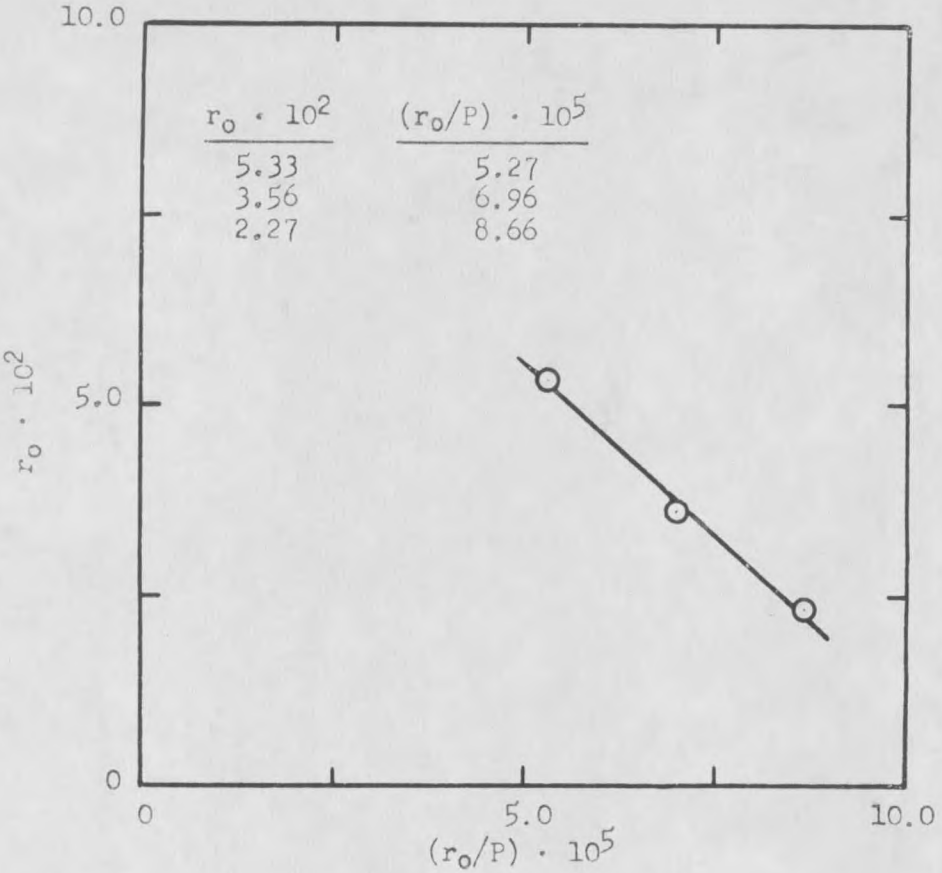


Figure 13b. Initial Reaction-Rate vs. Pressure, Penetek-Quinoline Hydrogenolysis, Lower Temperatures



$$r_o = \frac{aP}{(1 + bP)}$$

$$r_o = -(1/b)(r_o/P) + (a/b)$$

Figure 14. Test Curve for Form of r_o vs. P Curve, Penetek-Quinoline Hydrogenolysis

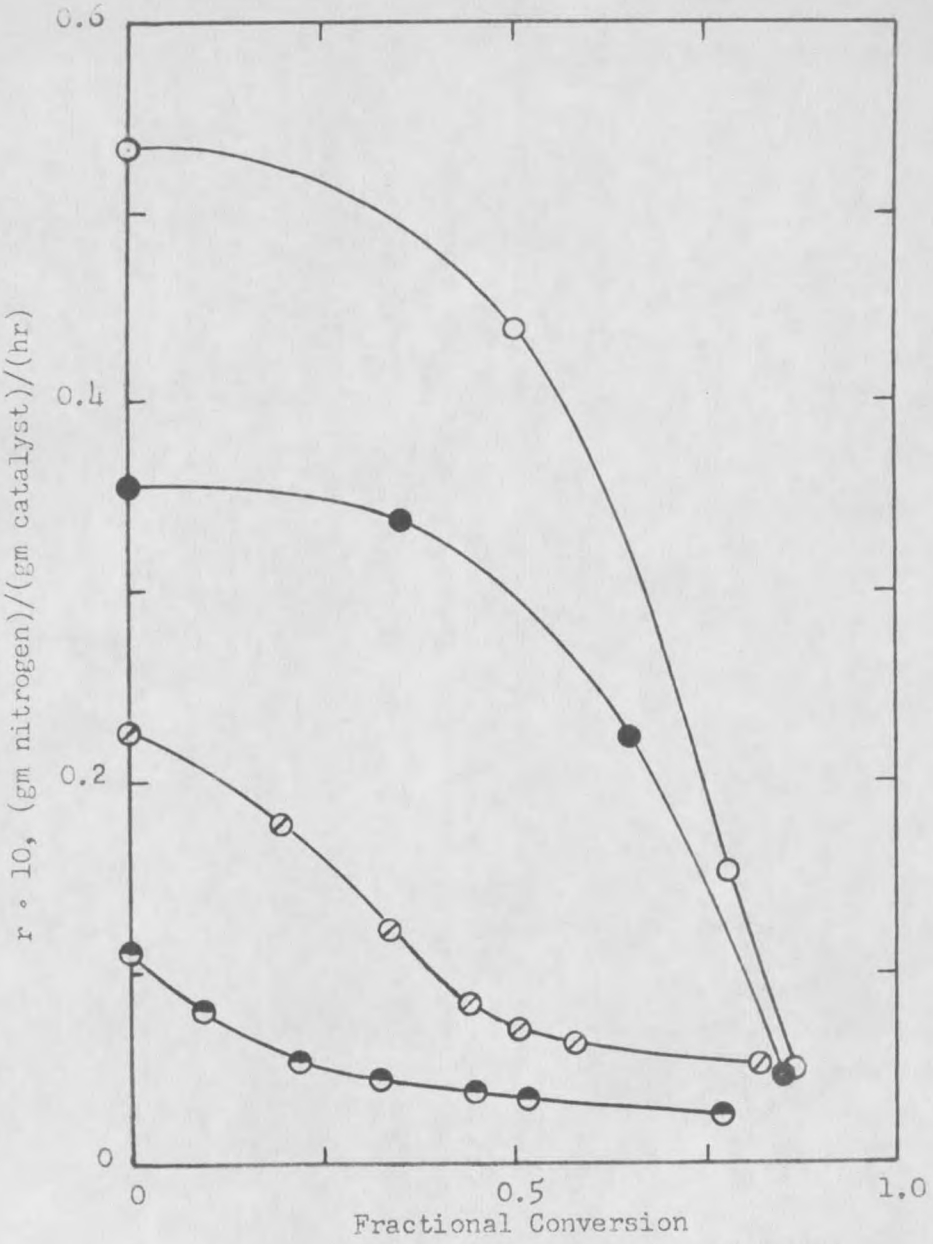


Figure 15. Reaction Rate vs. Conversion at Constant Temperature and Pressure

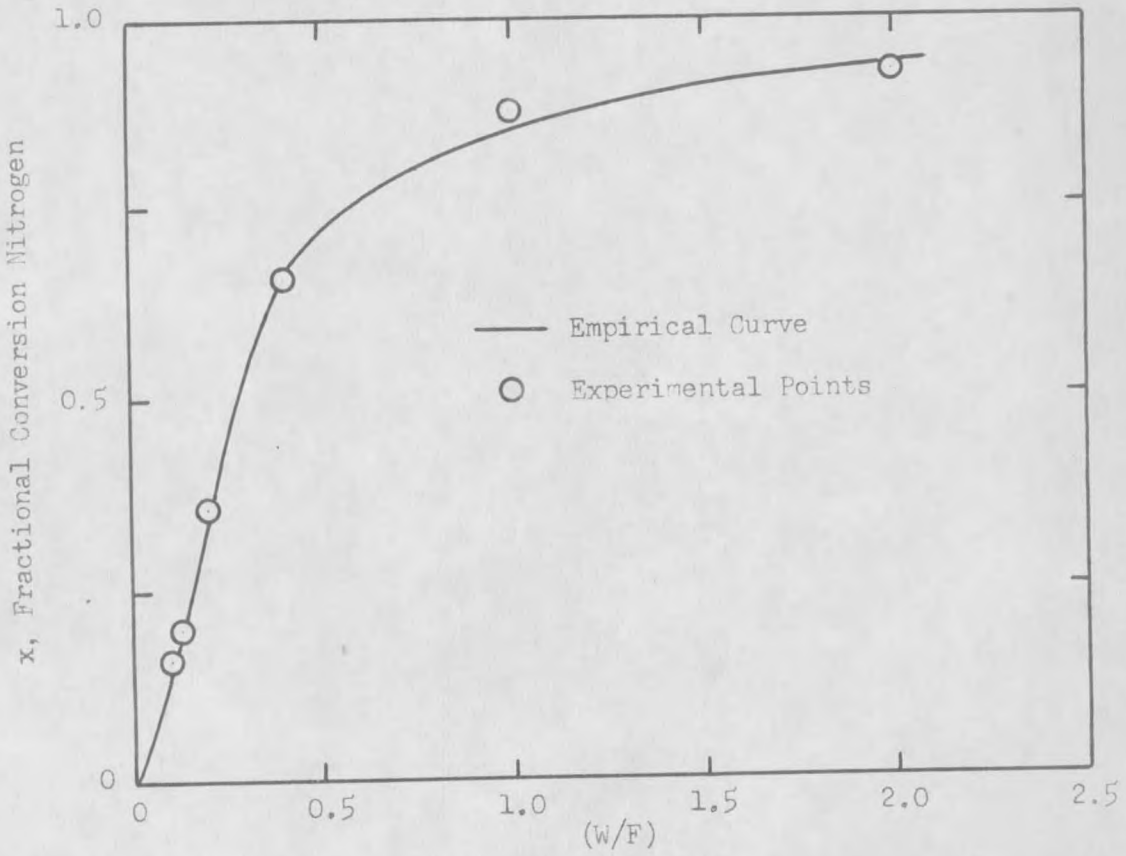


Figure 16. Empirical Curve; 830°F, 500 psig

VITA

Personal

Date and Place of Birth: July 21, 1932
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Educational

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Undergraduate: Montana State College, Bozeman, Montana 9/51 to 6/55; B.S. in Chemical Engineering

Graduate: Montana State College, Bozeman, Montana 6/55 to 12/58

Experience

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Assistant Production Engineer with the Shell Oil Company, Glendive, Montana; 6/54 to 9/54

Research Fellow in Chemical Engineering, Montana State College, Bozeman, Montana; 6/55 to 12/58

Assistant Instructor in Mathematics, Montana State College, Bozeman, Montana; 9/56 to 12/58

Assistant Professor of Chemical Engineering, University of Arizona, Tucson, Arizona; 1/59 to 8/61

Project Director and Consultant for plasma-jet research, Applied Research Laboratory, Tucson, Arizona; 3/59 to 8/61