Summary of the thesis:

"A COMPARATIVE STUDY OF THE EFFECTS OF THE NITRIDES OF THE TRANSITION ELEMENTS ON THE ACTIVATION ENERGY FOR THE AMMONIA DECOMPOSITION."

In the ammonia decomposition, the energies of activation associated with the nitrides of the transition elements: Ti, V, Cr, Mn, Fe, Co, and Ni, have been determined at 1 atmosphere pressure and temperatures ranging from approximately 400°C to 500°C. Wherever possible, similar preparative and experimental methods were used, so that the energies of activation could be compared directly.

In the introduction, it was stressed that these nitrides are interstitial structures, which exist as various phases, depending on the nitrogen content of the compound. Experimental difficulties were briefly mentioned, in particular those regarding the unstable nitrides of cobalt and nickel, in which cases very small quantities had to be used. For these catalysts a special experimental procedure was required. Previous experimental work was generally described, with reference to work regarding nitride formation during the reaction, and the possible participation of interstitial nitrogen atoms in the reaction mechanism.

The following section was a description of the apparatus used for determining the energies of activation. A flow system, interconvertible to a static system was used. The former system was found to be more satisfactory than the latter, which was only used for a few experiments.

A further section dealt with the preparation of the nitrides, in which ammonia was normally used as reactant gas with the metal or metal nitride starting material. It was shown that the stability of these nitrides varies systematically at operating temperatures: titanium nitride is stable,and on the other hand, nickel nitride is stable only under strictly controlled conditions.

The results show that in every case in which a wide temperature range of study was used, there was a change in activity at a definite temperature. Three energies of activation were shown by iron nitride, and two by each of the nitrides of vanadium, chromium amd manganese. Titanium nitride was found to become active at 480°C, above which temperature an energy of activation of 30 Kcal/mole was shown.In order to show which

nitride phase was used in each case, a brief resume of the structural chemistry of the nitrides was given in this section.

The results were such that a comparison of activation energies, based on the atomic numbers of the elements, led to no definite conclusions. Possible relationships were, however, discussed. It was shown that activation energy values may be grouped according to their general magnitude, which supports the view that different, parallel reaction mechanisms occursimultaneously, and in such a manner that the predominant mechanism determines the energy of activation. It was shown that a change in activity appears to be accompanied by a structural phase change. The similar activation energies, occurring at similar temperatures, suggest that such a change in structure is not a direct cause of a change of activity, but rather that it may create suitable conditions for different mechanisms to occur. Each mechanism would then result in similar energies of activation for different catalysts. There appeared to be a direct relationship between activation energies and the temperatures at which activity changes occur.

Further, the relationship between the energies of activation for the nitrides and the electronic character, in particular the d-character, of the metals, was considered. No marked relationship was shown. A comparison based on geometric factors did not result in any definite conclusions. It was shown that all the nitrides, under suitable conditions, show relatively low apparent energies of activation,and that the values determined are all similar to the energies of activation associated with a number of metals.

The electrical conductivities of the nitrides of titanium and vanadium were measured at temperature ranges including the temperatures at which activity changes occurred. Conditions were similar to those observed during activation energy determinations. There was no change in electrical properties at the temperatures of activity change.

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A Thesis Submitted to the

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by

C.R.Lotz B.Sc. (App. and Ind. Chem.)

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CONTENTS.

4. Results.

1. INTRODUCTION

In spite of the industrial importance of the catalytic synthesis of ammonia, accompanied as it has been by considerable research activity, no radical change in the nature of the catalyst employed has yet occurred. The widely used technical promoted iron catalyst is a development of a similar catalyst used in the initial experiments for the ammonia synthesis; this is particularly striking when the large number of other substances investigated in this connection is considered. Development has, however, been rapid, the more fruitful line of research being that in which the promoting action of various substances on the iron catalyst, and the mechanism of the reaction, were studied. In an illusive and complex problem, contributions such as that of Frankenburger [1.] and others, represent outstanding progress in the field of catalysis. It is true that various other catalysts are used in industry such as osmium, uranium and an iron-molybdenum mixture, but these are in general not superior to the promoted iron catalysts, which, for considerations such as sustained activity [2.] during use, rigidity of bulk structure and cost, is often preferred.

While various experiments have indicated that iron nitride itself is a poor synthesis catalyst [3.], it's role in the reaction mechanism has always been considered important, and it's formation as an intermediate product has been the basis of much theory. Activated adsorption of nitrogen is generally considered the rate determining step.[4.5.] The technical iron catalysts, which are produced by the fusion of iron oxide (magnetite) and various promoters (e.g. K_2O, CaO, Al_2O_3) followed by reduction, is probably changed finally, if only partially to a nitride when in use. Furthermore, the metals of the transition series are considered the active catalysts for the reaction, provided the heat of formation of the nitride is low[1.] On the other hand the nitridesof the elements which have a high heat of nitride formation, are also active. Examples are the well-known catalysts molybdenum, tugsten and uranium nitrides. Thermodynamic considerations put forth by Frankenburger require that, for efficiency, a catalyst must have a low heat of nitride formation, so that the adsorption or desorption of the metal-nitrogen bond can take place involving as little energy as possible. Oxygen poisoning experiments by Almquist and Black[6.] show that the activity and the retention of oxygen by the catalyst occur in similar surface regions, and that the last remaining oxygen atoms left on an almost completely reduced surface, cause smaller activity than when reduction is complete. This means that the catalytically active atoms are those of iron which have considerable free energy. It would therefore appear that the presence of other nonmetals, such as nitrogen, by causing a reduction in the free energy, would cause a diminution in activity. Such considerations lead one to expect that although nitride formation must bean **integral** part of the reaction mechanism, it's presence does not enhance catalytic activity. The active nitrides, it is thought, are active in a different sense, in that we have here to consider the introduction of a different electronic factor.

While not denying the import and significance of previous conclusions, it was thought justifieable to commence this series of experiments, in an attempt to shed more light on the role of the nitrides in catalysis. Greenhalgh, Slack and Trapnell [8.] have recently suggested that "slow adsorbed" interstitial nitrogen may well play a role in the reaction mechanism. The following series of experiments were made in order to obtain the values of the energies of activation for the decomposition of ammonia associated with the nitrides of the metals of the first transition series. Experimental conditions were such, that a comparison of the values could be based on the fact that all catalysts were subjected to similar treatment, as far as was practically possible. A survey of the pertinent literature shows somewhat divergent values of activation energy for a single catalyst, which, although depending to a large extent on the history of the catalyst employed, may partly be ascribed to the different methods used in the determination of the activation energy. This is illustrated in our experiments, for when using a static and a flow reactor for testing the activity of the same technical iron catalysts, different results of 45 Kcal/mole and 37 Kcal/mole respectively were obtained.

The general title of this thesis includes "transition metal nitrides", but it is necessary to be more specific. The nitrides of the first transition series, with the exception of scandium, copper and zinc nitrides were used. Scandium nitride [9.] forms at a temperature of 1700 to 1800°C, and equipment for obtaining this temperature was not available. Copper and zinc have complete electronic d-bands and behave in a different manner to the other transition metals. Active catalysts appear to be those which exhibit d-band character.[10.] Copper, in an excited (cupric) state, does show some d-band character, but the nitride decomposes at temperatures considerably below the operational temperatures used, and could therefore not be employed.[11.]

It should be made clear at the onset that the nitrides cannot in all cases be obtained as completely stoichiometric nitrides. The nitrides of titanium [12.] and vanadium [13.] are the only ones that can be obtained as complete stoichiometric interstitial structures. The other nitrides can only be obtained as structures in which some of the interstitial nitrogen positions are unoccupied, and chemical analyses consequently show a compostion approximating to a simple stoichiometric formula. The nitrides normally exist in various phases in which the structural type remains unchanged between two limits of nitrogen content. Cobalt and nickel nitrides presented special experimental problems, since they exist only under strictly controlled conditions.

The initial setup was a static system, and an attempt was made to obtain results for the ammonia synthesis at 1 atmosphere pressure. Equilibrium considerations [14.15.] show that micro-quantities of ammonia resulted, even over a good catalyst. Equilibrium shifted in favour of decomposition when higher temperatures were used. Attempts to measure the small yield of ammonia with sufficient accuracy and facility were unsuccessful. These included such methods as: ammonia absorption in acid and microtitration [16.17.] other micro-volumetric methods, heat transfer methods using a thermistor suspended in the centre of a spherical vessel and colourimetric methods. The real difficulty was the sampling of the gas, necessitating the efficient transfer of an accurately measured quantity of gas from a macro-scale reaction vessel to micro-scale equipment. For a more convenient and accurate method of experiment, a study of the reverse reaction, the decomposition of ammonia, was then attempted. The breakdown of the unstable catalysts in a static reaction vessel, however, introduced difficulties, since the accumulation of hydrogen, as the reaction proceeded, caused decomposition of the unstable nitrides.

It was then apparent that there was slender chance that the nitrides could have been preserved at all, during synthesis, because of the excess of hydrogen that was present. The first synthesis experiments were attempted because it was thought possible that at the relatively low temperatures which were necessary during synthesis, (derived from equilibrium considerations) at least some of the nitrides would have remained stable for a sufficient length of time to complete an experimental run. The apparatus was therefore modified to be inter-convertible from a static to a dynamic reaction system. This proved to be a judicious decision since increased efficiency and accuracy of measurement became possible, as well as an effective handling of the nitrides of cobalt and nickel.

A sample of technical promoted iron catalyst was used to aid as a trial catalyst in the development of the apparatus. Since the order of magnitude of it's activation energy was known, it served to some extent as a reference catalyst, the measured activity of which showed that a correct experimental procedure had been used. The catalyst was obtained by the reduction by hydrogen of iron oxide, supplied by African Explosives, from their Modderfontein plant, and being a technical catalyst, data regarding it's composition were not available. The results obtained by static and by flow method were somewhat divergent, yet reasonable

(45 Kcal/mole and 37 Kcal/mole respectively.) The reason for this divergence is uncertain. The inhibiting effect of hydrogen, which formed in the static reactor, may account for the high value shown by the static method. The flow-method value was derived indirectly. The decomposition was measured at a constant temperature with varying space velocity. Straight line plots of log % decomposition vs. log. space velocity resulted for various temperatures. The log rate vs $^1/T$ curve was derived from this plot, and showed a linear relationship. These are the relations normally obtained for iron catalysts, and since there appeared to be no error in the method, it was assumed to be justifiable to obtain Arrhenius plots directly, by measuring the decomposition at various temperatures and constant space velocity.

If it is assumed that the rate determing step is the same for synthesis and decomposition, the observed results should hold equally well for synthesis and decomposition. There has been mention of a "one-sided" catalyst, chromium nitride, [18]. which, it was suggested, should be an active decomposition catalyst and a poor synthesis catalyst. The chromium nitride catalyst used showed two different energies of activation, a low value at lower temperatures, and a rather high value of 58 Kcal/mole above approximately 490°C, and generally speaking appeared to be a rather poor catalyst.

A further limitation inherent in this type of experiment, restricting a comparative study of energies of activation, is the fact that observed energies of activation may deviate from the true values.[19]

Brief mention may be made of current problems in catalysis. These concern in general the relation between activity, and geometric and electronic factors. The d-band theory of metals in relation to catalysis has recently become prominent due to experiments by Dowden,[20] and Dilke, Maxted and Eley.[21.] When comparing the catalytic activity of various metals, the importance of electronic d-band structure as a fundamental cause of activity is clearly shown by Boudart[22.] Beeck's early comparison of heats of adsorption of gases on metals was based on the lattice structures of the metals. Boudart pointed out that when considering Pauling's theory of metals, the lattice dimensions are to be considered as an effect rather than a cause of activity, and that fundamentally the electronic factors are important. The phenomenon of slow adsorption of gas on metal surfaces must be clarified, and, of interest here, is the slow adsorption of nitrogen on iron discussed by Greenhalgh, Slack and Trapnell, mentioned previously in our introduction. It is interesting to note the suggestion submitted by these authors, that assuming slow adsorption of nitrogen to be a determing factor in the mechanism of the ammonia reaction, current rate laws probably require correction to incorporate a $\sqrt{p}$ relation, since this relation is obeyed by slow adsorption of nitrogen. Finally one may mention the undecided possibilities of "active sites" ie. heterogeneity of the surface, and migration of adsorbed atoms on the catalyst surface.

2. EXPERIMENTAL

2.1 APPARATUS.

2.11. Function.

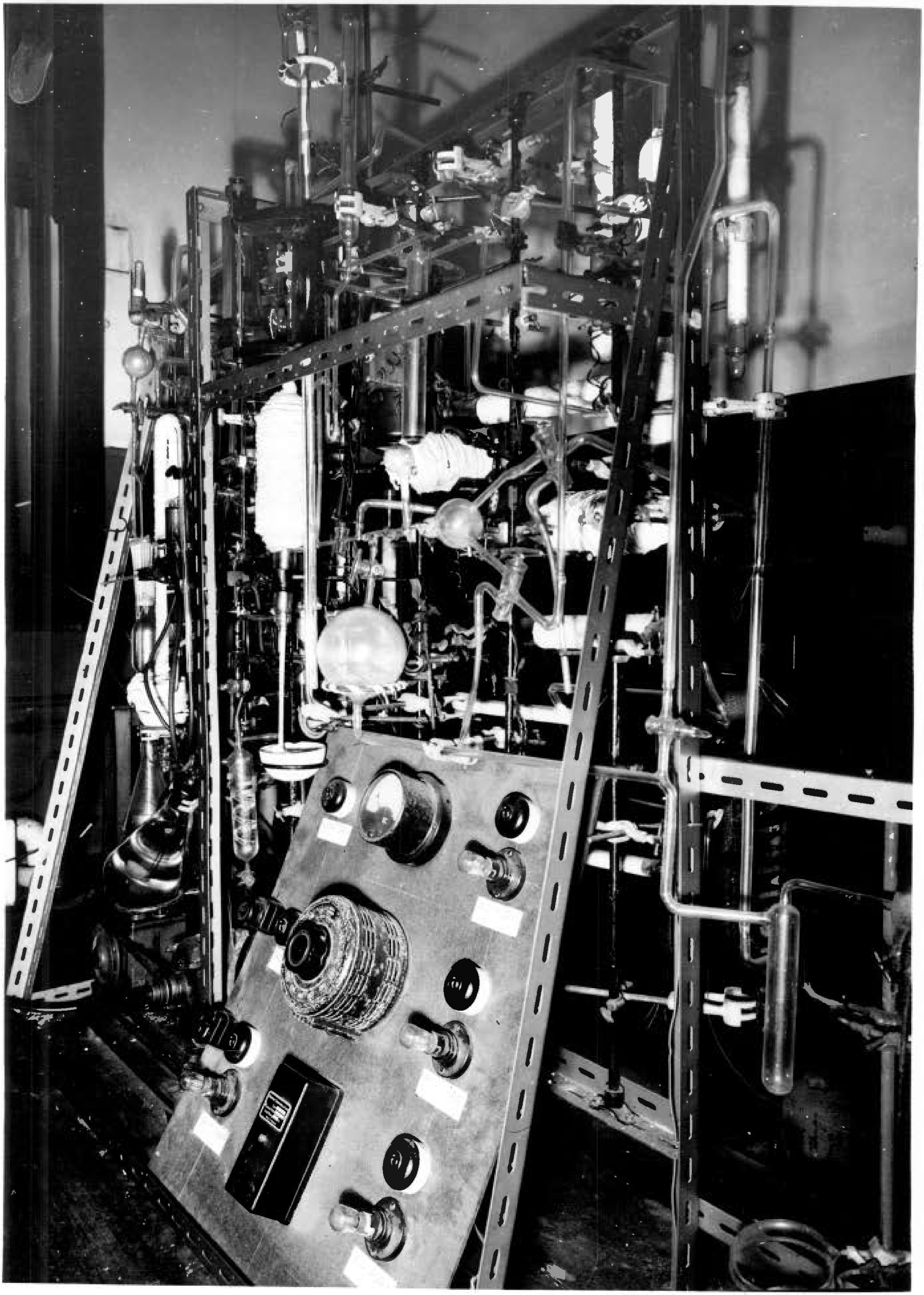
Activation Energy Determination.

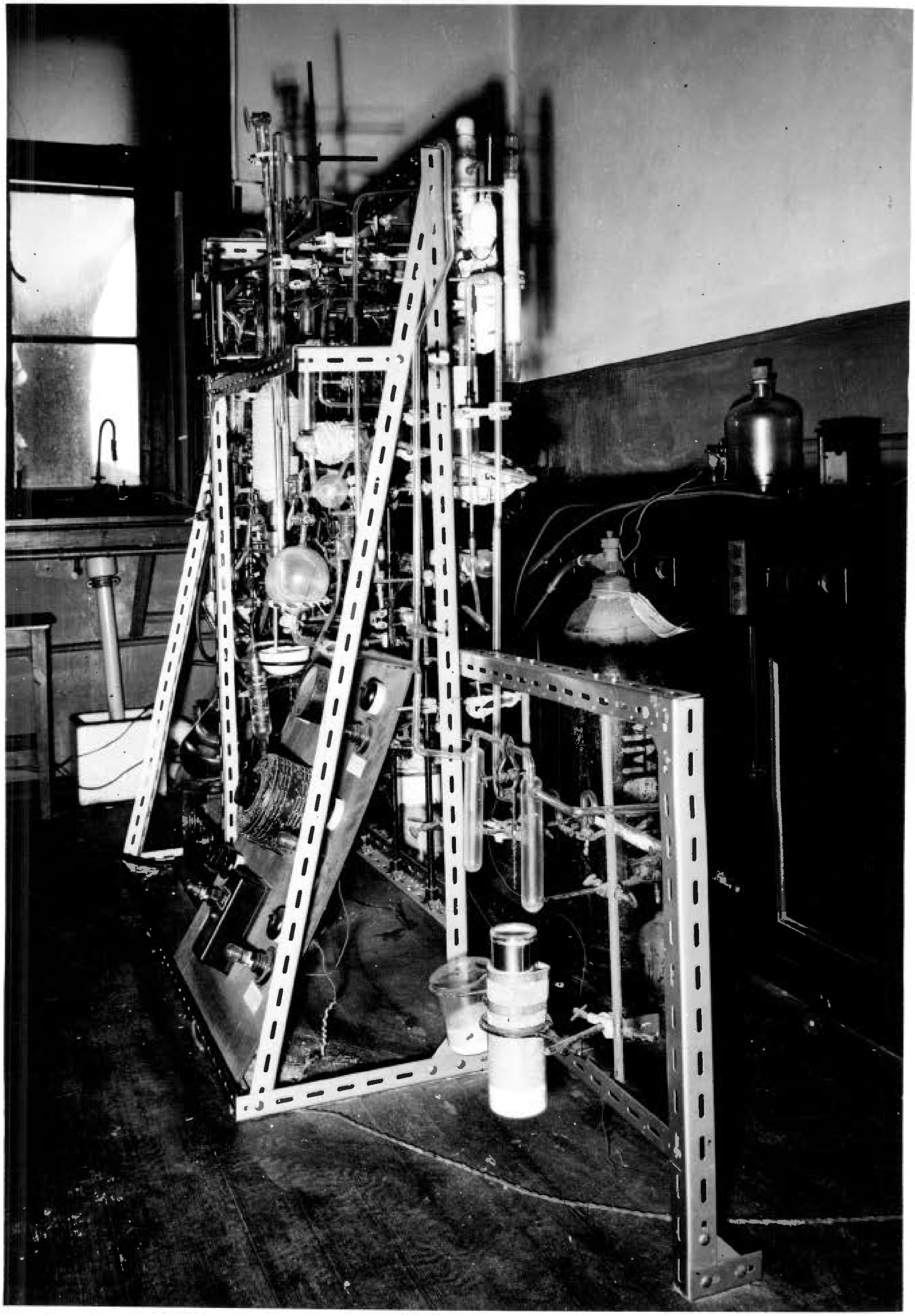
In order to determine the energy of activation associated with a catalyst, it is necessary to measure the rate of the heterogeneous reaction at known and varied temperatures.

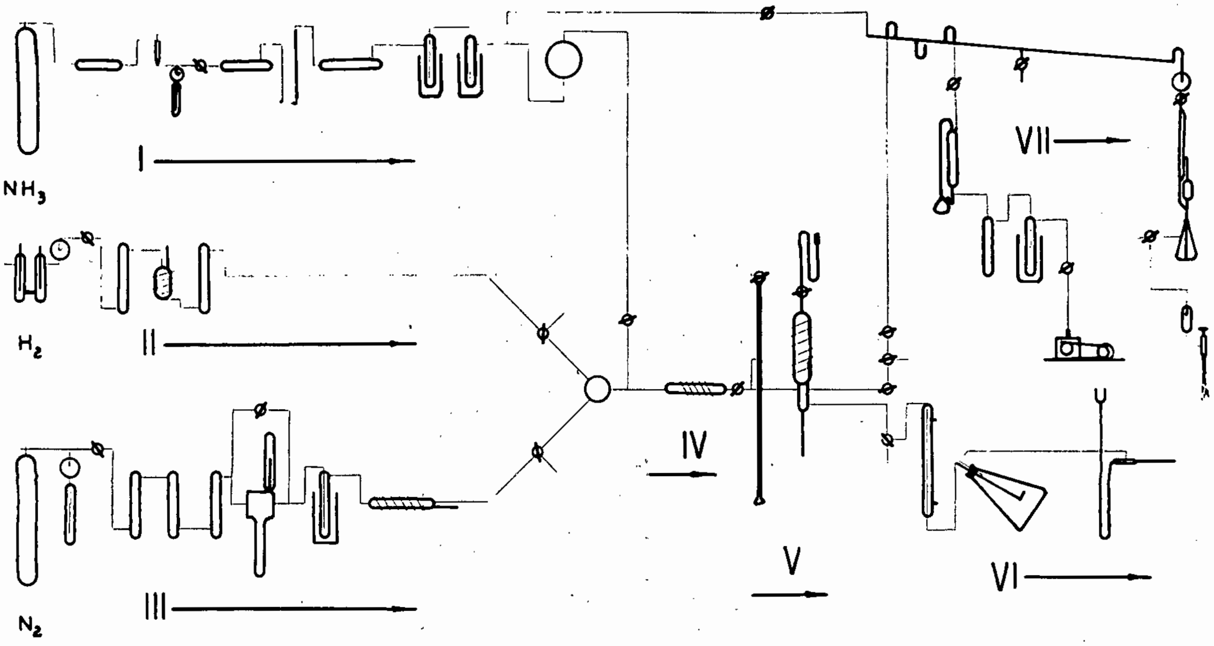
In the "flow" system, a constant flow of purified ammonia gas was passed over the catalyst which was contained in a thermostated reaction vessel. Undecomposed ammonia was absorbed in acid, and the combined flowrate of the remaining decomposition products was a measure of the extent of decomposition.

When functioning as a "static" system, the rate of pressure increase of an isolated volume of pure ammonia, in contact with the catalyst, was used as a measure of the rate of decomposition, since, according to the equation $2NH_3 \rightleftharpoons 3H_2 + N_2$, the decomposition products occupy twice the volume of the original ammonia.

Provision was made for creating a high vacuum, and for the supply of pure ammonia, hydrogen or nitrogen, where necessary, for use in the catalyst preparation, activation or safe storage.







I : AMMONIA GAS SUPPLY AND PURIFICATION TRAIN.
II : HYDROGEN GAS SUPPLY AND PURIFICATION TRAIN.
III : NITROGEN GAS SUPPLY AND PURIFICATION TRAIN.
IV : GAS PREHEATER.
V : MANOMETER AND REACTION VESSEL.
VI : AMMONIA ABSORPTION TRAIN AND FLOWMETER.
VII : VACUUM TRAIN.

DIAGRAM I : FLOWSHEET OF APPARATUS USED FOR THE DETERMINATION OF CATALYTIC ACTIVITY.

2.1.2. Design.

The apparatus used is shown in plate 1, and in a general diagram I. It consisted of ammonia, hydrogen and nitrogen gas trains, a preheater, a reaction vessel and manometer, a vacuum train, a gas absorption train and the necessary electrical system. All parts were rigidly clamped to a metal framework. "Pyrex" glass was used throughout. The whole system was vacuum-tight, and was periodically tested for leaks. The electrical controls were mounted on a centrally situated switchboard.

The ammonia gas train is shown schematically in diagram II. Specially distilled refrigeration grade ammonia, as supplied by "African Explosives and Chemical Industries Ltd", was used. The purity specified by the suppliers was 99.98% ammonia, with a water content of less than 0.02%. Further, there were traces of argon and methane dissolved in the liquid. Efficient drying was essential, since water vapour is a strong ammonia catalyst poison.[23.] Gas from a liquid ammonia cylinder (A) was dried over calcium oxide (C) & (F) previously ignited at approximately 1000 °C followed by phosphorus pentoxide (G), with which dry ammonia does not react [24.25]. As it is important that the ammonia be as pure as possible, a further purification step was included as a precaution. Non-condensible gases were removed by evacuating the system, while twice distilling a quantity of ammonia from the liquid oxygen traps (H) and (I). The

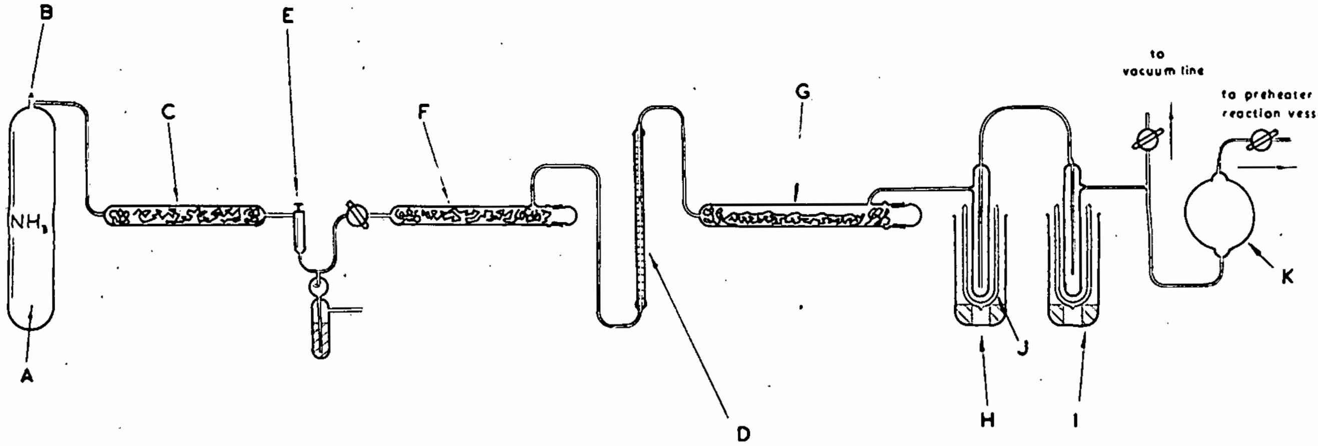


DIAGRAM II : AMMONIA GAS PURIFICATION TRAIN.

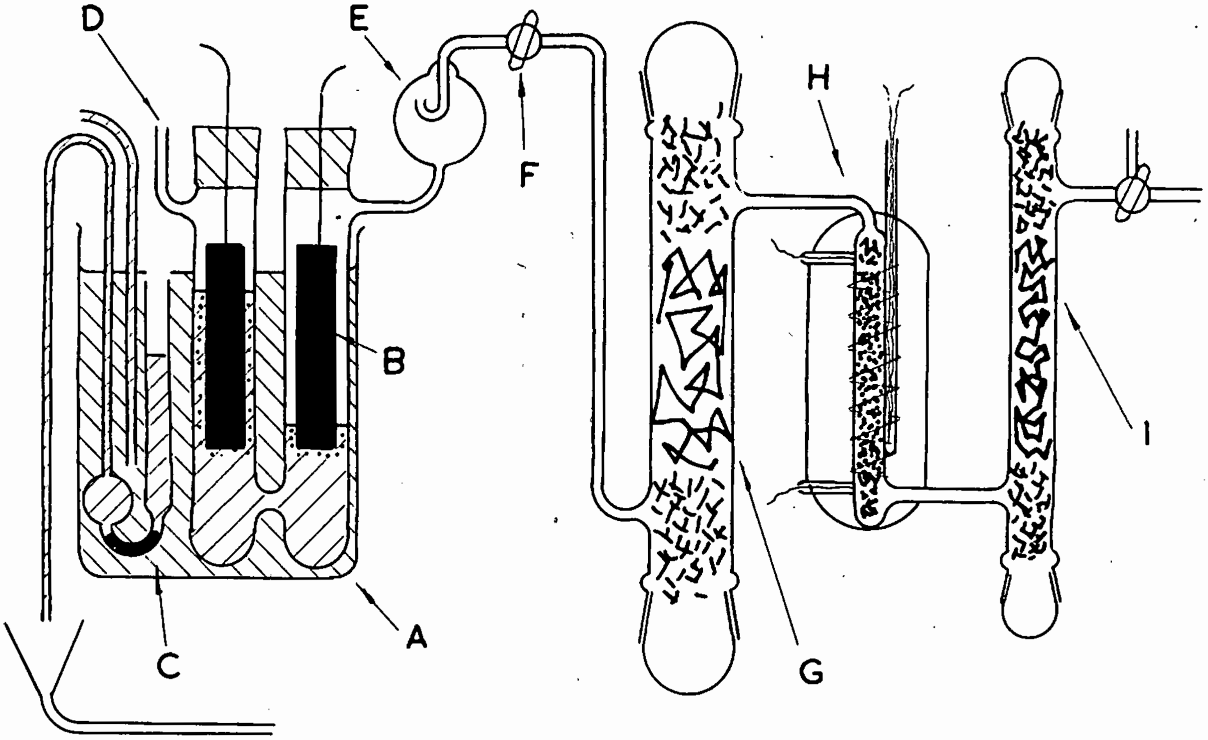
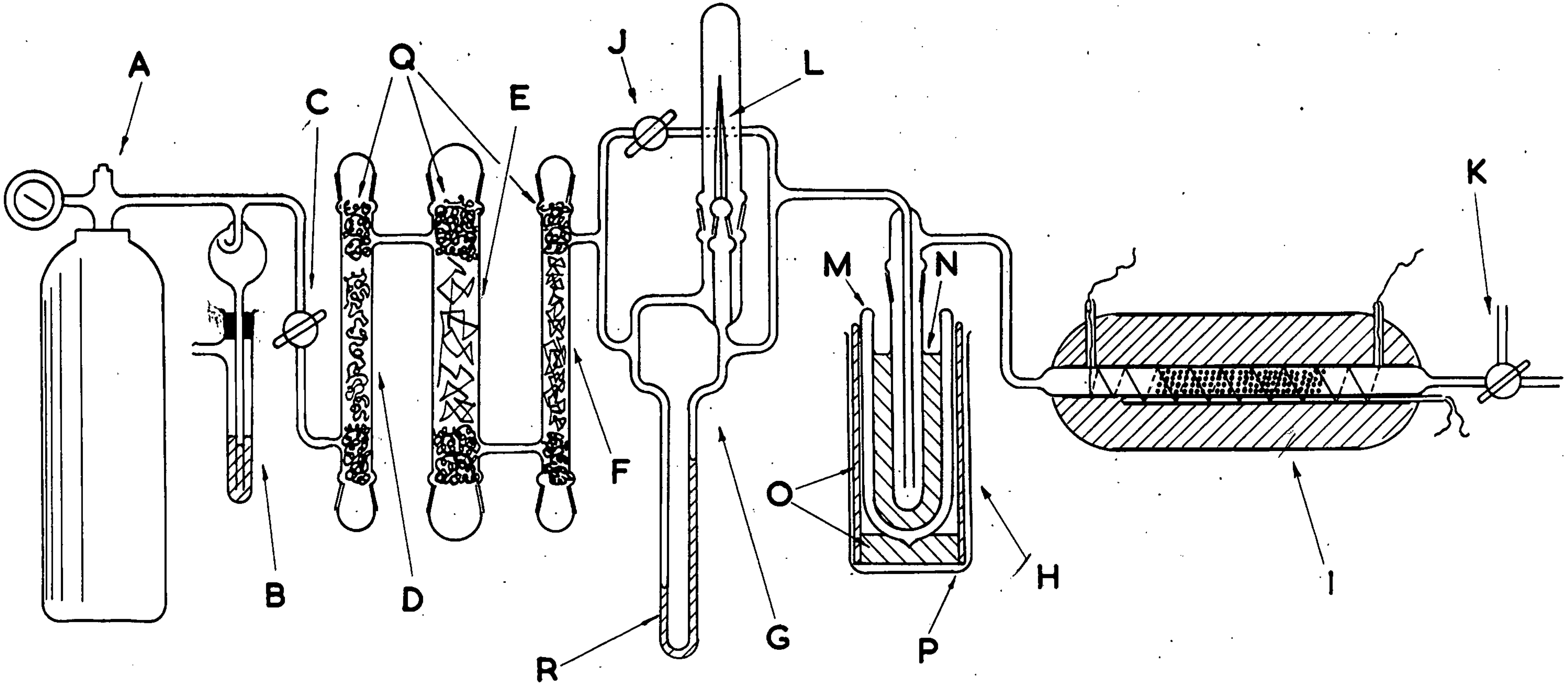


DIAGRAM III: HYDROGEN GAS SUPPLY

DIAGRAM IV.



DIAG: NITROGEN GAS SUPPLY TRAIN

The *nitrogen gas train* is shown in diagram IV. Cylinder nitrogen (A) passed over a pressure escape bubbler (B) and through tap (C). Carbon dioxide was removed by sodium hydroxide (D) and drying was done by passage over coarse calcium chloride (E) and magnesium perchlorate (F). Oxygen was removed by passage of the gases over hydrogen reduced copper foil in furnace (I) at 700^{0}C. Gas flowrate was measured on an orifice-manometer type flowmeter (G) containing di-butyl phthallate (R) as manometric liquid. A bypass tube (J) was used at times when the finely drawn-out capilliary orifice (L) became an undesirable constriction. Condensible material was removed in a liquid oxygen trap (H). The liquid oxygen (N) was contained in a Dewar flask (M) fitted into a cork-lined glass vessel (O,P)

A *gas preheater* was placed between the gas supply trains and the reaction vessel. The advantages were that (i) during static experiments, temperature equilibrium in the reaction vessel was rapidly regained after the ingress of gas into the initial vacuum, so that the necessary extrapolation of the data plot to zero time was more accurate, and (ii) during flow experiments the danger of a temperature gradient in the catalyst bed, due to cooling by the gas-stream, was minimised. The preheater was an electrically heated furnace of the normal design, filled with glass beads. The temperature was kept at approximately the

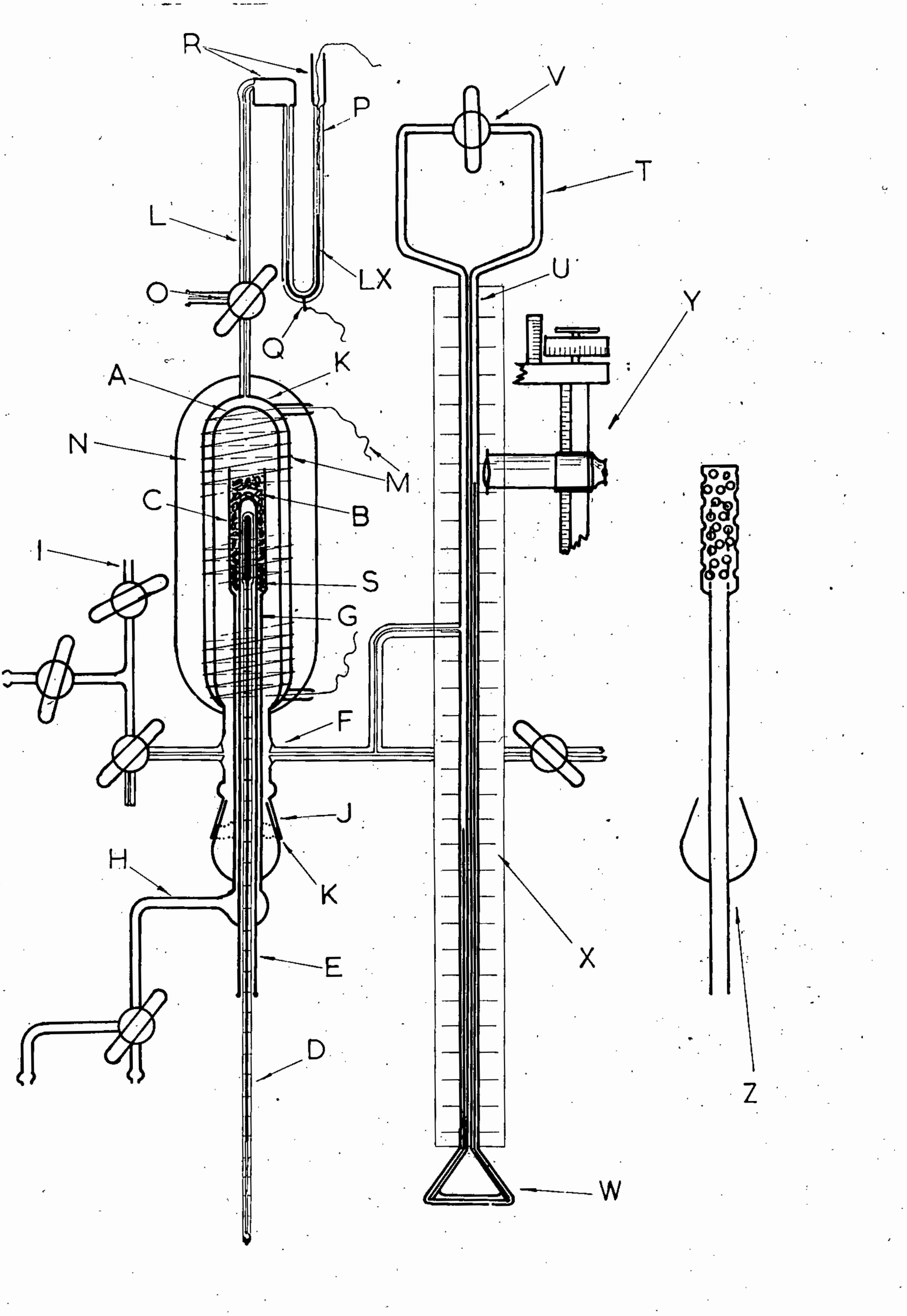


DIAGRAM : THE REACTION VESSEL

temperature of the reaction vessel.

The reaction vessel adapted for use in the flow method of experiment was an electrically heated, thermostated "pyrex" vessel of about 200 cc. capacity (A) (See diagram V) Gas entered at (F), flowed through the catalyst bed, down the annular space (G) and through (H) into the ammonia absorption system. The vacuum line was connected at (I). The pelleted catalyst (B) rested on glass-wool (S) in cage (C) which was inserted into the reaction vessel using ground-glass joint (J) sealed in with "**picien**" wax (K). The heater consisted of a nichrome element (M), thermally insulated by asbestos string (N). Expansion and contraction of air in the glass jacket (J) actuated an electrical "Sunvic" thermostat control via the make and break contacts of tungstan (Q) and nickel (P) and the mercury column (Lx). O is a 3-way tap, (R) mercury traps and (L) a 2mm capilliary tube. Temperature was measured on a 520 °C mercury thermometer (D) inserted into sheath (E) with the mercury bulb in the centre of the catalyst bed. The safe maximum working temperature in the "Pyrex" vessel was about 510 °C, and temperature change could be read to an accuracy greater than 0.5°C. No variation in temperature at equilibrium could be observed during the time required to obtain the necessary data, except in the case of lengthy static measurements of up to 30 minutes at a constant temperature.

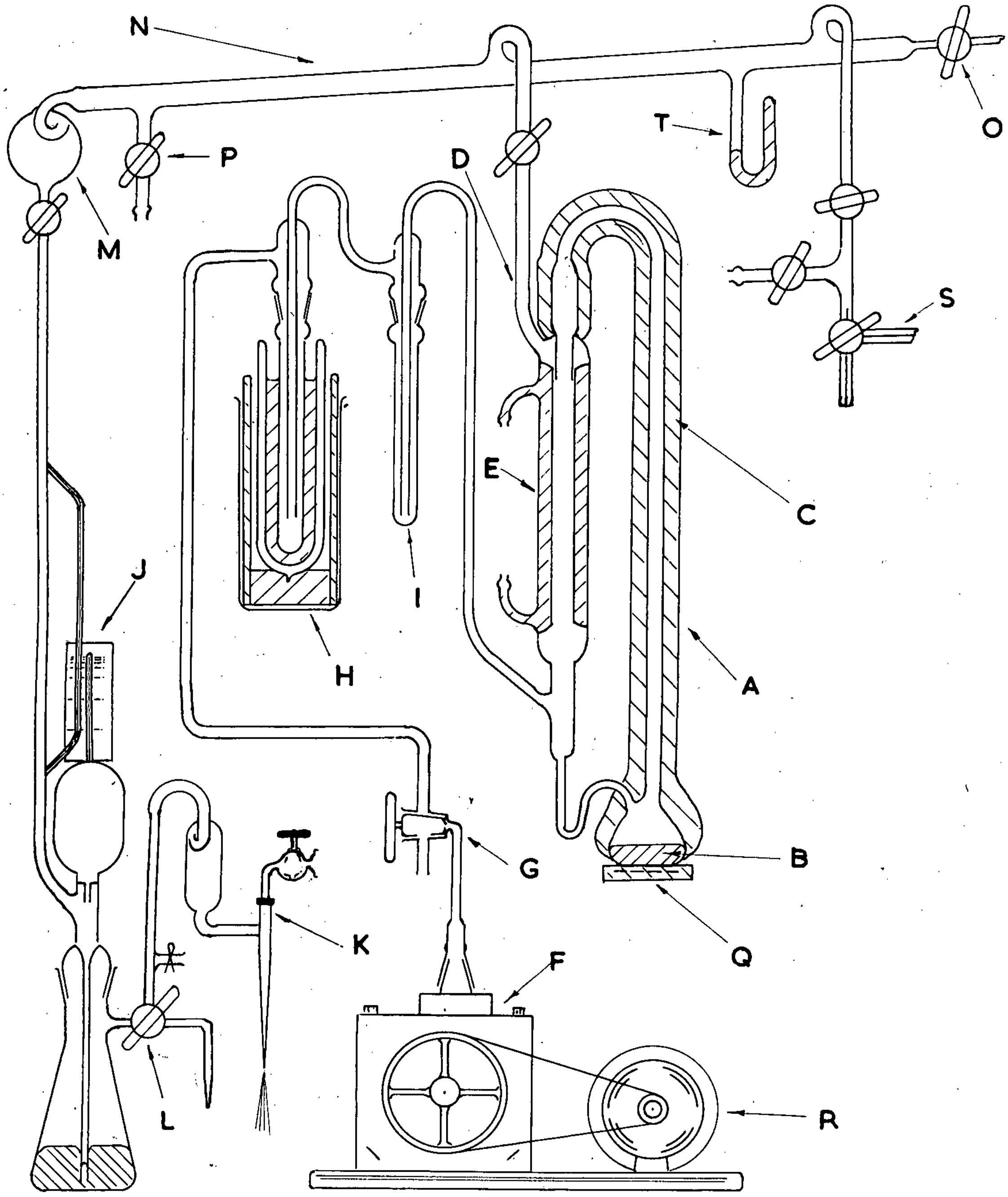


DIAGRAM THE VACUUM TRAIN

Pressure was indicated on a mercury manometer (T) of which arm (U) was under high vacuum, with tap (V) closed. The mercury level was indicated on scale (X) and pressure differences were measured with the aid of a rigidly mounted travelling microscope (Y).

The static method required the replacement of the catalyst cage, previously described by one shown in the diagram and labelled (Z). This cage, simply a perforated glass container, served only to hold the catalyst, while not obstructing free movement of the gas.

The <u>vacuum train</u> is shown in diagram VI. A vacuum of about 10^{-5}mm pressure was obtained by means of a mercury diffusion pump (A) backed by a mechanical vacuum pump (F). Between the two pumps a liquid air trap (H), a small air cooled trap (I) and a 3-way tap (G) were inserted. The traps protected the backing pump from ammonia gas and mercury. The pressure was measured by a Mcleod gauge (J), capable of measuring a pressure of 10^{-5}mm. and of indicating a pressure of approximately 10^{-6}mm. (K) was a waterjet vacuum pump, (M) a splashbulb, (T) a small manometer and (N) a tilted vacuum line placed above the apparatus to prevent mercury from entering the reaction vessel. The vacuum train was connected directly to the reaction vessel at (~~L~~S) and to the ammonia gas train at (O).

The <u>ammonia absorption train</u>. used during flow experiments is shown schematically in diagram VII. The decom-

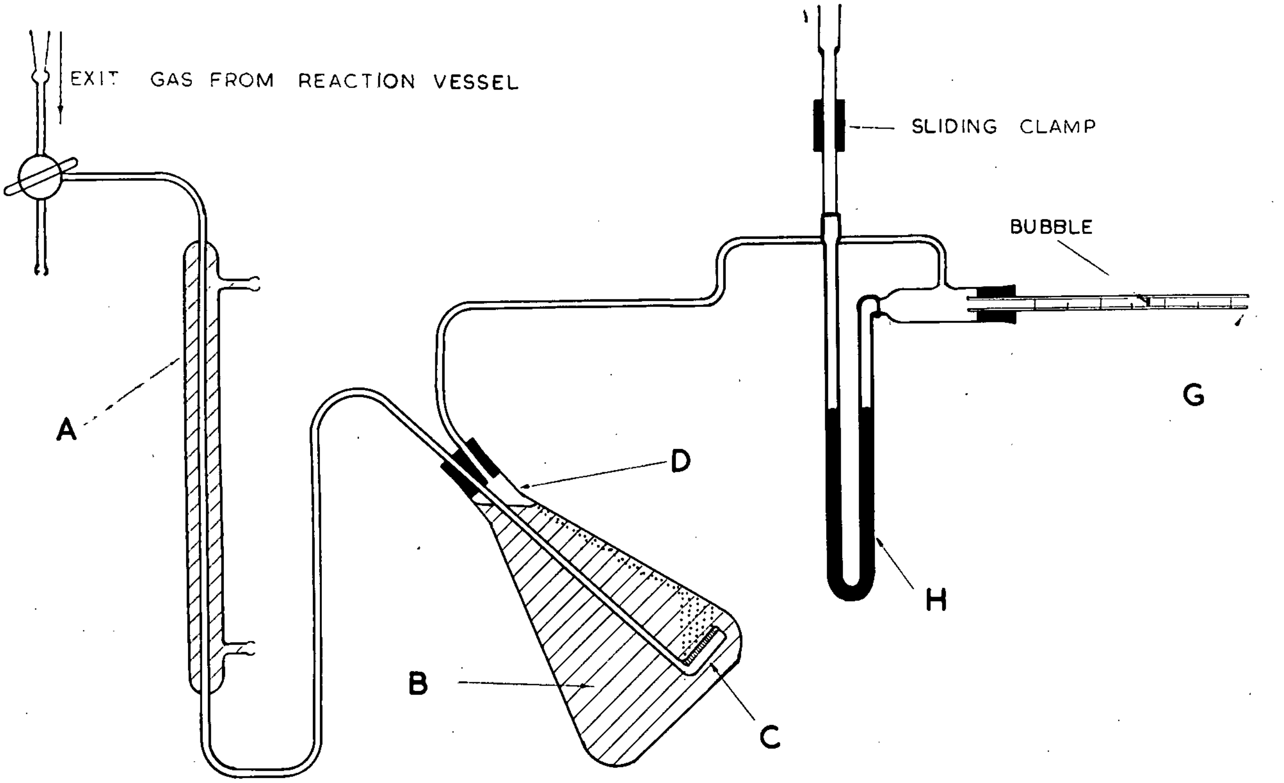


DIAGRAM VII. AMMONIA ABSORPTION TRAIN AND FLOWMETER...2.

position products leaving the reaction vessel were first cooled in a water-cooled tube (A) after which the ammonia was absorbed in hydrochloric acid (B), approximately 3 normal. A fine sparger (C), placed as shown in a large, tilted conical flask (D) caused an even stream of small bubbles to travel a considerable distance through the acid, without the gas pressure having to overcome a large pressure head.Methyl red indicator showed when spent acid required replacement.

The combined flowrate of the remaining decomposition products was measured on a soap-film flowmeter described by Gooderham[26]. It is shown in diagram VIII. The flowmeter shown in diagram VII is a modified one of this type and will be described later. The flowmeter originally used (diagram VII) functioned as follows: A thin film of "Teepol" or "Aerosol" solution was formed at the inner end of the tube (D) by lifting the mercury-sealed liquid reservoir (E) The film was carried up the graduated tube (F), (with the gas stream) and showed the gas flowrate without causing any resistance to the movement of the gas. It was highly sensitive, and could be used with equal efficiency over a wide range of flowrate by using interchangeable graduated tubes of varying bore. Three sizes were used: 20c.c., 2c.c and 0.5c.c capacity tubes, the respective internal diameters being 10mm, 4mm and 2mm. When measuring very small flowrates

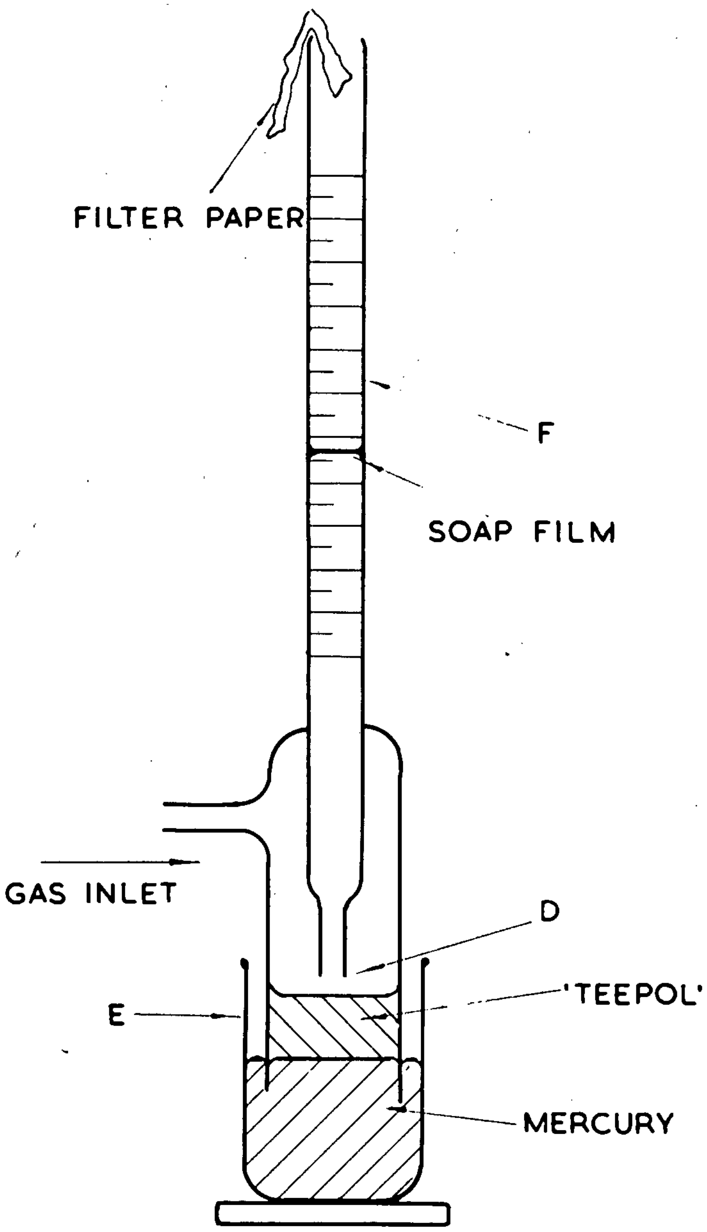


DIAGRAM VIII. FLOWMETER. 1

of the order of 0.02 c.c/minute, it was difficult and time-consuming to form a fine film in this way, as capilliary action in the upright tube caused errors in measurement, and the tube tended to resist motion of the film due to a certain amount of drying of the glass surface. At low flow-rates the film would often break when the mercury cup was lowered, since the rate of gasflow was insufficient to counteract the sucking effect of the lowered mercury cup.

The flowmeter was therefore modified to advantage for this experiment, as follows; (See diagram VII, flowmeter 2) The tube was placed horizontally. A "Teepol"-film was made to form over the outer end of the tube at (G) by touching the mouth of the tube with a "teepol"-moistened wad of cotton wool. The mercury-filled rubber tube (H) was then lowered, causing a reduced pressure in the system, which moved the film to the inner end of the tube, from which position it could move outward with the gas-stream. Thus it was not necessary to rely on the gas stream to form the film, but it could be formed independently when required. Furthermore, the tube could be rinsed by drawing water into it before each measurement. This arrangement worked equally well whatever size of graduated tube was used, provided that when necessary, the rubber U-tube was replaced by one of size corresponding to the size of the graduated tube.

The film flowmeter was ideally suited to most experiments. The lower limit of accuracy of measurement was of

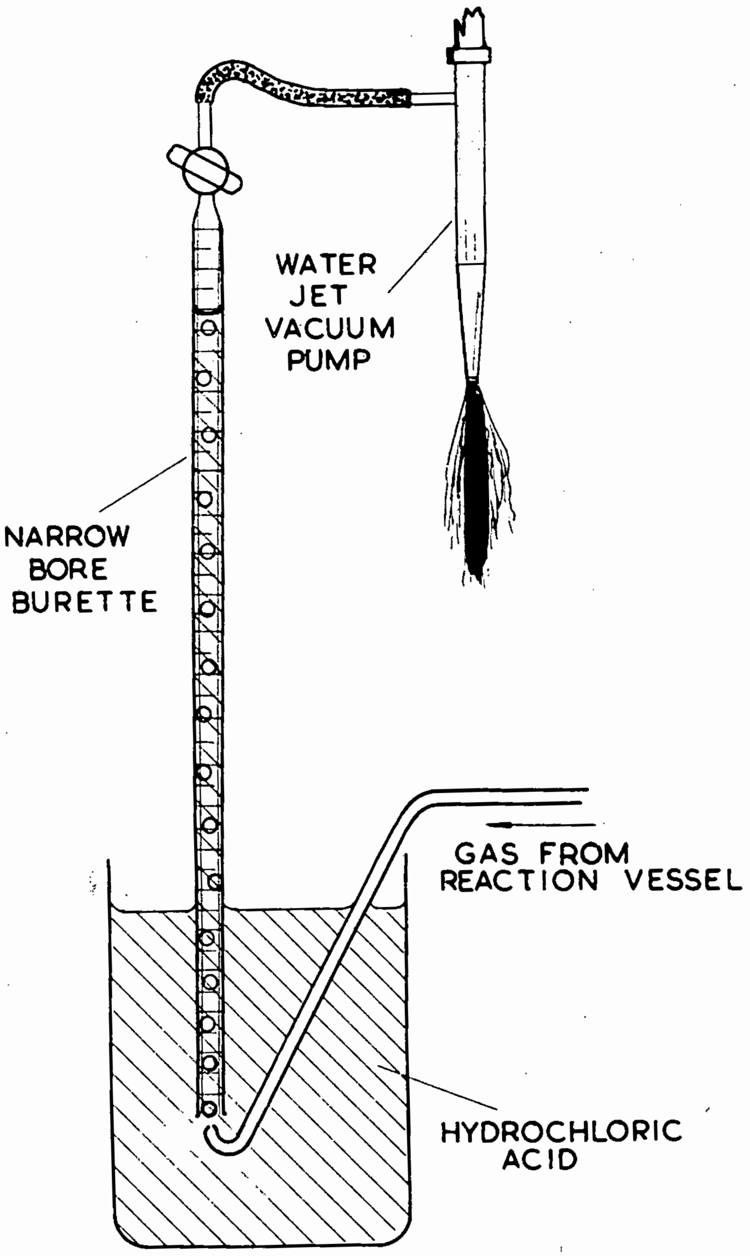


DIAGRAM IX: FLOWMETER

the order of 0.1 to 0.2 c.c/minute. (See Arrhenius plot for titanium nitride). This was due to the large dead space between the absorption vessel and the flowmeter, which was prone to slight volume changes with change of atmospheric pressure and local temperature. This was shown by a slight movement of the bubble in the 0.1c.c. capacity flowmeter (inner diameter circa 1mm.) When there was no flow of gas. The bubble did not always move outwards but in some instances backwards; the movement was always more pronounced in the early evening when temperatures dropped rapidly. It was noticed that when ammonia was flowing through the system at a rate of circa 100c.c./minute with no catalyst placed in the reaction vessel, the flowmeter indicated a flowrate of not more than 0.007 c.c./minute, which was confirmed by use of a more accurate flowmeter to be described. This reflects the efficiency of ammonia absorption and also the purity of the ammonia used, since unabsorbed gas constitutes only 0.01% of the total, this representing a maximum estimate. For reasons described in the section dealing with the preparation of the nitrides, cobalt and nickel nitrides were used in such small quantities, when determining the activation energies, that decomposition yielded a flow rate of less than 0.1 c.c/minute for decomposition products; the flowmeter system had thus to be replaced by a more sensitive arrangement. A graduated inverted narrow burette standing in an acid bath was used and arranged as shown in diagram IX The ammonia entered in small bubbles from a tube drawn out in a jet. Decomposition products collected in the burette, and the time taken to occupy a fixed volume indicated the rate of decomposition. A sparger was not practical, since in this case very tiny bubbles tended to adhere to the side of the burette. The acid was contained in a large beaker, and before each reading the locally neutralised acid, contained in the burette, was replenished from the acid bath by alternately emptying and filling the column several times. An indicator showed that the acid in the burette, was not neutralised during a single measurement, but soon became so if not replenished. The long tube allowed efficient ammonia absorption. In this way the dead space above the absorption liquid was eliminated, and measurements at low gas flowrates were found to be exactly reproducible. This method was limited in it's application to low flowrates of decomposition products, and for normal use the bubble flowmeter method, apart from being the neater and more rapid method, was preferred for greater accuracy. The reason is that at high flowrates, large bubbles form in the burette, which rise slowly with a consequent time lag in measurement. Plot 111 for manganese nitride (figure 4) resulted from data obtained by this method, and it is evident that at higher flowrates this plot is not as consistent as those obtained by the film flowmeter.

Another modification of the original vetically placed film flowmeter, may be mentioned, although it was used once only in this investigation. To eliminate the sucking effect of the lowered mercury cup, which tends to break a newly formed film, the lower end of the flowmeter was sealed off in glass, eliminating the mercury joint. The film was formed by raising a small cup placed inside the tube and containing the "Teepol" solution, with the aid of small bar magnets. One magnet was attached to the cup, which travelled along glass guides inside the tube, and a second external magnet served to lift and drop the cup.

The electrical system consisted of separate circuits for each furnace and for the vacuum pumps. The supply was 220V A.C. mains current distributed from a busbar system. The current input into the reaction vessel element was regulated by means of a "variac" auto-transformer. Pilot lights were placed in each circuit.

2.2 EXPERIMENTAL PROCEDURE.

The experimental procedure varied in detail for each individual catalyst used, depending on factors such as stability of the catalyst, mode of activation adopted, and the extent of ammonia decomposition caused by the catalyst. The flow method could be used in all cases, but the static method only when the most stable catalysts were used, and when these catalysts caused appreciable decomposition. The accumulation of hydrogen in the static reaction vessel resulted in a breakdown of the unstable catalysts. Furthermore, the dynamic system, apart from ensuring a low hydrogen partial pressure, was the more accurate method. A general outline of the experimental procedure will follow, and special procedures will be described where relevant.

2.2.1. <u>Static Method</u>.

The reaction vessel, containing the activated catalyst in pellet form, was evacuated strongly at the maximum working temperature, i.e. at about 500 °C. Pure, preheated ammonia was let in to a pressure of 200 mm. mercury, and a stopclock was immediately started. The crosswire of the travelling microscope was trained on the mercury meniscus, and the pressure difference was measured at one minute intervals for a period of 20 to 30 minutes. Since temperature equilibrium after letting in the gas was only regained after about 5 minutes, the plot of pressure change versus time at the temperature of experiment was only correct for values determined after 5 minutes. Initial gas pressure could not be measured accurately, but the time base was sufficiently accurate to allow extrapolation of the curve to zero time and hence to initial pressure. It was necessary to do this because the rate of decomposition decreases with time, due to an inhibiting effect of the continuously produced hydrogen.

This procedure was repeated at various randomly selected temperatures, so as to obtain data for a family of pressure change vs time curves, and hence for an Arrhenius plot of slop at zero time vs $^1/T$ °A.

2.2.2. Flow Method.

The pelleted, activated catalyst was contained in the appropriate catalyst cage, packed around the thermometer sheath, the depth of packing depending on the stability of the catalyst. The stable nitrides were packed in as deep a bed as the quantity available allowed. There was no danger of reduction of the nitride by hydrogen formed during reaction. The unstable catalysts were placed in as shallow a bed as was compatible with accuracy of measurement, and a high space velocity was maintained so that the partial pressure of hydrogen remained negligible.

The reaction chamber was initially evacuated to a very low pressure at room temperature. In order to avoid the denitriding of unstable catalysts in a vacuum, this step was omitted when using the nitrides of manganese, iron, cobalt and nickel. The reaction vessel was then flushed of all other gases by passing ammonia through it for several hours until the flowrate of exit permanent gas was less than 0.01c.c./minute. The preheater was then switched on, and the reaction vessel heated and kept at the maximum working temperature for an hour or more before the rate of decomposition was measured. It was kept at constant temperature until the extent of decomposition remained constant.

A graduated tube of convenient size was placed in the flowmeter, and the rate of flow of unabsorbed decomposition products was measured at various randomly chosen temperatures, replacing the flowmeter tube with a smaller or larger one when necessary. A 20-minute interval was allowed between readings, excluding the time taken for actual reading. In the case of the nitrides of cobalt and nickel, 45 minute intervals were allowed, so that the composition of the nitrides could reach equilibrium. The figures tabulated, i.e. those obtained at 20 or 45 minute intervals, were each the result of several consecutive measurements which without exception were almost exactly reproducible. Measurements taken during the equilibrium - reaching periods are not recorded, but a constant check showed that normally equilibrium was rapidly attained, and the rate of decomposition was virtually constant during the last 10 minutes of each period. The exception was nickel nitride, probably due to a slight change in structure when temperature was varied, but readings became constant before the termination of the 45 minute period.

The nitrides of cobalt and nickel, when stored overnight, were kept at room temperature in an atmosphere of nitrogen to prevent possible undue contact with hydrogen.

3. NITRIDE PREPARATION.

3.1. Introduction.

The nitrides of the following elements, arranged in order of their atomic number, were used as catalysts:

Ti, V, Cr, Mn, Fe, Co, Ni.

The ease of preparation and the stability of the products vary considerably, but in a systematic way. This is illustrated in table I. In order to prepare the nitrides of titanium and vanadium, special high temperature furnaces were required, but once the nitrides were obtained pure, they were easy to handle and quite stable. On the other hand, to prepare the nitrides of cobalt and nickel, a lower temperature is required, but the range has to be strictly controlled, otherwise the composition of the metal-metal nitride system changes.

3.2 Experimental.

In broad outline the experimental procedure was as follows: The metal or metal compound reactant material was heated in a tube-furnace, and a rapid stream of carefully purified reactant gas, usually ammonia, was passed over it. The required temperature was maintained for a sufficient length

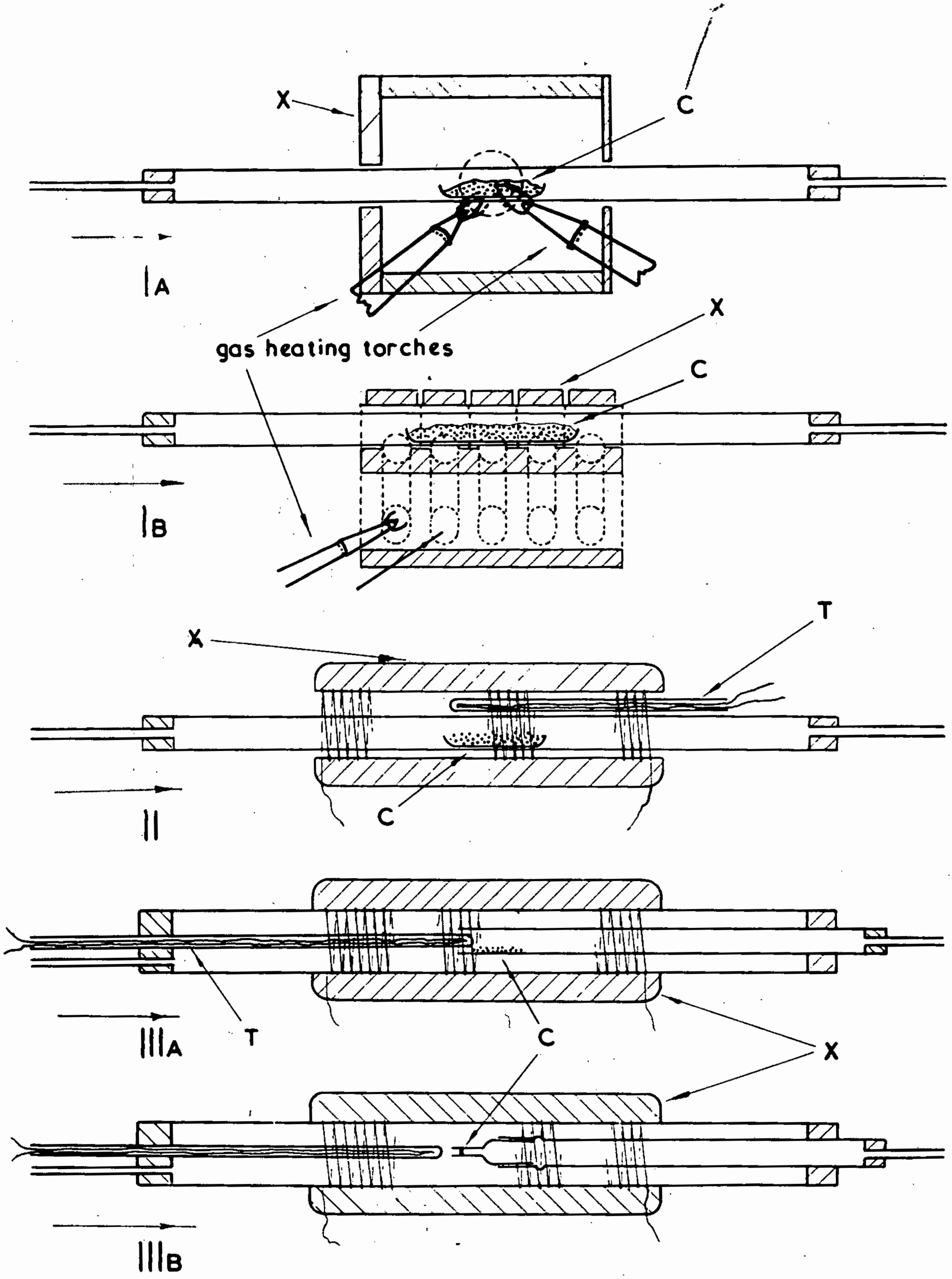


DIAGRAM X : FURNACE DESIGN: C : Reactant.
T : Thermocouple.
X : Heat insulation.

TABLE I.

NITRIDES : STABILITY.

METAL	FORMULA OF NITRIDE CORRESPONDING TO NITROGEN CONTENT AS ANALYSED †	TEMPERATURE REQUIRED FOR FORMATION IN AMMONIA	TEMPERATURE OF DECOMPOSITION	PURITY OF PRODUCT OBTAINED (BASED ON GIVEN FORMULA) †††	STABILITY DURING USE
		°C	°C	% NITRIDE	
Ti	TiN	1450[28]	MP.:2950[27]	99	Stable
V	VN	1100[29]	2000°[30]	99	Stable
Cr.	(Cr_3N_2)	850[31]	1000°	98	Stable
Mn.	(Mn_3N_2)	700-800[31,35]	Decomposes at approximately 500°C if ammonia not in excess.	95	Stable
Fe.	(Fe_2N)	450[38]	Decomposes at working temperature unless hydrogen partial pressure very low.	99	Practicaly Stable.
Co	(Co_2N)	475[40]		95	Stable only under strictly controlled conditions
Ni	(Ni_3N)	445[43]		97	

(†) These formulae are not intended to indicate the composition of a "pure" nitride, but the composition to which the analysed value approximates

(††) "% Nitride" indicates the variation from such composition.

of time for maximum conversion to the nitride to take place. The extent of nitride formation was determined by analysis of the product after cooling in a stream of the gas. It was alternately heated and analysed until three consecutive analyses showed no increase in the nitrogen content.

For consistency in method of preparation, ammonia was the reactant gas in all cases, but pure hydrogen was used to reduce technical iron oxide and cobalt oxide to metallic catalysts. Nickel and cobalt nitrides were stored in an atmosphere of nitrogen. The gas flowrate could be controlled and measured. Gas pressure was kept slightly above atmospheric pressure, so that there could be no diffusion of air into the furnace tube. This was particularly necessary when an alundum tube was used, since this material tends to become slightly porous after a period of use.

Two or more samples of nitride were prepared independently in each case.

Furnace design.

Three types of furnace were used, according to the temperature that was required. (See diagram X)

Type I. For maintained temperatures of either circa 1250°C or circa 1500°C, type Ia furnace was used. Two large gas torches were capable of heating a twelve inch length of alundum tubing, of which four inches could be maintained at white heat (circa 1500°C) When gas-oxygen was used; and a steady temperature of about 1250°C when a gas-air mixture was used. The nozzles of the air-cooled torches were outside a hole in the thick refractory heat insulating shell. The temperature was measured with an optical pyrometer, calibrated against an amyl acetate flame, and was checked by means of a Pt-Rh thermocouple calibrated to 1400°C. The maximum temperature exceeded 1500°C.

IB.

IB Furnace was of similar type to IA, but due to a smaller, more compact design was a more economical furnace, since it used far less oxygen to produce an equivalent temperature. The short heating length made it unsuitable for the preparation of titanium nitride, probably due to the fact that it could not preheat the entering gas sufficiently, with consequent cooling of the reactant in the tube. With oxygen-gas torches this furnace could heat a 2 inch length of tube to approximately 1500°C, while the adjacent tubing remained relatively cool. A temperature of 850°C was maintained when a row of "Bunsen"-type burners were used.

Type II furnace was used for temperatures up to 900°C. Electrically heated, it consisted of a nichrome resistance wire element wound round a silica core and insulated with several layers of asbestos string. A reaction tube of either silica (700°C - 900°C) or of combustion tubing (< 700°C) could be placed inside the silica core, independent of the core itself. The temperature was measured by means of a Pt-Rh thermocouple placed next to the reaction tube.

The above-mentioned furnaces all had the disadvantage that with the thermocouple outside the reaction tube, there was some error in the temperature reading, since the gas flowing through the tube cooled the reactant to a certain extent. For our purpose, however, this was not important.

Type III furnace was for use below 500°C. Accurately controlled temperature conditions required for preparation of the unstable nitrides necessitated the use of a furnace incorporating a thermocouple which reached into the reaction tube and next to the reactant. The reaction vessel which was used for determining catalytic activity itself was suitable and was at times used for this purpose. For convenience, a second furnace, IIIA, was made for independent use. Heating was done electrically, in the normal manner. The reactant was not placed in a boat, but was spread just inside one end of the long gas exit tube projecting into the heating area, as shown. In this manner a large reactant surface was exposed directly to the gas stream. If gas is not allowed to diffuse rapidly through the bulk catalyst, hydrogen partial pressure may cause nitride reduction in a deep bed. A~~n~~ Constantan – iron thermocouple was placed in a glass sheath, which extended into the reaction tube. It was calibrated against a 500°C mercury thermometer.

In order to adapt this furnace for use in preparing cobalt nitride the design was modified as shown: IIIB. The reactant metal was placed in a 4m.m. inner diameter tube to form a bed about 1m.m. deep. The tube fitted into the furnace as shown, by means of a ground-glass joint, so that it could be removed and fitted into the reaction vessel for an activation energy determination. The reason for using such small quantities of catalyst in this manner will be explained in a later section.

Using these furnaces it was possible to produce any temperature up to 1500°C.

Preparation of Individual Nitrides.

3.3 Titanium nitride.

O.Ruff [28] showed that titanium nitride forms when TiO_2 is heated in ammonia at 1400°C to 1500°C. This method was followed using pure white powdered titanium dioxide. It was heated in ammonia at 1500°C in type IA furnace. Type IB furnace yielded an incompletely formed nitride for reasons already stated, but it was used for initial treatment of the reactant before the final product was completely formed by using furnace IA. A molybdenum boat was used. After heating for one hour it was cooled and crushed in an agate bowl. At this stage a dark blue lower oxide of titanium had formed, which crumbled readily when crushed. When it was not crushed at this stage, the final product was a coarse powder, difficult to pulverise to fine consistency, consisting of blue oxide grains covered with a layer of the golden-yellow nitride. After this, it was heated for a total of approximately twenty hours at 1500°C, cooling and crushing the substance every four hours. After eight hours very little blue oxide could be seen, but inspection by microscope showed that each grain consisted partly of blue oxide and partly of yellow nitride. This excluded the possibility of separating the nitride from the oxide by physical means. All attempts to do so failed. Heating was therefore continued until microscopic examination showed no trace of the blue oxide. The product was then analysed chemically, followed alternately by further heating until consecutive analyses showed no increase in nitrogen content. The final analysis showed a product in agreement with the theoretical stoichiometric composition of TiN_1 within experimental accuracy limits. Estimation of nitrogen content showed circa 98% to 99% TiN. The main impurity was probably oxygen existing interstitially as atoms or ions in the lattice, either below the surface or attached to metal atoms associated with the highest free energy. It may be expected, however that the prolonged treatment in ammonia removed the normally tenacious oxygen atoms to such an extent that oxygen poisoning of the catalyst did not take place.

The nitrogen content of the nitride was determined by Duma's method i.e. by measuring in a nitrometer the volume of nitrogen quantitatively liberated by a heated mixture of the nitride and copper oxide. An error of approximately 0.5% to 1% could be expected, since the experiment was done on semi-micro scale, and since the nitride is exceptionally stable to chemical action, resulting in incomplete decomposition. That the nitride was not completely decomposed was evident from the fact that a very slow evolution of micro-bubbles of nitrogen still occurred when the determination was terminated. A semi-micro method was used to obviate wastage of rather scarce nitride. The results of the analyses are tabulated below:

TABLE II. ANALYSIS OF TITANIUM NITRIDE BY DUMA S' METHOD.

(Samples of the order of 0.02 gram)

TiN_1 requires 22.77% nitrogen.

Sample	% Nitrogen	% Purity TiN
1	22.6, 22.4	98.7
2	22.3, 22.4, 22.3	98.0

3.4. Vanadium nitride.

According to Epelbaum and Brager,[29] ammonium vanadate is quantitatively converted to vanadium nitride when heated in a stream of ammonia at 1100°C. These authors stated that the process is an auto-oxidation and-reduction of the vanadate, and by X-ray investigation found that the VN crystal lattice forms simultaneously with the reduction of the vanadate to VO. A distortion of the original lattice takes place to form the normal lattice of VN. Structural defects of the resultant lattice may therefore be expected. Friedrich and Sittig's[30] alternative method was not considered suitable, although an unused sample of VN was prepared as suggested by reduction of the pentoxide by admixture with carbon and the action of hydrogen at 1250°C. The resulting trioxide was nitrided with a mixture of nitrogen and hydrogen. The danger of carbide formation (1200°C) and the indirect method involved in the latter preparation made the former method more suited for our purpose. Furthermore, the use of ammonia instead of nitrogen as reacting gas corresponds more to the treatment of the other metals.

The procedure was as follows: Pure ammonium vanadate was heated in a stream of pure ammonia at about 1250°C in type IA furnace, using gas-air heating torches. This temperature, measured on an optical pyrometer and by a thermocouple outside the reaction tube, was probably slightly higher than the true temperature of the reactant within the tube. A molybdenum boat was used in preference to a carbon boat, which causes carbide formation at 1200°C, [30]. Analyses were done after 4 or 8 hours of heating until the product absorbed no more nitrogen. As in the case of titanium nitride, the conversion to vanadium nitride could be observed visually by the colour change from white vanadate to deep blue lower oxide and finally to the brown-violet nitride. Friedrich and Sittig describe the appearance of the pure nitride as being dark brown powder with a violet tinge, and our nitride has the same appearance. Final analysis showed the product to be approximately 99% VN. The results of the analyses are shown below.

TABLE III. ANALYSES OF VANADIUM NITRIDE BY DUMAS' METHOD

(Samples of the order of 0.02 gram)

VN_1 requires 21.57% nitrogen

Sample	% Nitrogen	Mean % Purity VN
1	21.18, 21.25	98.4
2	21.61, 21.16	99.2

Duma's method of analysis was used. All remarks regarding the analysis of titanium nitride hold as well for the analysis of vanadium nitride. The main impurity was probably oxygen, since an oxide is an intermediate product.

3.5 Chromium nitride.

Henderson and Galletly[31] prepared a nitride of chromium of composition corresponding to Cr_3N_2 by heating the metal in ammonia at 850°C. R.Blix[32] showed that the hexagonal close-packed phase β(Cr_2N) of 11% to 16% nitrogen content formed when electrolytic chromium was treated with ammonia at 800°C. It is mentioned by Hückel[33] that the nitride is formed most readily when the metal obtained from the amalgam is used, since in this case the metal lattice is incomplete. The normal ordered metal lattice of chromium does not absorb nitrogen readily.

Chromium nitride was prepared, as were the remainder of the nitrides in the series, by the action of ammonia on the metal. The metal used was "Matthey" electrolytic chromium flake of high degree of purity. It was spectrographically standardised by the suppliers, who reported only very faintly visible lines for impurities, and no visible lines for other transition metals.

The flake was crushed very fine in an agate bowl and heated in ammonia at 850°C in furnace IB until there was no increase in weight. Absorption of nitrogen was slow, and only after about 35 hours heating did analysis show virtually complete conversion to a nitride of composition corresponding to Cr_3N_2. No further absorption of nitrogen occurred. The suggestion that the chromium metal lattice should be incompletely formed for rapid nitride formation probably accounts for the prolonged treatment required for the preparation. A fine state of division of the initial powder was found to be an important prerequisite for enhanced efficiency in preparation. The substance was also pulverised every 10 hours, since the particles tended to adhere together as a hard mass. The final product was analysed for chromium content, and the results are shown below:

TABLE IV. ANALYSIS OF CHROMIUM NITRIDE BY SODIUM PEROXIDE FUSION AND IoDoMETRIC TITRATION.

(Samples of the order of 0.1 gram)

Cr_3N_2 requires 84.77% Cr.

Sample	% Chromium	Mean % Cr_3N_2
1	85.23, 83.99, 85.02	97.7
2	84.86, 85.15	98.5

The nitride was found to be extremely resistant to chemical reagents, and would not dissolve in any of the acids. Hydrochloric-sulphuric-, phosphoric-, and nitric acid or aqua regia, hot or cold, concentrated or dilute, had very small, or no effect on it. Kjeldahl digestion was attempted without success. Dumas' method produced extremely slow evolution of nitrogen. Finally, a successful estimation of chromium was done by fusion with sodium peroxide followed by iodometric titration, which gave practically reproducible results. The procedure described by Scott [34], was followed. It may be mentioned that it was found that the nitride is only completely converted to the green oxide when heated in air at a white heat, and in order to use this method for analysis a special refractory container is required.

It is unlikely that the nitride used was at all contaminated, and since it is an interstitial phase in which some interstitial positions may be vacant, the recorded "% Cr_3N_2" (Table IV) does not imply that the composition Cr_3N_2 is the pure form of nitride, but only the composition to which the nitride approximates.

3.6 Manganese nitride.

Nishiyama and Iwanaga [35] prepared manganese nitride by the action of ammonia on electrolytic manganese at 600°C. Henderson and Galletly [31] showed that manganese forms a nitride, approximately Mn_3N_2, when heated in ammonia at 800°C.

"Matthey" electrolytic manganese, spectrographically pure (impurities circa 0.005%) was crushed to a fine powder, which, in contrast to chromium could be achieved with very little difficulty. It was heated in a rapid stream of ammonia, for although this nitride may be considered stable for our purpose, a high space velocity in preparation and use was a precaution. After heating for 10 hours in type II furnace at 750°C, the mass remained constant, and analysis showed circa 13.8% nitrogen content. (i.e. approximately 95% of Mn_3N_2) There was a very slight increase in weight during a further period of 10 hours at 700°C. Final analysis showed no improvement on 13.8% nitrogen content, even at lower temperatures and higher space velocities. This result was obtained for two separate samples.

The final product, of dull grey appearance, dissolved in warm, dilute sulphuric acid, and the nitrogen was quantitatively converted to ammonia, which was determined by distillation from an alkaline solution, absorption in dilute acid and titration. The results are tabulated below:

TABLE V. ANALYSIS OF MANGANESE NITRIDE FOR NITROGEN CONTENT.

(Samples of the order of 0.2 to 0.5 gram)

Mn_3N_2 requires 14.60% nitrogen.

Sample	% Nitrogen	Mean % Mn_3N_2
1	13.80, 13.90, 13.80	94.8
2	13.87.	95.0
	13.82, 13.88	94.9

3.7 Iron nitride.

Iron nitride may be prepared by the action of ammonia on the metal at 450°C [35]. The NH_3: H_2 ratio, according to Lehrer [37] and others, determines the nitrogen content of the nitride, and hence the phase type. Jack [38] stated that the ζ phase (Fe_2N) richest in nitrogen content forms more readily just below 450°C, while the ϵ (Fe_3N) phase forms above 475°C.

"Matthey" iron sponge, prepared by reduction by hydrogen & spectrographically pure ($>99.995\%$ Fe) was heated in a rapid stream of pure ammonia at 475°C. After more than 15 hours consecutive analyses and weighing showed no increase in nitrogen content in a product containing about 11% nitrogen. It has been shown by Jack and others (See section 4.6) that this nitrogen content determines an ϵ (Fe_3N) phase and the ζ (Fe_2N) phase extends from 11.1%N to 11.3%N. Fe_2N. corresponds to 11.14% nitrogen.

The temperature range of decomposition of the nitride in the absence of pure ammonia coincides approximately with the temperature range of its formation [39]. The structure, during preparation and use therefore probably changed continuously in a dynamic equilibrium. The analytical method used for iron nitride was similar to that used for manganese nitride, and the results are shown below:

TABLE VI ANALYSIS OF IRON NITRIDE.

(Samples of the order of 0.3 to 1.2 gram)

Fe_2N requires 11.14% nitrogen.

Sample	% Nitrogen	Mean % Fe_2N
1	10.99, 10.47, 10.88	98.2
2	11.11, 11.03, 11.00	99.2

3.8 Cobalt nitride.

Beilby and Henderson [40], in 1901, obtained milligram quantities of cobalt nitride when a rapid stream of ammonia was passed over cobalt metal at, and slightly below 470°C. Their product contained 10.33% nitrogen. (Co_2N corresponds to 10.62% N) Recently Juza and Sachze [41] and Clarke and Jack [42] prepared the nitride at lower temperatures of 380°C and 350°C respectively. Juza and Sachze used cobalt reduced from the oxalate at 350°C in hydrogen, and prepared small quantities of nitride. Clarke and Jack readily obtained macro quantities of up to 1 gram of nitride of nitrogen content $10.61 \pm 0.01\%$ if they passed pure ammonia over 380 mesh cobalt powder at 350°C. For our purpose it was necessary to use such quantity of catalyst that it would not decompose at working temperatures of over 400°C. Therefore very small quantities of nitride

(0.02 gram) were prepared and used at temperatures specified by Beilby and Henderson. ($>470^{\circ}C$).

It may be mentioned that Juza and Sachze obtained the γ (Co_3N) phase by thermal decomposition of Co_2N at $276^{\circ}C$, a temperature considerably below our working temperatures. They could not obtain this nitride in pure form directly by the treatment of the metal with ammonia. For this reason we may assume that the catalyst used in our experiment was predominantly the δ (Co_2N) phase.

It was recognised by Beilby and Henderson that hydrogen formed by ammonia decomposition during preparation causes a reduction of the nitride. It was stated that it was essential to nitride formation that pure ammonia must be present in exess. It was for this reason that in our experiment, several early attempts to prepare the nitride failed, for when using normal quantities of several gram of metal, even with a rapid flow of ammonia, no detectable amount of nitride formed after more than 10 hours of treatment. Pure cobalt oxide, first reduced in hydrogen at circa $600^{\circ}C$ and then treated with ammonia at $470^{\circ}C$ yielded no nitride. When exposed to air, the substance warmed up, probably because the metal was in a pyrophoric state. Pure, hydrogen reduced "Matthey" cobalt was also used, without success.

The next step was to use a smaller quantity of approximately 0.5 gram of cobalt and a relatively high space velocity of ammonia of about 5000 c.c/c.c/hour, but after ten hours only about 3% nitrogen was absorbed. The measured decomposition of ammonia over such a small quantity of catalyst was of the order of 1 c.c/minute, and the use of less catalyst would have caused insufficient decomposition for accurate measurement by the normal method. It was clear that smaller quantities of catalyst had to be used, and therefore the absorption equipment was modified in design so that smaller gas flowrates could be measured. A more sensitive arrangement described in section 2.1.2. was used. It was possible to measure with unexpected accuracy the decomposition caused by as little as 0.01 gram of catalyst.

The final procedure was as follows: In two experiments respectively 0.03 gram and 0.01 gram of hydrogen reduced "Matthey" cobalt sponge, spectrographically pure (>99.99% Co) were used. A sample was placed in a 4m.m. inner diameter tube (see section 3.2.) to form a bed less than 1 m.m. deep, supported on a tightly packed plug of glass wool. The small diameter of the tube, through which the ammonia was passed, made possible the very high space velocities of ammonia of approximately 70,000 to 120,000 c.c./c.c./hour. It was placed in the modified furnace, type IIIB, described in section 3.2. and heated first at 470°C. The temperature was gradually reduced to 460°C during 20 hours, keeping the space velocity approximately 100,000c.c/c.c/hour. After cooling, the catalyst container was placed in the reaction vessel without removing the catalyst. Further similar treatment was continued for 5 hours at 465°C. The catalytic activity was then determined, the temperature being maintained in the region of 460°C. The product was analysed afterwards, and contained 10.1% nitrogen. The duplicate experiment gave a product assaying 10.2% nitrogen. During the latter experiment the catalyst was stored in an atmosphere of nitrogen when not in use. A similar analytical procedure to that used for iron nitride was followed. With care the results were reproducible, although the small quantity of nitride available were analysed in batches of 0.01 to 0.03 gram. The results are shown below:

TABLE VII. ANALYSIS OF COBALT NITRIDE.

(Samples of the order of 0.01 to 0.03 gram.)

Co_2N requires 10.62% nitrogen.

Sample	% nitrogen	Mean % Co_2N
1	10.1, 10.0	94.7
2	10.2	96.1

3.9 Nickel nitride.

Nickel nitride is less stable than cobalt nitride, but a similar preparative method was used, and the entire preparation was done inside the reaction vessel. According to Juza and Sachze,[43] 10 to 20 milligram of nickel absorbs 7.37% nitrogen when treated at 445°C ± 2°C in a stream of ammonia flowing at 22 cm./second. (Theoretically Ni_3N requires 7.37% nitrogen) Beilby and Henderson [40] prepared nickel nitride virtually in agreement with Ni_3N. Hagg [44] found no effect of ammonia on nickel at 300° to 1000°C, but Grandadam [45] found that nickel absorbed 9% nitrogen. The procedure of Juza and Sachze was decided upon as being the most suitable for our preparation, and the experimental conditions were followed closely where possible. A product containing 7.2% nitrogen resulted. It must be emphasized that the product was analysed only after the energy of activation had been determined, and that during the experiment the temperature was varied from about 440° to 450°C. According to Juza and Sachze the temperature range in which the nitride is stable is very narrow, and deviation from the specified temperature yields a product of low nitrogen content.

The metal used was hydrogen reduced "Matthey" nickel sponge (>99.99% pure). The final products in two experiments respectively contained 7.21 and 7.12% nitrogen. The analytical procedure was similar to that used for cobalt nitride, and the results are tabulated below:

TABLE VIII ANALYSIS OF NICKEL NITRIDE.

(Samples of the order of 0.01 to 0.03 gram)

Ni_3N requires 7.37% nitrogen.

Sample	% nitrogen	Mean % Ni_3N
1	7.21	97.8
2	7.21	96.6

4. RESULTS.

4.I . Graphs and mathematical relations.

The apparent energies of activation for the ammonia decomposition have been determined for several catalysts, using a plot based on the integrated Arrhenius equation.

$$k = Ae^{-E/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where k = rate constant.

A = frequency factor.

E = energy of activation.

R = gas constant : 1.987 $\mathrm{cal.deg^{-1}.\ mole^{-1}}$.

T = absolute temperature.

A plot of log (rate of reaction) vs.reciprocal of absolute temperature was made in each case. Hence, from equation,(1) assuming the frequency factor to remain constant with changing temperature, E was determined by the relation:

$$2.303 \times \text{Slope of plot} = -E/R$$

$$\text{i,e, } E = -\text{Slope} \times 2.303 \times 1.987 \text{ calories/mole.}$$

The energy, E, was determined at constant gas pressure, and no correction was made for the change in gas composition in the catalyst bed. A linear log (rate) vs reciprocal temperature plot was shown in each case, except for the smaller value of energy of activation determnied for chromium nitride, which showed an erratic plot which was not entirely due to experimental error. An approximately linear relationship was, however, shown.

The experimental "rate of reaction" was a value proportional to the rate constant, k. For the static method it was the rate of pressure increase at zero time of a constant volume of pure ammonia, based on the equation:

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

A series of plots of pressure change vs time (t) at constant temperature were made. In order to determine the rate of pressure increase at zero time, it was necessary to extrapolate each plot to zero time for reasons described in section 2.2.1. For the flow method it was the flowrate of residual decomposition products after removal of undecomposed ammonia. The ammonia flowrate before contact with the catalyst was constant, and it is assumed that the ratio of decomposition products nitrogen and hydrogen was at all times 1:3.

Tabulated data are given in the appendix (section8), the resultant plots being shown where pertinent to the discussion. Figures are only given for the nitride catalysts, but Arrhenius plots are shown for all catalysts used.

Table 9 shows, in summary energies of activation for the various nitride catalysts.

4.2. Titanium nitride.

The catalytic activity of titanium nitride was studied at temperatures ranging from 460°C to 506°C. Two samples were used, of mass 5 gram and 4 gram respectively, using a space velocity of 2000 c.c/c.c/hour in each case. The flowrate of the decomposition products produced in this way was very low. (0.02 c.c/minute to 0.32 c.c/minute), so that the Arrhenius plot (figure1) showed a series of somewhat erratic values. There was a change in activity at about 480°C, below which temperature the derived energy of activation of almost 100 Kcal/mole could only be interpreted qualitatively as showing no catalytic activity. At 480°C titanium nitride becomes catalytically active, and shows a relatively low energy of activation of about 30 Kcal/mole.

Analysis showed a stoichiometric proportion of nitrogen corresponding to the formula TiN_1. According to J.D. Fast[46] and P. Ehrlich[47] the lattice of titanium metal absorbs, with expansion, a stoichiometric quantity of nitrogen atoms into it's interstices, to form a face centred cubic lattice similar in structure to that of the metal.[48] Friedrich and Sittig[49] found that the metal lattice was reinforced and hardened, and according to K.Becker[50], metallic properties e.g.

TABLE 9.

NITRIDE CATALYSTS: ENERGIES OF ACTIVATION.

CATALYST	METHOD	SPACE. VELOCITY.	TEMP. RANGE °C	FIG.	PLOT	ACTIVATION ENERGY Kcal/mole			
						SAMPLES			
						1	2	3	MEAN
TiN	Flow.	2000	480-506	1	IA	29.8			30.7
		2000			IIA		31.6		
		2000	460.480		IB	91			95
		2000			IIB		98		
VN	Flow.	2000	420-470	2	I	35.8			34.8
		2000			IIA	35.0			
		2500			IIIA		34.4		
		2000			IVA	33.8			
		2000	-420		IIB	20			20.4
		2000			IVB	20.8			
Cr_3N_2	Flow.	2000	490°-510°	3	IA	57.0			57.8
		2000			IIA		58.5		
		2000	460-490°		IB	31.1			31.2
		2000			IIB		31.2		
Mn_3N_2	Flow.	10,000	460-500	4	IA	52.5			51.7
		2000			IIA		50.3		
		2000			IIIA			52.3	
		10,000	370-460°		IB	30.2			30.2
		2000			IIB		29.4		
		2000			IIIB			30.9	

								MEAN
Fe_2N	Flow.	2000		5	IA	48.5		
		2000			IIA	48.3		
		12000			IIIA	46.1		
		35000	440°-480°	6	IVA		48.2	47.5
		2000			VA		46.9	
		2000			VIA		46.9	
		2000		5	IB	32.6		
		2000			IIB	32.7		
		12000	375°-440°		IIIB	31.6		
		35000		6	IVB		32.2	
		2000			VB		31.4	
		2000			VIB		30.4	
		2000		5	IC	20.7		
		2000	340°-375°		IIC	22.2		
		12000			IIIC	20.1		22.2
		35000		6	IVC		25.1	
		2000			VLC		23.1	
Co_2N	Flow.	70,000	450°-480°	7	I	27.4		27.1
		120,000			II		26.7	
Ni_3N	Flow.	100,000	437-451	8	I	35		
		120,000			IIA		39	37
					IIB		36	

CATALYST : TITANIUM NITRIDE

Log cc/Min. vs. 1/T

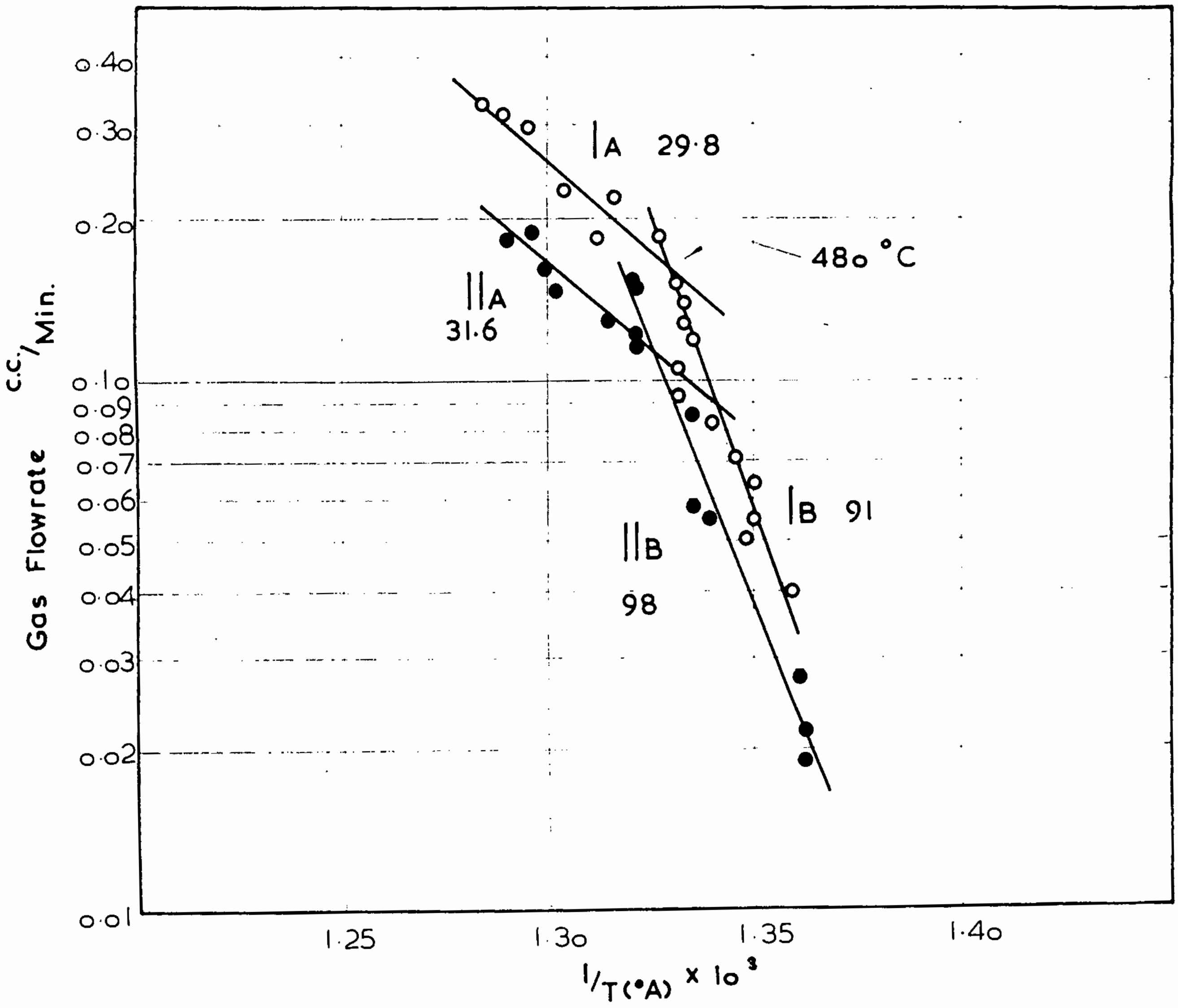


FIGURE 1.

metallic electrical conductivity are retained.

Two nitride phases are reported to exist. J.D. Fast [46] and P. Ehrlich [47] showed that one was a hexagonal close packed structure poor in nitrogen ($TiN_{0.23}$ to $TiN_{0.42}$). Fast, Ehrlich, and K. Becker and F. Ebert [51] showed that the other was a sodium chloride-type face centred cubic structure ($TiN_{0.42}$ to $TiN_{1.00}$). In the latter case structures deficient in nitrogen are due to unoccupied interstitial holes. A. Brager [52] has shown that a structure $TiN_{1.16}$ can exist. Here some metal positions in the lattice are vacant, but a face centred cubic structure, with a smaller lattice constant, remains. Brager's [52] work suggests that all phases revert to TiN, when treated in ammonia at 1400°C to 1500°C. The structure remains unchanged even up to 2950°C, which is its melting point. It may therefore be assumed that the nitride employed was a cubic face centred structure. According to A.E.van Arkel [53], Brager [52], Ehrlich [47] and Dawihl and Rix [54] the lattice constant $a = 4.23(5)$ Å.

While metallic titanium shows very poor catalytic activity, the nitride appears to be active under favourable conditions, one of which appears to be that the temperature must be in excess of 480°C.

The figures corresponding to the graphical representation are shown in the appendix, Tables IA and IB.

4.3. Vanadium Nitride.

Several runs were done by flow method, and a single run by static method, the results by the former method being described first.

The first two runs were made on a 5.5 gram sample of vanadium nitride (VN$_1$.) using a space velocity of 2,000 c.c/c.c/hour. The results are tabulated in the appendix, tables 2A and 2B, and are shown graphically in figure 2, curves I, IIA and IIB. The temperatures ranged from 400°C to 470°C. At the lower temperatures, a change of activity was shown, somewhat inaccurately. Above 420°C the energies of activation are 35.8 Kcal/mole (I) and 35.0 Kcal/mole (IIA), while below this temperature it is approximately 20 Kcal/mole. Two runs were then carried out on another sample of 3 gram, using space velocities of 2000 and 2500 c.c/c.c/hour. The energy of activation coincided with that found for sample 1., (Table 2C figure 2, curve III) i.e. 34.4 Kcal/mole. A change in activity was again observed at 420°C, but the results were not recorded, since they were inaccurate. In order to determine more exactly the temperature at which the activity changed, and the activation energy shown at lower temperatures, the two samples were combined. The space velocity was again 2,000 c.c/c.c/hour, and the extent of decomposition was increased, and the results were consequently more accurate. (See: appendix, table 2D

CATALYST: VANADIUM NITRIDE

Log $^{cc}/_{Min}$ vs. $^{1}/_{T}$

Combined sample: 1 & 2.: ●.

1st sample, run 1: •; run 2: ∘. 2nd. sample, run 1: o; run 2 ⊙.

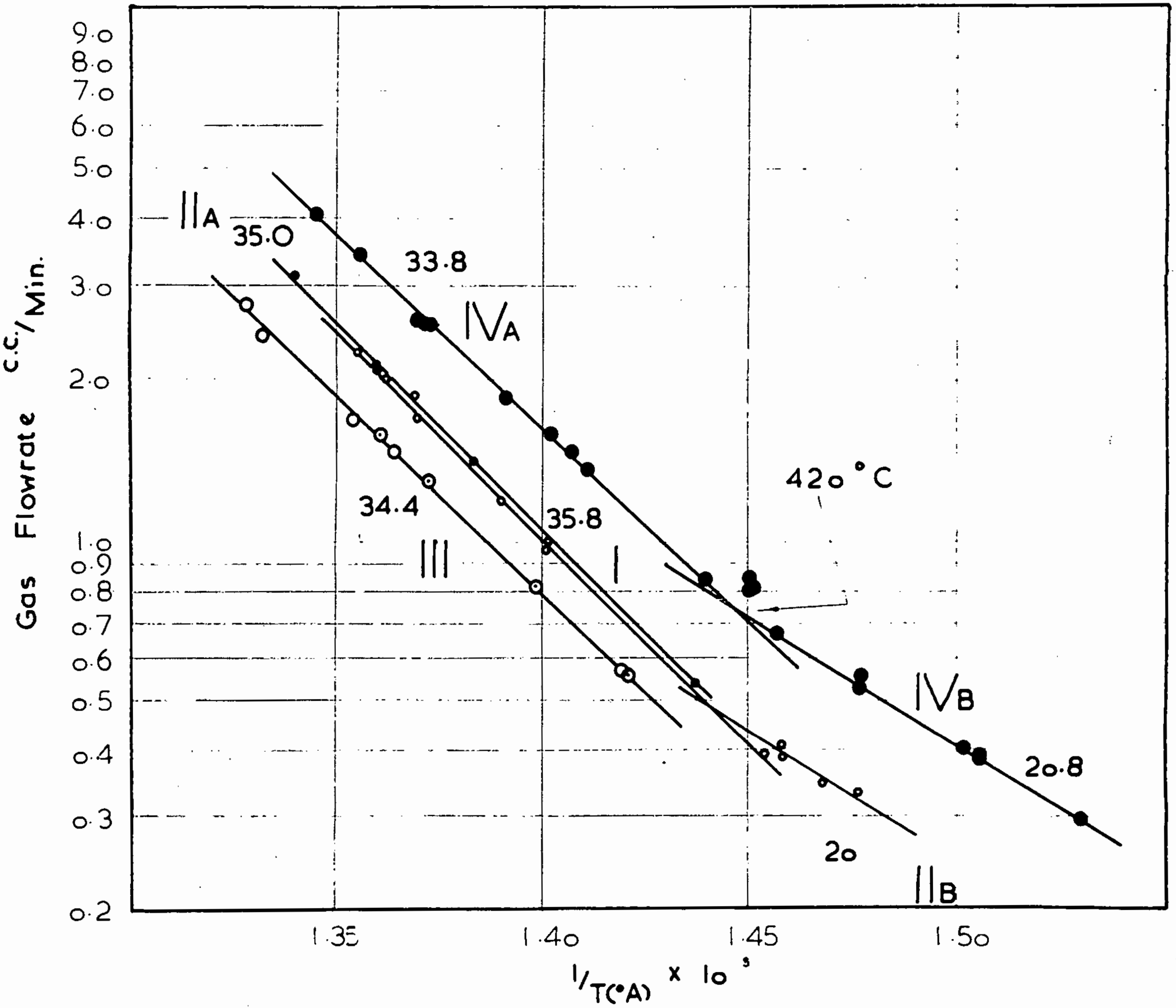


FIGURE 2.

and figure 2, plot IVA and IVB) The results coincided with the other values, i.e. 33.8 Kcal/mole (IVA) above 420°C and 20.8 Kcal/mole below this temperature. The temperature range of experiment was 380°C to 470°C.

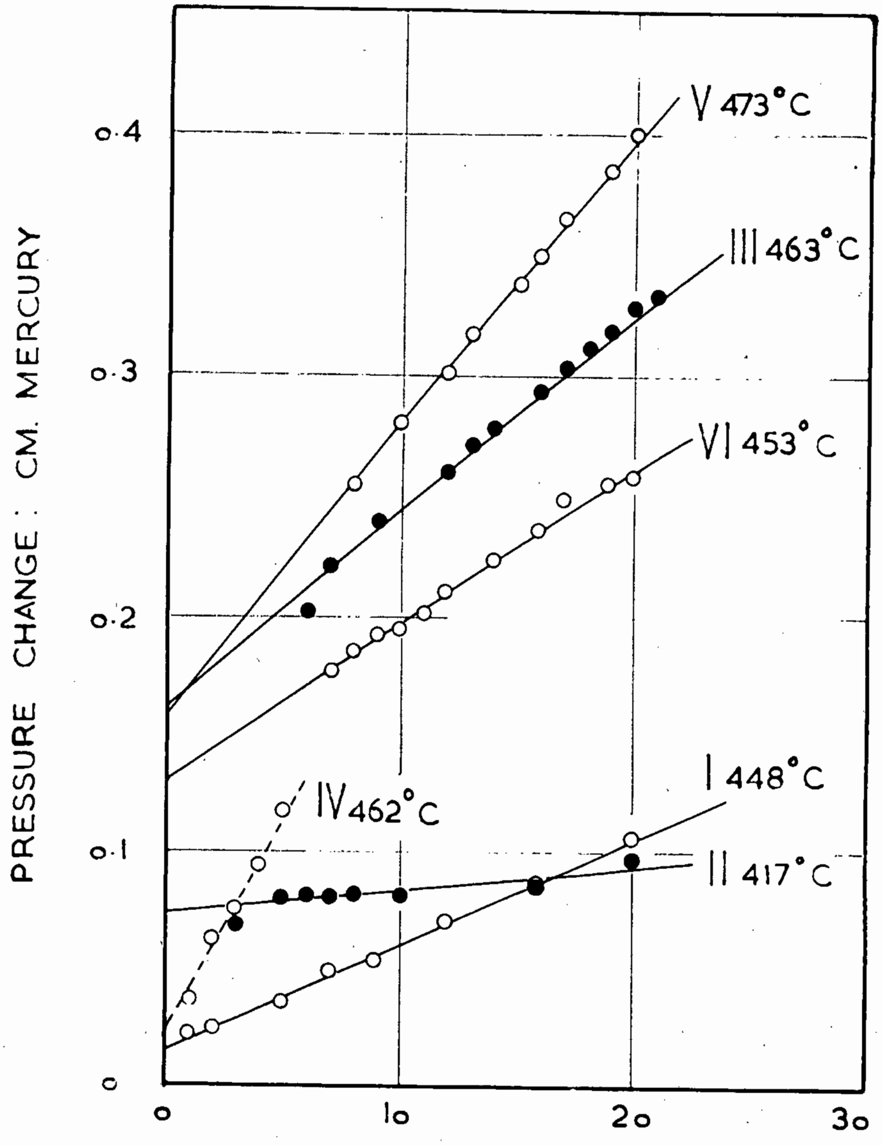
The static experiment gave a value for activation energy of about 39 Kcal/mole. The rate graph is shown in figure 9 and the resultant Arrhenius plot in figure 10. The accuracy of the result was not as high as that determined by flow method. Since the flow method had been found to be superior, and since the other stable catalysts caused insufficient decomposition of ammonia for accurate measurement by the static method, this method was not used for other nitride catalysts.

The close similarity between the structure and physical properties of TiN and VN would suggest similar catalytic behaviour, producing similar Arrhenius curves with the change of activity occurring at a high temperature, which might be outside the temperature range used. Since TiN became active close to the maximum experimental working temperature, the results were limited by a narrow temperature range of study.

H,Hahn[54], Becker and Ebert[55], Dawihl and Rix[68] and Brager and Epelbaum[56], showed that this nitride exists as a stoichiometrically composed interstitial sodium chloride type cubic face centred structure, which may exist as a homogeneous phase (γ) from $VN_{0.71}$ to $VN_{1.00}$. By a method of heat sintering vanadium

CATALYST: VANADIUM NITRIDE.

STATIC METHOD: ΔP vs. TIME.



TIME : MINUTES

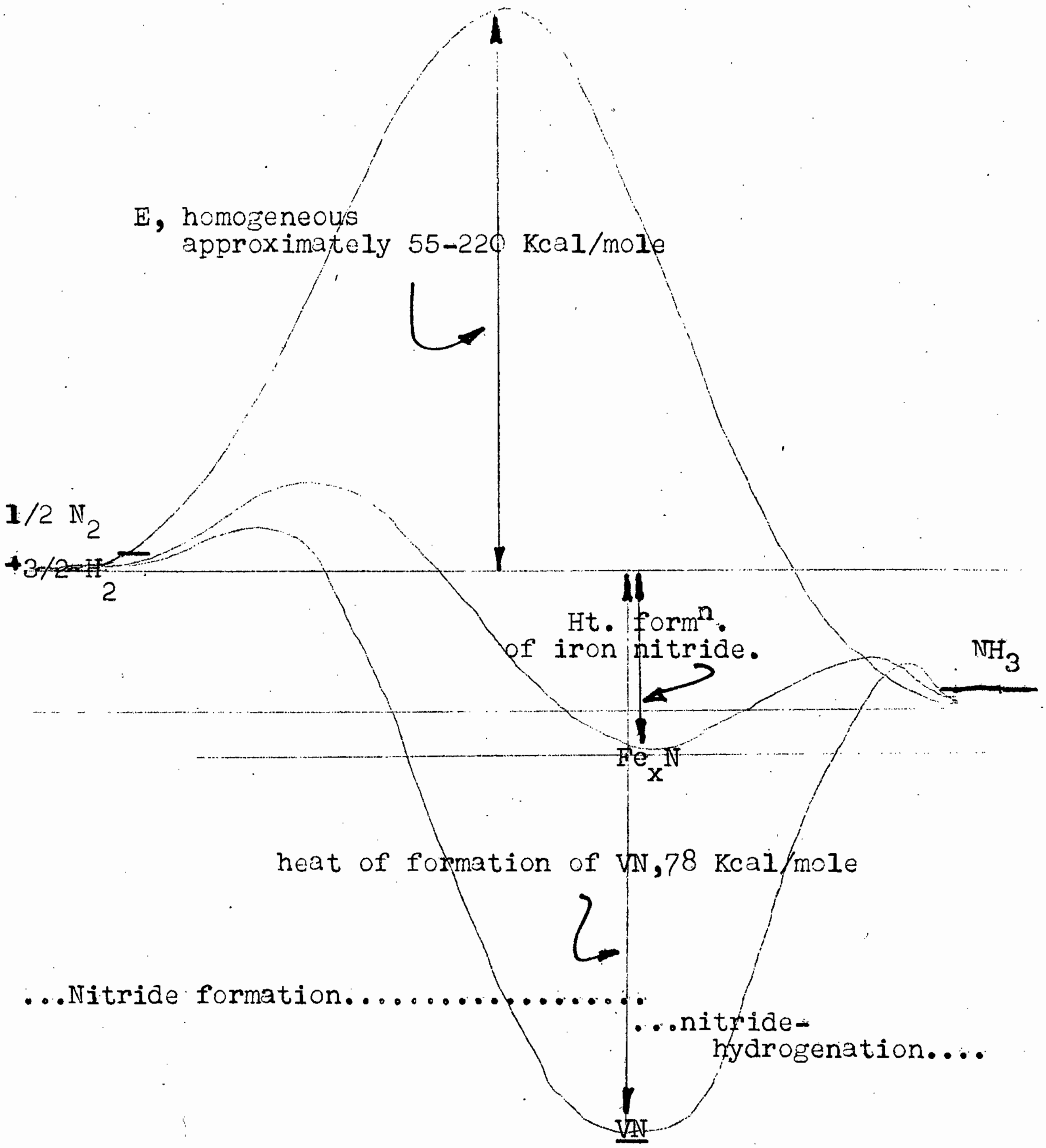
FIGURE 9.

metal with the nitride, VN, Hahn [54] showed that there is another nitride phase approximating to $V_3N(\beta)$, homogeneous between the limits $VN_{0.37}$ to $VN_{0.43}$, which has a hexagonal close packed lattice, with lattice constants: for $VN_{0.37}$, a=2.832 and c=4.33. and for $VN_{0.43}$, a=2.835 and ~~in~~ c=4.541. The nitride used in these experiments corresponded to the former phase, VN_1. According to Hahn the lattice parameter a is 4.126Å. Epelbaum and Brager [56], in a precision determination of the lattice constant, gave a value of a=4128Å. The method of preparation of the nitride used was similar to that employed by the latter authors. A comparison of the structures of TiN and VN shows similar structural properties, in that each may correspondingly exist as two phases: one a sodium chloride type lattice, and the other as hexagonal close-packed lattice.

Vanadium nitride appears to be an active ammonia decomposition catalyst, especially at temperatures below 420°C. This is in marked contrast with metallic vanadium. Frankenburger [1] in discussing the poor catalytic activity of metallic vanadium for the ammonia reaction, attributed it to the high heat of formation of the nitride, which was assumed to be an intermediate product during reaction. Diagram A is approximately reproduced from Frankenburgers paper, which illustrates this thermodynamic consideration. In contrast to a low heat of formation of iron nitride, vanadium nitride, with a high heat of formation, presents a considerable energy barrier to the reaction. Why the nitride is a relatively good catalyst is not clear, but this will be considered in the general discussion, together with the significance of the activity change.

It may be mentioned here that the variation of the electrical conductivity of each of titanium and vanadium nitrides, with temperature, was determined in a range which included the temperature at which a change in activity occurred. Conditions were exactly similar to those observed during a determination of the activation energy. A compressed pellet of a nitride was clamped between two platinum electrodes, connected with platinum leads to a bridge circuit. Ammonia was passed over the pellet, and the resistance was measured at progressively increasing and decreasing temperatures. This was done using two different samples of VN and one of TiN. There was no change in the linear relationship of resistance vs. temperature at temperatures at which the activity changed. It is therefore evident that a variation in activity in these cases is not accompanied by a change in electrical properties, and that the change is not due to semiconduction phenomena. The method of preparation of these nitrides, which involves an oxide reagent (TiO_2 and NH_4VO_3) probably results in impurities of oxygen atoms in the nitride lattice. Furthermore one can expect a certain proportion of vacant interstitial positions in the lattice, which could create extra permitted electronic

DIAGRAM A. (See page 52)



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energy regions in the forbidden energy zones placed below the conducting electron band, as in a p-type semi-conductor. It should be kept in mind that a completely ordered lattice cannot be expected, and electronic and structural defects may play some part in determining catalytic activity by creating "active sites" on a heterogeneous surface.

4.4 Chromium nitride.

Two samples of chromium nitride were used. Analysis showing about 15% nitrogen content suggests that the nitride used approximated to Cr_3N_2. Two nitride phases have been shown to exist. R.Blix [57] and G.Tammann suggested that one phase formulated CrN, which exhibits properties which are entirely unrelated to those of the metal, is not a normal interstitial compound. It is more akin to a salt-like compound. There is no "region of homogeneity", but it exists only as the stoichiometrically composed nitride CrN_1. Metallic properties shown by other interstitial nitrides are absent in this compound, and it's sodium chloride-type face centred cubic lattice is unrelated to the lattice of metallic chromium. According to Blix, the lattice parameter is 4.140Å. The β (Cr_2N) phase, states Blix, is a nitride in which nitrogen is probably distributed in a non-uniform manner in a hexagonal close packed lattice. Absorption of nitrogen is accompanied by an expansion of the metal lattice. Blix states that the β phase lattice

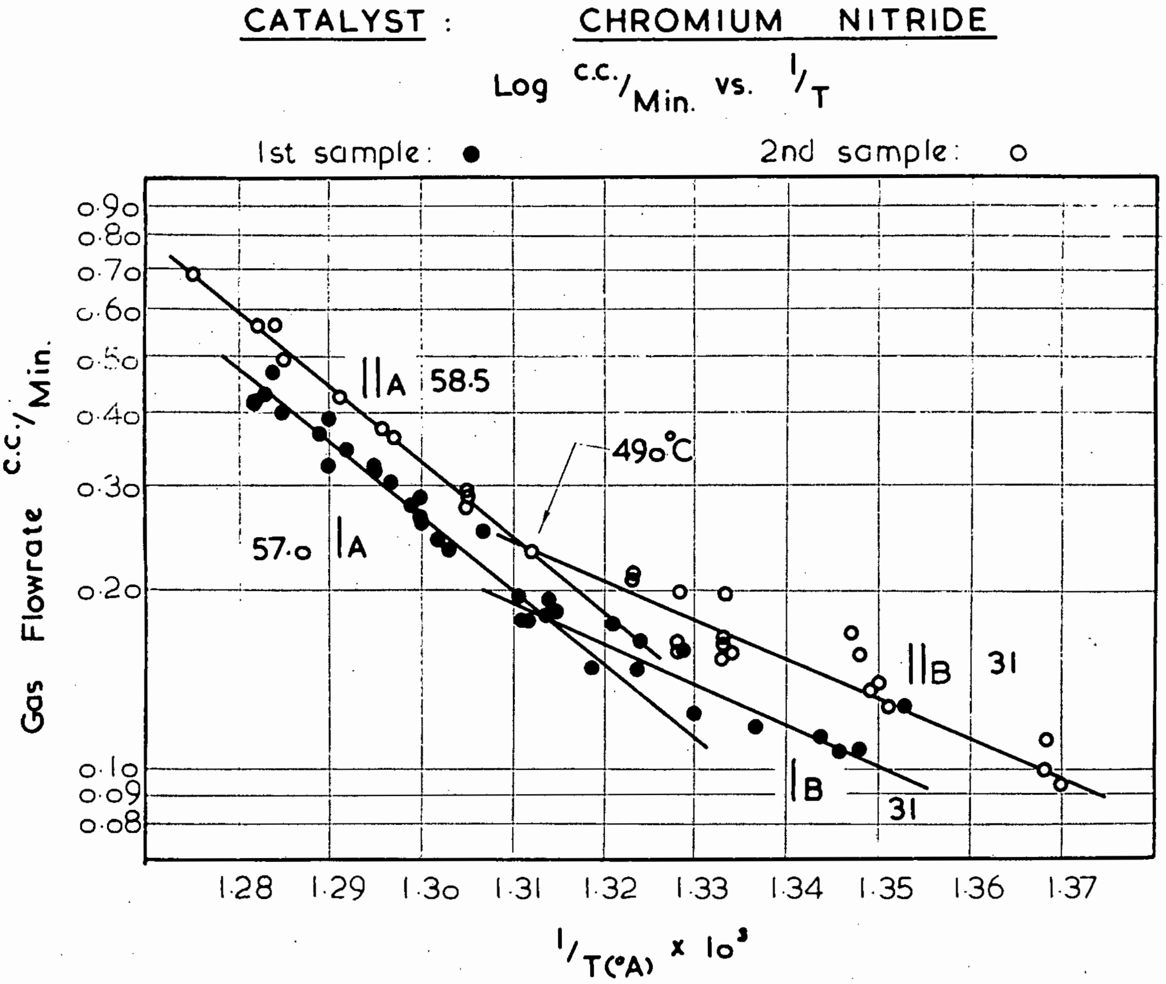
CATALYST : CHROMIUM NITRIDE
Log c.c./Min. vs. 1/T
1st sample: ●
2nd sample: ○
Gas Flowrate c.c./Min.
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.09
0.08
||A 58.5
57.0 |A
490°C
||B 31
|B
31
1.28
1.29
1.30
1.31
1.32
1.33
1.34
1.35
1.36
1.37
1/T(°A) x 10³

FIGURE 3 .

dimensions increase with increasing nitrogen content from a=2.747Å, c=4.439Å, to a=2.770Å, c=4.474Å. It is possible that the nitride used here consisted of both phases.

Manganese nitride (see section 4.5.) shows similar catalytic behaviour to chromium nitride, and one may argue that, by analogy the β chromium nitride, phase, which is a true interstitial phase like manganese nitride, is that which determines the catalytic activity.

The two samples used were approximately 5 gram each, and a space velocity of 2000 c.c./c.c./hour was used in each case. The investigation was made at temperatures ranging from 460°C to 510°C i.e. a range of 50°C. The chromium nitride catalyst caused little ammonia decomposition to occur. Consequently there was some error in measurement at lower temperatures. The erratic plot obtained in both cases was not entirely due to experimental error for the accuracy obtained was not as high as that expected. The reason for this behaviour is not known. The Arrhenius plot is shown in figure 3, and the corresponding figures are tabulated in the appendix, tables 3A and 3B. Above the point of activity change (490°C), the energy of activation is reproducible: 57.0 Kcal/mole (IA) and 58.5 Kcal/mole (IIA). Below this point there is a rough parallelism between the plots, showing an energy of activation of approximately 31 Kcal/mole (IB and IIB) Bauer and Voerman[18] suggested that chromium nitride should be an efficient ammonia decomposition catalyst while a poor synthesis catalyst. For the decomposition reaction, this nitride does not appear to be exceptionally good and it is unquestionably a poor catalyst above 490°C.

4.5. Manganese nitride.

The manganese nitride used was shown by analysis to contain about 13.9% nitrogen. $M\overset{n}{\cancel{N}}_3N_2$ corresponds to 14.6% nitrogen. Nishiyama and Iwanaga[59] observed the following three nitride phases: one face centred cubic structure containing about 21 atomic percent nitrogen corresponds to Mn_4N, with lattice parameter a=4.435Å and two face centred tetragenal structures. That which approximates to Mn_2N and which exists over a relatively large range of homogeneity has lattice constants a=4.154Å and c=4.037Å. On the other hand, existing in a narrow region of homogeneity is a nitride which corresponds almost to the formula Mn_3N_2. This phase has lattice constants a=4.211Å. & c=4.130Å This lattice expands with increasing nitrogen content, and according to Ochsenfeld[60] is considerably stabilised by interstitial atoms. The nitride used as catalyst probably consisted of mixed crystals of the two face centred tetragonal structures.

The catalytic activity of three samples (6, 8 and 3 gram) was investigated at temperatures ranging from 370°C to about 500°C. A space velocity of 10,000c.c/c.c/hour was maintained for sample 1. Samples 2 and 3 were tested at a space

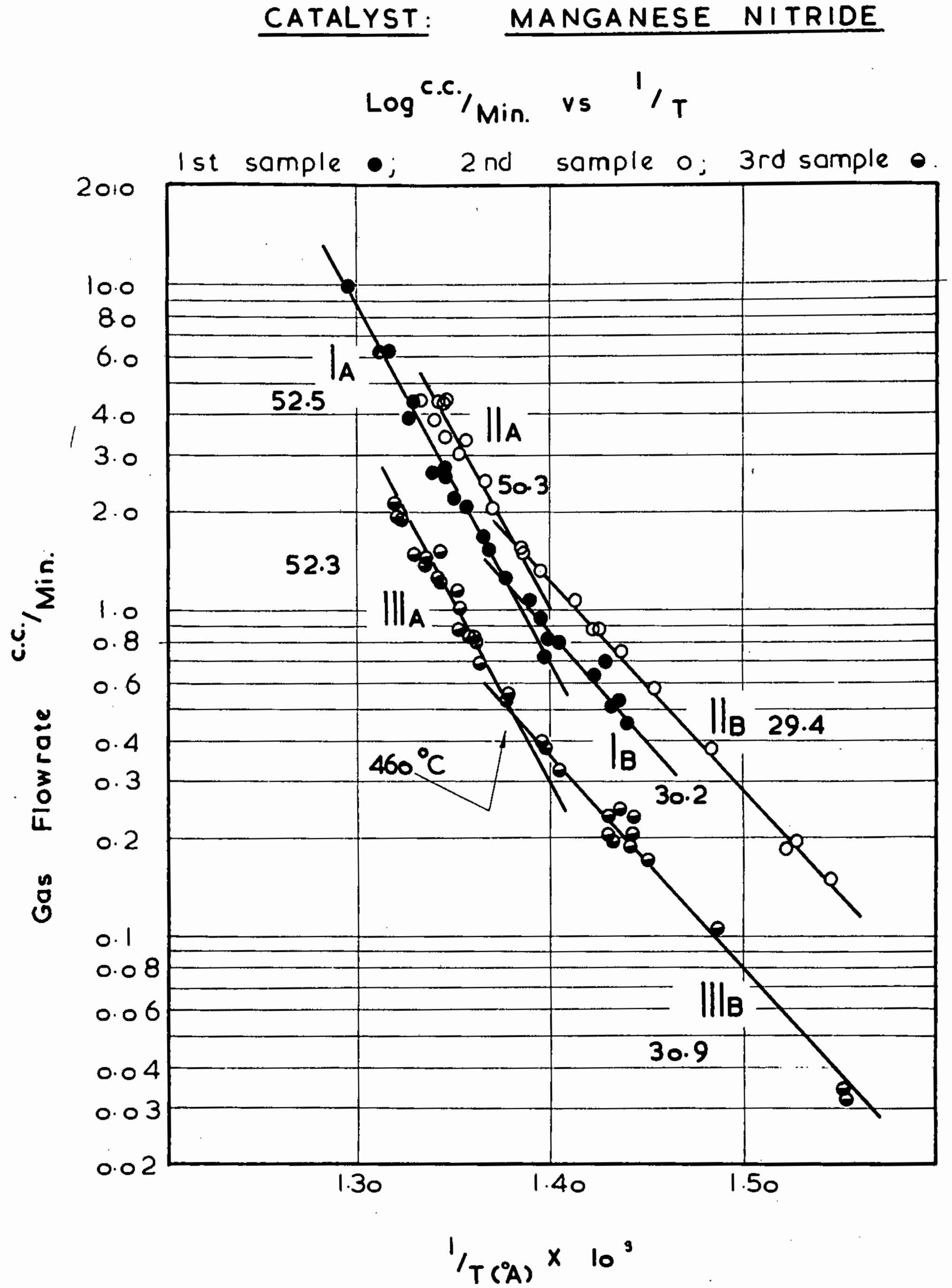
CATALYST: MANGANESE NITRIDE
Log c.c./Min. vs 1/T
1st sample ●; 2nd sample ○; 3rd sample ◒.
Gas Flowrate c.c./Min.
20.0
10.0
8.0
6.0
4.0
3.0
2.0
1.0
0.8
0.6
0.4
0.3
0.2
0.1
0.08
0.06
0.04
0.03
0.02
1.30
1.40
1.50
1/T (°A) x 10³
I_A
52.5
II_A
50.3
52.3
III_A
460 °C
I_B
30.2
II_B
29.4
III_B
30.9

FIGURE 4.

of 2000 c.c/c.c/hour. The results are shown to be reproducible. (See appendix, tables 4A, 4B and 4C: and figure 4) A change in activity occurred at approximately 460°C. The energies of activation shown above this temperature are 52.5 (IA), 50.3 (IIA) and 52.3 (IIIA) Kcal/mole respectively for the three samples. Below this temperature the energies of activation were 30.2 (IB), 29.4 (IIB) and 30.9 (IIIB) Kcal/mole respectively.

It is important to note that the change in activity indicated, is not a characteristic of the method of experiment. The measurements are based on the assumption that the $N_2:H_2$ ratio is at all times 1:3. A release or absorption of nitrogen of the catalyst would change this ratio, but it may safely be assumed that this effect was eliminated. This will be clarified by further consideration in the general discussion.

4.6. Iron nitride.

Six runs were performed using two samples of iron nitride. The samples used were probably mixed crystals of the ϵ (Fe_3N) and the γ (Fe_2N) phase. Since more than one phase is of interest to this investigation a brief resume of the possible structures will be given. As was shown by Brunauer, Jefferson, Emmett and Hendricks[61], the partial pressure of hydrogen in an ammonia hydrogen gas mixture determines the amount of nitrogen, iron will absorb. According to Lehrer[62], iron absorbs about

CATALYST: IRON NITRIDE

Log $^{cc}/_{Min.}$ vs $^{1}/_{T}$

1st sample, run 1: ● run2: ○ run3: ∘

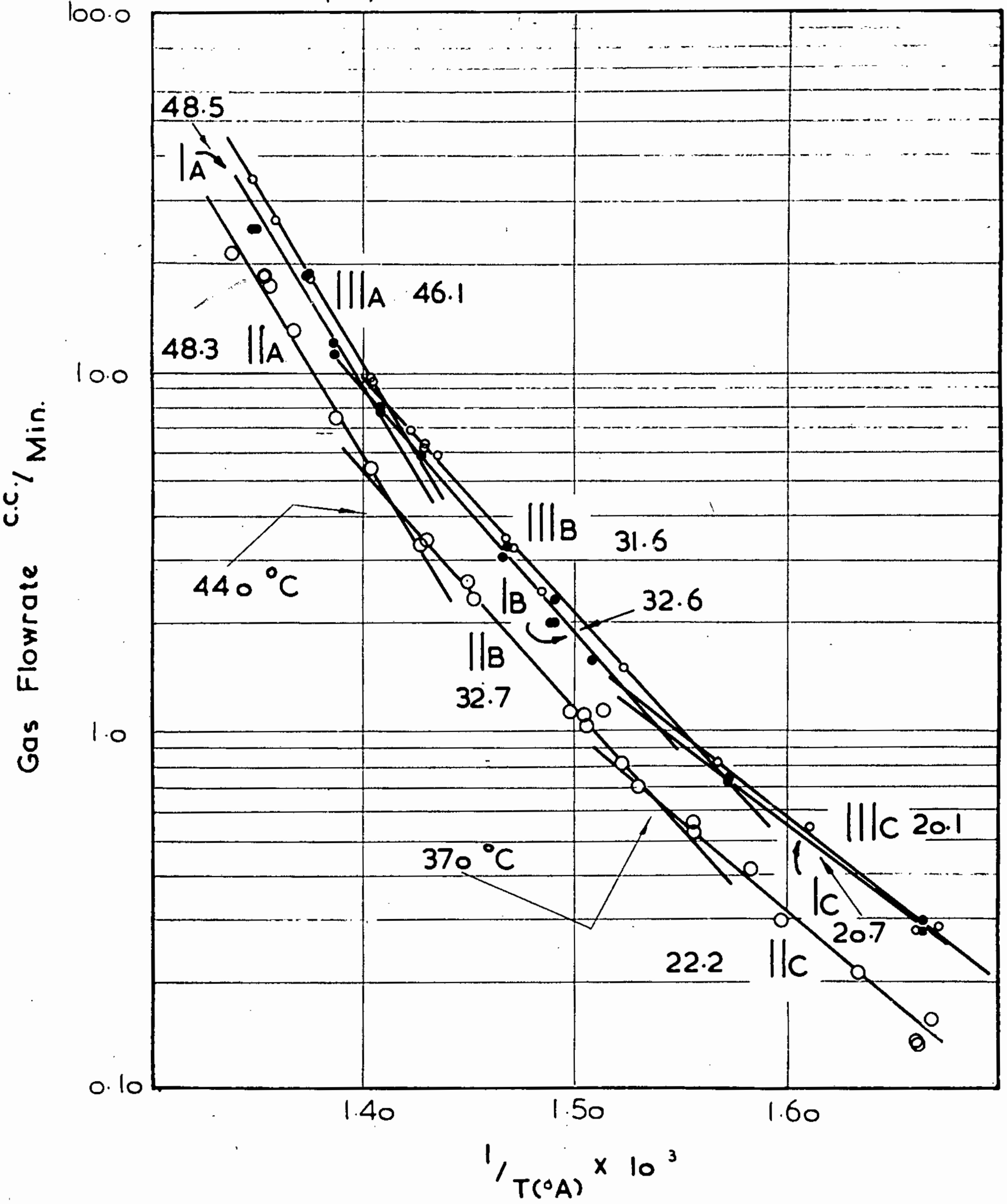

FIGURE 5.

0.5% nitrogen interstitially in a body centred cubic lattice. Hägg [63], Osawa and Iwaizumis [64], and Jack [65] have shown that γ' iron nitride exists in a narrow region of homogeneity ranging from 5.7 to 6.1%N. This is a face centred cubic nitride phase which includes Fe_4N. Hägg, and Osawa and Iwaizumis have shown that the $\epsilon(Fe_3N)$ closepacked hexagonal phase exists between limits of 7.3 to 11.1% nitrogen content. Jack has shown that the $\zeta(Fe_2N)$ phase forms in ammonia at temperatures just below 450°C, and exist from 11.1 to 11.3% nitrogen content. Hägg [66] stated that this phase has a base centred orthorhombic unit cell. Jack has described the structural unit cell more exactly as made up of two base centred orthorhombic units.

The nitride used as catalyst contained about 11% nitrogen. Fe_2N corresponds to 11.14% nitrogen. It was prepared at temperatures greater than 450°C, and it may therefore be assumed that the structure was mainly $\epsilon(Fe_3N)$ nitride and partly ζ (Fe_2N) nitride phase. Hendricks and Kosting [67] showed that the ϵ phase forms a continuous series of mixed crystals with the ζ phase.

Jack stated that in $\gamma'(Fe_4N)$ iron nitride, the nitrogen atoms occupy $\frac{1}{4}$ of the interstitial positions in a completely ordered array. The lattice constant was given as a=3.787 KX, and the Fe-N distance as 1.894 KX. Further, Jack gave the constants for the ϵ phase, at 11.0%N, as a=2.759, b=4.778 and c=4.411 KX and for the ζ phase, expanded anisotropically largely

CATALYST: IRON NITRIDE

Log c.c./Min. vs 1/T

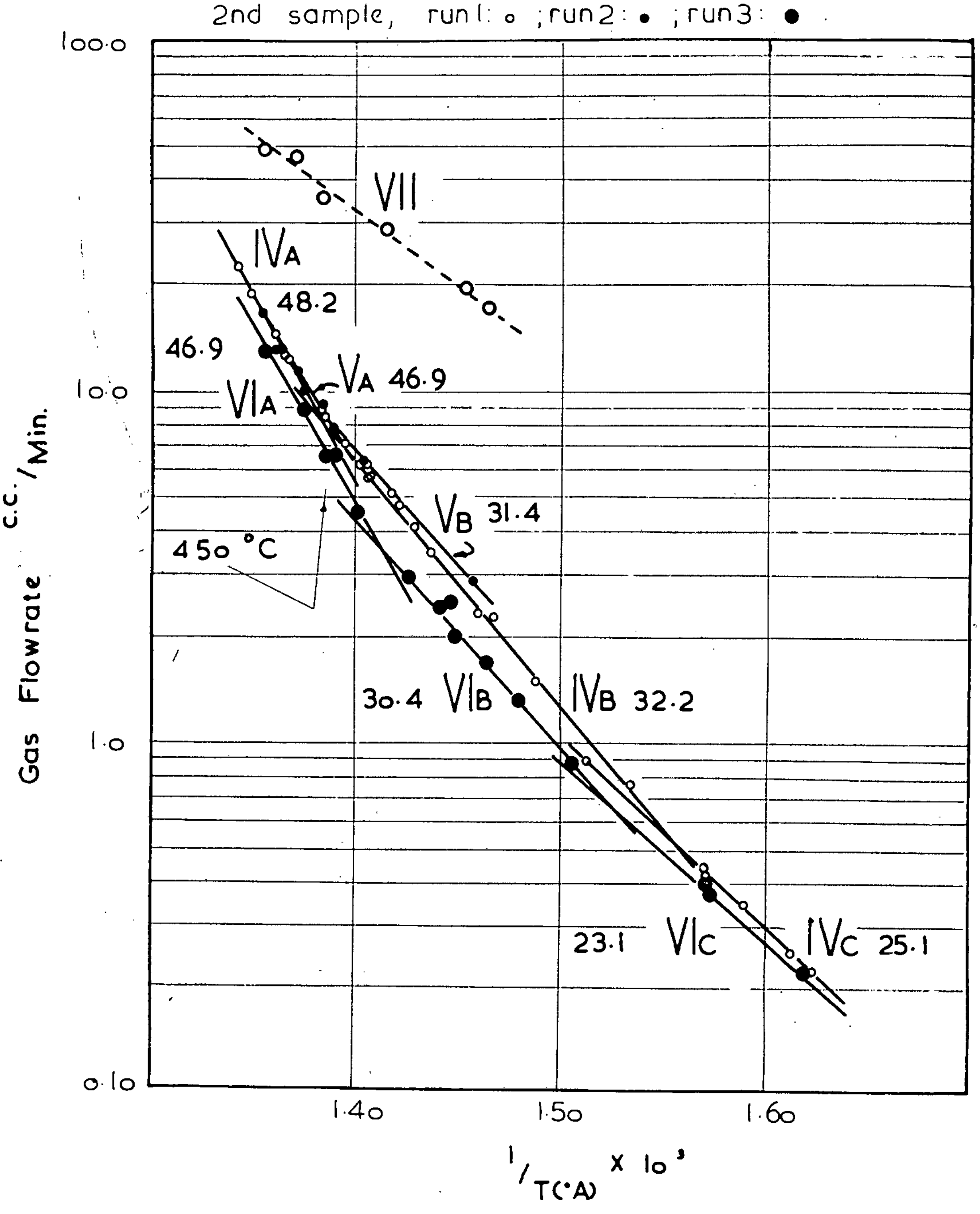

FIGURE 6.

in the b-direction, at 11.3%N as a=2.756, b=4.820 and c=4.416 KX while at 11.1%N, a=2.758, b=4.818 and c=4.416 KX. The relative positions of the nitrogen atoms in both the latter phases remains the same. According to Osawa and Iwaizumis and Hägg[66] the nitrogen atoms in the ε phase are so placed that six interstices surrounding each atom in the same plane, and the two directly above and below it, are vacant. Jack maintained that in the ζ (Fe_2N) phase, ½ the number of interstitial positions in each layer of atoms are occupied, in such a manner that there are vacant positions directly above and below an occupied position. The average iron-nitrogen distance, according to Jack, is 1.943 KX. His description of the true orthorhombic base-centred unit results in lattice constants stated thus: $a'=2a=5.512$, b=4.820, c=4.416 KX.

The first sample was used for three runs (using 7,5 and 5 gram respectively) at space velocities of 2000, 2000 and 12,000 c.c/c.c/hour, and at temperatures ranging from 330° to 480°C. (See: tables 5A, 5B, 5C, in the appendix, and figure5.) The Arrhenius plot showed linear, reproducible relationship with a change in activity occurring at two temperatures, approximately 440°C. and 375°C. Increasing temperature showed a stepwise increase in activation energy from about 21 Kcal/mole changing at 375°C to about 32 Kcal/mole changing at 440°C to approximately 48 Kcal/mole. Three runs on the second sample (2gram) showed that these results were reproducible (See tables 6A, 6B, 6C, and figure 6) The space velocities were 35,000, 2,000 and 2000 respectively for the three runs. Somewhat differing behaviour of plots is shown in figure 6, but although the curves are not quite parallel the energies of activation are shown to be approximately equal at similar temperature ranges. The greatest deviation is exhibited by plots IIIc (20.1 Kcal/mole) and IVc (25.1 Kcal/mole) which show a difference of about 5000 calories. IVc, however, is an exception. PlotVII is shown to indicate the effect of a high partial pressure of hydrogen. A deep bed of catalyst was used in this case, and extensive decomposition of ammonia no doubt caused a breakdown of the nitride deeper down in the bed. This breakdown was due to reduction of the nitride, and since hydrogen that should have been measured in the exit gas mixture was converted to ammonia, the resultant plot was a curve of smaller slope (VII) than the true plot for activation energy.

The striking feature of these plots, is that the change of energy of activation occurs at the temperature (450°C) below which the ζ nitride phase forms more readily, and above which the ϵ (Fe_3N) phase forms as mixed crystals with the nitride. The γ' (Fe_4N) phase forms partly at lower temperatures, and a structural change may once more account for the change in activity. Analysis of our nitride showed practically no change in nitrogen content before and after use at temperatures ranging from 340°C to 470°C, but catalysis, depending on surface properties as it does, make it quite probable that the surface structure could have changed at the transition temperatures, causing variable activity of a single catalyst. The significance of this observation will be discussed in the general discussion.

4.7. Cobalt nitride.

Tables 7A and 7B (appendix) and figure 7 show the results obtained when using two samples (0.03 and 0.01 gram) of cobalt nitride as catalyst. The reasons for using such small quantities and the high space velocities of 70,000 and 120,000 c.c/c.c/hour respectively are given in the section on the preparation of the nitrides. The temperature range of investigation was from 450°C to 480°C. Since the nitride is unstable, measurements were done at intervals of more than 45 minutes, in order to allow the nitride to reach it's equilibrium composition at any temperature, and consequently the plots consist of few points. The modified ammonia absorption system described in section 2.1.2, page 19 was used. Initial measurements were not recorded until consecutive readings became constant. The results obtained were reproducible, and the energy of activation was found to be about 27 Kcal/mole (I = 27.4, II = 26.7 Kcal/mole) Figure 13 shows the activation energy plot for cobalt metal. The energy of activation for cobalt was found to be about 20 Kcal/mole, reproducible for two samples. One sample was pure hydrogen reduced "Matthey" cobalt sponge, the other being prepared inside the reaction vessel by the action of hydrogen on pure cobalt

CATALYST: COBALT NITRIDE

Log $^{c.c.}/_{Min.}$ vs. $^{1}/_{T}$

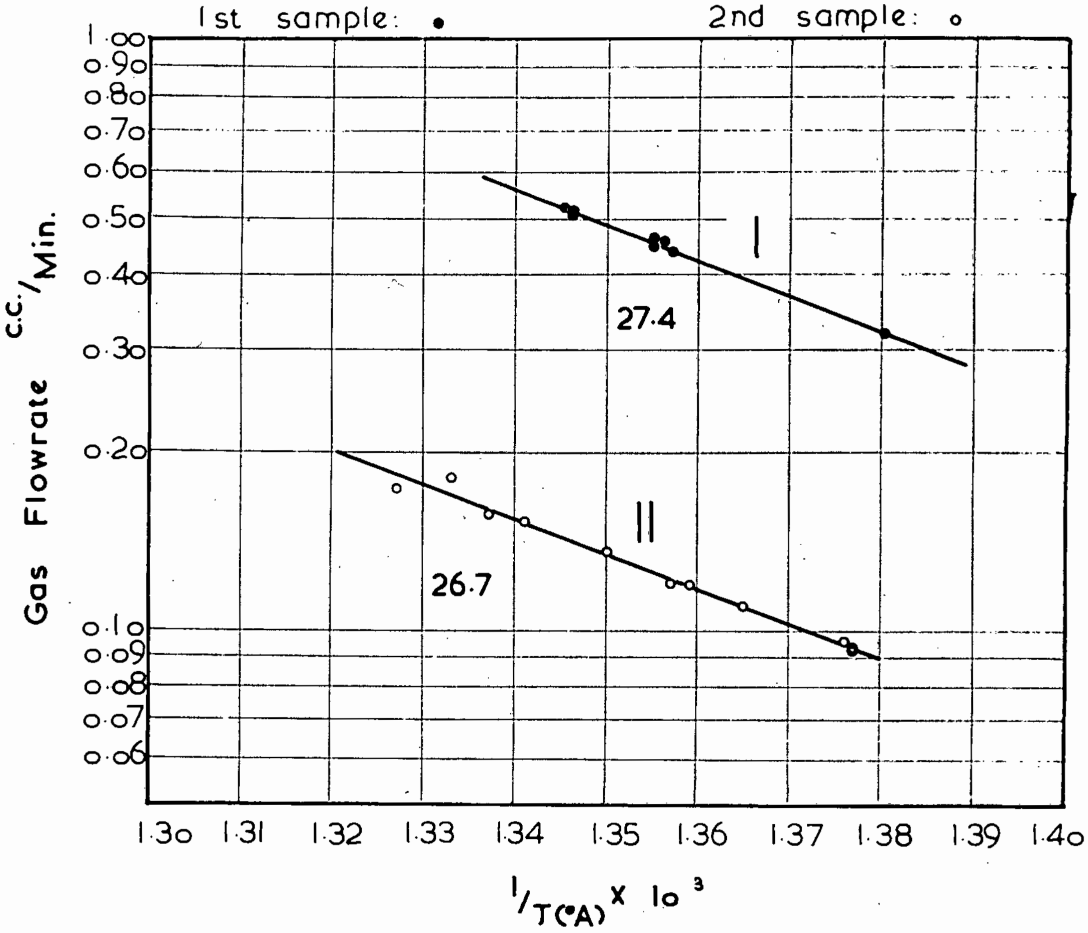

FIGURE 7.

CATALYST : NICKEL NITRIDE

Log cc./Min. vs. 1/T

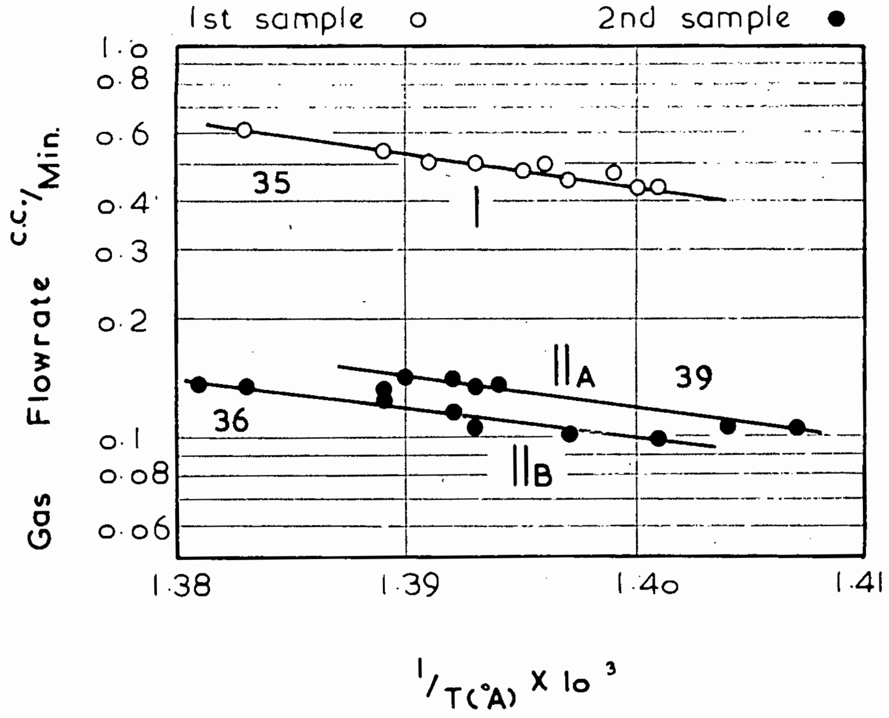

FIGURE 8.

4.8. Nickel nitride.

Nickel nitride is less stable than cobalt nitride, and consequently required accurate control of experimental conditions. For this reason the investigation could only be done within a 14°C range of temperature from 437.5°C to 451°C. The space velocities were respectively 100,000 and 120,000 c.c./c.c/hour. Similar precautions to those mentioned regarding cobalt nitride, were observed. Two samples were used (0.02 and 0.01 gram) and the results were reproducible. (See appendix: tables 8A and 8B and figure 8) The results, which were obtained at very low flowrates of decomposition products, showed an accurate Arrhenius curve. This was made possible by the use of the special measuring equipment previously described, used in the case of cobalt nitride. Curves IIA and IIB are the result of a single run, but have been drawn separately, since each curve was plotted from consecutively measured data showing linear relationship, each resulting during several hours of experimental observation. The small temperature range used makes it impossible to state the magnitude of the energy of activation exactly. Curve I represents an energy of activation of about 35 Kcal/mole, curves IIA and IIB energies of approximately 39 and 36 Kcal/mole, respectively. It would, however, be more correct to state that the energy of activation lies approximately within the limits of 30 to 40 Kcal/mole.

TECHNICAL PROMOTED IRON CATALYST

ΔP. vs. TIME

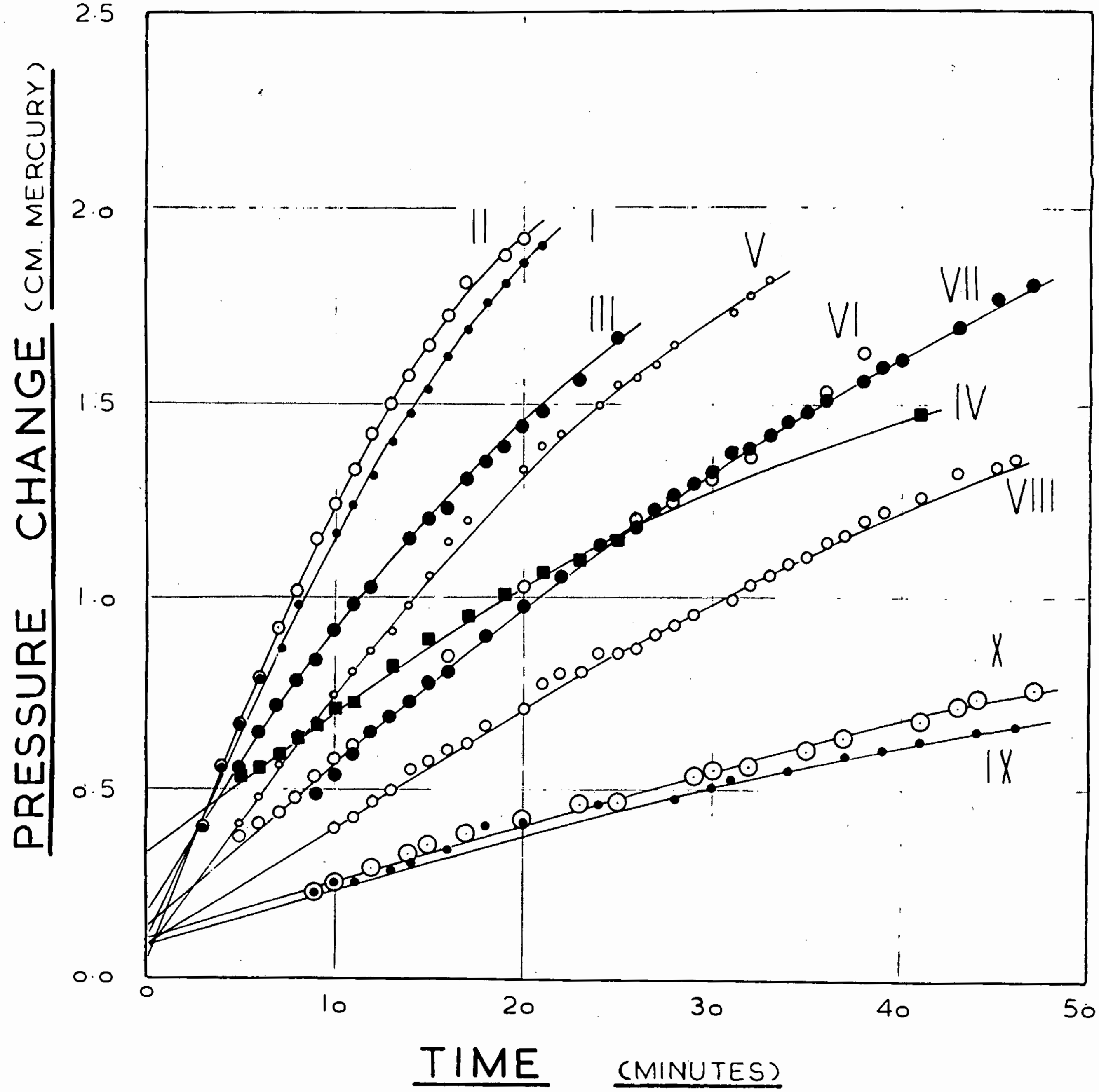

FIGURE 11.

CATALYST: TECHNICAL PROMOTED IRON.

LOG CM./MINUTE VS 1/T
(DERIVED FROM FIGURE 11.) STATIC METHOD.

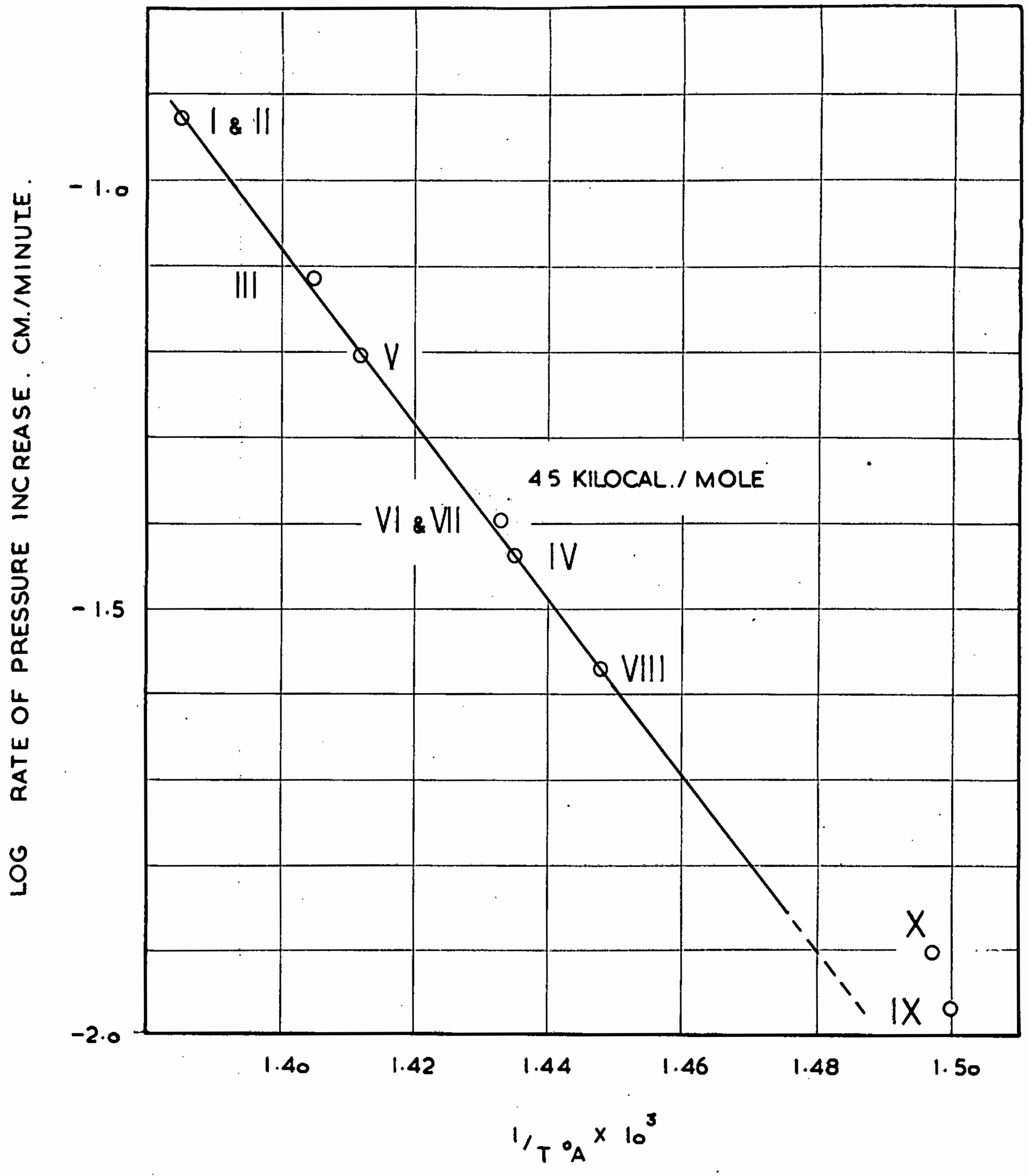

FIGURE 12.

Juza and Sachze [43] showed that the nickel nitride phase, which includes the compound Ni_3N, exists in a narrow range of homogeneity as a hexagonal close packed interstitial structure, with lattice constants a=2.664, c=4.298Å, and with nitrogen atoms existing in the centre of the octahedron formed by nickel atoms. The Ni - N distance was stated to be 1.877Å, and the N-N distance 3.423Å. The nickel nitride used in our experiment corresponds approximately in composition to Ni_3N, and is assumed to exist as the nitride phase described above.

4.9. Technical promoted iron catalyst.

Since the composition of this catalyst was not available, the results warrant only a brief mention. Technical iron oxide, as supplied by the Modderfontein ammonia manufacturing plant, was reduced in hydrogen at a temperature slightly above 400°C. An energy of activation determination by the static method resulted in the rate graph shown in figure II and the Arrhenius plot shown in figure 12. The energy of activation was shown to be about 45 Kcal/mole, a relatively high value. By flow method the energy of activation was approximately 37 Kcal/mole (See figure 12B) The difference cannot be readily explained. The flow method is probably the more accurate method, and it is possible that the extrapolation of rate curves to zero time for static method was not correct.

ENERGY OF ACTIVATION vs ATOMIC NO.

PLOT...... 1

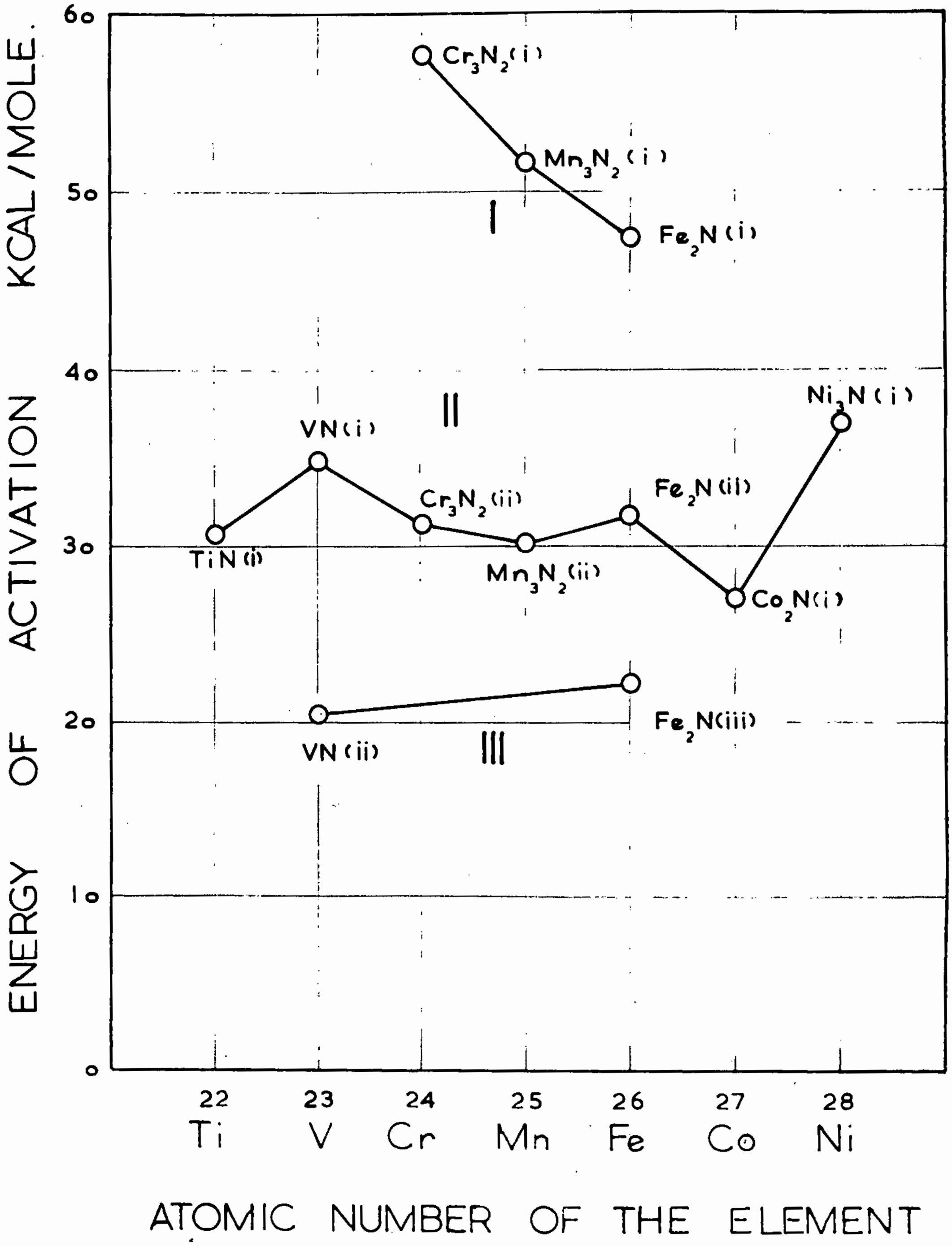

FIGURE 14.

5. DISCUSSION.

Figures 14, 15 and 16 show the energies of activation associated with seven nitride catalysts, plotted against the atomic numbers of the elements. Each plot is labelled for convenient reference by using the approximate formula for the nitride followed by the number (i) (ii) or (iii). Each figure represents a possible relationship of values, and the results are such that few definite conclusions can be drawn until the following questions are answered: Do all nitrides show variable activity if studied over a sufficiently wide range of temperature? Is VN(i), for example, akin to Cr_3N_2(i) or to Cr_3N_2(ii); or Ni_3N to Fe_2N(i) or to Fe_2N(ii)? Is iron nitride unique in showing three distinct energies of activation? Before proceeding, the reservation must be made that a discussion can for this reason be little more than conjectural, and each relationship will be dealt with, bearing this in mind.

Inspection of the plot shows a systematic behaviour of Cr_3N_2 (i), Mn_3N_2 (i) and Fe_2N (i), in which case no other relation apart from those shown in the three figures can reasonably be assumed. Characteristic of all three plots is that activation energy values may be grouped in two or three separate ranges. In figure 14, values of similar magnitude are grouped: those approximating to 50 Kcal/mole, Cr_3N_2 (i), Mn_3N_2 (i) and Fe_2N (i) being distinct from those approximating to 30 Kcal/mole. The three values for iron nitride suggests a further group of values approximating to about 20 Kcal/mole. Figure 15 shows three groups which consist of generally decreasing values. This

ENERGY OF ACTIVATION vs ATOMIC NUMBER.

PLOT...... 2.

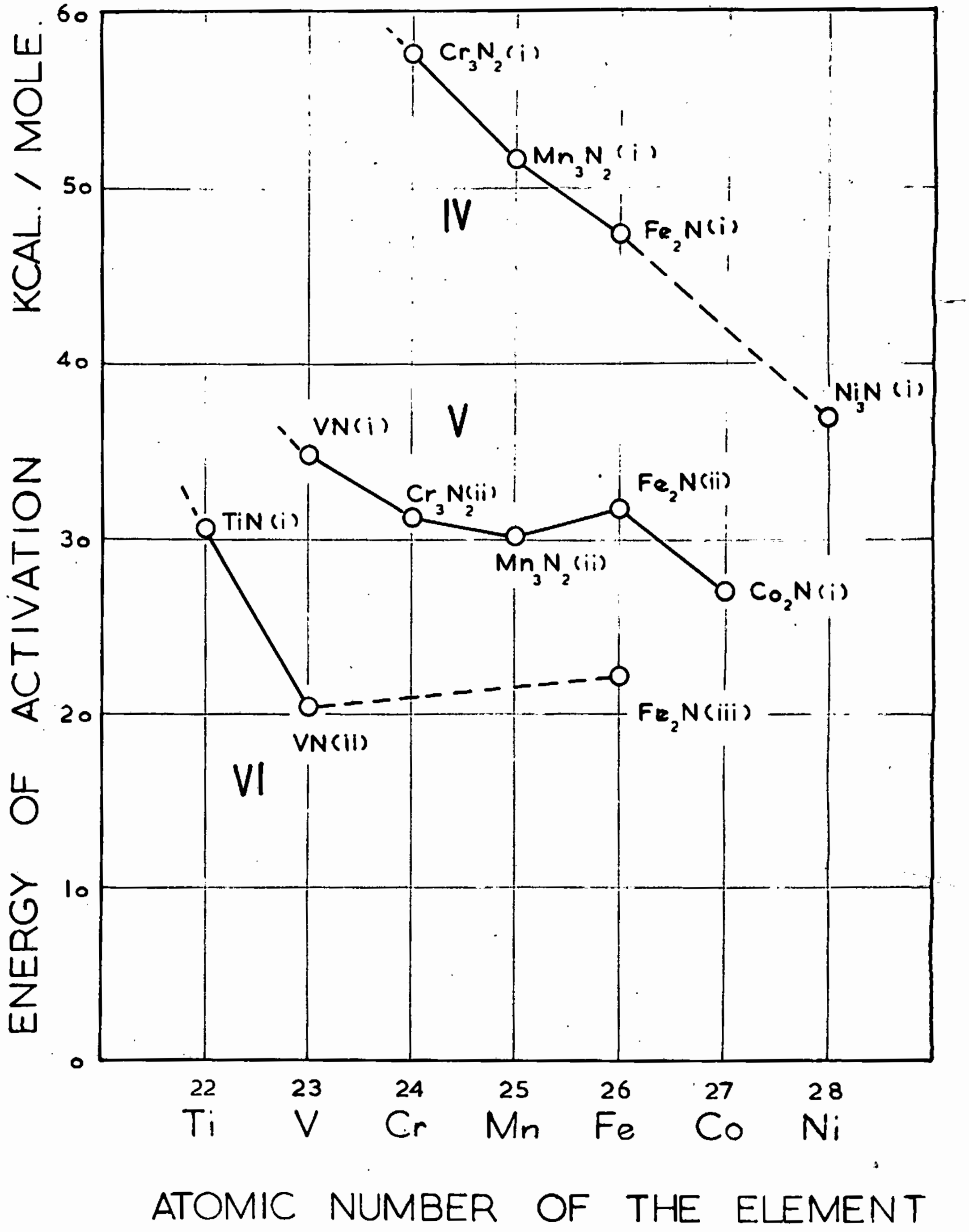

FIGURE 15.

relationship results from a consideration of the similar structural and physical properties of the two catalysts, vanadium nitride and titanium nitride. Following the suggestion, made in section 4.3., that similar catalytic behaviour may be expected, titanium nitride should show a further energy of activation at higher temperatures which would more correctly be associated with VN (i), so that TiN (i) would be related to VN (ii), as shown. An alternative relation shown in figure 16 is based on the assumption that the highest values determined for each catalyst are related, and that vanadium nitride, for example, does not show a third energy of activation which may more correctly be associated with Cr_3N_2 (i), Mn_3N_2 (i) and Fe_2N (i). This relation shows a rough parallelism between two sets of grouped values, but shows that nitrides in the middle of the series have a maximum of activity. A further consideration, however, does not support the grouping of VN (i) with Cr_3N_2 (i) This is shown in figure 17, which is a plot of activation energy values with respect to the temperatures at which activity changes occur. Considering first the activation energies observed at higher temperatures than the temperature of activity change, it is found that those nitrides where the changes of activity occur at the higher temperatures, show a correspondingly higher value for activation energy. (CurveI)

ACTIVATION ENERGY VS TEMPERATURE OF ACTIVITY CHANGE.

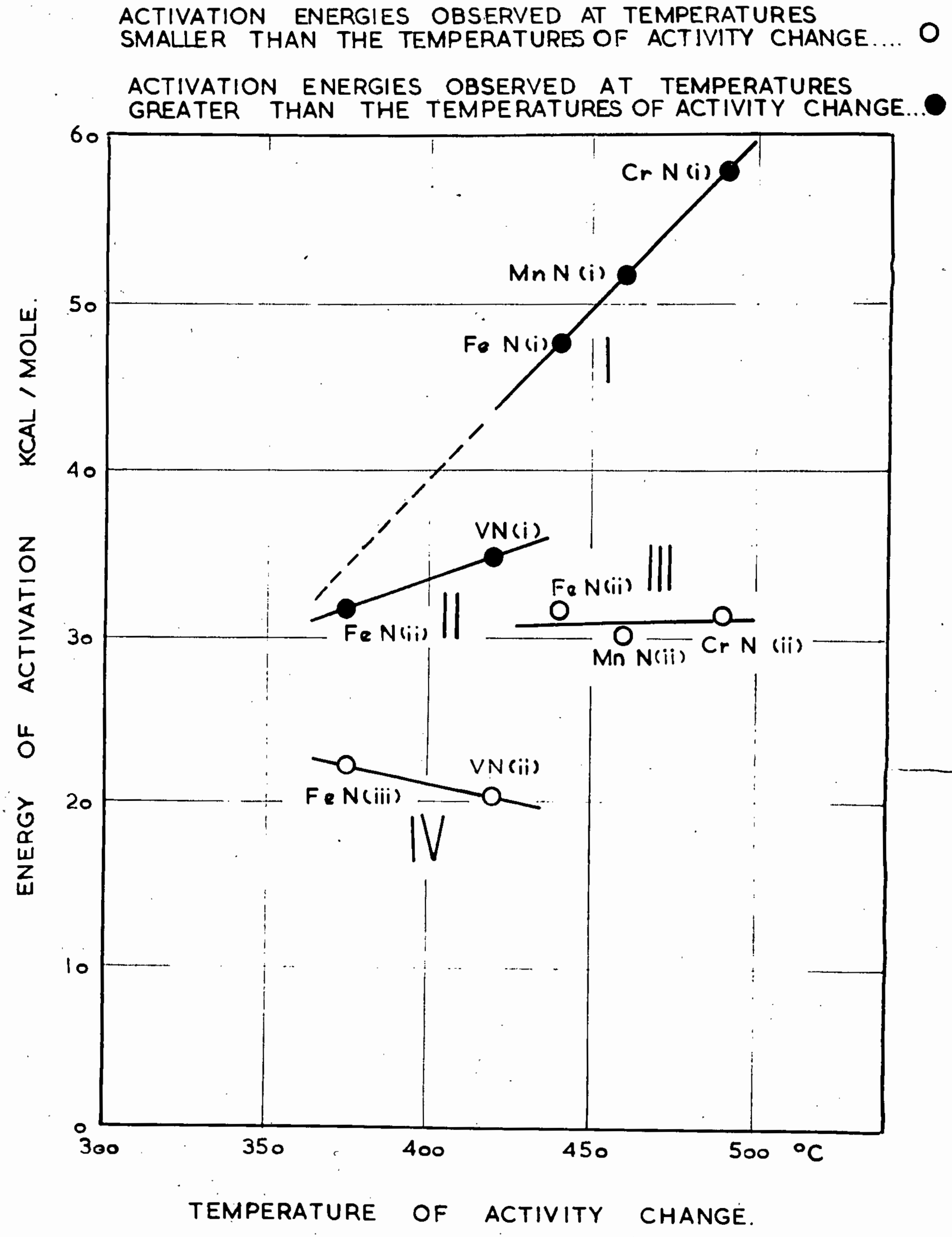

FIGURE 17.

Cr_3N_2 (i), Mn_3N_2 (i) and Fe_2N (i) again show systematic behaviour. A linear relation, I, includes the points VN (i) and Fe_2N (ii), but it may be more correct to relate VN (i) to Fe_2N (ii) (curveII) as distinct from Cr_3N_2(i), Mn_3N_2(i) and Fe_2N(i), since VN (i) does not follow the series V-Cr-Mn-Fe in correct order, and since the Fe_2N (i) and Fe_2N(ii) values are unlikely to be related. Similar arguments apply as well for the plot of values determined below the point of activity change. (Curves III and IV)

It appears, therefore, that the relationships shown in figures 14 and 15 are more correct than that shown in figure 16.

Activity change.

A distinction will be made between the general magnitude of a group of activation energies and the variation in magnitude of values within a group, and each will be dealt with separately. First, the factors which may cause variable activity, and so determine the general magnitude of a group of values, will be discussed.

A change in activity at a distinct temperature is shown for the nitrides of vanadium, chromium, manganese and iron. Titanium nitride may show such behaviour, but as it could only be studied in a narrow range of temperature, since it only became active close to the maximum operating temperature, this could not be observed. The narrow range of thermal stability of the nitrides of cobalt and nickel precludes an investigation of their catalytic behaviour at other temperatures.

A considerable change in activity of a single catalyst may be caused by a radical change in geometric or electronic structure of the catalyst. It is unlikely, however, that such activity change is solely due to a structural change, unless the structural change is accompanied by a change in reaction mechanism. Each group of activation energies will then be associated with a single mechanism, probably involving either of the radicals $\cdot N$, $\cdot NH$ or $\cdot NH_2$. Furthermore, Hinshelwood [69] suggested that an Arrhenius plot showing two straight lines merging asymptotically into each other, in which the lower value of activation energy is shown at lower temperatures, results from separate reaction mechanisms occuring simultaneously and in parallel. This is typified by the Arrhenius plots for the nitrides of vanadium, chromium, manganese and iron, the latter showing three values of activation energy.

Various experiments have shown that structural phase changes appear to coincide with changes in activation energy. The occurrence of similar activation energies in the case of nitrides so varied in properties as, for example, vanadium nitride and iron nitride, suggests that a phase change does not cause an activity change directly , but rather it may create suitable conditions for a particular mechanism to take place.

The statement that an activity change is not entirely due to a structural change, without a change in mechanism, is therefore not contradicted. The iron nitride catalyst shows a change in activity close to the structural transition point, 450°C, above which temperature the ϵ (Fe_3N) phase predominates, and below which the ζ (Fe_2N) is readily formed. A second activity change occurs at approximately 375°C, and it is possible that this change is accompanied by a phase change to the γ' (Fe_4N) nitride, which exists at lower temperatures. Analysis before and after use for several hours at temperatures ranging from 340°C to 470°C showed virtually no change in nitrogen content, but this does not exclude the possibility of a surface structural change, which would be of considerable importance in catalysis. This argument applies as well for the other catalysts. Vanadium nitride, for example, exists as either of two phases approximating to VN or V_3N, and although the nitride is stable at the temperature of activity change, and does not change from the composition VN_1, a surface structural change may once again occur at the temperature at which the activity changes. As a further example one may cite an experiment performed by Fischbeck and Salzer [3], in which the catalytic activity of a length of iron wire was determined at the transition point: α iron $\rightarrow$ δ iron, working at temperatures close to 1000°C. A marked reduction in activity occurred when the temperature dropped below the transition point (800°C). It is significant that it was a transition point from a non-nitride forming region to a nitride-forming region.

A nitride catalyst of variable activity is not uncommon. Kunsman[70], for example, using metallic tungsten, molybdenium and nickel catalysts at 600°C to 1200°C, found a change in activity in each case. The energy of activation was found to be approximately 45,000 calories for each catalyst, the activity changing to 35, 32 and 26 Kcal/mole respectively at higher temperatures. The author suggested that it was due to a change of the surface of the catalyst; a structural change of the surface atoms, or a change in the nature or quantity of adsorbed gas, or a change in the "composite surface" of the metal and the adsorbed gas, or a combination of all three factors. Love and Emmett, using three technical promoted iron catalysts, observed a change in activity occurring in two cases. A possible explanation was suggested, that the change was due to a change in reaction mechanism, in which $\cdot NH$ or $\cdot NH_2$ radicals take part. It was suggested that the desorption of adsorbed nitrogen atoms, i.e. the step presenting the greatest energy barrier, was facilitated by the formation of $\cdot NH$ or $\cdot NH_2$ radicals previous to desorption of nitrogen and hydrogen. From thermodynamic considerations these authors showed that this was feasible, keeping in mind that thermodynamic relations may be profoundly modified when applied to surface properties. Frankenburger and Hodler [71] showed that $\cdot NH$ radicals exist on a tungsten surface during ammonia decomposition. The existence of intermediate products during reaction, facilitating the path of reaction by a stepwise process has long been recognised [1]. Frankenburger[1] expressed the synthesis reaction as proceeding generally in two stages, nitride formation and nitride hydrogenation, the latter stage apparently proceeding in stepwise manner involving the nitride radicals, thus:

$$\begin{aligned}
M + N_2\,(gas) &\rightarrow M - N_{(ads.)} \\
M - N_{(ads)} + H &\rightarrow M - NH_{(ads)} \\
M - NH_{(ads)} + H &\rightarrow M - NH_{2(ads)} \\
+ H &\rightarrow M - NH_{3(ads)} \\
M - NH_{3(ads)} &\rightarrow M + NH_3.
\end{aligned}$$

The nitrogen molecule has a high heat of dissociation, and adsorption or desorption of nitrogen atoms during synthesis and decomposition was assumed to be the slow reaction step. A catalyst showing a change in activity, with the $\cdot NH$ or $\cdot NH_2$ or $\cdot N$ radicals participating in different reaction mechanisms occurring in parallel requires a modification of the stepwise type of reaction mechanism mentioned above.

It is not known which mechanism would cause a low energy of activation. As was previously mentioned, Love and Emmett showed that desorption of nitrogen and hydrogen from an adsorbed •NH or •NH_2 radical may occur with smaller energy than desorption of nitrogen from an adsorbed nitrogen atom. The role of interstitial nitrogen atoms, if such atoms take part in the reaction at all, must, however, be considered. Recently Greenhalgh, Slack and Trapnell[8] suggested that desorption may occur from an iron surface following the formation of an •NH group consisting of an adsorbed hydrogen atom and an interstitial nitrogen atom. The suggestion was based on several observations: Firstly that slow adsorption of nitrogen occurs simultaneously with the normal rapid adsorption, and these authors showed that this slow adsorption was less likely to be caused by a surface migration of atoms, than by the alternative cause, the slow penetration of nitrogen atoms into the metal interstices; secondly, Emmett and Brunauer suggested that iron in use at catalytic temperatures contain interstitial atoms, probably due to this slow adsorption, and finally, Goodeve and Jack found that the denitriding of iron nitride occurs more rapidly in an atmosphere of hydrogen than in vacuo.

The participation of interstitial nitrogen in the reaction mechanism could be the factor that determines the general magnitude of the energy of activation. In a nitride-forming temperature range of a metal, the interstitial nitrogen may be so firmly bound that it is not allowed to participate in the reaction. The example of iron nitride may be cited. It is generally considered that the metal is a better catalyst than the nitride. In these experiments, the energy of activation for iron nitride at temperatures above 440°C, i.e. in the nitride forming range, is higher than that observed at lower temperatures, where iron has smaller affinity for nitrogen.

On the other hand interstitial nitrogen may form a weaker bond with the already saturated nitrides of vanadium and titanium than with the metals, which show great affinity for nitrogen. This would then account for the greater activity of the nitrides over the metals.

Considering Almquist and Black's experimental data regarding catalyst poisoning, which show that the iron atoms, exposed by the removal of the last atoms of oxygen on reduction of the oxide, are most active, it may be of interest to determine whether oxygen atoms on an iron surface will inhibit slow adsorption of nitrogen. If this happens, surface migration of adsorbed atoms to active iron sites may be the cause of slow adsorption, because oxygen atoms should not hinder absorption of nitrogen into the metal lattice, whereas they may prevent surface migration to active sites.

While the grouping of similar energies of activation may be due to such factors as suggested above, variation in structure, electronic properties or other properties of the catalysts are likely to cause the variation of activation energies within each group.

Electronic factors.

The limited information regarding the exact electronic state of the interstitial nitrides together with the complicating factor of the uncertain behaviour of the surface of solids in this respect makes it impossible to attempt more than a qualitative comparison of values. The fact that the nitrides retain to a large extent the metallic properties of the parent metal, and only modify the metal lattice in dimension and not in type, leads one to expect that the electronic properties of the metal are not grossly modified by incorporation of the metalloid. One may further assume that the absorption of interstitial nitrogen is a function of the electronic properties of the metal, in particular due to the extent of d-band character, and that a comparison of energies of activation based on the electronic properties of the metals may not be completely in error. It has been suggested that interstitial nitrogen may be partly ionised in some if not all cases. Jack[72], determining the structural properties of the ϵ and ζ carbonitrides of iron, found that the effective atomic radius of nitrogen in iron is greater than that of carbon, and suggested that there may be an electron transfer from metalloid to metal, and mentioned a possible significance in the fact that those metals which have an incomplete inner quantum shell are the only ones that form true interstitial alloys.

Accordingly it would appear that the donated electrons enter this shell. In support of possible ionisation, Clarke and Jack[42], having determined the structure of cobalt nitride, explained that while the apparent radius of the interstitial nitrogen is 0.665Å, the covalent radius of the nitrogen atom is 0.71Å. The former value was of similar order to that determined by Jack[73] for nitrogen in iron. S.A. Nemnonov[74] said that the bonds in chromium nitrides are homopolar. The cubic phase (CrN), however, shows no similarity in properties to other interstitial alloys[57]. Nemnonov suggests that it is possible that the nitrides of other metals, in particular those metals that show little electron defect, have similar homopolar bonds and that the nitrides formed by a series of transition elements will have bonds varying from metallic to homopolar, depending on the electron deficiency shown by the metal. Li_3N appears to be the only known nitride with completely heteropolar bonds[75]. While bond types appear to differ in character from one transition metal nitride to the next, the effect of interstitial atoms on the magnetic properties of a metal may illustrate the difference in bonding properties of a metal and it's nitride. Manganese nitride forms as a similar or slightly modified phase type to the metal. In one manganese phase, the absorption of nitrogen causes a change to ferromagnetism[76], which indicates a change in electronic arrangement, and hence in bond type. Generally speaking, however, one may say that the electronic structures of titanium and vanadium are modified to a lesser extent on incorporation of nitrogen atoms than those of the other metals in the series.

That the transition metals are normally active catalysts has long been recognised. As expressed by Frankenburger,[1] the active catalysts for the ammonia reaction are those that have a partially filled electronic level under the outer shell, so that electron exchange can take place. More recently the "d-band" relation to catalysis has been developed by Dowden[20], Dowden and Reynolds[77], Couper and Eley[78], Beeck[7], Dilke, Maxted and Eley[21] and others. Chemisorption values have shown decided relationship to d-character of the adsorbents. Adsorption has been shown by Dilke, Maxted and Eley to result in a change in magnetic behaviour of the adsorbent. Other experiments, based on calculated d-character involving the bond radius of the metal atom and the number of electons in the outer shells, have shown striking relation between the d-character and beats of chemisorption. It was shown that covalent bonding occurs with atomic d-orbitals. These experiments were performed by Beeck[7], who compared the results with respect to geometric factors, but Boudart[22] pointed out that the fundamental cause was the d-character shown by the metal, and verified this suggestion by pointing out that there is a marked relation between log of activity and % d-character. Furthermore, Trapnell[79], studying the adsorption of six gases, including nitrogen and hydrogen, on twenty-two different metal surfaces, showed that, adsorption activity was associated with d-band character, and increases with increasing atomic number at the approach of a transition period, and decreases towards the end. This was clearly indicated for the series of elements potassium to zinc, which, with exception of calcium, showed this behaviour. Nickel did not chemisorb nitrogen, but titanium and iron were shown to adsorb all the gases. Experiments showing the relation of d-band character to catalysis were done by Couper and Eley and Dowden and Reynolds, who used alloys as catalysts. The choice of alloys were such that the effect of one metal on another was to diminish the d-character. A relationship between d-character and catalytic activity was evident.

With this knowledge, and always bearing in mind the remarks made about the electronic structure of the nitrides, one may attempt a comparison of the energies of activation for the nitrides with the d-band character shown by the metals, assuming that the electronic structure of the nitrides are determined directly by that of the metal, and that an approximate parallelism exists for both.

Pauling[80] determined the d-character of a metal from the formula;

$$R_1 = 1.825 - 0.043z - (1.600 - 0.100)\delta$$

R_1 = single band radius of the metal

z = number of electrons in outer shells

δ = d-band character.

and designated each transition metal with a corresponding value. These values were used by Boudart as base for the comparison of Beeck's heats of chemisorption on various surfaces as was mentioned above, and there was a decrease in heat of adsorption of hydrogen and ethylene with increasing percentage d-character. Of the first transition series, chromium, iron and nickel were shown to obey this rule.

When comparing the energies of activation for the nitrides with respect to Paulings d-band character , we find a similar behaviour in the case of the greatest values determined for chromium, iron and nickel nitrides. Here any similarity ends. Manganese nitride deviates from the plot. Cobalt nitride should not be included since the energy of activation measured appears to be more akin to the lower activation energy values associated with the other nitrides. This applies as well for the nitrides of titanium and vanadium, and these show no relation to the

VARIATION OF ACTIVITY OF THE NITRIDES SUPERIMPOSED ON A PLOT OF ENERGY LEVEL DENSITIES IN THE 3-d BAND.

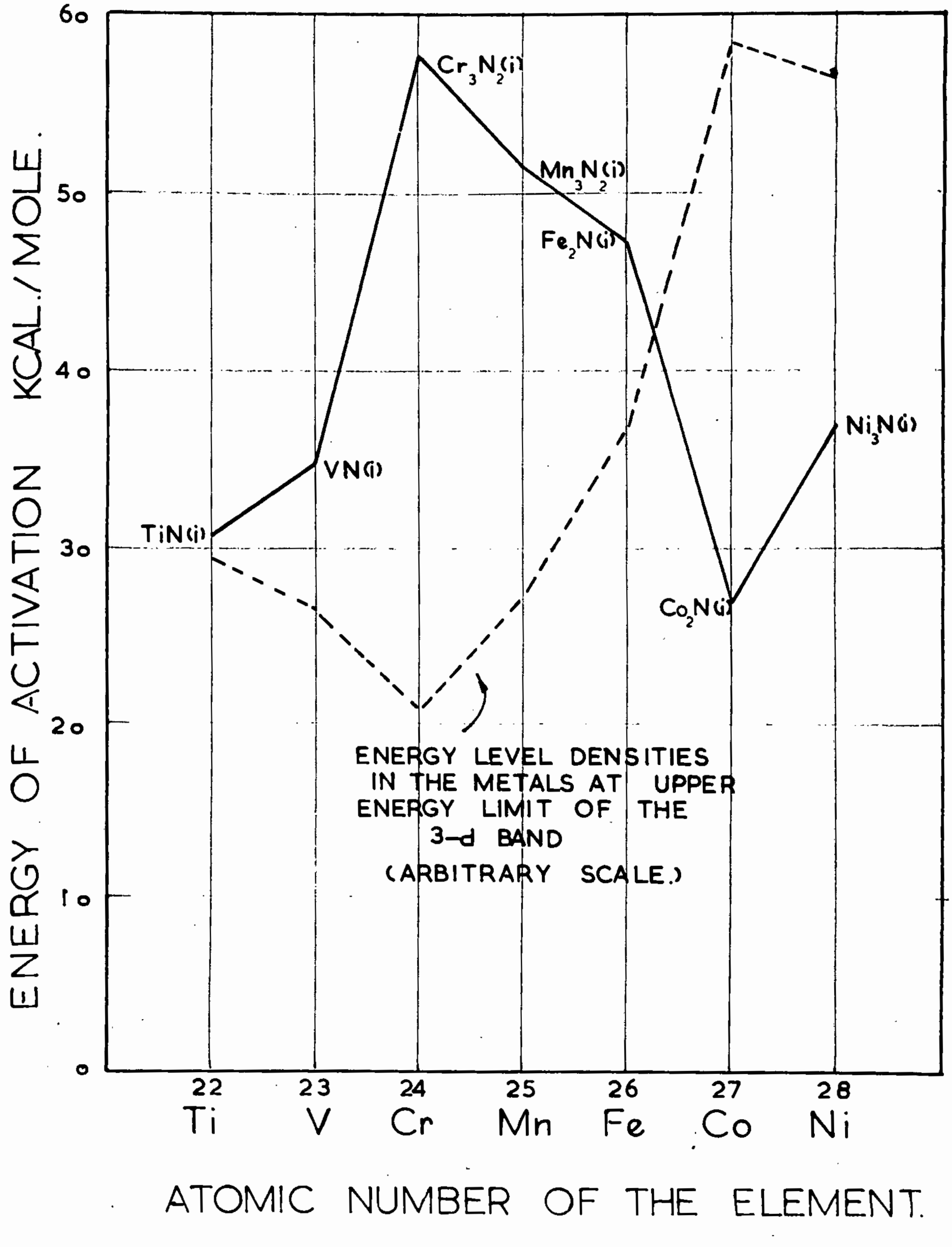

FIGURE 18.

Cr - Fe - Ni nitride plots. The lower values of energy of activation show no relation to this d-character. It is with some reluctance that attention is drawn to the fact that there appears to be a relation between the variation of the highest values of activation energy shown in figure 16 and the energy level densities of the 3d-band of the pure metals. The energy level densities of each metal at the upper limit of energy vary, with increasing number of electrons associated with the metal, in opposite behaviour to the activation energies. This is shown in figure 18. The uncertainty lies in the fact that the figure 16 relation may not be correct, and also that the electronic properties of the metals, and not the nitrides are considered. Furthermore, the choice of the energy level densities at the upper energy limit does not take into account the density of energy levels at lower energy values The uneven manner in which energy level densities vary with increasing number of electrons associated with the metals is represented in a plot after Slater, shown in "Catalysis, volume II" by Emmett.

TABLE IX.

X shows the phase which is regarded as the predominant phase present in each catalyst used.

NITRIDE FORMULA.	PHASE TYPE	LATTICE CONSTANTS, Å. a	b	c
TiN_1	f.c.cubic .x.	4.23 (5)		
$TiN_{0.23-0.42}$	hex. c.p.			
VN_1	f.e. cubic .x.	4.128		
V_3N	hex c.p.	2.83		4.33
CrN	f.c. cubic	4.140		
Cr_3N_2	hex c.p. .x.	2.747- 2.770		4.439- 4.474
Mn_3N_2	f.e. tetr .x.	4.211		4.130
Mn_2N	f.e. tetr .x.	4.154		4.037
Mn_4N	f.e. cubic	4.435		
Fe_4N	f.e. cubic	3.787 KX		
Fe_3N	c.p. hex .x.	2.759 KX	4.778KX	4.411KX
Fe_2N	orthorhomb base centred	2.756KX	4.820KX	4.416KX

Co_3N	rhomb. deformed hex. c.p.	.x.	2.842	4.351
Ni_3N	hex. c.p.		2.664	4.298

Geometric factors.

Although the nitride lattice parameters may be a function of the electronic character, the relation to catalytic activity will be briefly considered. Table IX shows, in summary, the nitride phase types and lattice constants. It is shown that the nitrides used as catalysts varied in phase type. Cr_3N_2, Mn_3N_2 and Fe_3N, which show systematic catalytic behaviour exist respectively as a hexagonal close packed-, a face centred tetragonal-and a hexagonal close packed phase, and therefore it appears that the phase type does not bear any relation to the energy of activation. Since varied phase types exist, the lattice parameters cannot be compared. Other properties of the nitrides, stability and heat of formation show a general decrease in value with increasing atomic number, and this corresponds to the activation energy variation shown in figure 15. Here again, such considerations lead only to a speculative discussion.

In conclusion, it may be mentioned that the activation energies determined are in general not very different from energies of activation shown by many other catalysts. One may cite a number of cases where the activation energy is either of the order of 40 to 50 Kcal/mole, or of the order of 30 Kcal/mole. Some examples of the former case are: Molybdenum, tungsten and nickel (Kunsman), previously mentioned; copper, 46 Kcal/mole (Dixon[81]) ; platimum, 44 Kcal/mole (Schwab, Schmidt[85]); iron, approximately 40 to 50 Kcal/mole (Kunsman[82.83.]) and of the latter: iron at high temperatures, 20 Kcal/mole (Kunsman[82]) ; ruthemium, rhodium and palladium, 30.5, 30 and 31.6 Kcal/mole, respectively (Amano and Taylor[84]); and the lower values of activation energies found by Kunsman for the molybdemum, tungsten and nickel catalysts.

The results, however show that the majority of the nitrides used show good catalytic activity under certain conditions, and such behaviour does not differ much from the behaviour of the metals.

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TABLE 1A. **CATALYST: TITANIUM NITRIDE**

Sample............1
Run...............1
Space velocity....2000cc/cc/hour
Mass..............5 gram
Analysis..........22.5% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T^\circ A$	seconds	c.c.	cc/min.
1	477	1.333	238	0.5	0.126
2	476	1.335	255	0.5	0.118
3	487	1.316	137	0.5	0.219
4	503	1.289	96	0.5	0.312
5	506	1.284	92	0.5	0.326
6	499	1.295	101	0.5	0.297
7	480.3	1.327	163	0.5	0.184
8	478.5	1.331	200	0.5	0.150
9	477.5	1.333	216	0.5	0.139
10	489.2	1.312	164	0.5	0.183
11	494	1.304	134	0.5	0.224
12	463	1.359	151	0.1	0.040
13	473	1.340	73	0.1	0.082
14	468	1.350	110	0.1	0.055
15	468	1.350	94	0.1	0.064
16	469	1.348	120	0.1	0.050
17	478	1.332	56	0.1	0.11
18	478	1.332	64.8	0.1	0.093
19	470	1.345	84.5	0.1	0.071

ENERGY OF ACTIVATION, E: IA = 29.8 Kcal./mole
IB = 91 Kcal./mole.

(See figure 1)

TABLE 1B. CATALYST: TITANIUM NITRIDE

Sample............2
Run...............1
Space velocity....2000cc/cc/hour
Mass..............4 gram
Analysis..........22.3% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T^oA$	seconds	c.c.	cc/min.
1	461	1.362	319	0.1	0.019
2	462	1.361	221	0.1	0.027
3	461.5	1.361	221	0.1	0.027
4	474	1.339	110	0.1	0.055
5	476	1.335	70.5	0.1	0.085
6	476	1.335	105	0.1	0.057
7	488	1.314	47.0	0.1	0.128
8	484	1.321	52	0.1	0.12
9	484	1.321	39	0.1	0.15
10	484	1.321	52	0.1	0.12
11	484	1.321	40	0.1	0.15
12	484	1.321	52	0.1	0.12
13	484	1.321	50	0.1	0.12
14	502	1.290	33	0.1	0.18
15	498	1.297	32	0.1	0.19
16	497	1.299	36	0.1	0.17
17	495	1.302	41	0.1	0.15

ENERGY OF ACTIVATION, E: IIA = 31.6 Kcal./mole.
IIB = 98 Kcal./mole.

(See figure 1)

TABLE 2A. **CATALYST: VANADIUM NITRIDE**

Sample............1
Run...............1
Space velocity....2000cc/cc/hour
Mass..............5.5 gram
Analysis..........21.2% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T^oA$	seconds	c.c.	cc/min
1	462.0	1.361	55.0	2.0	2.07
2	462.5	1.360	56.0	2.0	2.14
3	463.0	1.359	55.8	2.0	2.15
4	473.0	1.340	38.4	2.0	3.12
5	473.0	1.340	39.0	2.0	3.08
6	473.0	1.340	38.6	2.0	3.11
7	450.0	1.383	86.0	2.0	1.39
8	450.0	1.383	86.8	2.0	1.38
9	423.0	1.437	223.5	2.0	0.537
10					

ENERGY OF ACTIVATION, E: I = 35.8 Kcal./mole.

(See figure 2)

TABLE 2B. CATALYST: VANADIUM NITRIDE

Sample............1
Run...............2
Space velocity....2000cc/cc/hour
Mass..............5.5 gram
Analysis..........21.2% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T°A$	seconds	c.c	cc/min
1	465.0	1.355	13.2	0.5	2.27
2	465.0	1.355	13.4	0.5	2.24
3	465.0	1.355	13.6	0.5	2.20
4	465.0	1.355	13.2	0.5	2.27
5	465.0	1.355	13.2	0.5	2.27
6	446.5	1.390	25.2	0.5	2.00
7	462.0	1.361	15.0	0.5	2.00
8	462.0	1.361	15.0	0.5	2.00
9	458.0	1.368	17.8	0.5	1.69
10	462.0	1.361	14.8	0.5	2.03
11	441.0	1.401	31.2	0.5	0.961
12	441.0	1.401	30.4	0.5	0.986
13	414.5	1.455	76.5	0.5	0.392
14	413.0	1.458	78.0	0.5	0.385
15	413.0	1.458	70.0	0.5	0.405
16	404.0	1.477	91.0	0.5	0.330
17	408.0	1.468	87.0	0.5	0.345

ENERGY OF ACTIVATION, E: IIA = 35.0 Kcal./mole.
IIB = ^{n}20 Kcal./mole.

(See figure 2)

TABLE 2C. CATALYST: VANADIUM NITRIDE

Sample............2
Runs..............1&2
Space velocity....2500cc/cc/hour
Mass..............3.1 gram
Analysis..........21.4% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T^\circ A$	seconds	c.c.	cc/min
1	460.0	1.364	20.2	0.5	1.49
2	460.0	1.364	19.8	0.5	1.52
3	460.0	1.364	20.4	0.5	1.47
4	460.0	1.364	20.4	0.5	1.47
5	465.0	1.355	18.0	0.5	1.67
6	465.0	1.355	18.0	0.5	1.67
7	465.0	1.355	18.5	0.5	1.62
8	455.5	1.373	23.2	0.5	1.29
9	443.0	1.397	36.5	0.5	0.822
10	443.0	1.397	36.8	0.5	0.815
11	443.0	1.397	36.8	0.5	0.815
12	431.0	1.420	54.3	0.5	0.552
13	432.0	1.418	53.5	0.5	0.561
14	463.5	1.358	19.0	0.5	1.58
15	478.0	1.332	12.5	0.5	2.40
16	480.0	1.328	10.8	0.5	2.78
17	480.0	1.328	10.8	0.5	2.78
18	480.0	1.328	10.8	0.5	2.78
19	480.0	1.328	11.0	0.5	2.73

ENERGY OF ACTIVATION, E: IIIA = 34.4 Kcal./mole

(See figure 2)

TABLE 2D. CATALYST: VANADIUM NITRIDE

Sample............1 & 2 combined
Run...............1
Space velocity....2000cc/cc/hour
Mass..............7.5 gram
Analysis..........21.3% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T°A$	seconds	c.c	cc/min
1	440	1.403	19.0	0.5	1.58
2	438	1.406	20.5	0.5	1.46
3	436	1.410	21.9	0.5	1.37
4	471	1.344	7.4	0.5	4.1
5	465	1.355	8.8	0.5	3.4
6	465	1.355	8.8	0.5	3.4
7	465	1.355	8.8	0.5	3.4
8	415	1.453	35.0	0.5	0.857
9	416	1.451	37.2	0.5	0.806
10	415	1.453	36.8	0.5	0,815
11	391	1.506	77.0	0.5	0.390
12	391	1.506	78.0	0.5	0.384
13	437	1.408	20.2	0.5	1.49
14	456	1.372	11.6	0.5	2.59
15	453	1.377	12.2	0.5	2.46
16	446	1.391	16.2	0.5	1.85
17	458	1.368	11.6	0.5	2.59
18	456	1.372	11.8	0.5	2.54
19	455	1.374	12.0	0.5	2.50
20	421	1.441	35.6	0.5	0.842
21	414	1.456	45.0	0.5	0.667
22	394	1.499	74.5	0.5	0.403
23	400	1.486	54.2	0.5	0.553
24	400	1.486	57.7	0.5	0.520
25	381	1.529	100.2	0.5	0.294

ENERGY OF ACTIVATION, E: IVA = 33.8 Kcal./mole
IVB = 20.8 K al./mole

(See figure 2)

TABLE 3A. CATALYST: CHROMIUM NITRIDE

Sample............1
Run...............1
Space velocity....2000cc/cc/hour
Mass..............5 gram
Analysis..........15.2% N.

(See figure 3)

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T^oA$	seconds	c.c	cc/min
1	465.5	1.354	248.0	0.5	0.121
2	469.	1.348	281.4	0.5	0.107
3	482.5	1.324	182.6	0.5	0.164
4	489	1.312	169.8	0.5	0.177
5	490	1.311	170.0	0.5	0.177
6	494.5	1.303	128.5	0.5	0.234
7	495	1.302	123.1	0.5	0.244
8	498	1.297	98.9	0.5	0.304
9	503	1.289	81.5	0.5	0.368
10	501	1.292	87.3	0.5	0.343
11	506	1.284	64.0	0.5	0.468
12	507	1.282	71.7	0.5	0.418
13	506.5	1.283	70.0	0.5	0.428
14	496.5	1.300	104.0	0.5	0.288
15	497.5	1.299	107.5	0.5	0.279
16	499.5	1.295	93.7	0.5	0.320
17	496.5	1.300	112.9	0.5	0.266
18	492	1.307	120	0.5	0.250
19	505	1.285	75.0	0.5	0.400
20	487.5	1.315	164	0.5	0.183
21	479.5	1.329	187.4	0.5	0.160
22	482.5	1.324	204.0	0.5	0.147
23	484	1.321	171.2	0.5	0.175
24	488	1.314	163	0.5	0.184
25	488	1.314	155.5	0.5	0.193
26	488	1.314	155.8	0.5	0.193
27	490	1.311	154.5	0.5	0.195
28	496	1.300	115.1	0.5	0.261
29	502.5	1.290	76.9	0.5	0.390
30	502	1.290	93.5	0.5	0.321
31	466	1.353	237	0.5	0.127
32	470	1.346	281	0.5	0.107
33	471	1.344	268	0.5	0.112
34	475	1.337	255	0.5	0.117
35	475	1.337	260	0.5	0.116
36	485.5	1.319	206	0.5	0.146
37	479	1.330	244	0.5	0.123

ENERGY OF ACTIVATION, E: IA=57.0, 1B=31.1 Kcal/mole.

TABLE 3B. **CATALYST: CHROMIUM NITRIDE**

Sample............2
Run...............1
Space velocity....2000cc/cc/hour
Mass..............5 gram
Analysis..........15.0% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T°A$	seconds	c.c	cc/min
1	469.5	1.347	179	0.5	0.168
2	469	1.348	194.5	0.5	0.155
3	468	1.350	216	0.5	0.139
4	476.5	1.334	191	0.5	0.157
5	477	1.333	151	0.5	0.199
6	477	1.333	184.4	0.5	0.161
7	477	1.333	179	0.5	0.168
8	477	1.333	196	0.5	0.153
9	480	1.328	150.8	0.5	0.199
10	480	1.328	183.0	0.5	0.164
11	480	1.328	194	0.5	0.155
12	468.5	1.349	222	0.5	0.135
13	467	1.351	238	0.5	0.126
14	457	1.370	323	0.5	0.0929
15	458	1.368	270	0.5	0.111
16	458	1.368	320	0.5	0.0935
17	483	1.323	141	0.5	0.213
18	483	1.323	146	0.5	0.206
19	498	1.297	82.8	0.5	0.362
20	498.5	1.296	80.4	0.5	0.373
21	505	1.285	61	0.5	0.493
22	507	1.282	54	0.5	0.555
23	506	1.284	52.8	0.5	0.567
24	501	1.292	70.6	0.5	0.425
25	493	1.305	108.5	0.5	0.277
26	493	1.305	101.5	0.5	0.295
27	511.5	1.275	44.1	0.5	0.680
28	493.5	1.305	104.7	0.5	0.287
29	489	1.312	128.6	0.5	0.233

ENERGY OF ACTIVATION, E: IIA = 58.5 Kcal/mole.
IIB = 31.2 Kcal/mole.

(See figure 3.)

TABLE 4A. CATALYST: MANGANESE NITRIDE

Sample............1
Run...............1
Space velocity....10,000cc/cc/hour
Mass..............6 gram
Analysis..........13.8% N.

NO	TEMPERATURE		GAS FLOWRATE		
	$^{\circ}C$	$10^3/T^{\circ}A$	seconds	c.c	cc/min
1	424	1.435	56.5	0.5	0.531
2	422	1.439	65.8	0.5	0.455
3	439	1.404	37.8	0.5	0.793
4	427	1.429	43.0	0.5	0.697
5	444	1.395	31.8	0.5	0.943
6	443	1.397	41.5	0.5	0.722
7	442	1.399	36.9	0.5	0.813
8	430	1.422	47.2	0.5	0.636
9	459	1.366	17.8	0.5	1.69
10	458	1.368	19.7	0.5	1.52
11	447	1.389	27.8	0.5	1.08
12	425.5	1.432	59.5	0.5	0.504
13	453.5	1.377	23.8	0.5	1.26
14	467	1.351	13.5	0.5	2.22
15	464	1.357	14.4	0.5	2.08
16	473	1.340	11.4	0.5	2.63
17	470	1.346	11.0	0.5	2.73
18	470	1.346	11.6	0.5	2.59
19	481	1.326	31.0	2.0	3.87
20	480	1.328	27.8	2.0	4.32
21	499	1.295	12.2	2.0	9.83
22	487	1.316	19.2	2.0	6.24
23	489	1.312	19.3	2.0	6.22
24	432.5	1.417	43.4	0.5	0.690
25	403	1.479	82.2	0.5	0.365

ENERGY OF ACTIVATION, E: IA = 52.5 Kcal/mole.
IB = 30.2 Kcal/mole

(See figure 4)

TABLE 4B. CATALYST: MANGANESE NITRIDE

Sample............2
Run...............1
Space velocity....2000cc/cc/hour
Mass..............8 gram
Analysis..........13.9% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^{3}T^{\circ}A$	seconds	c.c	cc/min
1	374	1.546	200	0.5	0.150
2	383.5	1.523	163	0.5	0.184
3	383.0	1.524	152	0.5	0.198
4	401	1.484	80.0	0.5	0.375
5	423.5	1.436	40.2	0.5	0.745
6	430	1.422	34.6	0.5	0.866
7	429	1.425	34.8	0.5	0.861
8	444	1.395	22.9	0.5	1.31
9	415	1.453	51.7	0.5	0.580
10	449	1.385	19.2	0.5	1.561
11	435	1.412	28.0	0.5	1.07
12	459	1.366	12.0	0.5	2.50
13	457	1.370	59.0	2.0	2.03
14	466	1.353	40.0	2.0	3.00
15	473	1.340	31.4	2.0	3.82
16	470	1.346	35.1	2.0	3.42
17	477.5	1.333	26.8	2.0	4.47
18	478	1.332	27.4	2.0	4.37
19	470	1.346	35.0	2.0	4.43
20	448.5	1.386	80.0	2.0	1.50
21	464.0	1.357	36.3	2.0	3.32
22	471.0	1.344	27.8	2.0	4.32

ENERGY OF ACTIVATION; E: IIA = 50.3 Kcal/mole.
IIB = 29.4 Kcal/mole.

(See figure 4)

TABLE 4C. CATALYST: MANGANESE NITRIDE

Sample............3
Run...............1
Space velocity....2000cc/cc/hour
Mass..............3 gram
Analysis..........13.9% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T$°A	seconds	c.c	cc/min
1	460	1.364	86.8	1.0	0.692
2	466	1.353	68.8	1.0	0.872
3	472	1.342	49.5	1.0	1.214
4	461	1.362	75.0	1.0	0.800
5	462	1.361	73.4	1.0	0.817
6	443	1.397	153.5	1.0	0.391
7	452	1.379	112.8	1.0	0.532
8	452	1.379	108.4	1.0	0.554
9	425	1.433	306.4	1.0	0.196
10	426	1.431	256.4	1.0	0.234
11	426	1.431	295.0	1.0	0.204
12	438	1.406	186	1.0	0.323
13	466	1.353	52.0	1.0	1.16
14	471	1.344	40.0	1.0	1.50
15	420	1.443	260	1.0	0.231
16	423	1.437	248	1.0	0.242
17	400	1.486	583	1.0	0.103
18	416.5	1.450	354	1.0	0.170
19	371	1.553	190	1.0	0.032
20	420.0	1.443	293	1.0	0.205
21	484.5	1.320	28.6	1.0	2.10
22	463.0	1.359	71.4	1.0	0.840
23	421.0	1.441	31 .6	1.0	0.190
24	442.5	1.398	156	1.0	0.385
25	465.5	1.354	59.7	1.0	1.01
26	483.0	1.323	31.8	1.0	1.89
27	483.5	1.322	31.0	1.0	1.94
28	471.0	1.344	49.6	1.0	1.21
29	475.5	1.336	42.8	1.0	1.40
30	475.5	1.336	42.0	1.0	1.43
31	479.0	1.330	40.4	1.0	1.49
32	371.0	1.553	171.4	1.0	0.035

ENERGY OF ACTIVATION, E: IIIA = 52.3 Kcal/mole.
IIIB = 30.9 Kcal/mole.

(See figure 4)

TABLE 5A. CATALYST: IRON NITRIDE

Sample............1
Run...............1
Space velocity....2000cc/cc/hour
Mass..............7 gram
Analysis..........10.8% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T\,^{\circ}A$	seconds	c.c	cc/min
1	456	1.372	6.6	2.0	18
2	437	1.408	15.0	2.0	8.00
3	449	1.385	10.0	2.0	12.0
4	469	1.348	4.8	2.0	25
5	470	1.346	4.8	2.0	25
6	455	1.374	6.4	2.0	19
7	450	1.383	10.8	2.0	11.1
8	437	1.408	15.4	2.0	7.78
9	428	1.427	20.2	2.0	5.94
10	408	1.468	37.0	2.0	3.24
11	409	1.466	39.0	2.0	3.08
12	398	1.490	52.0	2.0	2.31
13	399	1.488	58.0	2.0	2.07
14	399	1.488	60	2.0	2.0
15	398	1.490	15	0.5	2.0
16	390	1.508	19	0.5	1.58
17	363	1.572	41	0.5	0.73
18	363	1.572	40	0.5	0.75
19	328	1.664	101	0.5	0.297
20	328	1.664	109	0.5	0.275

ENERGY OF ACTIVATION, E:

IA = 48.5 Kcal/mole.
IB = 32.6 Kcal/mole.
IC = 20.7 Kcal/mole.

(See figure 5)

TABLE 5B. CATALYST: IRON NITRIDE

Sample............1
Run...............2
Space velocity....2000cc/cc/hour
Mass..............5 gram
Analysis..........10.8% n.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T°A$	seconds	c.c	cc/min
1	392	1.504	27.0	0.5	1.11
2	395	1.497	26.5	0.5	1.13
3	391	1.506	29.0	0.5	1.03
4	428	1.427	9.0	0.5	3.3
5	427	1.429	8.8	0.5	3.4
6	417	1.449	11.5	0.5	2.61
7	388	1.513	26.6	0.5	1.13
8	415.5	1.452	12.8	0.5	2.34
9	440	1.403	5.5	0.5	5.5
10	329	1.661	228.2	0.5	0.132
11	329	1.661	224	0.5	0.134
12	328	1.664	190	0.5	0.158
13	359	1.582	73	0.5	0.41
14	370	1.555	57	0.5	0.53
15	370	1.555	53	0.5	0.57
16	384	1.522	37	0.5	0.81
17	353	1.597	101	0.5	0.297
18	381	1.529	42.6	0.5	0.705
19	339	1.634	14.1	0.5	0.213
20	459	1.366	9.24	2.0	13.0
21	448	1.387	16.2	2.0	7.40
22	469	1.348	6.1	2.0	19.6
23	468	1.350	6.4	2.0	19
24	465	1.355	7.0	2.0	17
25	475	1.337	5.7	2.0	21

ENERGY OF ACTIVATION, E:
IIA ≃ 48.3 Kcal/mole.
IIB ≃ 32.7 Kcal/mole.
IIC ≃ 22.2 Kcal/mole.

(See figure 5)

TABLE 5C. CATALYST: IRON NITRIDE

Sample............1
Run...............3
Space velocity....12000cc/cc/hour
Mass..............5 gram
Analysis..........10.8% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T^oA$	seconds	c.c	cc/min
1	456.5	1.371	6.2	2.0	19
2	464.0	1.357	4.6	2.0	26
3	470	1.346	3.6	2.0	33
4	455	1.374	6.6	2.0	18
5	439	1.404	12.4	2.0	9.67
6	384	1.522	80	2.0	1.5
7	407	1.471	37	2.0	3.3
8	401	1.484	49	2.0	2.5
9	430	1.422	17.2	2.0	6.97
10	427	1.429	19.2	2.0	6.25
11	424	1.435	20.5	2.0	5.85
12	334	1.647	350	2.0	0.343
13	334	1.647	348	2.0	0.345
14	365	1.567	148	2.0	0.810
15	348	1.610	222	2.0	0.540
16	329	1.661	437	2.0	0.275
17	325	1.672	426	2.0	0.282

ENERGY OF ACTIVATION, E:
IIIA - 46.1 Kcal/mole.
IIIB = 31.6 Kcal/mole.
IIIC = 20.1 Kcal/mole.

(See figure 5)

TABLE 6A. CATALYST: IRON NITRIDE

Sample............2
Run...............1
Space velocity....35,000cc/cc/hour
Mass..............2 gram
Analysis..........11.0% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T°A$	seconds	c.c	cc/min
1	444	1.395	17	2.0	7.1
2	440.5	1.402	19.5	2.0	6.2
3	438	1.406	21.2	2.0	5.65
4	437.8	1.407	21.2	2.0	5.65
5	427	1.429	29.2	2.0	4.11
6	422.5	1.438	34.4	2.0	3.49
7	410	1.464	52.8	2.0	2.27
8	399	1.488	81.8	2.0	1.47
9	388	1.513	134.4	2.0	0.894
10	343	1.623	535	2.0	0.224
11	379	1.534	39	0.5	0.77
12	364	1.570	68	0.5	0.44
13	363.5	1.571	71	0.5	0.42
14	356	1.590	87	0.5	0.35
15	347	1.613	120	0.5	0.250
16	412	1.460	13	0.5	2.3
17	432	1.418	5.8	0.5	5.2
18	430	1.422	25.2	2.0	4.76
19	438	1.406	19.5	2.0	6.15
20	450	1.383	13.5	2.0	8.88
21	449	1.385	14.2	2.0	8.45
22	459.5	1.365	9.4	2.0	13
23	458	1.368	9.8	2.0	12
24	472	1.342	5.3	2.0	23
25	468.5	1.349	6.4	2.0	19
26	462.5	1.360	8.2	2.0	15

ENERGY OF ACTIVATION, E:
IVA = 48.2 Kcal/mole.
IVB = 32.2 Kcal/mole.
IVC = 25.1 Kcal/mole.

(See figure 6)

TABLE 6B **CATALYST: IRON NITRIDE**

Sample............2
Run...............2
Space velocity....2000,cc/cc/hour
Mass..............2 gram
Analysis..........11.0% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T$ °A	seconds	c.c	cc/min
1	439.5	1.404	19	2.0	6.3
2	447	1.389	15	2.0	8.0
3	462	1.361	9.2	2.0	13
4	460	1.364	9.2	2.0	13
5	456	1.372	10.6	2.0	11.3
6	455	1.374	12	2.0	10
7	450	1.383	13.2	2.0	9.08
8	465	1.355	7.2	2.0	17
9	413.5	1.457	41.8	2.0	2.87

ENERGY OF ACTIVATION, E: VA = 46.9 Kcal/mole.
VB = 31.4 Kcal/mole.

(See figure 6)

TABLE 6C. CATALYST: IRON NITRIDE

Sample............2
Run...............3
Space.velocity....2000cc/cc/hour
Mass..............2 gram
Analysis..........11.0% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T°A$	seconds	c.c	cc/min
1	437	1.408	30	2.0	4.0
2	418	1.447	48	2.0	2.5
3	410	1.464	71	2.0	1.7
4	417	1.449	60	2.0	2.0
5	429	1.425	41	2.0	2.9
6	402.5	1.480	91	2.0	1.3
7	440.5	1.402	26.4	2.0	4.54
8	446	1.391	18.2	2.0	6.60
9	464.5	1.356	9.2	2.0	13
10	454.5	1.375	13.4	2.0	8.95
11	421	1.441	49.4	2.0	2.43
12	344	1.621	136	0.5	0.221
13	362.5	1.573	81	0.5	0.37
14	363.5	1.571	75	0.5	0.40
15	391	1.506	34.2	0.5	0.88
16	399	1.488	18.2	0.5	1.65
17	448.5	1.386	18.2	2.0	6.59

ENERGY OF ACTIVATION, E:

VIA = 46.9 Kcal/mole.
VIB = 30.4 Kcal/mole.
VIC = 23.1 Kcal/mole.

(See figure 6)

TABLE 7A. CATALYST: COBALT NITRIDE

Sample............1
Run...............1
Space velocity....70,000cc/cc/hour
Mass..............0.03 gram
Analysis..........10.1% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T$°A	seconds	c.c	cc/min
1	464.5	1.356	131.2	1.0	0.457
2	465.0	1.355	130.2	1.0	0.462
3	470.5	1.345	116.7	1.0	0.515
4	470.0	1.346	119.0	1.0	0.504
5	470.0	1.346	118.4	1.0	0.507
6	465.0	1.355	133.6	1.0	0.449
7	464.0	1.357	136.8	1.0	0.439
8	452.0	1.379	187.5	1.0	0.320

ENERGY OF ACTIVATION, E: 27.4 Kcal/mole.

(See figure 7)

TABLE 7B. **CATALYST: COBALT NITRIDE**

Sample............2
Run...............1
Space velocity....120,000cc/cc/hour
Mass..............0.01 gram
Analysis..........10.2% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T°A$	seconds	c.c	cc/min
1	453.5	1.376	627	1.0	0.096
2	463.0	1.359	507	1.0	0.119
3	453.0	1.377	650	1.0	0.092
4	475.0	1.337	385	1.0	0.156
5	472.5	1.341	395	1.0	0.152
6	480.5	1.327	352	1.0	0.171
7	480.0	1.328	334	1.0	0.180
8	453.0	1.377	649	1.0	0.193
9	459.5	1.365	547	1.0	0.110
10	468.0	1.350	460	1.0	0.134
11	464.0	1.357	501	1.0	0.120

ENERGY OF ACTIVATION, E: 26.7 Kcal/mole.

(See figure 7)

TABLE 8A. CATALYST: NICKEL NITRIDE

Sample............1
Run...............1
Space velocity....100,000cc/cc/hour
Mass..............0.02 gram
Analysis..........7.2% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T$°A	seconds	c.c	cc/min
1	442	1.399	126.8	1.0	0.473
2	450	1.383	99.8	1.0	0.602
3	447	1.389	113.8	1.0	0.527
4	443	1.397	132.0	1.0	0.454
5	443.5	1.396	121.0	1.0	0.496
6	444	1.395	125.0	1.0	0.480
7	446	1.391	119.0	1.0	0.504
8	445	1.393	120.0	1.0	0.500
9	441.5	1.400	138.1	1.0	0.435
10	441.0	1.401	138.0	1.0	0.435

ENERGY OF ACTIVATION, E: I = 35 Kcal/mole

(See figure 8)

TABLE 8B. CATALYST: NICKEL NITRIDE

Sample............2
Run...............1
Space velocity....120,000cc/cc/hour
Mass..............0.01 gram
Analysis..........7.1% N.

NO	TEMPERATURE		GAS FLOWRATE		
	°C	$10^3/T°A$	seconds	c.c	cc/min
1	439	1.404	563	1.0	0.107
2	444.5	1.394	437	1.0	0.138
3	445	1.393	450	1.0	0.133
4	446.5	1.390	425	1.0	0.141
5	445.5	1.392	425	1.0	0.141
6	437.5	1.407	571	1.0	0.105
7	447	1.389	459	1.0	0.131
8	450	1.383	449	1.0	0.134
9	443	1.397	594	1.0	0.101
10	445	1.393	569	1.0	0.106
11	445.5	1.392	523	1.0	0.115
12	447	1.389	485	1.0	0.124
13	441	1.401	607	1.0	0.099
14	451	1.381	435	1.0	0.138

ENERGY OF ACTIVATION, E:

IIA = 39 Kcal/mole.
IIB = 36 Kcal/mole.

(See figure 8)