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I hereby recommend that the thesis prepared under my supervision by Harry L. Kahler, Jr.
entitled Heterogeneous Catalysis in Liquid Ammonia Solution.

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy.

Approved by:

W. M. Burgess, director.
W. M. Burgess, Chairman.

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A STUDY OF HEREROGENEOUS CATALYSIS
IN LIQUID AMMONIA SOLUTION

A dissertation submitted to the

Graduate School
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1934

by

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To Dr. Wayland M. Burgess, director of this research, my sincere appreciation of his unfailing cooperation, foresight and wise counsel.

Harry L. Kahler, Jr.

II INTRODUCTION

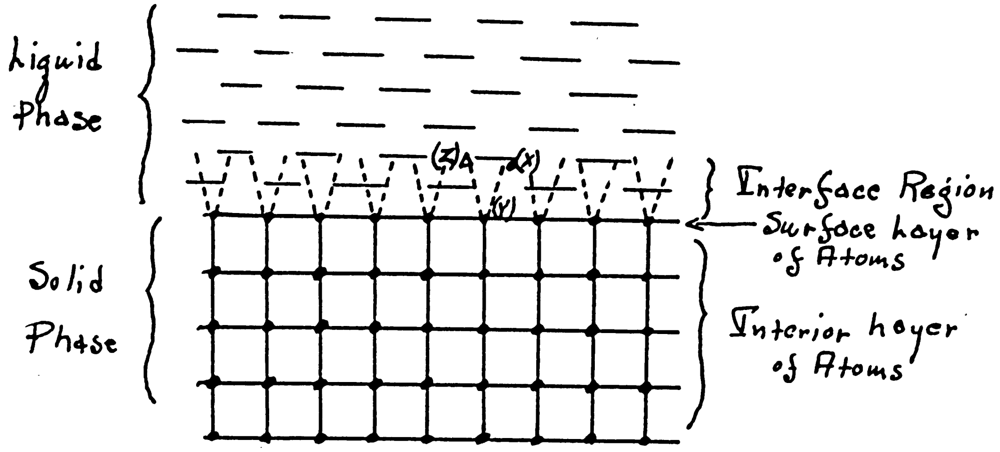
The introduction of this thesis will present discussions on heterogeneous catalysis, the nature of the system in which this work was done, viz., alkali metal - liquid ammonia solution, and the object of the investigation.

A. Discussion of Heterogeneous Catalysis

This general discussion will include the following topics in the order named: A brief history of heterogeneous catalysis,[1] a concept of adsorption and the seat of catalytic activity,[2 3 4] discussion of order of reaction in heterogeneous systems, and a few of the important theories of heterogeneous catalysis.

Centuries ago,[1] agents were used to facilitate various reactions, such as the conversion of alcoholic liquor to vinegar. The Arabians were familiar with the preparation of ether and the part that dehydrating acids played. From these early times, up to the present time, we learn that investigators were continually finding these phenomena, which are now commonly known as catalyzed reactions. Scheele, in 1792, studied the effects of acids and bases on esterification and saponification. Clement and Desormes discovered the role of nitrogen in the Chamber Process of sulphuric acid. In 1913, Thenard studied the decomposition of ammonia in the presence of metals. Davy, in 1817, observed that certain combustible gas mixtures were oxidized in the presence of heated platinum wire. Berzelius was of the opinion that all these curious reactions involved a new chemical force and to him is given credit for suggesting that the phenomenon be called "Catalysis" from the Greek, meaning wholly loose. Ostwald, in 1888, broadly defined a catalyst as a "substance which, without appearing in the final product, influences the speed of a chemical reaction." At this time, contact catalysis was coming into industrial prominence through the epic work of Sabatier, on the hydrogenation and dehydrogenation of organic compounds. From Sabatier's time up to the present time, utilization of catalysis as an industrial tool increased at a rapid pace. In addition, the theoretical aspects of the problem began more and more to focus the attention of many of our illustrious scientists, among whom can be included Langmuir, Taylor, Hinshelwood, Sabatier, and Lewis. The labor of these men and many others has given to us a deeper insight into the intricacies of heterogeneous catalysis and its many interesting manifestations.

It is universally accepted that the process of adsorption takes place before the process of catalysis,[2] Therefore, it is necessary to have a clear conception of adsorption prior to the presentation of the mode of action of heterogeneous catalysis itself. The following representation, purely diagrammatic, gives a picture of the process involved when a substance becomes attached to a solid.[3] The diagram also serves to illustrate the nature of the solid surface of the catalyst and the seat of catalytic activity; a discussion of these follows the one on adsorption. The example which is chosen for this illustration is taken from the liquid ammonia system in which this work was done.



The upper portion of the diagram indicates the liquid phase, which constitutes a solution of potassium in liquid ammonia. The lower portion of the diagram pictures the solid phase, in this case, a platinum catalyst. The valences of the interior atoms of the platinum are represented as being saturated by neighboring platinum atoms. In the surface layer, complete saturation is not obtained, due to a lack of a layer of platinum atoms, above and contiguous with this surface layer.

The dotted lines protruding into the liquid phase represent the free valences of the platinum atoms on the surface. It is by these free valences that the constituents in the liquid phase, ammonia and potassium, become attached, i.e., adsorbed to the platinum. These surface atoms of the platinum, because of unsaturation, exert a force towards the platinum. A discussion of the nature of this force is beyond the scope of this thesis and is not presented; it is sufficient for the present means just to call it a force.

To be more explicit concerning the process of adsorption, let us examine this case. A molecule of ammonia (x) and an atom of potassium (z) are in close proximity to one of the catalyst atoms (Y) on the surface of the catalyst. This atom (Y), because of its force, reaches out, so to speak, and comes in contact with the particles (x) and (z) and, in order to satisfy this proclivity, draws these two particles toward the solid, where they are held. It can be pointed out here that there are many views concerning whether one solid atom has the power of adsorbing only one particle or whether its power is such as to allow more than one to be held. Langmuir[3] is the advocate of the theory that one particle of adsorbed material is held by one atom of the solid. Taylor[4] advocates that more than one particle can be held. I, personally, favor Taylor's views and, therefore, use his idea in this work, giving the platinum atom in the surface layer, for sake of illustration, two unsaturated valences. Thus the platinum atom (y) is now completely saturated by the two particles it has adsorbed. It must be understood that in the case just presented the atom (y) has a special attraction for these particles (x) and (z). Adsorption is a specific phenomenon, each solid possessing a definite adsorptive value for each substance under definite conditions. This specificity is only recognized here and not discussed. With this rough idea of the process of adsorption in mind, it is now the purpose to present a brief discussion on the seat of catalytic activity.

The study of heterogeneous catalytic reactions is always concerned with the process occurring at the interface between at least two phases. In the diagram, the seat of catalytic activity is, therefore, lodged within the confines of the dotted lines above the surface of the solid. Any catalyzed reaction outside these confines exemplifies homogeneous catalysis and not heterogeneous catalysis. The lines of force are represented as protruding an appreciable distance into the liquid phase; in reality, this distance is so small that it can be said, for all practical purposes, that the adsorbed materials are on the surface of the catalyst proper. The reaction between potassium and ammonia takes place directly on the surface of the catalyst. Immediately after adsorption, the particles (x) and (z) react, due to the effect of the platinum atom (y). The mechanism of how the catalyst can effect this change is reserved for a later discussion. The products of the reaction are now considered. When potassium and ammonia react, hydrogen and potassium amide are formed. This catalyst, platinum, under consideration, has no strong attraction for these products and they are released immediately after formation and escape into the liquid phase. As soon as the products are eliminated, adsorption of more reactants again takes place and the reaction repeats, thus allowing a continuous operation. If it is assumed, for the sake of illustrating the effect of the products of reaction, that the products are strongly attracted by the platinum, they are retained and vary the succeeding operations. If the escape of the products is slow, eventually they will be eliminated, after which adsorption and reaction occur again. If they are permanently held, all catalytic activity is shut off. In this discussion, one atom of the catalyst was chosen as a base for the reaction. This was done for simplicity of presentation. The solid catalyst, platinum, is composed of an innumerable number of these atoms, so that catalytic activity is dispersed over the entire surface. An innumerable number of reactions similar to the one on (y) is, therefore, taking place. The discussion has now progressed to the point where order of reaction in heterogeneous catalytic systems may be presented.

After the discovery of the Law of Mass Action and its kinetic interpretation, it was taken for granted that the same principle would apply, unaltered, to heterogeneous catalytic reactions, that is, it was assumed that the reaction velocity, in contact with a solid, would be proportional to the concentration of one or more of the reactants.[5] Experimentally, it was found that there was at least one more factor to be considered, the removal of products. In any heterogeneous catalytic reaction, these two factors, the rate of the chemical reaction, determined by the concentrations of the reactants, and the rate of diffusion of the products of reaction away from the catalyst, are always occurring concurrently. The net velocity of reaction will then be determined by the rate of the chemical reaction, if the diffusion process is faster than this, or by the rate of diffusion if the chemical reaction is faster; in other words, the slower of these two reactions is always the determining factor in the final velocity. The effect of the concentration of the reactants is now discussed. Three cases and discussions are presented.

1) If the concentration of the reactant relative to the surface is sufficiently great, it is to be expected that the whole of the active surface of the catalyst will be steadily and continuously saturated with the reactant, the concentration of which at the surface will, therefore, be constant. Under

such conditions, the amount of reaction change per unit of time will be constant, in other words

$$\frac{dx}{dt} = k$$ which is known as a zero order.

2) If the relation between the concentration of the reactant in the liquid and the contact surface is such that the amount of the surface covered by the reactant is proportional to a fractional power of the concentration of the latter in the liquid phase, the reaction velocity obtained will be represented by

$$\frac{dx}{dt} = k(a-x)^N$$ where N is any number between 0 and 1.

3) If the relation between the concentration of the reactant in the liquid and the contact surface is such that the amount of the surface covered by the reactant is proportional to the concentration of the latter in the liquid phase, then the reaction velocity obtained will be that of an "apparent" unimolecular order as given by

$$\frac{dx}{dt} = k(a-x)$$

This case is also obtained if more than one reactant is present and if all but one are present in higher concentration. The general equation is

$$\frac{dx}{dt} = k(bcd\text{-----})(a-x)$$ b,c and d being other reactants of high concentration.

or $$\frac{dx}{dt} = k'(a-x);\ k' = k(bcd\text{-})$$

For reactions involving two or more reactants, at approximately the same concentration, interacting at a surface, the complexities are naturally so much the greater. Not only are the concentration ratios between surface and solution, in the cases of the individual reactants, of determining import, but the relative ratios of the two or more reactants on the surface are, likewise, fundamental. No large body of experimental evidence is available which enables a quantitative presentation of such relationships to be made.

Theories of Heterogeneous Catalysis

At the close of the eighteenth century, men had already begun to attempt to visualize just what was occurring in a heterogeneous catalytic reaction and the mechanism by which such reactions took place. Many indefinite theories in these early times were propounded and discarded. As time progressed, two major theories that received attention and and support were the Intermediate Compound Theory and the Adsorption Theory. These theories still command attention today, although the original postulates have been greatly altered and extended. In addition to these, many other theories have been put forward with more or less success. A few of the chief ones are briefly presented, among which are the Intermediate Compound Theory, the Adsorption Theory and the Theory of Reduction of Activation Energy. They are presented in the order given.

Intermediate Compound Theory[6]

The main premises of this theory are that at least one of the reactants of a reaction unites with the catalyst to form a definite chemical compound which is very reactive and this, in turn, unites with the other reactant, liberating the catalyst. Let us examine the well-known hydrogen peroxide reaction

$$H_2O_2 \xrightarrow{Hg} H_2O + \frac{1}{2}O_2$$

The hydrogen peroxide reacts with the mercury catalyst, forming the mercuric peroxide and liberating two atoms of hydrogen.

$$H_2O_2 + Hg \longrightarrow HgO_2 + 2H$$

The mercuric peroxide then reacts with the nascent hydrogen, forming mercury, water and oxygen.

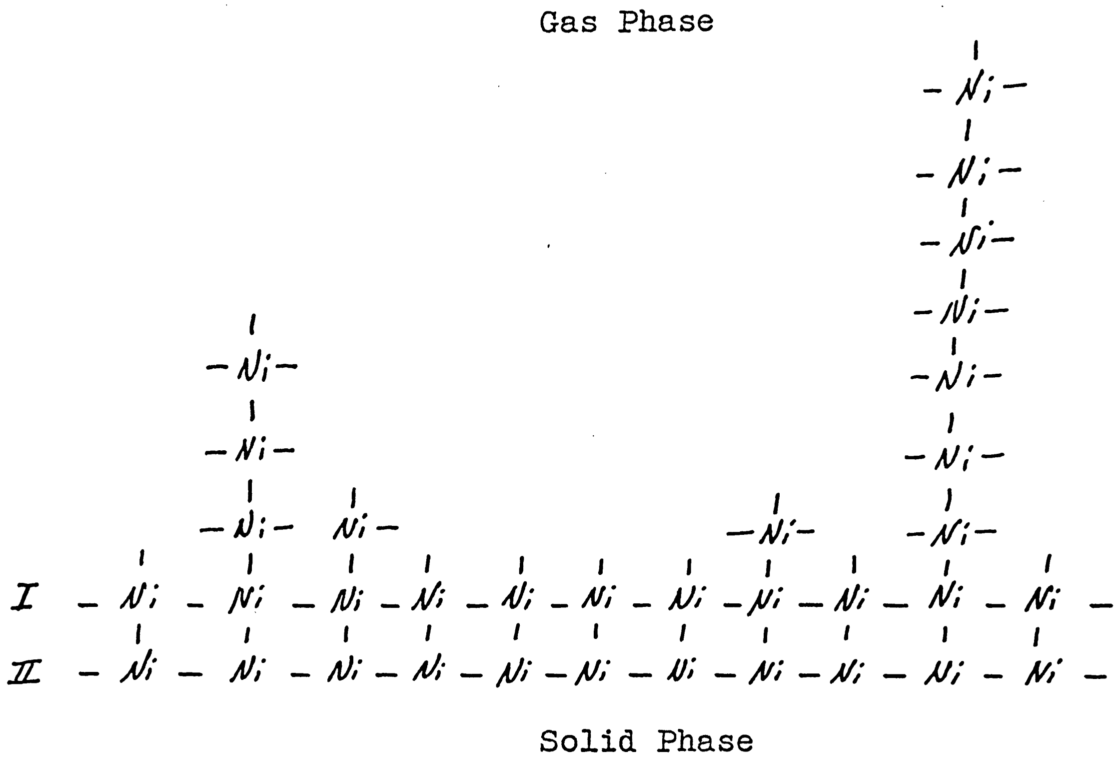
$$HgO_2 + 2H \longrightarrow H_2O + Hg + \frac{1}{2}O_2$$

The mercuric peroxide is the intermediate compount in this reaction. Definite formation of it can be detected by the naked eye - the film of mercuric peroxide intermittently forming and breaking down. One of the requisites of this theory is the pitting of the solid catalyst, that is, when the catalyst combines with one of the reactants the surface of the catalyst is eroded because of the removal from the surface of the catalyst of some of the surface atoms to form the intermediate compound.

The Adsorption Theory

In the latter part of the nineteenth century, Fusinera was the first to see the correlation between adsorption and heterogeneous catalysis. His views and those of many investigators following him were vague and untenable. Around this period of time many theories were propounded and discarded. Among the many theories trying to correlate adsorption with heterogeneous catalysis, the two that have weathered the storm of scientific opinion are those of Taylor and Langmuir. The following is a presentation of Taylor's[8] views.

It is experimentally known that a catalyst shows a varying capacity both as to the gas adsorbed and the promotion of the catalytic change. In addition, catalysts are sensitive to heat and poisons, the reduction of catalytic power being more pronounced than the reduction of adsorptive power. X-ray examination of metallic catalysts show that they possess, even when they are prepared by low temperature reduction, a definite lattice structure of crystalline material. A granule of the catalyst must, therefore, possess in part the ordered arrangement of atoms found in crystals of the metal. The sensitivity of the product, even to moderate heat, whereby marked sintering occurs, suggests that this ordered arrangement of atoms has not been attained and that here and there on the surface of a crystalline granule are groups of atoms in which crystallization is not complete. The following representation, purely diagrammatic, of a cross section of a minute portion of a granule of nickel is an example.



The atoms in the second layer (11) of the granule proposed are surrounded on six sides in three dimensions by other nickel atoms. The atoms in the first layer (1) are surrounded by neighboring nickel atoms in all directions except towards the gas phase. The nickel atoms in the planes above (1) are the atoms not yet crystallized in a definite lattice pattern, and extend out into space. The degree of saturation, imposed on this orderly arrangement, becomes less and less as we proceed outward from the granule proper. Further, we note that the atoms on the edge of a granule have one less degree of saturation than those on the surface proper. Atoms at a corner have two less degrees of saturation than those of the surface proper and one less degree of saturation than those at an edge.

Thus, a surface of a granule might be regarded as composed of atoms in various degrees of saturation by neighboring metal atoms, varying from those one degree less saturated than interior atoms to those which are held to the solid surface by only one bond, thus possessing multiple unsaturation. Accordingly, Taylor gives a picture of a surface which possesses, in spots, inhomogeneously scattered on that surface, certain metal atoms of great chemichal activity. The possession of this activity is the key to adsorption, for by these unsaturated metal atoms gases are easily adsorbed and are markedly changed in their physical and chemical properties. Taylor's theory allows a metal atom to adsorb more than one atom or melecule of gas, depending on the free valences which that metal possesses. For example, if two gases, A and B, are adsorbed on a very unsaturated metal atom, the metal atom provides a base for the interaction of A and B. Taylor's theory, however, goes no further and fails to provide a mechanism by which A and B are activated and ultimately react. He is justly accused of having a Theory of Solid Surface and not of Heterogeneous Catalysis. Langmuir's[9] theory on heterogeneous catalysis is presented in the following discussion.

Langmuir holds that a gas adsorbed on a solid surface is held chemically by the unsaturated atoms at the surface. The atoms in the plane surface of any face of a crystal, for instance, a Face-Centered Cubic lattice of nickel, are practically saturated by neighboring atoms in three dimensions with the exception that there is a certain degree of unsaturation towards the gas phase. In a sufficiently large plane surface of this type, each atom is identical in properties with the majority of the atoms in the surface. There is a certain variability in the surface fields of attraction with variations in the exposed face. The fields are weakest in the closely packed faces, i.e., the 111 planes, stronger in the 100 planes and strongest in the 110 planes. Atoms at the edges of such a crystal are one degree less saturated than the atoms on the surface by reason of the fact that they are to a less degree surrounded by nickel atoms. For this reason they posses stronger attractive forces for impinging gaseous atoms. In an incompletely ordered crystal, the attractive force progressively increases as the degree of saturation by neighboring nickel atoms becomes less and less until, finally, in atoms which are only held to the granule by an attachment, nickel-nickel, the unsaturation of the metal atoms and the attractive force for the impinging gaseous substances are at a maximum. This conception of "extra lattice" atoms is somewhat similar to Taylor's idea but much more vague. Unlike Taylor, he also postulates that only one gaseous atom or molecule is adsorbed by one metal atom. He emphasizes that the distribution of the catalyst atoms varies the distances between adjacent adsorbed molecules or atoms over a wide range and some of these distances are exactly right for the reaction to occur at the highest possible speed. Langmuir's theory can be justly accused of also being a theory of Solid Surface and not a theory of Heterogeneous Catalysis.

The Theory of Reduction of Activation Energy

This theory presents views that heterogeneous catalytic reactions can take place more easily than non-catalyzed reactions, because the energy relationships required in the catalytic reactions are more easily met than in the non-catalytic reactions.[7 10] Before a chemical reaction can take place, the reacting substances must possess sufficient energy to react; if they do not possess this energy of their own accord, it must be supplied. The theory does not postulate that the energy required is supplied by the catalyst but that the catalyst has the power to change the channel of reaction by inducing a different order of reaction, thus altering the energy relations to the extent that the catalyzed reaction possesses a higher velocity than the non-catalyzed reaction. This energy mentioned is called the critical increment, E, which is the amount of energy that must be added per gram mol of reacting substance in excess of the average energy these substances carry ordinarily, in order to bring these substances into a position to react. Experimental evidence exists that proves that the higher the critical increment of a substance, the lower its reactivity and the rate which it exhibits in a reaction; conversely, the lower the critical increment, the higher its reactivity. Hence, this theory postulates that the catalyst has the power to lower the critical increment of the substances in a reaction and, therefore, increase the velocity of that reaction. A typical example is the decomposition of nitrous oxide. Homogeneously, this gas is decomposed thus:

$$2 N_2O \longrightarrow 2N_2 + O_2 + 58500 \text{ calories}$$

The order of the reaction has been determined as a bimolecular one, depending on the collision of 2 molecules of N_2O. Heterogeneously, this gas is decomposed thus:

$$2 N_2O \xrightarrow{Pt} 2N_2 + O_2 + 32{,}500 \text{ calories}$$

The order of reaction has been determined as unimolecular. The role of the platinum is, therefore, to change the order from second to first, thereby lowering the energy required for this reaction to proceed and, consequently, due to this decrease in critical increment, the reaction proceeds more rapidly. This theory shows promise but, unfortunately, the advocates have not as yet advanced any plausible mechanism as to how the catalyst is able to change the order and therefore, be the agent by which the energy change is facilitated.

As is evident from this discussion, these various theories, while interesting, are very difficult to definitely prove or disprove, with the data available at present. Most of the reactions studied to date have been carried out in the gas phase. Less data have been obtained concerning heterogeneous reactions in the solution phase. The present investigation deals with this latter type, being a study of heterogeneous catalysis in liquid ammonia solution, the specific reaction involving the alkali and alkaline earth metals and ammonia. It is most essential that a clear insight into the nature of this liquid ammonia system be obtained.

B. The Nature of the Metal - Liquid Ammonia Solution

The alkali and alkaline earth metals dissolve in liquid ammonia, forming deep blue solutions, considered by some to be solutions of the metals, by other, solutions of the compounds of the metals and ammonia. Seeley[11] was the first to favor the former view, basing his conclusion upon a consideration of the optical properties and general behavior of these solutions. Joannis[12] carefully investigated these systems and decided that a compound between the metal and ammonia was formed, and called these compounds "metal ammoniums", MNH_3. Kraus[13], however, proved beyond doubt that these "metal ammoniums" did not exist and that true solutions of the metals were formed. This view has been established through a study of the variation of vapor pressure with composition in the cases of solutions of lithium, sodium[14], and potassium.[15] Kraus[13 16] also developed the theory of the nature of these solutions that is most generally accepted today. A brief description of this theory will be next presented.

The metal, M, is assumed to ionize according to the following equation

$$M \rightleftharpoons M^+ + e^-$$

The cation is identical with the cation resulting from a soluble salt of the metal. The anion is a new species of ion and is identical with the negative electron of radioactive transformations. It is solvated to a more or less degree, thus:

$$e^- + x\,NH_3 \rightleftharpoons e^-(NH_3)_x$$

The value of x increases with dilution. It is to this anion that these solutions owe their charactdristic properties. Thus they have an abnormally high conductance, the equivalent conductance of sodium, in concentrated solutions, reaching a value of 80,000 mhos. In dilute solutions, the value is as low as 500 mhos. The values of the conductance increases as the degree of solvation of the electron decreases. The significance of the values for a concentrated solution is realized when it is noted that its specific conductance at 0°C. is approximately one-half that of mercury at the same temperature. Another important property of these solutions is their strong reducing power. This again is attributed to the presence of the free electron. The color and appearance of the metal solutions resemble each other. In concentrated solutions, they possess metallic lustre and a bronze color. Dilute solutions do not show metallic lustre but have a characteristic deep blue color, which persists to extreme dilution. Thus it is distinct at a dilution of .000025 N. To what constituent of the solution this color is due is not known. Since none of the metal, the metal ion nor the solvated electrons are known to be colored, the color may be attributed to some combination. Perhaps it should be ascribed more to the solvated electron, since the blue, as far as it is possible to determine, is the same, irrespective of the metal used to produce it. Whatever the explanation, the sensitiveness of this blue color is of the utmost importance in determining the presence or disappearance of free metal in liquid ammonia solutions.

While liquid ammonia solutions of metals appear stable for a considerable length of time, nevertheless, a slow reaction takes place, forming metal amides and hydrogen. This reaction requires the dissociation of ammonia into hydrogen and amide ions, a dissociation which is so small that no accurate determination of the specific conductance of pure liquid ammonia has been carried out. Yet, the early workers in this field, Joannis[17], Franklin and Strafford[18], prepared the amides of sodium and potassium in this way, waiting, insome cases, for days and even months for the reaction to go to completion. The reaction may be formulated thus:

$$\begin{array}{ccccc} 2M & \rightleftharpoons & 2M^+ & + & 2e^- \\ & & + & & + \\ 2NH_3 & \rightleftharpoons & 2NH_2^- & + & 2H^+ \\ & & \downarrow\uparrow & & \downarrow \\ & & 2MNH_2 & & H_2 \end{array}$$

That the rate of the reaction between metals and liquid ammonia could be appreciably speeded up by the presence of other substances was first observed by Franklin[19]. He noticed that in certain tubes containing bits of asbestos fiber(from filters introduced into the tubes) the time of preparation of KNH_2 was markedly shortened. This suggested the use of other catalyzing agents to accelerate the reaction and spongy platinum and oxides of iron[20,21] were found to be of value. Franklin[19] stated that a few milligrams of spongy platinum so greatly increased the reaction that as much as a gram of potassium was converted into KNH_2 in the course of 15 minutes. It is still customary to prepare $NaNH_2$ and KNH_2 from the metals and ammonia, using oxides of iron as a catalyst. In other instances, particularly in the work on conductance and electromotive force measurements, catalysis and resulting formation of amide and hydrogen were reported. In the majority of these instances, electrodes of platinum or gold served as the catalytic agent. In these cases, catalysis was not complete but was appreciable enough to introduce errors in the experimental values.

If the theory of these solutions proposed by Kraus is correct, it would seem that the real reaction, in all cases, is the following:

$$2e^- + 2NH_3 \longrightarrow H_2 + 2NH_2^-$$

On this basis, little difference w~~h~~ould be observed with various metals. Definite information on how the rate of this reaction varies with the metal, as well as with the catalyst employed, would be of value in the interpretation of these reactions

C. Object of Investigation

The object of this investigation was to study, quantitatively, the catalyzed reaction between alkali and alkaline earth metals and liquid ammonia, using various metallic catalysts. The work carried out in pursuance of this problem is presented in the following discussion, in order as it is discussed in this thesis.

The research was started by the measurement of the hydrogen obtained from the reaction and the determination of the variable factors which were of importance for future determinations. These factors were the behavior of the catalysts with respect to constant activity, the effects of the products of the reaction, hydrogen and metal amide and the effect of the rate of stirring. The next main body of work effected was accomplished on the relative catalytic powers of a series of catalysts. Under this section also the variability of the catalysts under certain conditions and the procedure of elimination of this variability were determined. Following this, the effect of the concentration of the alkali metal on the time of reaction was measured, in addition to the relative reactivities of potassium, sodium and calcium and the effects of their products of reaction. The final step in the completion of the work embodied the determination of order of reaction.

III APPARATUS AND EXPERIMENTAL PROCEDURE

A. Apparatus

In studying reactions in liquid ammonia, there are three general methods of procedure: first, to work at low temperature, second, to work at room temperature and, third, to work at high temperature. The first method requires working at a temperature near the boiling point of ammonia, -33°C. and one atmosphere pressure. The second involves room temperature and pressures that approximate ten atmospheres, thereby requiring a sealed apparatus capable of withstanding these pressures. The third requires high temperature around the critical point and pressure which necessitate apparatus capable of withstanding extreme ranges of these two conditions. The first method is more adaptable to studying the progress of this reaction and was adopted for this work. A thesis for a Master's degree at the University of Cincinnati in 1931 was done on the reaction between potassium and sodium and liquid ammonia in the presence of powdered catalysts. This apparatus proved satisfactory in carrying out the reactions in all the determinations performed, such as gas collection, time of reaction, effect of concentration of alkali metal, et cetera. This same apparatus was taken for use in this work with the following alterations: a better method of stirring, addition to the absorption train of bottles and better equipment for the determination of order of reaction.

Facsimiles of the apparatus, Figures 1, 2, and 3, are now presented with an appropriate discussion on each.

Legend of Figure 1

Figure 1 represents the reaction and condensation systems and embodies the following parts:

A. DeWar flask. This flask served to carry the reaction tube, and provided a cooling bath of impure liquid ammonia for the system. The stopper in this flask carried the thermometer to measure the temperature of reaction and the inlet and outlet tubes of air which were used to control the temperature of the bath.

B. Air inlet tube. Dried air entered this tube from a compressed air supply, was conducted through the liquid ammonia and conducted out at the exit (C).

C. Air outlet tube. This tube was an exit for the air admitted by inlet tube (B).

D. Reaction tube. Vessel in which the reaction between alkali metal and liquid ammonia took place. The upper right hand section of this tube had a side arm which was used for the introduction of samples of alkali metal and also for the admittance of gaseous ammonia which was used in producing the liquid ammonia for the reaction and for sweeping out the hydrogen which was formed by the reaction. The mouth of the reaction tube had a two-hole stopper which carried the stirrer (F) and the outlet tube (N) for the ammonia and hydrogen.

E. Sweeping-out tube. This tube was connected to the inside extension of the ammonia entrance (Q) and extended to within 3 inches of the top of the liquid ammonia. It was made of rubber so as to facilitate easy introduction in each experiment. The gaseous ammonia was admitted to the reaction tube at the bottom of the tube and swept the hydrogen upwards and ultimately out through (N). In the side arm section, this tube was fitted for sweeping out the hydrogen in this "pocket".

F. Stirrer shaft. From the motor (T), a steel shaft extended down through the mercury seal (P) into the reaction tube, culminating at a point about 15 centimeters above the surface of the liquid ammonia. The shaft was of steel and could not be used in the reaction fluid for attaching the catalyst (I).

G. Glass tube for catalyst attachment. This tube was fastened to the stirrer shaft (F) and extended into the liquid ammonia. Near its bottom in the reaction fluid, it had two series of ferrules for the attachment of the catalyst (I).

H. Ammonia exit. This tube served as the outlet for ammonia from the condensation system. After the ammonia passed through this exit, it was absorbed in a water reservoir (reservoir not shown).

I. Catalyst. The catalyst was attached to the glass tubing in the following manner: at each end of the catalyst, wires, size 20 and approximately 3 inch long, were fastened and these, in turn, were wound around the ferrules on the glass tubing (G).

J. Thermometer. This thermometer was used to measure the temperature of the bath. Both a pentane and an alcohol thermometer were employed.

K. Leveling pear. This pear was reservoir of the mercury used in the condensation system and was connected to part (U) of that system by rubber pressure tubing.

L. Condensation system. This system was composed of parts(U) and (L) and carried a column of mercury which opposed the flow of ammonia from the reaction tube.

M. Liquid ammonia. This was the pure liquid ammonia distilled from a dilute sodium solution. The volume in all reactions was 50 cc. This volume was convenient to handle and covered the catalyst by 2 centimeters.

N. Reaction tube exit. This exit led from the mouth of the reaction tube to the condensation system, when that system was being used, and to bottles (C) in Figures 2 and 3 when they, respectively, were being used.

O. Hole in sweeping-out tube. This hole was in the part of the sweeping-out system that was confined in the side arm of the reaction tube. Its aperature was such that approximately 1/5 of the ammonia entering (Q) was emitted here at (O).

P. Mercury seal stirrer. In order for the reaction tube to be gas tight and, at the same time, provide stirring facilities, the usual type of mercury seal stirrer was used, carrying approximately 2 inches of mercury. This seal prevented the escape of any gas that might enter the seal through (X).

Q. Ammonia entrance. This tube provided for the entrance of gaseous ammonia into the reaction tube for both condensation and sweeping purposes. It had its source in a small 5-lb. tank of ammonia (not shown), in which several grams of sodium were placed to insure absolute dryness.

R. Speed adjustment on motor. The adjustment had sufficient sensitivity to provide easy duplication and adjustment of speeds.

S. Commercial liquid ammonia. This ammonia was used in the DeWar flask as a cooling bath for the reaction system.

T. Motor. The motor was of the 1/8 H.P. type, operating on 110 AC and 30 Amp. It furnished consistent performance in long runs, varying around 5 RPM. at a speed of 250RPM. The speed was determined by the use of a revolution counter applied at the top of the speed adjuster (R).

U. Part of the condensation system. With tube (L), it composed the condensation system.

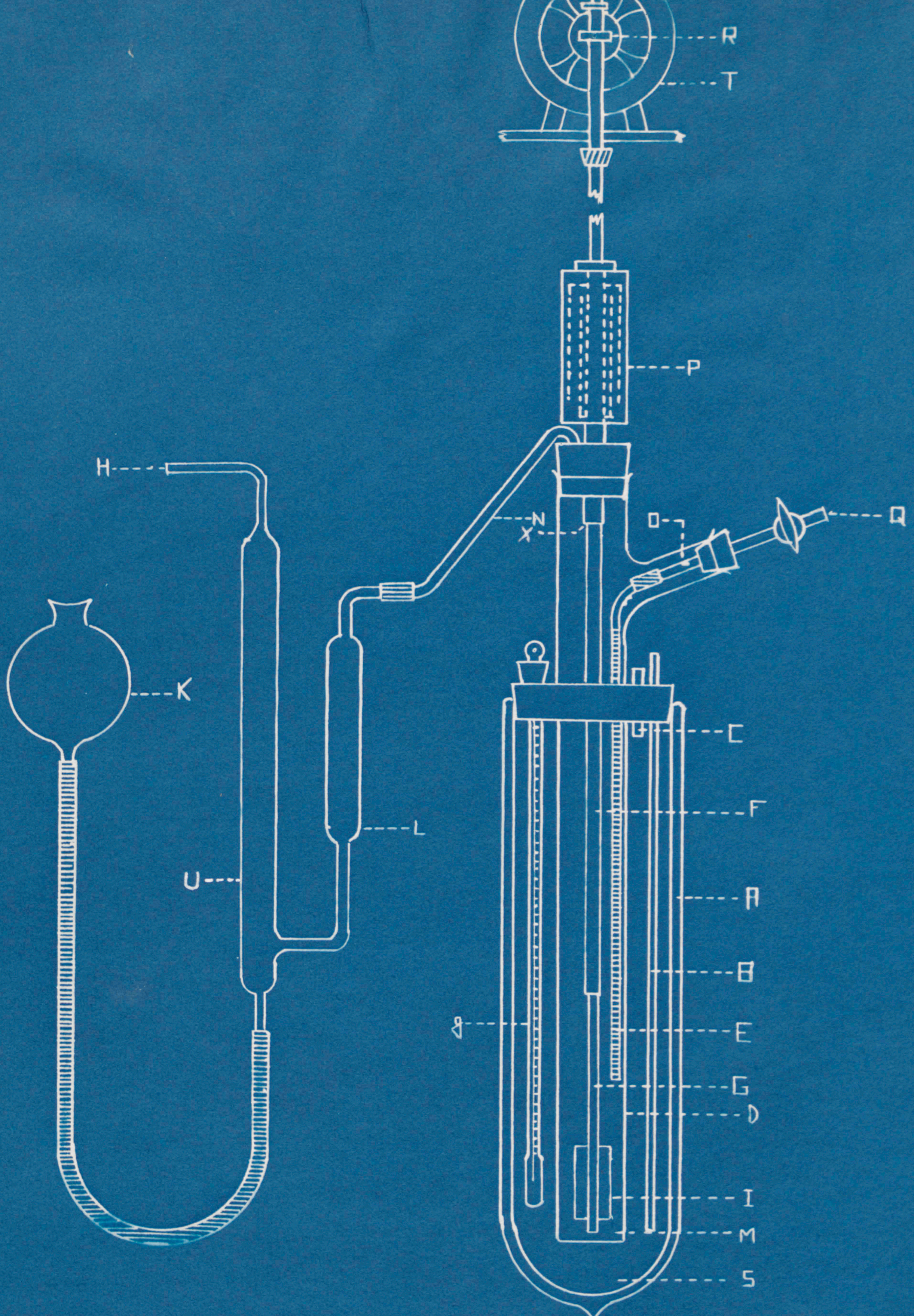


FIGURE 1
APPARATUS FOR MEASUREMENTS IN HETEROGENEOUS CATALYSIS

Legend of Figure 2

Figure 2 represents the adsorption train and the gas collection system and is connected to the reaction system by bottle (C) of this Figure and tube (N) of Figure 1. The Figure contains the following parts:

A. Gas reservoir. This reservoir was filled with water and carried tube (B).

B. Sampling tube. This tube allowed the withdrawal of a sample of hydrogen from the total volume in (A), for the determination of purity of hydrogen.

C. Safety bottle. The bottle, when this system was in use, was attached to (N) of Figure 1. The bottle was dry and carried 1/2 inch of mercury. The special purpose of it was for use in a reaction when a poor catalyst was in use and it performed the duty of allowing no water vapor to diffuse back into the reaction system.

D. Safety and adsorption bottle. This bottle was filled with 1/2 inch of mercury and a dilute solution of hydrochloric acid. The mercury served as a safety column in case the reaction sucked back. The dilute acid was used to adsorb the ammonia from the reaction, allowing the hydrogen to pass into the collection tube (A).

E. Dish of water supply. This porcelain dish supported tube (A) and furnished the water for this tube.

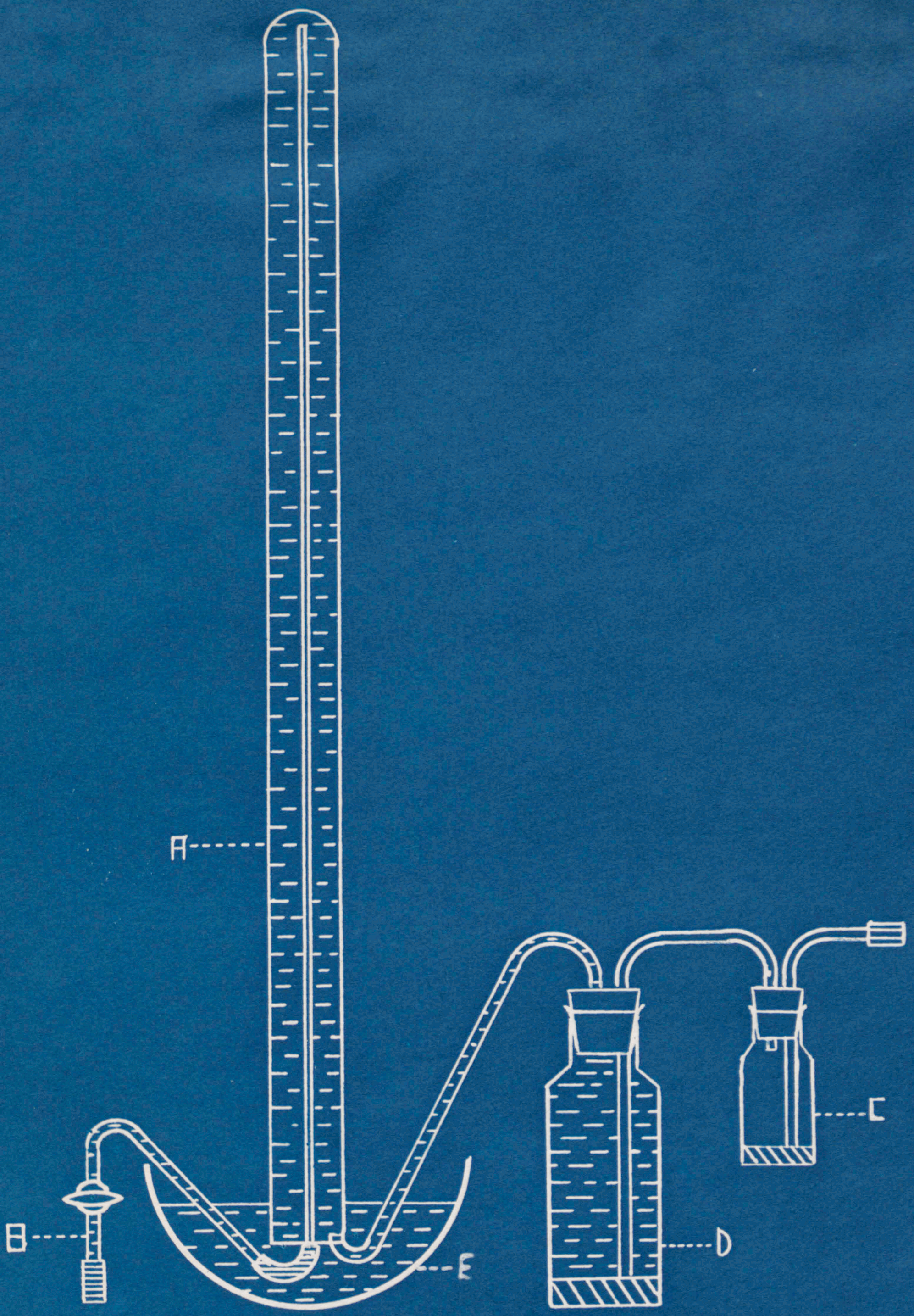


FIGURE 2
APPARATUS FOR TOTAL GAS COLLECTION

Legend of Figure 3

This Figure represents the gas collection apparatus used in the determination of order of reaction. When in use, tubing from bottle (C) is connected to (N) of Figure 1. The Figure includes the following parts:

A. Water trough. Water was used as the collecting medium for hydrogen and this trough served as a supply.

B. Safety and adsorption bottle. The bottle was filled with 1/2 inch of mercury and a dilute solution of hydrochloric acid. The mercury served as a safety column in case the reaction sucked back. The dilute acid absorbed the ammonia from the reaction, allowing only hydrogen to pass into the gas collection tubes.

C. Safety bottle. This bottle was anhydrous and carried 1/2 inch of mercury. The special purpose of it was for use in reactions where poor catalysts were used and it performed the duty of allowing no water vapor to diffuse back into the reaction system.

D. Support for test tube colony. The test tube colony was composed of a group of test tubes which were fastened on the outer edge of a wooden circular disc, the entire system being held up by this support. The support allowed rotation so that different tubes could be put in position to receive hydrogen from bottle (B).

E. Test tubes. These tubes were of large size (90 cc.) and were used in collecting the hydrogen.

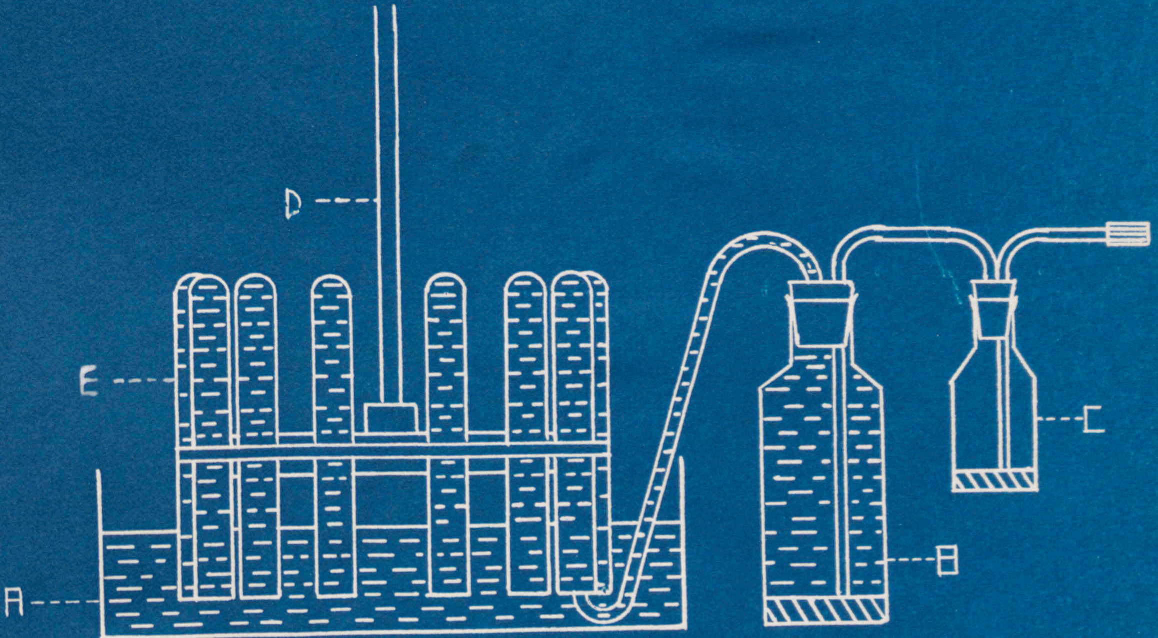


FIGURE 3

APPARATUS FOR GAS COLLECTION IN THE DETERMINATION OF ORDER OF REACTION

B. Manipulation

In order that a clear idea concerning the use of the apparatus be obtained, the steps involved in a complete run or experiment will be presented. This discussion of a general run will involve the collection of hydrogen for the determination of the total gas from a complete run. Following this description will be presented the procedure of gas collection employed in the determination of order of reaction. The topic will be concluded by a discussion of the procedure of evacuation of the catalyst.

The reaction tube (D), (unless otherwise noted, these letters represent parts included in Figure 1), was placed in DeWar flask (A), containing impure liquid ammonia (S), which served as a cooling bath. Air line (B) was connected to air supply and exit tube (C) to a water reservoir (not shown) where the ammonia, vaporized in a DeWar flask, was adsorbed by the water reservoir. The temperature of the cooling bath was controlled by varying the rate at which air bubbled through the DeWar flask. Prior to its introduction, the reaction tube was cleaned with cleaning solution, rinsed with alcohol and ether and dried by anhydrous nitrogen and finally by gaseous ammonia (distilled from sodium solution) to insure its being strictly anhydrous. Next, the catalyst (I) was attached to the stirring rod (G) and placed in the reaction tube. The reaction tube was then attached to the mercury column(L) by tube (N). With this connection complete, gaseous ammonia was passed through the system until all air that perchance entered the reaction tube during the introduction of the catalyst was swept out. The system was then ready for condensing the ammonia for the reaction.

The ammonia used for this purpose was distilled from a dilute solution of sodium to insure high quality. The temperature of the bath was lowered by a stream of air through (B) and the mercury in the column(L) increased slightly. The increase of pressure and the decrease of temperature caused the ammonia to condense in the reaction tube. Condensation was carried out until the arbitrarily adopted level of 50 cc. was reached. The outlet (M) was then changed from the mercury column (L) to the safety bottle (C) in Figure 2, to which was attached an ammonia adsorption bottle (D), Figure 2. The stirrer (F) was then set at the desired speed. Following the stirring adjustment, the system was ready for the introduction of the alkali metal.

A digression here from the main procedure will be made in order to give the necessary information concerning the handling of the alkali metal prior to its introduction. The alkali metal was prepared for the reaction by cutting the proper size under petroleum ether in a suitable dish. The best efficiency was obtained in cutting by the use of a small pair of tweezers to hold the metal and a razor blade to cut it.

After the proper size had been cut, a weighing bottle of dimensions 2 x 6 centimeters was filled with dried nitrogen gas, the metal quickly inserted in the bottle and the bottle again swept out. Evaporation of the adhering petroleum ether cooled the bottle and sufficient time had to be alloted for it to regain room temperature, after which it was quickly weighed. It was then ready for introduction.

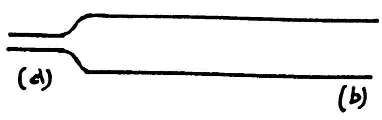
Returning again to the description of the main procedure, the weighed metal was introduced into the reaction tube by the removal of the stopper in the side arm. The introduction was effected by long tweezers which were capable of reaching the metal on the bottom of the weighing tube and, in addition, so constructed as to allow speedy entry through side arm, where metal was dropped to the liquid below. From the time the stopper was removed, until replaced, ammonia was swept into the reaction tube. This prevented air from entering and introducing water vapor found to be injurious to the reaction. As soon as the metal entered the liquid ammonia, the stirrer was switched on, the stop watch was snapped and contact with gas collection apparatus (C), Figure 2, was established.

As the reaction progressed, the temperature was regulated to suit the catalyst employed. There were two classes of catalysts of this work, fast and slow. The former required a bath temperature of -35.5°C., and the latter, a temperature of -34°C. The nature of the reaction necessitated these two different temperatures. The fast catalysts gave a vigorous reaction, liberating hydrogen at a relatively high rate, accompanied by evaporation of solvent and the splashing of solution up the sides of the tube. It was found that this temperature and the proper rate of entry of ammonia kept the sides clear of solution and the volume constant. The slow catalysts exhibited the same type of reaction but it was far less intense. Very little splashing and loss of solvent accompanied the reaction. The temperature was, therefore, higher so that the rate of ammonia introduced did not increase the volume of the solvent above the usual level.

At the finish of the run, the blue color was gone, as all potassium had reacted. The stop watch was snapped and the time of reaction recorded. Ammonia was swept through the reaction tube and all hydrogen collected in the collection system. The operation involved in sweeping out the bydrogen required 10 minutes. The reaction solution containing amide was discarded. This completes the procedure involved in a typical run, which included the gas collection for a complete run. The gas collection procedure followed in order of reaction is now presented.

The method used in the foregoing presentation for the collection of gas was employed when total gas for a desired reaction was to be estimated. The method, when order of reaction was determined, was afforded by the use of the same procedure as already described, with the exception that the method of gas collection was different. The procedure employed was that of collecting gas for certain intervals of time from which data for order computations could be drawn. This collection per interval was accomplished by connecting one tube of the test tube colony presented in Figure 3 to the reaction tube for the desired interval, at the end of which time the tube was detached and the next one connected, et cetera. For each interval, all the hydrogen liberated from the reaction had to be swept out of the system into the gas collecting tube. This was accomplished by issuing a rapid current of ammonia through reaction tube by way of rubber tubing (E). This sweeping-out period was usually started 2 minutes before the finish of the interval and stopped when the interval was reached. The gas in all cases was analyzed by use of the Hempel Explosion Method. This concludes the discussion on gas collection for order of reaction determination and will be followed by procedure for evacuating catalysts.

The procedure by which the catalysts were evacuated was as follows;:the catalyst was enclosed in an evacuating tube of this construction



The catalysts, all except platinized platinum and rusted iron, were wet cleaned with bon ami, polished with No. 3 carborundum powder, dried and inserted in the tube. The tube was sealed off at (b) while under an atmosphere of nitrogen, which entered at (a). This procedure eliminated any possibility of moist air being admitted and effecting the catalysts. In order that the catalysts be subjected to as little heat treatment as possible, the evacuating tube was at least a foot long and, during the sealing-off process, the catalyst was placed near (a) end of tube. Upon completion of sealing-off, part (a) was sealed onto an evacuating system, equipped with an oil pump and a McCleod guage. The time required for evacuation of .02 mm. of mercury was usually 10 minutes, after which the evacuation tube was sealed-off at (a). Thus, with the evacuation tube sealed off at both (a) and (b), the catalyst was in a closed system under .02 mm. of mercury pressure.

When the catalyst was needed, it was removed in this manner. A rubber tube, leading from an ammonia supply, was attached to the closed end of (a). The seal was broken and the ammonia admitted to the tube. The rubber tubing was replaced by a plug to keep the ammonia from escaping. The tube was then cut off at (b) end, the catalyst removed, attached to the stirrer and introduced into the reaction tube, after which the customary procedure of the run was followed.

In that the removal of the catalyst from the evacuation tube to the reaction tube necessitated contact with air, this operation was done as rapidly as possible, usually requiring less than 15 seconds. In that most of our measurements were relative, and all catalysts were subjected to this error, most of its injurious effects were cancelled. All foils, except of platinized platinum, were evacuated at .02 mm. of mercury and allowed to stand one-half hour. The platinized platinum catalyst was evacuated at some indefinite pressure around 1 mm., the evacuation being accomplished by using a desiccator as an evacuating vessel, an oil pump and a mercury manometer. The deposite on the catalyst necessitated this special treatment.

C. Materials and Catalysts

The important materials used in this work are enumerated now, each material being discussed as to use, source and purity. After the discussion on materials, catalysts will be given.

Liquid Ammonia. This impure product was used as a source of pure ammonia for the reaction by distillation from a dilute sodium solution of it and as a bath for the reaction. It was obtained from Mathieson Alkali Company, Inc. The product was clear and of fair purity.

Potassium. This metal was employed in the liquid ammonia reaction. It was a Merck product. Purity analysis by Francis Holden of this laboratory. Weight of potassium sample .0770, .0674. Weight of potassium chloroplatinate .4776,.4189. Calculated for potassium 99.75% and 99.95%. Chloroplatinate method. Treadwell and Hall Volume 11, 7th ed., page59.

Calcium. This metal was employed in the liquid ammonia reaction. Kalbaum product. Purity analysis by Francis Holden of this laboratory. Weight of calcium sample .2412, .3419. Weight of calcium oxide .3344, .4740. Calculated for calcium 99.05%, 99.07%. Oxalate method used.

Sodium. This metal was employed in the liquid ammonia reaction. Kalbaum product. Listed as containing only slight trace of any impurity.

This completes the list of materials used in this work. The next topic presented will be on catalysts.

The catalysts employed in the pursuance of this work are presented with a discussion of purity on each.

Silver. Bell and Coleman product. Purity 100%.

Smooth Platinum. Purity 100%

Platinized Platinum. This catalyst was a smooth platinum foil, carrying a deposite of finely divided platinum.

Gray Platinum. This was obtained by subjecting the platinized platinum to red heat.

Nickel. Purity unknown. Believed to be high, however.

Iron. Obtained from the American Rolling Mill Company. Purity 99.80%.

Rusted Iron. This catalyst was obtained by allowing a pure iron foil to rust in moist air.

Zinc. Purity unknown. Believed to be high, however.

Tantalum. Purity 99.90%, established by Metallography Department of the University of Cincinnati.

Columbium. Purity 99.90%, established by Metallography Department of the University of Cincinnati.

This completes the list of the catalysts and their respective purities and a presentation of the preparation of catalysts will be given at this point.

One of the main objects of this work was to find out the relative catalytic powers of a series of catalysts.

To do this, the prime requisite was to have catalysts of corresponding size. Therefore, an arbitrary surface area of 5.5 x 2.55 centimeters was adopted and adhered to. It is desired to make clear that these 13.01 square centimeters are plane surface area and not real surface exposure. Thus, for the metals, nickel, pure iron, silver, smooth platinum, zinc, tantalum, and columbium, a true comparison was possible. This was not true of platinized platinum, gray platinum and rusted iron, for here is, in addition to plane surface area, a surface exposure, due to the very nature of the deposite, a surface many times that of the plane surface; so, in this sense, a true comparison has not been attained for these catalysts. The thickness of these foils varied from .01 to .15 centimeter. Even though this presented a variation in surface exposure, it was of minor importance.

Catalysts that needed no special preparation, other than size definition, were silver, smooth platinum, nickel, pure iron, zinc, tantalum, and columbium. Catalysts that required special preparation were platinized platinum, gray platinum and rusted iron foils, and are now discussed.

Preparation of platinized platinum. The smooth platinum was subjected to hot cleaning solution to eliminate grease, et cetera. The platinizing solution employed was of unknown strength, approximately 3% platinic chloride. No lead acetate was used to insure an adhering coat.

Three to four volts and low amperage were employed in the electroplating. The electroplating apparatus was so constructed that the foil was sandwiched between two large electrodes of platinum which served as cathodes and were conveniently arranged so that the electrodes did not have to be moved to insure proper deposition. It was found that reversing the current at regular intervals was of no particular advantage. The time of electrolysis depended on the strength of the plating solution. On the average, the foil was plated until a coat, black and rich-looking, was obtained. No more precautions were taken than this, in that it was not desired to keep the exposed area of the deposite constant, except within rough limits. Immediately following the platinizing, the foil was subjected to a second electrolyzing, in dilute sulphuric acid for ten minutes, at the same voltage and amperage, current being reversed every minute. All authorities on platinized platinum recommend this as an excellent way to clean the foil of the majority of gaseous impurities. The foil was then rinsed with distilled water and preserved in this solvent until used.

Gray Platinum. The gray variety of platinum was prepared by subjecting the platinized platinum to a dull red heat for a few minutes. The catalyst was preserved in a phosphorous pentoxide disiccator until used.

Rusted Iron Foil. The pure iron was wetted and allowed to remain in contact with air. Length of exposure to air depended on what amount of rust was desired. It was found advantageous to use a film of rust that was distributed over the surface in small patches, because these small patches had greater stability to high-speed stirring. Following the preparation, the foil was preserved in a phosphorus pentoxide desiccator.

This ends the discussion on this section of the thesis and is followed immediately by presentation of experimental results.

IV EXPERIMENTAL RESULTS

The total experimental work accomplished in pursuance of this work is presented under this heading. The results of the work are presented in five divisions, A, the preliminary results including many determinations which were necessary for future work, B, the determination of the relative catalytic powers of a series of catalysts, C, the effect of concentration of alkali metals on the time of the reaction, D, the relative reactivities of potassium, sodium, and calcium, and E, the determination of order of reaction. Each of these topics will be properly introduced by a discussion of the manner inwhich each determination was carried out, followed by the presentation of the experimental results obtained and concluded by a discussion of results. The first of these divisions will now be presented.

A. Preliminary Results.

Several preliminary measurements were of fundamental importance in the pursuance of this work, for without them the majority of the succeeding work would have been impossible. These initial determinations included the standardizing of the apparatus with respect to the hydrogen collected, and such variables as the constancy of the catalyst, the effect of the products of reaction and the rate of stirring. Before considering these topics, however, certain qualitative observations on the nature of the solution necessary for interpretation of the work will be presented.

(1) Nature of the solution before, during, and after a run.

When the apparatus was completely assembled and ready for a run, the liquid ammonia was examined to see that it was perfectly clear of foreign particles. As soon as the sample of alkali metal was introduced into the liquid ammonia, a deep blue color was formed which was totally opaque above a concentration of .0001 normal. If the concentration was above approximately .5 normal, the solution presented a coppery lustre. In very dilute solutions, in the region of .00005 normal, the solution was translucent. As soon as the alkali metal was in solution, a reaction between the metal and the liquid ammonia occurred as evidenced by the evolution of hydrogen and a gradual lessening of the blue color. The reaction is:

$$K + NH_3 \rightarrow KNH_2 + \frac{1}{2} H_2$$

In vigorous reactions, obtained with a high concentration of alkali metal and a rapid catalyst, a spray of solution was shot up as high as 4 inches in the tube, depositing the alkali metal and amide on the sides of the reaction tube. These were washed down into solution by liquid ammonia produced by the condensation of a stream of gaseous ammonia. As the reaction neared the finish, the evolution of hydrogen diminished, the blue color became translucent and finally the evolution of hydrogen stopped and the blue color entirely disappeared. The resulting liquid ammonia solution possessed its normal color, except when high concentrations of potassium were employed, in this case, the resulting solution was yellow due to the presence of soluble potassium amide. The difficultly soluble amides of sodium and calcium were white and did not color the solution, being left deposited as crystalline solids.

In the beginning of this work, difficulty was experienced in obtaining an anhydrous medium. Many of the initial runs resulted in the production of a white gelatinous precipitate, which was though to be either the hydroxide or oxide of the alkali metal. This faulty procedure was eliminated by taking special precautions in making every member of the system absolutely dry. As a result of this care, only occassionally was the work interrupted by the formation of precipitates and these few occurrences were due to mistakes in the drying process. Most of these precipitates were due to humid conditions of the atmosphere, as many of the parts of the system before use were exposed to air and were of such construction that permitted only mechanical drying. The results of the experiments that had precipitates of this type in them are not included in this presentation.

(2) Collection of hydrogen from the reaction.

When the alkali metal reacted with liquid ammonia, hydrogen and the amide of the metal were formed according to the equation presented in (1). The determination of the hydrogen lent itself to four very important uses: The check on the empirical equation itself as presented in (1), the standardization of the apparatus and gas collection system as applicable for good gas collection, a good criterion of whether the catalysts were adsorbing any hydrogen and the detection of any side reactions. The hydrogen determination was carried out using various size samples of alkali metal, the hydrogen being swept into and preserved for analytical tests in the gas reservoir, Figure 2. The gas was analysed by the Hempel explosion method. The results of a small percentage of the total work accomplished are embodied in Table I.

Table I

Hydrogen obtained from Reaction

No. of run	Potassium in grams	H_2 in cc. N.T.P. Theory	H_2 in cc. N.T.P. collected	Atomic Ratio of $K:H_2$
221	.1016	29.1	27.5	1:.958
305	.3563	102.1	102.0	1:1
310	.5578	159.8	156.8	1:.993
601	.3260	93.2	93.4	1:1
312	.5318	152.4	150.3	1:.973
314	.5301	151.8	151.0	1:.995

In this table, the first column presents the number of the experiment, the second the amount of potassium in grams in the reaction, the third the volume of hydrogen calculated from the potassium-ammonia equation in cc. at N.T.P., the fourth the volume of hydrogen collected in cc. at N.T.P., and the fifth the relation between the gramsatoms of hydrogen and potassium.

The good agreement between the amount of hydrogen in relation to the potassium used showed decisively that one atom of potassium interacted with one molecule of ammonia, thus supporting the empirical equation advanced in (1). It showed, in addition, that the apparatus was applicable for the use for which it was intended with respect to gas collection; it showed that if any hydrogen was adsorbed by the catalysts, the volumes were very small and could be considered negligible. Lastly, it showed the absence of those side reactions which would use the hydrogen in diverse ways and prohibit its recovery.

(3) Behavior of catalysts with respect to constancy or inconstancy of catalytic power.

This discussion on the behavior of the catalyst will have two parts, the first dealing with the results showing theconstancy of the catalysts, and the second showing the inconstancy. These vitally different behaviors were obtained by different treatment of the catalysts. The treatment that effected constancy will now be presented.

The treatment that brought about constancy in the catalysts was the evacuation of these catalysts. With rusted iron an additional treatment was necessary and will be explained in the second portion of this section. The procedure that was employed has already been advanced. The four catalysts on which this work was done were nickel, rusted iron, smooth platinum, and platinized platinum, the former three being evacuated to .02 mm. of mercury and allowed to stand in this degree of evacuation for one-half hour and the latter one being evacuated to 1 mm. of mercury and allowed to stand this same length of time. The constancy of any one catalyst was established in this manner. Successive identical samples of the alkali metal were introduced into the solution and their times of reaction were recorded. A comparison of these times was a direct measure of the constancy of the catalyst. These successive samples were added to the same set up of apparatus, one sample being introduced immediately after completion of the previous one. In this table to be presented, and in all tables in this thesis, these samples will be indicated thus: the run of the initial sample will be represented by a number, the first successive sample by the next higher number followed by a small (a), the second successive sample by the next higher number followed by a small (b), et cetera. The results of these determinations are presented in Table II.

Table II

Constancy of Catalysts

Number of run	Catalyst	Potassium grams	Time of Reaction Minutes
628	Platinized	.1141	9.5
629a	Platinum	.1164	9.3
630b		.1151	9.1
538	Nickel	.0054	22.2
539a		.0059	21.1
558	Nickel	.0058	21.0
559a		.0058	20.9
507a	Smooth	.0057	65.0
508b	Platinum	.0059	65.0
511	Smooth	.0061	69.0
512a	Platinum	.0057	66.0
570b	Rusted Iron	.0307	5.5
579f		.0304	5.8
646b	Rusted Iron	.2332	12.6
647c		.2300	12.2

This table is divided into four sections, one being reserved for each of the foure catalysts. Each section has four columns, the first giving the number of the run, the second the catalyst, the third the potassium in grams, used in the reaction, and the fourth the time in minutes required for the potassium to react. The temperature of reactions with platinized platinum and rusted iron was $-35 \pm .5^{\circ}$C.; that for nickel and smooth platinum being $-34 \pm .5^{\circ}$C. All reactions were stirred at 250 ± 5 RPM.

The results in the table show that each catalyst was constant under the conditions imposed on it. Only four catalysts were used here but many more examples of this constancy have been obtained among them being those presented later in Table X.

The preceeding presentation showed that when catalysts are evacuated they exhibit constant behavior which was reproducible. It is advantageous now to show briefly that without the imposition of this evacuation the catalytic power of the catalyst was not constant and not of reproducible power.

The results of nickel and smooth platinum will first be presented and discussed after which separate discussions of platinized platinum and rusted iron will be given. The variability of the former two was detected by the employment of the same size sample of alkali metal on different days of work with the same catalyst. Their times of reaction were used as measures of their variability. The measurements made on nickel and smooth platinum are presented in Table III.

Table III

Variability of Nickel and Smooth Platinum

Nickel			Smooth Platinum		
Number of run	Potassium grams	Time of Reaction Minutes	Number of run	Potassium grams	Time of Reaction Minutes
322	.4120	135	231	.0065	130
324a	.3570	198	476	.0055	29
275	.3990	500	485	.0056	169
276	.0059	11.8			
461a	.0051	20.1			

This table embodies the experimental data obtained with two catalysts, nickel and smooth platinum. The columns of the table are identical with Table II. Temperature and stirring were held constant.

An examination of the table will show that the behavior of each catalyst was different. Thus for example, smooth platinum on one day converted .0055 gram of potassium in 29 minutes and on another day in 169 minutes. With nickel for the same size sample the variability was not as great, times of 11.8 and 20.1 minutes being recorded. In higher concentrations with the same catalyst, extreme variability was obtained, one run in particular never finishing at all after hours of running. This presentation will suffice to show that without evacuation these two catalysts were not of constant activity. The variability of platinized platinum will now be given.

This catalyst showed the same type of irreproducibility as given above for nickel and smooth platinum, one day being a rapid catalyst and on another day a slow one. Instead of presenting results on this work, a more interesting variability will be given. This variability manifested itself on the first run following the preparation of the catalyst, and was observed by a comparison of the reaction times for successive identical samples of alkali metal. An illustration of one series of these successive runs is presented in Table IV.

Table IV

Variability of Platinized Platinum

Number of run	Potassium grams	Time of Reaction minutes
393	.0531	48.1
394a	.0508	19.8
395b	.0533	15.0
396c	.0540	12.2
397d	.0537	10.5
398e	.0527	10.1

The columns of this table are identical to those presented in Table II.

The results of this series of runs show that the catalyst gradually increased in power as the samples of alkali metal were added, ultimately reaching a constant value. In all the experiments of this type, where the catalyst was used after a fresh deposit had been placed on it, the catalyst showed a great tendency to increase in power. This increase in activity was not observed when the catalyst was evacuated. This same proclivity to increase in power was also shown by rusted iron catalyst. Its method of detection was slightly different, a discussion of which follows the table of results which are now given.

Table V

Variability of Rusted Iron

Number of run	Potassium grams	Time of Reaction minutes
259	.0072	5.8
260a	.0225	7.5
261b	.1033	8.4
262c	.4109	8.1
265f	.0232	4.6
266g	.0075	3.4

This table presents the data showing the increase of activity of rusted iron when successive samples were added. The table is composed of the same column material as Table IV.

With this catalyst, the successive samples were not always identical in weight. However, there are several samples of the same weight and a comparison of their times of reaction will show that the catalyst was not constant, showing a tendency to increase in power. Thus the first sample of .0072 gram of potassium took 5.8 minutes while the last one of the same weight only required 3.4 minutes. A comparison of 261b and 262c will also show clearly that the catalyst in the latter sample required less time to convert more than three times as much potassium as the catalyst in the former sample, thus indicating that the catalyst increased greatly in power. This type of variability described here was due to a change in the deposite on the catalyst and not to lack of evacuation. Evacuation of this catalyst prior to use did not correct for the behavior brought about by the change of deposite.

The behavior of the catalysts, nickel, smooth platinum, and platinized platinum will be discussed together as their variabilities were of the same type. The explanation of rusted iron will follow this discussion. Because evacuation of the catalysts obtained constancy, it was postulated that a film of air was the cause of the variability of the catalysts. It was supposed that this air covered up the active spots on the catalyst and thus provided not only a depressing catalytic effect but a variable one in that on different days of work the amount of air on the catalyst was not constant. Burk[29] says "A rather disheartening point arises in catalytic work in that the real catalysts may not be what we think they are. Most of them have small amounts of adsorbed gases on them, the removal of whidh varies the value of the catalyst. Thus we are on dangerous ground in dealing with these catalysts for we do not know when a catalytic reaction takes place on the film or on the catalyst." Bancroft[30] says "One of the most striking things about catalysis by solids is the way in which the catalytic actions of the solids may be reduced by the presence of relatively small amounts of substances now universally termed 'poisons'."

In conjunction with this work on nickel, the investigator would like to state that some limited work done indicated that a long time of evacuation was not a factor in the obtaining of constancy, ten minutes being as effective as three hours. The degree of evacuation did however enter in, the higher the evacuation the better the catalyst. It was also found that separate exposures of this evacuated catalyst to oxygen and nitrogen showed that both of these constituents of air were instrumental in depressing the activity of the catalyst, and bringing about variability.

The variability of the rusted iron catalyst was attributed to two causes, the first of which was a film of adsorbed gas as explained above and second of which was due to a chemical reaction occurring on the surface of the catalyst during the course of the reaction. The increase of power shown in the results, Table V, was credited to the latter cause. The catalyst before use was red in color, while after the reaction the foil was black. It was postulated that during the course of the reaction the red deposite, which undoubtably was mainly ferric oxide, was changed to a black deposite, which was though to be composed of ferrous oxide. Additional support was given this premise by the experimental data obtained in the Master's work of 1931 by the same investigator at this University. In this work it was found that ferrous oxide was a better catalyst than ferric oxide. The fact that the black deposite on the catalyst was a better catalyst than the red agreed with this work of 1931. No mechanism will be offered as to how the ferric oxide was changed to ferrous in the presence of alkali metal. However, it is suggested that in such an excellent reducing medium where the free electron and nascent hydrogen abound, this reduction should present no difficulties.

(4) Effect of the products of reaction.

In heterogeneous catalytic reactions it is common occurrence that the products of these reactions are able to exert influence on the course the reaction takes and the time for the reaction to go to completion. Because of this, it was advisable to determine the effects of the hydrogen and the metal amide in the reaction between potassium and ammonia. The effect of one of these products, hydrogen, can not be stated as no evidence was obtained which would justify any statement. The effect of this other product, the metal amide, was determined in this way. A sample of the metal was introduced, allowed to react and the time for reaction recorded. Successive samples of potassium in larger amounts were added to increase the amide content in solution. A sample, identical to the initial sample, was then introduced and time for reaction obtained. This initial and final sample, being of equal size allowed a comparison to be made of their times of reaction. The results with two catalysts, platinized platinum and rusted iron will be respectively presented in Table VI.

Table VI

Effect of Potassium Amide on the Reaction

Number of run	Catalyst	Potassium grams	Potassium Amide grams	Time of Reaction minutes
337b	Platinized	.0354	0	5.7
342g	Platinum	.0364	.6088	5.8
187	Platinized	.0523	0	6.9
193f	Platinum	.0521	2.0817	7.1
571c	Rusted Iron	.0057	0	3.0
576h		.0057	.5942	2.9
599h	Rusted Iron	.0057	0	3.1
602k		.0057	.4124	3.1

The table is divided into four sections, each exemplifying one series of runs in which the effect of the amide was determined. The first three columns need no further discussion. The fourth gives the amount of potassium amide in grams present at the beginning of each run. The fifth column gives the times of reaction obtained from each experiment. All variables such as the behavior of the catalyst, speed of stirring and the temperature of reaction were held constant during all the runs.

The results of this section of work prove that the potassium amide formed in the solution from the reactions was no determining factor in the reaction within the range of these concentrations, as the times of the initial runs when no considerable amide was present, were the same as the times of the final runs which took place in a solution where considerable amide was present.

(5) Effect of stirring on the time of reaction.

In this reaction between alkali metal and liquid ammonia, little reaction is known to take place without the presence of a catalyst. Practically all the reaction therefore occurs on the surface of the catalyst. Because of this, the rate of supplying the reactants to the surface is a dominating factor in the reaction and this rate of supply is entirely dependent on the speed of stirring. The effect of stirring on the time of reaction was determined by making a series of successive runs in which the same weight of alkali metal was used, varying the speed of stirring for different samples and recording their times. These times of reaction furnished the basis for determining the effect of stirring. This effect with two catalysts, platinized platinum and rusted iron, is presented in Tables VIII and IX.

Table VIII

Effect of Stirring

Number of run	Potassium grams	Time of Reaction minutes:seconds	Rate of Stirring RPM.
288a	.0201	12:38	104
289b	.0203	12:29	104
290c	.0203	10:34	196
291d	.0208	10:22	196
292e	.0204	9:41	250
293f	.0198	9:46	246
294g	.0199	9:25	300
295h	.0205	9:23	384
296i	.0208	9:20	440
297j	.0207	12:33	104
298k	.0202	28:20	0
408	.0556	6:32	256
409a	.0552	6:10	254
410b	.0538	8:14	112
411c	.0548	7:20	146
412d	.0541	6:46	196
413e	.0544	6:6	304
414f	.0543	6:2	356
415g	.0540	32:0	0

Table IX

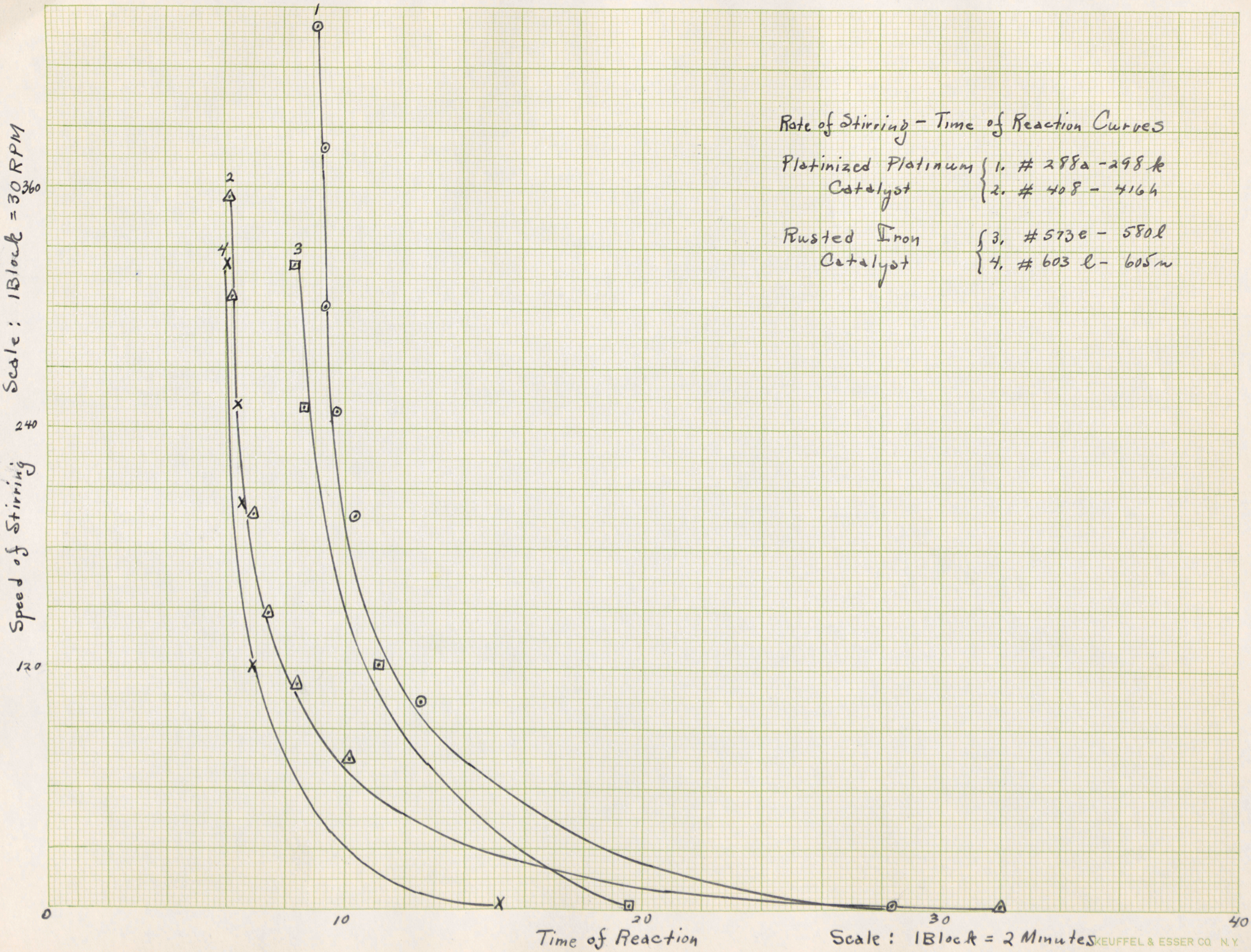
Effect of Stirring

Number of run	Potassium grams	Time of Reaction minutes:seconds	Rate of Stirring RPM.
573e	.0647	6:23	252
577i	.0653	6:55	120
578j	.0647	6:31	200
579k	.0658	6:8	320
580l	.0660	15:3	0
603l	.1527	11:10	120
604m	.1510	8:25	320
605n	.1502	19:46	0
X*	.1500	8:36	250

*The material for this run was obtained from another section of this work.

Tables VIII and IX are identical in column material and so they can be discussed as one. Columns one and two respectively present the number of the run and the amount of potassium used in the reaction in grams. The third column gives the times required for each sample of potassium to react, in minutes and seconds. The last column embodies the rate of stirring in revolutions per minute. All other variables that could effect this work, such as behavior of the catalyst and temperature of reaction, were maintained constant. It must be made clear that the values obtained when stirring was listed as zero represented zero mechanical stirring by the motor. There was another type of stirring inherently present in the system, however, --that of the evolution of gas. This, of course, was small in relation to the stirring by motor but its effect never-the-less was present. This effect becomes evident when run 415g in Table VIII is compared to 5801 of Table IX. In the former, platinized platinum was used with .0540 grams of potassium and gave a time of 32.0 minutes, while in the latter, rusted iron was used with .0660 gram of potassium and gave a time of only 15.3 minutes. The reason for this appreciable difference in time was due to the fact that the reaction with rusted iron was more vigorous and the evolution of hydrogen, therefore, more effective, shortening the time. The stirring effect of this gas evolution decreased in its intensity as mechanical stirring increased, the effect of it being negligible in the region of 250 RPM.

The results of this work with both catalysts are embodied in curves 1, 2, 3, and 4. In all cases, they showed that an increase of stirring decreased time of reaction until a minimum of time for a maximum of stirring was reached. The slope of the curves shows that above approximately 250 RPM., an increase of stirring had no effect. This rate of stirring was, therefore, adopted for use in all of the other determinations



Rate of Stirring - Time of Reaction Curves

B. Determination of the Relative Catalytic Powers of a Series of Catalysts

One of the prominent characteristics of a catalyst is its specificity, i.e., each catalyst possesses a certain definite catalytic value towards a chemical reaction under constant conditions. It was the desire of this investigation to see just how a group of catalysts lined up in order of activity in relation to this reaction. To do this an arbitrary set of conditions was selected and adhered to for each catalyst, so that true comparisons of their relative catalytic activities could be obtained. These conditions were: Speed of stirring 250 ± 5 RPM., temperature of reaction -34 ± .5°C., evacuation of the catalyst for one-half hour at .02 ± .005 mm. of mercury, and a sample of potassium of .0055 ± .0005 gram. These conditions were followed in all cases where it was possible to employ them. The results obtained with all catalysts are presented in Table X.

Table X

Relative Catalytic Powers of Catalysts

Number of run	Catalyst	Potassium grams	Time of Reaction minutes
631c*	Platinized Platinum	.0057	2.6
576h	Rusted Iron	.0057	2.9
602k		.0054	3.1
558a	Nickel	.0058	21.0
676		.0053	22.0
621	Pure Iron	.0050	44
622		.0051	44
507a*	Smooth Platinum	.0057	65
511		.0061	69
623	Zinc	.0058	86
624		.0059	71
565	Silver	.0054	252
567		.0059	245
555	Gray Platinum	.0058	556
634	Tantalum	.0056	>1000
642	Columbium	.0058	>1000
620	No Catalyst	.0051	>1500

*The evacuation of platinized platinum and smooth platinum was at 1 mm. and not at .02 mm. of mercury. For the former of these two catalysts, it was necessary due to the delicacy of the deposite, to handle it with exceeding care. This evacuation, therefore, could not take place in the customary manner and was effected by the use of a desiccator as an evacuating vessel, the pressure being read on a closed manometer. The work on smooth platinum was accomplished before this more drastic evacuation was employed.

All the columns presented in this table have occurred in other tables and need no further discussion.

In this table platinized platinum was given preference over rusted iron. The results show that the times were so close that rusted iron may just as well have been chosen to head the list as platinized platinum. Tantalum and Columbium also were determined to have about the same catalytic power and thus were listed together. The other catalysts were more diversified in their activities and presented no difficulty in representing their relative powers. The entire series of catalysts investigated can be lined up in order of decreasing catalytic activity as follows:

(1) Platinized Platinum
(2) Rusted Iron
(3) Nickel
(4) Pure Iron
(5) Smooth Platinum
(6) Zinc
(7) Silver
(8) Gray Platinum
(9) & (10) Tantalum and Columbium

C. Effect of Concentration of Alkali Metal on the Time of Reaction

Previous work, presented in this paper, has already indicated that with any one particular catalyst the amount of time required to convert a given sample of alkali metal increased as the weight of the sample increased. It is the desire of this section to show just how the time of reaction did vary with the concentration of the metal. This was done in the following manner. Successive samples of increasing weight were added and the corresponding times of reaction obtained, from which it was possible to determine how the time varied with weight of sample. It will be noticed that weight of sample and concentration of sample are used to denote one and the same thing; this is true because the volume of liquid ammonia was the same in all this work, so that a comparison of concentrations of metals is realy the same as a comparison of weights of samples. The results of three experiments using three catalysts are presented in Table XI.

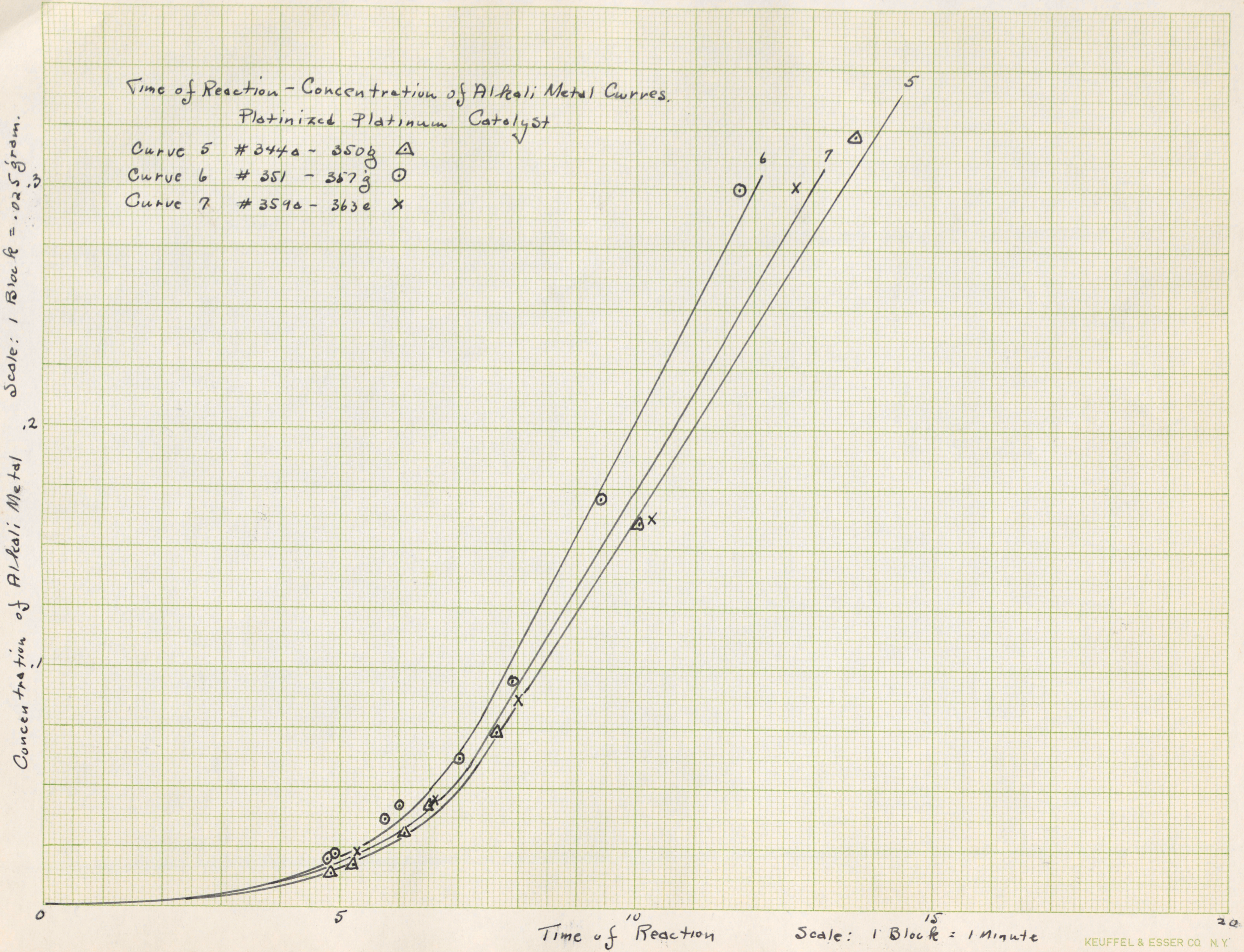
Table XI

Effect of Concentration of Alkali Metal on the Time of Reaction

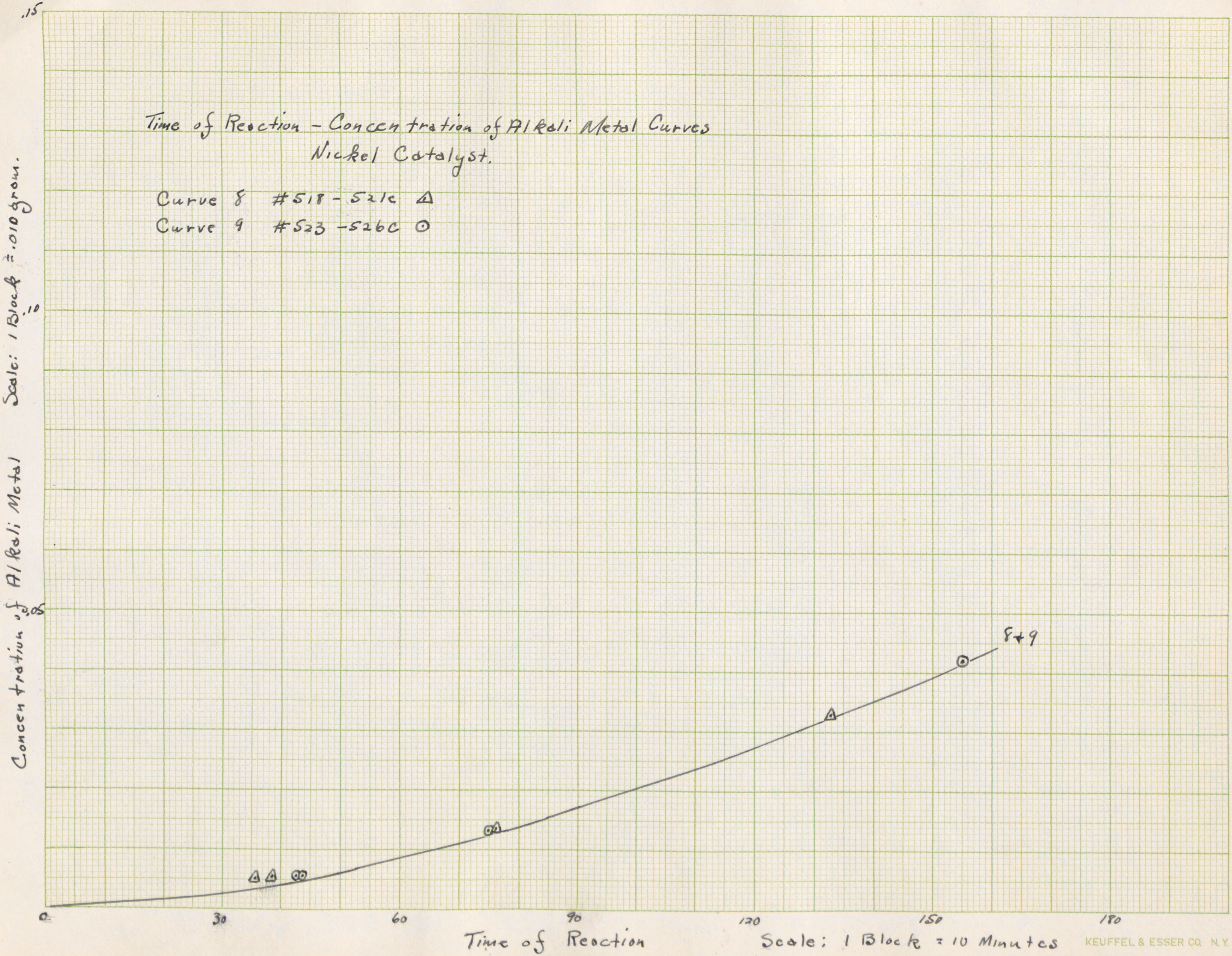
Platinized Platinum			Nickel			Rusted Iron		
Run	K	Time	Run	K	Time	Run	K	Time
351	.0170	5.3	518	.0050	36	595d	.0304	6.0
352b	.0151	4.8	519a	.0052	39	596e	.1910	9.6
353c	.0443	6.5	520b	.0136	76	597f	.0304	5.8
354d	.0734	7.6	521c	.0330	133	598g	.0057	3.1
355e	.1596	10.1				600i	.0807	7.0
356f	.3261	13.7				601j	.3260	10.8
357g	.0299	6.0						
344a	.0212	4.9	523	.0054	43	472d	.1328	9.2
345b	.0416	6.0	524a	.0055	44	472e	.0860	7.8
346c	.0587	7.0	525b	.0138	75	473f	.2591	10.7
347d	.0942	7.9	526c	.0420	155	475h	.0081	4.1
348e	.1704	9.5						
349f	.3000	11.7						
350g	.0388	5.7						
359a	.0241	5.3				570b	.0301	5.5
360b	.0448	6.5				571c	.0057	3.0
361c	.0858	8.0				572d	.0163	4.2
362d	.1635	10.2				573e	.0647	6.4
363e	.3019	12.7				574f	.1160	7.2
						575g	.3972	8.9
						576h	.0057	2.9

This table has three sections, each representing the material obtained with one catalyst. The first column in each series presents the number of the run, the second the weight of potassium in grams used in the reaction and the third the time of reaction in minutes.

The material that the table sets forth shows that as the size of the alkali metal sample increased, the time of reaction increased. The curves, 6,7,8,9,10,11, and 12 which follow this discussion show that the rate of increase in the time for an increase in weight of sample was gradual, each series of points representing a smooth curve. The one curve presented using nickel as a catalyst is really two curves superimposed upon each other. This is additional support that at different times of work, evacuation made the catalyst reproducible. The curves using platinized platinum and rusted iron do not show this constancy for in all these runs as the catalysts had different deposites on them. However, the curves for both of these catalysts are very close in the region of low concentration, appreciable variation only making its appearance in the region of high concentration. It will be noticed that the curves for platinized platinum and rusted iron are similar in type, while both of them differ from the type exhibited by those curves for nickel. This is attributed to different orders of reaction, the discussion of which appears later in this presentation.

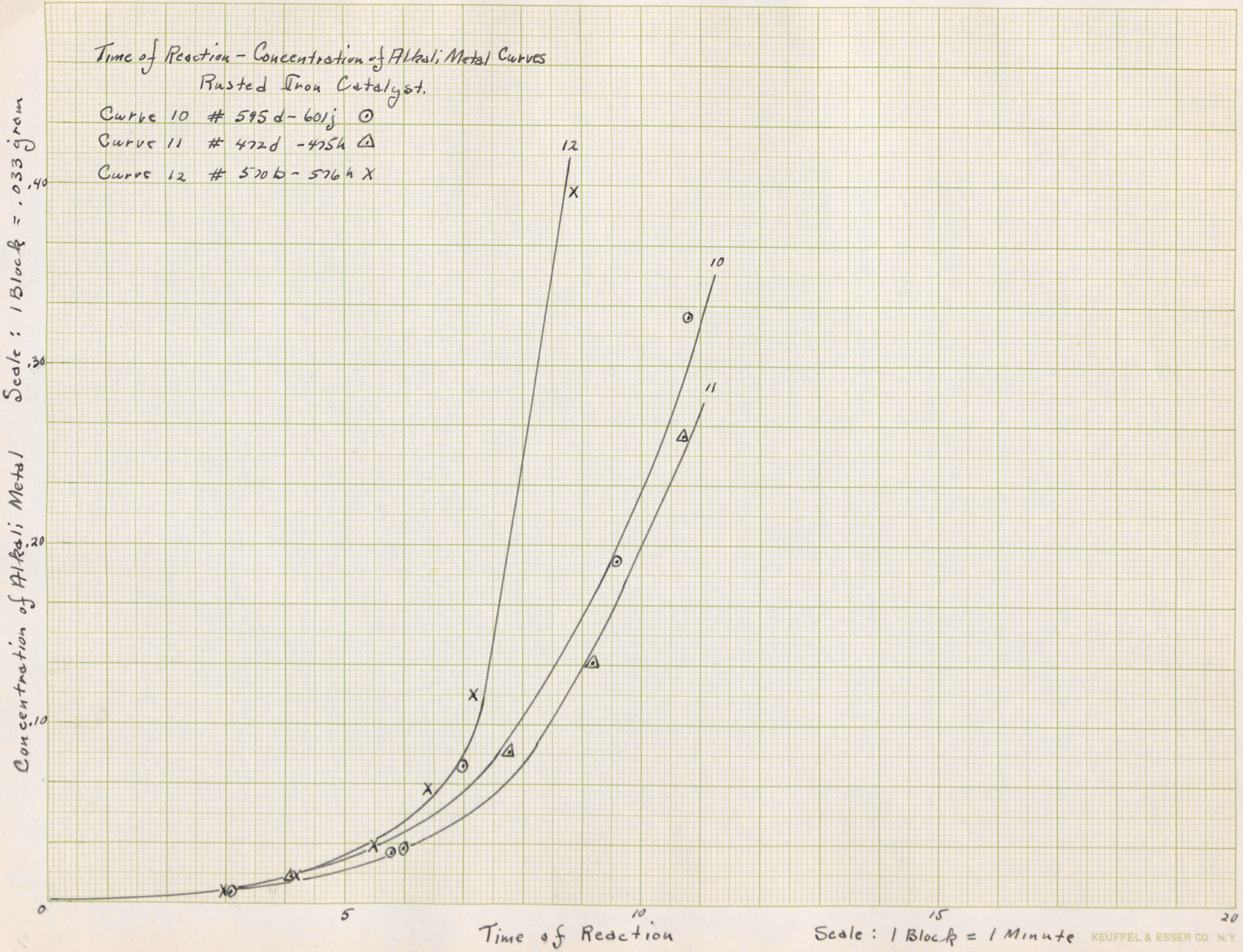


Time of Reaction - Concentration of Alkali Metal Curves.
Platinized Platinum Catalyst



Time of Reaction - Concentration of Alkali Metal Curves
Nickel Catalyst.

Curve 8 #518 - 521c △
Curve 9 #523 - 526C ⊙



Time of Reaction - Concentration of Alkali Metal Curves

Rusted Iron Catalyst.

D. The Relative Reactivities of Potassium, Sodium and Calcium

In the introduction of this thesis, it was suggested that should the products of reaction of these alkali and alkaline earth metals be of no influence on the reaction that the times of reaction of these metals in equivalent amounts should be the same. On the other hand, should the products exert influence, the times of reaction for equivalent amounts would be different. It is the purpose of this topic to show, first that under certain conditions imposed upon the system the three metals reacted identically and, second that without these conditions that they reacted differently.

(1) Identical relative reactivities of potassium, sodium and calcium.

The condition which was imposed on the reacting system in order to prove that the relative reactivities of these three metals were identical was the use of an agent which offset the injurious effects of the amides of sodium and calcium. This agent was potassium amide. The comparison between these metals was carried out in this way. The scheme entailed the conversion of a relatively large amount of potassium to potassium amide. With this in solution the sampleof potassium to which equivalent amounts of sodium and calcium were to be compared was then introduced and times of reaction determined. Successive separate samples of sodium and calcium were then added and times determined. In this manner, the time of reaction to be used as definite evidence whether the three metals in equivalent amounts were reacting identically.

The table embodying the results obtained with the use of two catalysts, platinized platinum and rusted iron is now given.

Table XII

Series	Run	Catalyst	KNH_2	K	Na	Ca	Time
1	434c	Platinized	2.67		.16		1.9
	435d	Platinum		.16			1.8
2	439c	Platinized	2.01		.14		2.3
	440d	Platinum		.14			2.3
	441e			.14			2.5
3	701	Platinized				2.20	>30
	702a	Platinum		2.55			>30
	703b			15.6			42
	704c			2.36			14.0
	704d		18.1			2.20	13.9
	705e					2.19	18.3
4	659b	Platinized		3.85			10.1
	660c	Platinum		3.90			9.9
	661d		15.4		3.90		13.0
	662e			3.85			13.6
	663d			3.92			14.2
	664e					3.90	13.8
5	616e	Rusted Iron	16.4	.13			2.7
	617f				.12		2.8
6	648c	Rusted Iron	16.7	.14			3.6
	650e				.13		3.6
	651f			.46			5.4
	652g					.44	5.9
	653h			.44			5.2
	654i			2.53			9.0
	655j				2.43		15.4
	656k			2.52			8.9
7	668c	Rusted Iron	11.4	2.14			7.6
	669d				2.19		9.5
	670e			2.13			7.8
	671f					2.12	7.3
	672g			2.15			7.4

The first column in Table XII presents the series number. The second and third columns present respectively the run number and the catalyst used. The fourth presents the amount of potassium amide in millimols present in solution. This value is placed opposite to the run in which it was present at the start. The fifth, sixth and seventh columns present respectively the amounts of potassium, sodium and calcium in milliequivalents used in the reaction. The last column gives the time of reaction in minutes. All variables, such as the behavior of the catalyst, temperature of the reaction and speed of stirring were maintained constant.

In Table XII several series of runs using each catalyst are given. These individual series will be given separate discussions, In the first series, samples of potassium and sodium were introduced into a liquid ammonia solution containing 2.67 millimols of potassium amide. These metals gave the same times of reaction. The second series was almost identical to the first series and established that these metals reacted in the same time. The third series employed a different preliminary procedure. Instead of having an excess of potassium amide in solution prior to the comparison of metals, a calcium sample was initially introduced. This proved to be a slow reaction and never finished. Samples of potassium, equivalent to 18.10 millimols of potassium amide were then added to this unfinished reaction. The table shows that all this potassium plus what remained of the calcium reacted in 42 minutes. Comparison samples of potassium and calcium were then successively added and required the same time to react. An additional calcium sample took approximately 5 minutes longer than the previous calcium sample. The reason for this time difference and an explanation of the whole run will be presented in a discussion following the presentation and discussion of different relative reactivities of potassium, sodium and calcium. In series four, the normal procedure of having an excess of potassium amide present was again used. The first two runs established the time required for approximately 3.9 milliequivalents of potassium to be 10 minutes. An equivalent sodium sample was then added and a time of 13 minutes was recorded. Successive equivalent samples of potassium and calcium also gave time values varying from 13 to 14 minutes. It will be noticed here that the samples of potassium and calcium following the sample of sodium check the time of that sample but that the potassium values are 3 to 4 minutes higher than the two initial equivalent samples of potassium. These discrepancies will be discussed later.

In the fifth, sixth and seventh series of this table, similar work on the reactivities of potassium, sodium and calcium were carried out using rusted iron as a catalyst. The procedure presented under potassium was employed in obtaining this data. In series five, the results clearly show in this solution containing 16.4 millimols of potassium amide, that equivalent amounts of potassium and sodium reacted identically. In the first portion of series six, the same thing is true. In the latter portion, it will be noticed that the sodium sample in 655j required more time than its comparison samples of potassium. This will be discussed later in this section, along with an example of the same type that took place in series seven. The last runs of each of these two series were made to check on the behavior of the catalyst and to determine whether the potassium samples were reacting normally. The data shows that times of both of these were identical to previous values. All other values in this series strongly support the contention that the relative reactivities of the metals are the same.

(2) Different relative reactivities of potassium, sodium and calcium

Having just presented evidence that equivalent amounts of these metals react in the same time in the presence of excess potassium amide, it is the purpose now to show that these metals in solutions of only their own amides possessed different relative reactivities. The procedure for doing this is illustrated in the following description. In comparing these metals, it was necessary to adopt an arbitrary size of sample for each comparison. Because of the slowness with which sodium and calcium reacted, it was advisable to use small samples. For each catalyst, each one of these samples was used in an individual reaction and their times of reaction were taken as a criterion of their relative reactivities. Table XIII illustrates the results obtained.

Table XIII

Different Relative Reactivities of Potassium, Sodium and Calcium

Number of run	Catalyst	Potassium milli-equivalents	Sodium milli-equivalents	Calcium milli-equivalents	Time of Reaction minutes
632	Platinized Platinum	2.45			10.3
695			2.55		14.0
701				2.21	>100
573e	Rusted Iron	1.65			6.4
678			2.35		56
686				2.29	>100
538	Nickel	.15			22
528			.11		360

The third, fourth and fifth columns of this table contain respectively samples of potassium, sodium and calcium in milliequivalents used in the reactions. All other columns are familiar to the reader, as the headings in them have been presented many times previously.

With each catalyst except nickel in Table XIII the reactivities of potassium, sodium and calcium have been determined; with nickel, only the first two metals were used. The results of the metals are grouped for each catalyst so that a comparison can easily be obtained. It is concluded from this work that the relative reactivities of equivalent amounts of the metals, in solutions of their respective amides are different for each catalyst and stand thus in order of decreasing reactivity, potassium, sodium and calcium. With rusted iron, there is a greater difference between potassium and sodium than with platinized platinum. With nickel, these same metals gave decisively different times of reaction. The calcium runs for platinized platinum and rusted iron do not lend themselves to any comparison of this kink, as both were so slow that they did not finish in 100 minutes. The author would like to point out that the differences between potassium and sodium in runs 632 and 695 is misleading as it might suggest that the reactivity of sodium closely approximates that of potassium. Successive samples of sodium (not shown here) following run 695 showed that the reaction slowed up gradually, the first successive sample of the same weight requiring 135 minutes and the second never finished at all, thus indicating that whatever was causing the depressing effect on the catalyst was increasing as the amount of sodium added to the solution was increased. This was attributed to be sodium amide. It is now advisable to axamine the reasons why the reactions of sodium and calcium were depressed by their amides and why excess of potassium amide allowed normal activity of catalysts and the same relative reactivity of the metals.

It is postulated that the differently soluble amides of sodium and calcium depressed their respective reactions due to their forming a coating on the catalyst thereby shutting off catalytic action. As these reactions progressed, the influence of the amides gradually increased as borne out by the sodium run cited in the previous paragraph. If this conception of the depressing effect of these amides is correct, the removal of them from the surface of the catalyst should allow normal activity. This has direct experimental support in the calcium runs 701 to 705e in Table XII. To bring out this point, a few of the main features of these runs will be repeated. The first sample of calcium produced enough $Ca(NH_2)_2$ to shut off a portion of the catalytic power of the catalyst as shown by the failure of this run to finish. In runs 702a and 703b, sufficient potassium equivalent to 18.10 millimols of KNH_2 were added and nullified the effect of the $Ca(NH_2)_2$. The comparison samples of potassium and calcium next added gave identical times. Thus, in this run, it can be thought that the $Ca(NH_2)_2$ was coated on the catalyst and the activity of the latter depressed. The KNH_2 then removed the $Ca(NH_2)_2$, by a process which will now be presented.

The manner in which the KNH_2 is though to offset the deleterious effects of the amides is by combining with these two differently soluble compounds in forming more soluble complexes. Franklin[31] has shown that a mixture of potassium amide and sodium amide, in liquid ammonia, forms a complex more soluble than the sodium amide, which after crystallization conforms to the formula $NaNH_2 \cdot 2KNH_2$. He also has found that analogously $Ca(NH2)_2$ forms with KNH_2 the compound $Ca(NH_2)_2 \cdot KNH_2$. Definite solubilities of these compounds are not known; qualitatively they are said to be more soluble than the amides from which they are formed. On the basis of these facts, it is postulated that the sodium and calcium amides were removed from coating the catalyst by the interaction mentioned above and allowed the catalyst to function normally. The author would like to point out here that all solutions in which these relative reactivities of potassium, sodium and calcium were determined, had variable amounts of these complex amides which were not in solution, depending on the amounts of the various metals used.

As mentioned in the previous paragraphs, some of the results gave discrepancies in time values. It is the purpose now to show that some of these results can be explained on the basis of the theories presented while others do not lend themselves to plausible explanation and do not support the theories advanced. For instance, the runs 704d and 705e of Table XII indicated that as the $Ca(NH_2)_2$ increased, due to these two fairly large samples of calcium successively added, the difference in time was approximately 5 minutes. It appears that as the $Ca(NH_2)_2$ increased in amount, the efficiency of the catalyst was reduced. In runs 655j and 669d in the same table, this appears true of the sodium runs. This behavior was not always the same however, for in 655j the sodium run was long while the successive check by potassium was normal. This was true also of runs 670e to 672g. These two cases were different from the one in 661d and 662c where the potassium and calcium samples, instead of returning to check the normal value, maintained the same value that sodium gave. In these cases where values obtained were longer than normal times, the author can only say that the efficiency was somehow reduced by the presence of large amounts of sodium or calcium amide. In run 695, Table XIII, it will be noted that the time values for sodium approximate that of potassium, while in 678 with another catalyst, the times for potassium and sodium under the same concentrations. The author is unable to account for this variance in behavior. It is altogether possible that the catalyst enters here in some manner not known. It cannot be explained on basis of solubility for under the conditions in 678, the same result was not obtained. It has already been mentioned that the successive sodium values(not shown) that followed 695 required progressively appreciably longer times, the second taking 135 minutes and the third, never finishing at all. It is also pertinent to note that the addition of very large samples of potassium were never able to speed up the reaction.

E. Order of Reaction

The importance of order of reaction in heterogeneous catalytic work was alluded to in the introduction. Suplementing this, it can be said that this importance lies in the fact that a knowledge of an order of reaction is not only essential for determining the rate of reaction but it is helpful in adopting a mechanism by which a reaction takes plase. It was for these purposes that the order of reaction, for various catalysts employed in this reaction, was measured.

(1) Procedure employed in the determination of order of reaction.

The general procedure employed in this work was one involving the collection of one of the products of reaction, hydrogen. From this, by computation, a measure of how far the reaction had progressed at a certain time interval, could be ascertained. The two methods used for this gas collection are given below.

(a) One method employed was to collect the hydrogen from one sample of potassium at definite intervals of time, the gas corresponding to each interval being collected in one of the collection tubes in Figure 3. Gas analysis, by the Hempel explosion method was performed separately on each of these samples. Knowing the initial amount of the alkali metal and being able to calculate the amount of this metal, from the gas analysis, at various stages of the reaction, it was possible to determine, by substitution of the values of time and weight of metal in the various order equations such as zero, first, second, et cetera, a series of reaction constants for a complete run. The equation which the data fitted thus gave the order of reaction for this reaction.

(b) The second method used included the work of two successive runs. In the first run, a small sample of alkali metal was introduced and the hydrogen collected for a definite time interval. In the second run, a successive sample of larger size was used and the hydrogen collected for the same time interval. Experimental data of this type was of use in determining order because it has already been established that in a zero order, the rate of reaction is constant over a period of time, that in a first order reaction the time taken for a given fraction to react is independent of the initial concentration, that in a bimolecular reaction the time taken for a given fraction to react is inversely proportional to the initial concentration, that in a termolecular reaction the time taken for a given fraction is inversely proportional to the square of the initial concentration, et cetera.

(2) Experimental results

Order of reaction, for this reaction between potassium and ammonia, were determined with four catalysts, platinized platinum, rusted iron, nickel and smooth platinum by the methods prescribed. The results of each will be presented separately in the order given.

Table XIV

Order of Reaction Using Platinized Platinum

Run	K Total	Time Int.	H_2 Theory	H_2 Coll.	K Reacted	Fr. K Reacted	Const. x 10^{-2}
354d	.0734	6.0	21.0	19.2	.0670	.913	38.3
355e	.1596	6.0	45.7	41.2	.1438	.901	38.5
405e	.0659	5.5	18.8	17.6	.0616	.934	49.6
406f	.1077	5.5	30.9	29.2	.1018	.945	52.8
221	.1016	4.0	29.1	22.1	.0780	.759	36.5
222a	.2775	4.0	79.5	54.7	.1937	.688	30.0

Table XIV presents in the first column the number of the run, in the second column total potassium in grams used in the reaction, in the third the time interval in minutes in which hydrogen was collected, in the fourth the theoretical hydrogen for the completed reaction, in the fifth the volume of hydrogen in cc. at N.T.P., which was collected in the time interval, in the sixth the potassium in grams reacted in the time interval equivalent to the hydrogen collected, in the seventh the fraction of potassium which had reacted during the time interval (fraction is equal to weight of metal reacted divided by sample weight), and in the ninth the constant of the reaction obtained by substituting the necessary experimental values in the first order equation. All variable, other than concentration of alkali metal, were held constant.

With all of these experiments, it can be clearly seen that regardless of the size of the sample, approximately the same fraction of it was converted in the same time, thus determining, with the aid of laws presented, the order to be first. With these same runs, the data was substituted in the first order reaction equation

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

where k is the reaction constant, t is the time of reaction in minutes, a the initial amount of potassium in grams and x the amount of potassium in grams used up in time t. The constants show very good agreement and lend support to the statement that the reaction proceeds as a first order. It will be noted that constants for the first two series of runs were different. This can be attributed to the fact that these catalysts had different deposites on them. It was also true that the deposite for the third series of runs was not the same as for the others but coincidentally was of about equal power to the first. This concludes the work on platinized platinum and will be followed by similar work on rusted iron, in which identical procedure wor this determination were employed. The experimental material is presented in Table XV.

Table XV

Order of Reaction Using Rusted Iron

Run	K Total	Time Int.	H_2 Theory	H_2 Coll.	K Reacted	Fr. K Reacted	Const. x 10^{-2}
472e	.0860	5.0	24.6	22.1	.0773	.898	45.8
473f	.2591	5.0	74.2	66.7	.2330	.899	45.9
614c	.1464	6.0	41.9	40.8	.1422	.972	59.2
615d	.3216	6.0	92.1	87.6	.3060	.954	50.4
600i	.0807	5.0	22.8	21.9	.0774	.960	63.9
601j	.3260	5.0	93.4	82.4	.2875	.882	42.8

The column material presented in this table is identical in type with the previous table. The computations arrived at in completing this table are the same as were used in the platinized platinum work.

Analogously the results showed that the reaction between potassium and liquid ammonia was first order. As with platinized platinum, the constants show dissimilarities when different series are compared and, like this catalyst, the dissimilarities were due to different deposites. In the third series of this table, run 601j, it will be noticed that the second constant was appreciably lower than the first. This is easily explained in that all the gas for that five minute interval could not be swept out due to the rapidity with which it was forming at the end of that interval, hence less hydrogen was collected than should have been. The reaction constant for the second run of this third series is therefore low. An examination of the equation will show that the less hydrogen collected the larger is the denominator of the fraction and hence the lower the constant.

Before the additional experimental results are presented on order of reaction with other catalysts, the writer deems it advisable to present a general discussion supplementary to the conclusions drawn from the work on platinized platinum and rusted iron. In the reaction betweenn liquid ammonia and potassium, there are two reactants which are changing concentration, potassium and ammonia. However, only potassium changes appreciably, as the mols of ammonia present are at least some twenty times more than the mols of potassium. Hence it can be said that the ammonia, for all practical purposes, is constant and offers no influence on the reaction. Another factor which also must be considered in this respect is the presence of the catalyst. This, too, was constant in all cases. If all these variables such as time, potassium, ammonia and catalyst were considered, however, the proper equation of first order is

$$k' = \frac{1}{tbc} \ln \frac{a}{a-x}$$

All parts of this equation have been presented except b and c which respectively represent the concentration of ammonia and catalyst. However since b and c were constant in this work, the equation suitable for use here is best used with these terms concerned about relative constants of reaction than it was about absolute values and k gave these as well as k'.

The results of order of reaction determinations with nickel were obtained by the employment of both methods as described in the beginning of this section. Table XVI presents the results obtained by the use of method (a). One experiment using method (b) will be presented following the discussion of the results included in the table.

Table XVI

Determination of Order of Reaction with Nickel

Number of run	Potassium grams	H_2 collected for interval of 30 minutes in cc. N.T.P.			H_2 Theory cc. N.T.P.
		1	2	3	
522d	.6104	8.9	8.0	7.6	174.9
527d	.6012	7.5	7.7	7.3	172.2

The central portion of this table represents the volumes of hydrogen collected for the time intervals stated. The catalyst in both cases was evacuated and allowed to stand one-half hour at 1 mm. of mercury. Stirring and temperature were the same for all experiments.

The limited work done on this catalyst was indicative of the fact that the reaction between potassium and ammonia with nickel catalyst was of zero order. This indication is drawn from the gas collection which showed that approximately the same volume of hydrogen came off the reaction for each interval of time. The additional determination made with nickel is now presented. This involved the use of method (b). In run 529, .1303 gram of potassium was used and 16.1 cc. hydrogen at N.T.P. were collected while in run 530, 1.0483 grams of potassium were used, 25.6 cc. of hydrogen at N.T.P. being collected. This work showed that the first order of reaction was not in operation for this order would have given 129.5 cc. of hydrogen at N.T.P. for the second sample. This work also showed that the zero order was not strictly in operation either, as the same volume of gas would have been obtained in both cases. The results indicate, however, that the order more closely approximated zero order than it did the first, and in addition indicate that some order between zero and first could have been in operation. In respect to these different orders, the following cases can be visualized. If the concentration is high enough, in relation to the active portion of the catalyst, the latter will be completely and continuously saturated and the rate of reaction will be constant, i.e. a zero order. If, however, the concentration is low enough so that the rate is proportional to the concentration, the order will be first. If the concentration is moderate, the rate of reaction will be proportional to some fractional power of the concentration and a fractional-power order will be obtained. The order determination for smooth platinum will now be presented in Table XVII.

Table XVII

Determination of Order of Reaction

with Smooth Platinum

Number of run	Potassium grams	H_2 collected for interval of 60 minutes in cc. N.T.P.			H_2 Theory cc. N.T.P.
		1	2	3	
641	.8630	4.4	4.9	4.4	247.0

This table is constructed in the same way as Table XVI with one exception--60 minute intervals were used instead of 30.

The few intervals over which gas was collected indicated a zero order in this reaction. However, due to the limited work accomplished, this result is only indicative and not conclusive.

F. Mechanism of Reaction

In the introduction of this thesis, an example was advanced to show how the reaction between potassium and ammonia was brought about on the surface of a catalyst. In it one atom of potassium was conceived to react with one molecule of ammonia, forming one molecule of potassium amide and one atom of hydrogen. This was only an illustration and as such it served its purpose. The author has no experimental evidence to show that the reaction proceeded by such a mechanism.

The order of reaction measurements with the rapid catalysts, platinized platinum and rusted iron, showed that potassium and ammonia proceeded as a first order reaction. With these same catalysts, it was also shown that potassium, sodium and calcium reacted identically in a system where the depressing effects of the amides of the two latter metals were rectified. It can be inferred, then, that in such a system sodium and calcium also would exhibit first order reactions with ammonia. Such being the case, it seems apparent that the individual characteristics of these metals were not determining factors in the reaction. Something, therefore, common to all these reactions was the determining factor. Kraus has already postulated that the free electron is that factor and presents the following equation which is set up to illustrate the mechanism by which the reaction proceeds.

$$e^- + NH_3 \longrightarrow NH_2^- + \frac{1}{2} H_2$$

where the free electron e^- comes from the metal in the following manner

$$M \rightleftharpoons M^+ + e^-$$

This mechanism can be postulated for the reaction only on the assumption or on the proof that the ammonia, amide ion and hydrogen relationships with the catalyst are of no consequence. The potassium amide and the amides of sodium and calcium under the proper conditions have been shown to have no influence by this work. From this it seems logical to state that the metal ions and the amide ions had no influence. What parts the ammonia and hydrogen played are not known. The author, however, believes that the adsorption of ammonia (if it is adsorbed) or its decomposition into ions,

$$NH_3 \rightleftharpoons NH_2^- + H^+$$

could not be determining factors as it is inconceivable that either of these two processes would proceed as first order reactions, and to be dominating factors in this reaction they would have had to go by this process. Analogously, it is believed that the rate of desorption of hydrogen from the catalyst did not proceed as a first order reaction for if it did, then it in itself was not the determining factor as its rate would be proportional to its concentration and this very concentration of hydrogen would be proportional to the amount of the alkali metal present, so the metal and not hydrogen would be the determining factor. The examination of all these views and facts leads the author to state that the mechanism could be either that postulated by Kraus, given in (1) or by the author in (2).

$$(1)\ e^- + NH_3 \longrightarrow NH_2^- + \tfrac{1}{2} H_2$$

$$(2)\ e^- + H^+ \longrightarrow \tfrac{1}{2} H_2$$

The free electron e^- in both equations comes from the metal

$$M \rightleftharpoons M^+ + e^-$$

The hydrogen ion in (2) comes from the ammonia equilibrium

$$NH_3 \rightleftharpoons NH_2^- + H^+$$

There is no evidence at hand for the author to state which of these two mechanisms is in operation and therefore he presents both as possibilities. The author prefers the equation presented in (2) as it is believed that the ammonia decomposes into amide and hydrogen ions before reacting. These mechanisms were mainly derived by the use of the experimental evidence obtained with the fast catalysts. It is believed, however, that they apply to the slow ones also, even though these catalysts exhibited something approximating a zero order. It is postulated that whichever reactant in the above mechanisms is the determining factor, this factor so completely saturates the active portions of these slow catalysts that an approximate zero order is exhibited. So far the discussion presented has given no prominent place as to what part the catalyst played in this mechanism. A brief discussion of this is now given.

It has been definitely established in heterogeneous catalysis that at least one of the reactants of a reaction must be adsorbed on the catalyst. In each of the two mechanisms advanced, two reactants are involved. Along with not being able to postulate which is the true mechanism due to lack of experimental evidence, the author is also unable to postulate which one of the two reactants is adsorbed. It is not inconceivable that both are adsorbed.

V CONCLUSION

A. Summary

The following general conclusions, drawn in this work, are grouped under apparatus, catalysts and the reaction.

(1) Apparatus

The apparatus employed was found to be applicable for the pursuance of this work, as it could be operated as a strictly anhydrous system, it allowed gas collection very closely approximating the theoretical and in general was amenable to the discharge of the functions for which it was constructed.

(2) Catalysts

(a) The catalysts, under proper treatment of evacuation were of constant activity and of reproducible behavior. Without treatment they varied widely in their activities

(1') Explanations were advanced to explain the variability due to lack of evacuation and the constancy due to it.

(b) The catalytic powers of a series of catalysts were investigated and their activities, in relation to this reaction, evaluated. They possessed this order of decreasing activity:

Platinized Platinum
Rusted Iron
Nickel
Pure Iron
Smooth Platinum
Zinc
Silver
Gray Platinum
Tantalum and Columbium

(3) The Reaction

(a) The hydrogen from the reaction proved that the reaction went to completion. In addition, it showed that the catalysts adsorbed no appreciable amounts of this gas and that the main reaction was unaccompanied by side reactions.

(b) The products of reaction had the following influences:

Potassium Amide; no effect
Sodium Amide; slowed up reaction
Calcium Amide; slowed up reaction
Hydrogen; effect undetermined

A procedure was used that eliminated the effects of the sodium and calcium amides involving the use of potassium amide. Explanations were also advanced to show why the sodium and calcium amides produced their effects and why potassium amide eliminated these effects.

(c) The time of reaction was effected by the rate of stirring, and increase of stirring decreasing time of reaction. Time of reaction--rate of stirring curves are presented to show this influence.

(d) The time of reaction was effected by the concentration of the alkali metal, an increase of concentration increasing time of reaction. Time of reaction--concentration of metal curves are presented.

(e) The relative reactivities of potassium, sodium and calcium were determined. For platinized platinum and rusted iron, these metals in equivalent amounts in a solution of excess potassium amide gave identical times of reaction. These metals when tested in solutions containing only their respective amides gave different times of reaction. With nickel and smooth platinum determinations, similar to the ones in the preceding sentence, were carried out with the results that all the metals gave decidedly different times of reaction. No work with the latter group of catalysts was accomplished in the presence of excess potassium amide to see if, under such conditions, the reactivities would be the same. Where the three metals reacted differently, the order of decreasing activity was potassium, sodium and calcium for all catalysts. An explanation why the excess potassium amide allowed the reactions to procede in the same times is advanced.

(f) The order of reaction was determined in the presence of platinized platinum, rusted iron, nickel and smooth platinum. The reaction for the former two catalysts proceeded as a first order reaction, while the same reaction with the latter two indicated a zero order.

(g) Two mechanisms were advanced for the reaction of the alkali and alkaline earth metals with ammonia in the presence of catalysts. They are:

(1) $e^- + NH_3 \longrightarrow NH_2^- + \frac{1}{2} H_2$

(2) $e^- + H^+ \longrightarrow \frac{1}{2} H_2$

B. Suggestions of some Future Problems in the extension of this work

1. The sintering effect of temperature on these catalysts.
2. Poisons for these catalysts.
3. Adsorption measurements on these catalysts.
4. Effect of temperature on the reaction.
5. Effect of more intense evacuation.
6. Extension of work on order of reaction using smooth platinum and nickel.

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