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Decomposition of Potassium Azide Melts in the Presence of Metal Catalysts

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The thermal decomposition of molten KN_3 in the presence of selected metals and metal oxides was studied by following the pressure change in a constant volume vacuum system. Decomposition rates were observed to be increased by several orders of magnitude. The increase with oxides as additives was not due to the oxides but to the catalytic activity of the metals formed from the oxides in the initial phases of KN_3 decomposition. The characteristics of the decomposition curves were determined by this metal formation and the catalytic properties of the formed metals. Manganese, iron, cobalt, and nickel metals were highly active catalysts and lowered the activation energy of KN_3 decomposition from 49 to 32 kcal./mole. Copper, silver, and gold did not exert an influence of similar magnitude. The activation energy with copper was found to be 44.5 kcal./mole. The frequency factors (related to the unit surface area of catalyst) increased progressively in the sequence from nickel to manganese. For copper, the frequency factor is two to three orders of magnitude larger than for the metals mentioned above. The data of this work seem to indicate that holes in the d-band of the catalyst play an important role in lowering the activation energy for KN_3 decomposition.

Introduction

The thermal decomposition of inorganic azides has been widely investigated. This reaction has been found to be autocatalytic with the rate of nitrogen liberation starting slowly and increasing rapidly as metal is formed. When KN_3 is decomposed *in vacuo*, the metal formed evaporates and the major portion of the KN_3 sample decomposes with a linear rate.[1] In the presence of potassium vapor the rate of decomposition is considerably increased.[1,2] This was attributed to a reduction of the activation energy from 49 kcal./mole *in vacuo* to 41.5 kcal./mole in 16 mm. of potassium vapor.[1]

In this paper the thermal decomposition of molten KN_3 was investigated from the viewpoint of heterogeneous catalysis. The decomposition rate was increased several orders of magnitude by the presence of metals and metal oxides. Some metals lowered the activation energy of the KN_3 decomposition considerably while others lowered it only slightly. To account for this, current theories on the relation between electronic structure of metals and their catalytic activity were used. The first parts of this paper deal mainly with the influence of reducible oxides. Subsequently, quantitative results of the catalytic action of selected metals are presented.

Experimental

Potassium azide and the additive were mixed in an agate mortar to a high degree of homogeneity. A small pellet of this mixture (in most cases less than 1 mg.) was placed on the glass spoon of the decomposition apparatus and kept there for at least 1 hr. under high vacuum. Figure 1 shows a schematic representation of this apparatus. By rotating the spoon the sample was dropped into the vessel, which was surrounded by a heated brass block, the temperature of which was held constant electronically. The decomposition was followed by recording the increase in pressure measured by an ionization or alphatron gage automatically. Although the ionization gage was applied in the pressure range of 0.05–5 μ and the alphatron gage in the range of 1–100 μ, the same curves were obtained from both gages. For the work presented here the alphatron gage was used and the sample sizes were chosen so that the nitrogen pressure did not exceed 100 μ. The outgassing rate of the vacuum system was checked before each run and normally was negligible. Two cold traps were included in the decomposition apparatus. One was part of the system in which the nitrogen accumulated; the other separated this system from the pumps. All experiments were conducted at temperatures above the melting point of KN_3.

Results

The decomposition of pure, molten KN_3 was a very slow process at 350° and required many hours even at temperatures above 400°. At the beginning of decomposition different samples resulted in different initial shapes of the decomposition curves. However, the main portions of the samples decomposed with linear rates in all cases. Using the split run technique (decomposing the same sample at different temperatures) the activation energy was found to be in the neighborhood of the literature value of 49 kcal./mole.

The decomposition rates were increased when the outgassing time was increased. This might be due to the reduced presence of water traces which react with the potassium nuclei formed during decomposition. When catalysts were present, all such parameters became unimportant in comparison and the reproducibility was satisfactory. The gaseous decomposition products of pure KN_3, KN_3–metal, and KN_3–metal oxide mixtures were analyzed mass spectrometrically. They were identical and consisted almost exclusively of nitrogen. In the case of decomposition with catalysts, the evolved nitrogen volume could be related to the decomposed KN_3 sample by the equation $2KN_3 \rightarrow 2K + 3N_2$ within the limits of experimental accuracy.

Decomposition with Fe_3O_4 or Iron Metal as Additive.—Figure 2 shows the decomposition curves for KN_3 with different amounts of Fe_3O_4 as an additive. Although the decomposition was very much accelerated by the presence of Fe_3O_4, it can be concluded from Fig.

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[1] P. W. M. Jacobs and F. C. Tompkins, *Proc. Roy. Soc.* (London), **A215**, 265 (1952).

[2] W. E. Garner and D. J. B. Marke, *J. Chem. Soc.*, 657 (1936).

2 that Fe_3O_4 itself was not acting as a catalyst. This is shown by the following four points: (1) It was known from similar experiments that the warming-up time of the samples when dropped into the reaction tube was less than 1 sec. With Fe_3O_4, however, there was little decomposition in the first 10 sec. and the reaction velocity increased in the form of an acceleration period. (2) The length of the acceleration period was proportional to the Fe_3O_4 concentration, provided this concentration was not excessively high as in the case of curve 4. (3) The decomposition velocity did not increase linearly with the amount of Fe_3O_4 present. (4) Experiments which have not been included in Fig. 2 show that the decomposition velocity is almost independent of the specific surface of the added Fe_3O_4 powder. All of these observations indicate that Fe_3O_4 is not the catalyzing agent, but is involved in a reaction which produces the catalyst. The activation energy was obtained from plots of the linear rates of curve 1 and curve 4 against $1/T$ (°K.) and was found to be 32 kcal./mole.

Figure 3 shows the decomposition curves for KN_3 with iron metal powder as a catalyst. In this case the reaction started within 1.5 sec. after the sample drop, and there was no acceleration period observed except when large quantities of iron metal were present. The very small acceleration period (below fractional decomposition $\alpha = 0.01$) which was observed in the latter case was due to the oxide layers which covered the metal surface. This was indicated by the observation that an increase in the amount of surface reoxidation caused a lengthening of the acceleration period. (The iron powder has been obtained by reduction of Fe_3O_4 with hydrogen at 850° and cooling in hydrogen.)

Up to approximately $\alpha = 0.04$, there was a rapid linear decomposition when iron metal was present (Fig. 3). In the interval $\alpha = 0.04$ to approximately $\alpha = 0.15$ a retardation of the reaction velocity occurred, after which the decomposition became linear again. The broken curve in Fig. 3 is for a catalyst concentration which was smaller by an order of magnitude and therefore was plotted on a time scale which is ten times larger. In order to keep this figure clear only these two KN_3-iron ratios have been plotted. The fact that the curves fall closely together shows that the characteristics of the decomposition are the same for different KN_3-iron metal ratios, and that the decomposition velocity is proportional to the amount of iron present. Because of these facts, it is evident that the iron metal acts as a catalyst.

The experiments with Fe_3O_4 and with iron metal led to the conclusion that iron oxides are completely reduced to iron metal during the acceleration periods. This has been confirmed by X-ray analysis of the residues of KN_3 decompositions with Fe_3O_4. The observed iron powder pattern was seen to be broad and diffuse, indicating a very small particle size for the iron formed. This enables one to understand why high decomposition velocities are obtained with metal oxides.

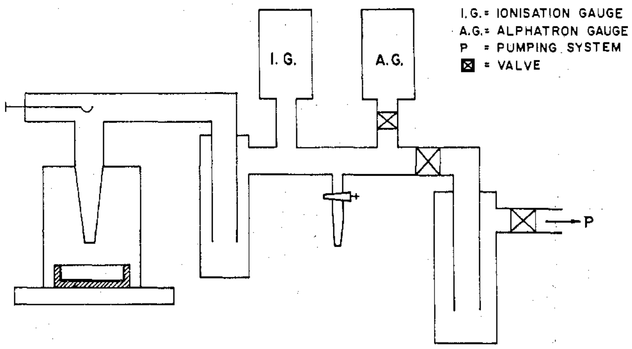

Fig. 1.—Schematic representation of the decomposition apparatus.

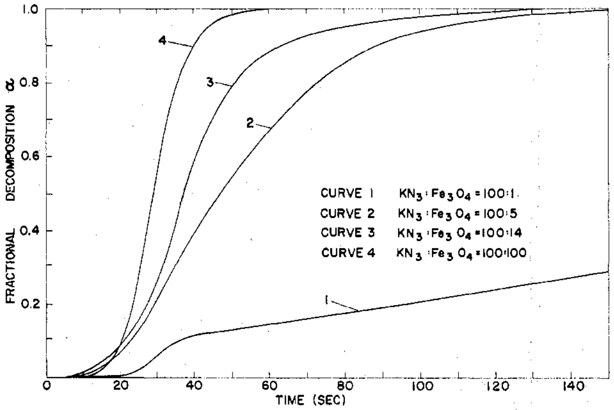

Fig. 2.—Fractional decomposition, α, *vs.* time; $T = 360°$, four different KN_3/Fe_3O_4 ratios.

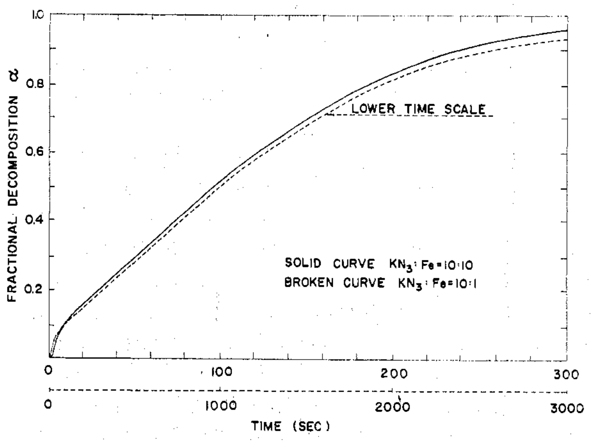

Fig. 3.—Fractional decomposition, α, *vs.* time; $T = 360°$, iron additive.

In view of this, the iron oxide curves may be interpreted in the following way: The beginning of the decomposition is slow since no iron metal is present. The slight decomposition of KN_3 which occurs without metallic iron present yields some potassium metal which then reduces some iron oxide to iron. These iron specks are the sites of primary KN_3 decomposition and they grow, increasing the decomposition velocity until all of the oxide is reduced and the highest decomposition rate is obtained.

The decomposition of KN_3 with 5 parts or more of Fe_3O_4 in 100 parts of KN_3 is so fast that the retardation of reaction velocity observed with iron metal is not easy to see. However, with 1 part of Fe_3O_4 in 100 parts of KN_3 (curve 1, Fig. 2), the decomposition is slow

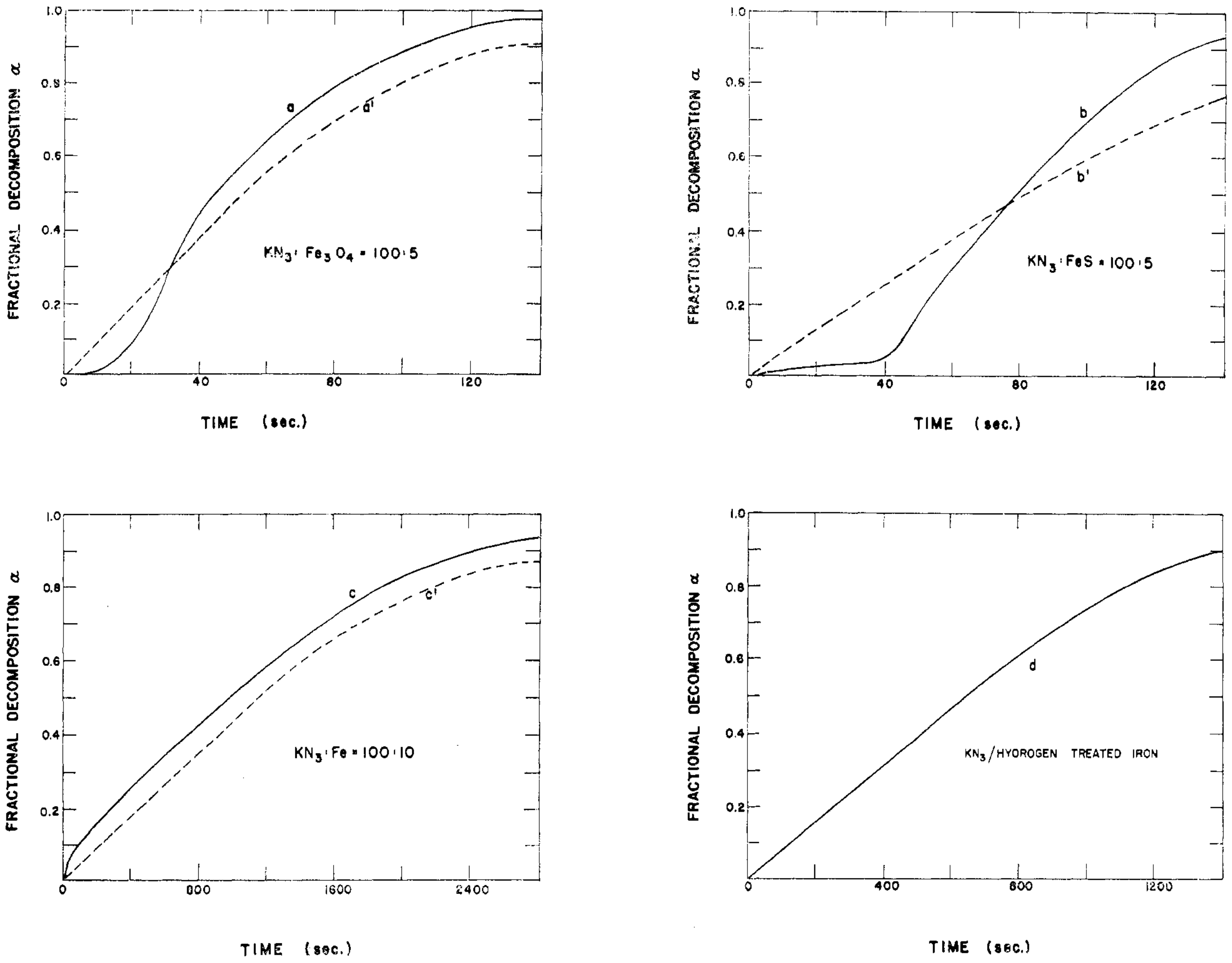

Fig. 4.—Fractional decomposition, α, *vs.* time; $T = 360°$: (a) Fe_3O_4 additive; (b) FeS additive; (c) Fe additive (broken curves are for the same catalyst used a second time); (d) iron, hydrogen treated *in situ*, as catalyst.

enough that the retardation of reaction velocity can be observed very clearly. The energy of activation for the decomposition of KN_3 with iron metal was found to be 32 kcal./mole, as expected. This value was obtained from the temperature coefficients of both the initial linear decomposition rate and the main linear decomposition rate. This shows that the retardation of the decomposition velocity is due to a change in the pre-exponential factor of the Arrhenius equation only.

Decompositions with Repeatedly Used Iron Catalysts.—The experiments with iron metal and Fe_3O_4 seem to indicate that after the catalyst surface has stabilized the decomposition of KN_3 proceeds on the iron surface according to a zero order reaction. To establish this, experiments were carried out using the same catalyst two or three times. This was accomplished by pumping out the nitrogen from the first experiment and dropping a sample of pure KN_3 by means of a second spoon on the catalyst which remained from the previous run. This procedure could be repeated again by using a third spoon. In this way, three experiments were performed without breaking the vacuum in the apparatus. The results of these experiments are given by the broken curves in Fig. 4, and show that the decomposition rates on previously used catalysts are constant from the beginning of the reaction to $\alpha = 0.5$ or more. This seems quite reasonable since the concentration of KN_3 is constant and the specific surface of the catalyst is the determining factor for the reaction velocity. The decomposition rate cannot be expected to remain linear throughout the reaction since some catalyst particles lose contact with the KN_3. Curve b of Fig. 4 shows the decomposition with FeS as an additive. There is an induction period which might be due to a delay in the formation of iron nuclei. On all parts of the curve after the induction period the activation energy for KN_3 decomposition again was found to be 32 kcal./mole.

It also seemed desirable to investigate the catalytic behavior of iron metal surfaces which had been freed from oxide layers by hydrogen treatment. A very small sample of iron powder was placed in the reaction tube and the decomposition apparatus repeatedly flushed with hydrogen. A heat treatment was carried out after filling the apparatus with one atmosphere of hydrogen. With the re-establishment of high vacuum, a sample of pure KN_3 was dropped on the hydrogen-treated iron. Curve d of Fig. 4 shows that the decomposition rate on hydrogen-treated iron surfaces also is constant for a considerable portion of the curve.

Decompositions with Various Oxides.—All of the above experiments using iron and iron oxides have been carried out with nickel, cobalt, and their oxides. The decomposition characteristics with these oxides are similar to those of the iron oxides. The slight difference in the shapes of the curves observed with iron, cobalt, and nickel oxides can be understood by considering the different degrees of retardation observed with iron, cobalt, and nickel metal. More about this retardation will be presented in a subsequent section of this paper. X-Ray analysis of the residues with NiO and Co_2O_3 indicated again that the oxides were reduced to the metals. Second runs with the same catalyst also resulted in constant rates.

Manganese dioxide had little effect although manganese metal was a highly active catalyst. From this it is obvious that manganese oxides are not reducible to metal under the conditions of KN_3 decomposition. This also is indicated by the chemical potentials of the manganese oxide reduction and potassium metal oxidation.

Cuprous oxide influenced KN_3 decomposition much less than the oxides of iron, cobalt, and nickel. Around 360° the decomposition was very slow. Therefore, most of the experiments with Cu_2O were carried out above 400°. Multiple runs with the same catalyst again resulted in constant rates. The energy of activation was found to be 44.5 kcal./mole. The decomposition curves with Cu_2O show long and slowly rising acceleration periods. This indicates that the reduction of Cu_2O to copper takes place slowly, which very likely is a consequence of the low catalytic activity of copper. The slow reduction of copper oxides can be observed with a microscope. A sheet of copper tarnishes when it is put on a hot stage of a microscope. After a droplet of KN_3 is placed on this dark gray copper oxide layer, red spots begin to appear which increase in size and number with time. These red spots are the preferred sites of nitrogen bubble formation.

Vanadium pentoxide behaves differently from other oxides. It reacted vigorously with KN_3 but the rapid decomposition ceased with the depletion of the V_2O_5 since the product of this reaction does not catalyze. No vanadium metal was formed in the reaction between KN_3 and V_2O_5. This agrees with the observation of Stern,[3] who found, during a study of the solubility of metal oxides in molten NaCl, that NaCl melts are vigorously decomposed by V_2O_5.

Chromium oxide (Cr_2O_3) and titanium dioxide (TiO_2) did not influence the decomposition of KN_3.

Decomposition with Selected Metals as Catalysts.—The transition metals from titanium to nickel as well as copper, silver, and gold have been studied. With the exception of iron and copper the metal powders were obtained by grinding commercially available metals with a mechanical alumina mortar and pestle. The purity of these metals was greater than 99%. The iron powder could not be obtained in this way since it oxidized to a greater extent during the grinding operation. The use of ground iron resulted in decomposition curves which were typical for the presence of iron oxide. Therefore, the iron metal powder was prepared by a 2-hr. reduction of Fe_3O_4 in hydrogen at 650° followed by cooling in hydrogen. Copper powder was obtained by the same procedure at 250°.

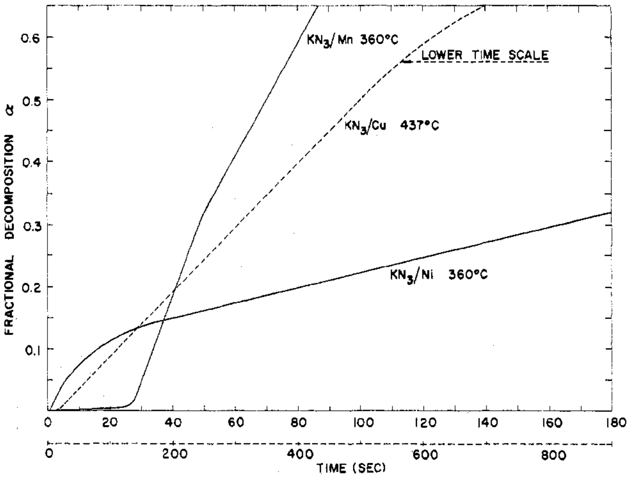

Fig. 5.—Fractional decomposition, α, *vs.* time; Ni and Mn additive, $T = 360°$; Cu additive, $T = 437°$.

Iron, cobalt, and nickel are very active catalysts for KN_3 decomposition. The presence of each of these metals resulted in essentially the same type of decomposition curve described for iron in a previous section. In Fig. 5 the curve using nickel is plotted as an example.

Manganese metal was the most active catalyst used. The decomposition characteristic (Fig. 5) showed an induction period terminating abruptly with a very fast decomposition which has a constant rate up to $\alpha = 0.25$. After this, an insignificant retardation of the reaction velocity occurred followed by another constant rate decomposition. When the same manganese metal is used a second time no induction period is observed and the decomposition rate is constant from the beginning to about $\alpha = 0.5$. The induction period observed with manganese may be caused by a delay in the formation of manganese metal nuclei from the surface oxide layer. The thermodynamic situation for the reduction of these oxide layers cannot be very favorable since bulk MnO is not reducible by potassium.

Iron, as well as nickel, cobalt, and manganese, lowers the activation energy for KN_3 decomposition from about 49 to 32 kcal./mole. In view of this it would be of considerable interest to determine if the other transition metals with partially filled d-bands also act as catalysts. This could not be established since the oxides covering chromium, vanadium, and titanium are irreducible by potassium, making the real metal surface unavailable for catalysis. This can be deduced from arguments based on chemical potentials and can be observed experimentally.

While manganese, iron, cobalt, and nickel are very effective catalysts for KN_3 decomposition, copper, silver, and gold did not display an influence of similar

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[3] K. H. Stern, "Chemical and Thermodynamic Properties at High Temperatures," a symposium, XVIII International Congress of Pure and Applied Chemistry, Montreal, Canada, 1961.

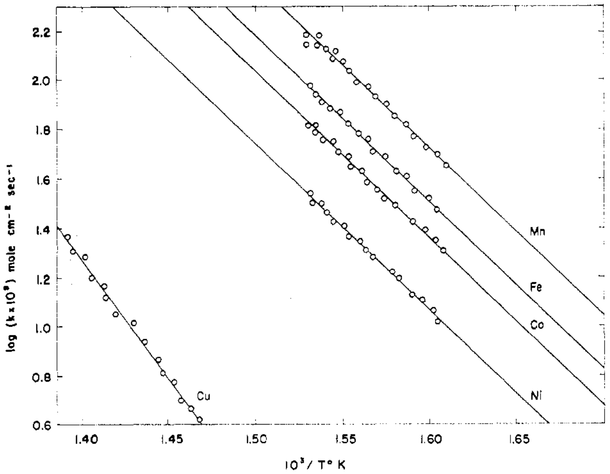

Fig. 6.—Log ($k \times 10^9$) (mole cm.$^{-2}$ sec.$^{-1}$) of the initial linear decomposition *vs.* $10^3/T$ (°K.) (Arrhenius plot).

magnitude. Figure 5 shows a decomposition curve taken at 437° with copper powder as catalyst. After a short period, which again can be considered as the period of surface oxide reduction, there was a constant rate decomposition from $\alpha = 0.005$ to $\alpha = 0.55$. No slowing down of the reaction velocity was observed before the stage of general decline of reaction velocity. The energy of activation was found to be considerably higher than in the case of manganese, iron, cobalt, and nickel, namely, 44.5 kcal./mole.

Activation Energy and Frequency Factor.—The specific surface of the manganese, iron, cobalt, nickel, and copper powders has been determined by the B.E.T. method.[4] Using these data, the reaction velocity constant, k, was expressed in moles of KN_3 decomposed per cm.^{2} of catalyst surface per second ($dx/dt = k$ (mole cm.$^{-2}$ sec.$^{-1}$), where dx/dt is the rate of KN_3 decomposition as calculated from the rate of nitrogen pressure increase). The contribution of the non-catalytic decomposition of KN_3 is negligible in the presence of manganese, iron, cobalt, or nickel and not important with copper. The temperature dependence of the reaction velocity constant was well represented by the Arrhenius equation, $k = B \exp(-E/RT)$. Figure 6 is an example of the many Arrhenius plots obtained in this investigation. The activation energies were determined by 15–20 runs at temperatures between 348 and 380° with manganese, iron, cobalt, and nickel and at 400–450° with copper. The maximum uncertainty is ±1.5 kcal./mole with the latter metal and ±1.0 kcal./mole with manganese, iron, cobalt, and nickel. The activation energy data obtained with the metals agreed with the data using metal oxides. The results are displayed in Table I.

Table I

Activation Energy, E (kcal./mole), Frequency Factor B_i of the Initial Rapid Decomposition, and Frequency Factor $B_{\alpha=0.4}$ of the Main Portion of the Decomposition[a]

	E	B_i	$B_{\alpha=0.4}$
Mn	32	9.8×10^3	6.8×10^3
Fe	32	7.1×10^3	1.2×10^3
Co	32	5.7×10^3	1.0×10^3
Ni	32	2.3×10^3	1.4×10^2
Cu	44.5	1.0×10^6	1.0×10^6

[a] Frequency factors in mole cm.$^{-2}$ sec.$^{-1}$.

B_i in Table I represents the frequency factor of the initial rapid constant rate decomposition, and $B_{\alpha=0.4}$ the frequency factor of the main portion of the decomposition. B_i seems to represent the activity of the newly formed metal surfaces. It can be seen from Table I that the B_i values increase from nickel to manganese. This leads to the speculation that the frequency factor might be influenced by the number of holes in the d-band of the catalyst. The frequency factor can be represented by a lattice frequency $\nu \sim 10^{13}$ sec.$^{-1}$ multiplied by the number of moles covering the unit surface of catalyst. With this, the speculation mentioned above implies that more adsorption will occur on a metal with a greater number of holes in the d-band. The dependence of the specific activity on the number of holes per atom in the d-band was postulated theoretically by Dowden.[5]

It must be mentioned that more experimental evidence is necessary before a correlation between frequency factor and the electronic structure of the catalyst actually could be proposed on the basis of these experiments. For instance, deviations of the activation energy within the limits of experimental accuracy would disrupt the trend of the B_i values. However, it seems that the same process of activation occurs with manganese, iron, cobalt, and nickel as catalysts, and it is not unlikely that the activation energy is the same with all four metals. The uncertainty associated with the B.E.T. measurements is not large enough to permit a change in the trend of the B_i values. It should be noted that the increase of the frequency factor from iron to manganese is not paralleled by the number of singly occupied atomic d-orbitals of these two metals.[6,7] The high value of the frequency factor with copper as a catalyst agrees with the catalysis rule that high activation energies are associated with high frequency factors.

Table I also shows that the retardation of the decomposition velocity, which was observed with nickel, cobalt, iron, and manganese metal, is due solely to a change in the frequency factor. By comparison of B_i and $B_{\alpha=0.4}$ it can be seen that this retardation is enhanced with nickel, less with iron and cobalt, and very little with manganese. Hydrogen treatment of iron, nickel, or cobalt resulted in constant rates of decomposition. This might imply that the portion of the catalytically active surface which becomes poisoned in the course of KN_3 decomposition already is poisoned by the previously adsorbed hydrogen. Poisoning by the developed nitrogen seems to be a possibility when KN_3 is decomposed. However, nitrogen should be

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[4] The B.E.T. surface determinations were carried out by "Isotopes Inc.," 123 Woodland Avenue, Westwood, N. J.

[5] D. A. Dowden, *J. Chem. Soc.*, 242 (1950).

[6] L. Pauling, *Phys. Rev.*, **54**, 899 (1938).

[7] L. Pauling, *Proc. Roy. Soc.* (London), **A196**, 343 (1949).

adsorbed more strongly by manganese and iron than by nickel according to Trapnell.[8]

Discussion

Catalysis at the interface between solids and fluids is a complex phenomenon, dependent on a number of parameters. For instance, it can be expected that the adsorption of N_3^- and K^+ alters the work function of the metal catalyst. Nevertheless, considerations based on the work functions of the metals do not seem to lead to an understanding of the catalytic activities observed in this work.

The data contained in this paper seem to indicate that holes in the d-band of the catalyst (free electron theory) or singly occupied atomic d-orbitals (valence bond theory) are important for catalytic action. Reactions affected by the rate of formation of a chemisorbed positive ion (electron transfer to the catalyst) or a covalent substrate–catalyst bond are favored by the presence of holes in the d-band. The formation of N_3^+ ions is energetically impossible under the conditions of KN_3 decomposition. However, it seems a likely possibility that N_3^- ions which have sufficient excitation energy form a partly covalent bond with the catalyst. This bond will be relatively strong with manganese, iron, cobalt, and nickel since singly occupied atomic d-orbitals are available. With copper this is not the case and the bond can be formed only with the unused fraction of surface bonding orbitals. This seems to explain the higher catalytic activity of manganese, iron, cobalt, and nickel as compared with copper. Two N_3 groups, chemisorbed on adjacent sites of the catalyst surface, may react to yield three molecules of nitrogen while two potassium ions may become reduced to potassium metal.

Acknowledgment.—The author wishes to thank Dr. B. deB. Darwent for his comments on this paper and Mr. M. D. Kemp for supplying the KN_3 used in the experiments.

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[8] B. M. W. Trapnell, *Proc. Roy. Soc.* (London), **A218**, 566 (1953).

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Precipitation of Silver(I) Halides in Molten Lithium Nitrate–Potassium Nitrate Eutectic[1]

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Using a glass reference electrode, the precipitation of AgCl, AgBr, and AgI in $LiNO_3$–KNO_3 eutectic was studied by a potentiometric titration technique. Titrations were performed at a series of temperatures and solubility products and other thermodynamic properties were calculated for the reaction: $Ag^+ + X^- \rightleftharpoons AgX(s)$. Employing a method suggested by Gurney, the entropy associated with the co-sphere of each anion was calculated for aqueous solution and for the molten solution. By comparing these unitary entropy terms, it can be shown that the interaction between molten solvent and halide ion is the same for each of the three halide ions studied. This is considerably different from the interactions in aqueous solution.

Introduction

The behavior of silver ions in molten nitrates has been studied by several investigators. Laity measured activity coefficients in the silver–sodium nitrate system in concentration cells with transference.[3] Flengas and Rideal, in a classic study, demonstrated that the silver electrode behaved ideally,[4] and using a concentration cell they carried out electrometric titrations of silver ions with various halides in 1:1 $NaNO_3$–KNO_3 melts. Blander, *et al.*, measured the e.m.f. of cells containing $AgNO_3$ and KCl in molten KNO_3 and NaCl in molten $NaNO_3$.[5,6] In a previous report the present authors have shown that a reference electrode consisting of a mercury filled glass bulb functioned very well in Li–K nitrate eutectic.[7] The potential of the glass reference electrode differs for different electrodes, but in the case of potentiometric titrations one is interested only in differences rather than absolute values. The object of the present study was to investigate the behavior of silver(I) halides in Li–K nitrate eutectic *via* electrochemical techniques employing the glass reference electrode.

Experimental

All chemicals used, except the $AgNO_3$, were reagent grade and were used directly without further purification other than oven drying at 120°. The silver nitrate was also reagent grade but only hand-picked clear crystals were used in the investigation. Silver wire was B & S gage 18 of 99.99% purity. All nitrogen used was of extra-dry quality.

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[1] Part of the work submitted by H. Ti Tien to Temple University in partial fulfillment of requirements for degree of Doctor of Philosophy.

[2] Author to whom all inquiries should be sent.

[3] R. W. Laity, *J. Am. Chem. Soc.*, **79**, 1849 (1957).

[4] S. N. Flengas and E. K. Rideal, *Proc. Roy. Soc.* (London), **A233**, 443 (1956).

[5] M. Blander, F. F. Blankenship, and R. F. Newton, *J. Phys. Chem.*, **63**, 1259 (1959).

[6] M. Blander and J. Braunstein, *Ann. N. Y. Acad. Sci.*, **79**, 838 (1960).

[7] G. W. Harrington and H. T. Tien, *J. Phys. Chem.*, **66**, 173 (1962).