2. Two mercury-arc systems suitable for the preparation of hydrogen atoms have been described.

3. The presence of hydrogen atoms at cathodes during electrolysis as well as in oxyhydrogen flames has been indicated.

4. The mechanism of the Cario-Franck method has been discussed and further lines of study have been outlined.

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DISPLACEMENT OF METALS FROM SOLUTIONS OF THEIR SALTS BY LESS ELECTROPOSITIVE ELEMENTS. III. THE ACTION OF LIQUID AMMONIA SOLUTIONS OF SALTS OF THE ALKALI AND ALKALINE EARTH METALS ON MAGNESIUM AND OTHER ELEMENTS[1]

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Introduction

A metal in general precipitates a less electropositive metal from solutions of its salts. Thus, as copper reacts with mercuric nitrate in water solution to form metallic mercury and cupric nitrate, so we should expect sodium or potassium to displace the less electropositive elements calcium, barium, magnesium and aluminum from water solutions of their salts were it not for the vigorous action of the alkali and alkaline earth metals with water. Indirect evidence that such replacements take place has been obtained by G. McPhail Smith and his pupils[4] who have shown that aqueous solutions of salts of sodium and barium, for example, react with potassium amalgam in the manner represented by the equations, $K + NaI \rightleftharpoons KI + Na$ and $2Na + BaCl_2 \rightleftharpoons Ba + 2NaCl$. Jellinek, with Czerwinski and others, has shown that similar reactions take place in fused salt media.[5] Thus, barium reacts with fused sodium chloride in accordance with the equation, $Ba + 2NaCl \rightleftharpoons 2Na + BaCl_2$, while, inversely, sodium reacts with barium chloride in accordance with the above equation read from right to left.

A direct study of reactions of this type at ordinary temperatures may be carried out in liquid ammonia, in which the alkali and alkaline earth metals dissolve as such with the formation of relatively stable blue solu-

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[1] Papers of this series previously published are (a) THIS JOURNAL, **45**, 2788 (1923); (b) **47**, 1836 (1925).

[2] National Research Fellow.

[3] A preliminary version of this paper was received on September 2, 1925. (Editor.)

[4] (a) Smith, *Am. Chem. J.*, **37**, 506 (1907). (b) Smith and Rees, THIS JOURNAL, **40**, 1802 (1918). (c) Smith, *ibid.*, **37**, 76 (1915). (d) Smith and Ball, *ibid.*, **39**, 179 (1917); and other articles.

[5] Jellinek and Czerwinski, *Z. physik. Chem.*, **110**, 192 (1924).

tions. Dilute solutions of the alkali metals in liquid ammonia have been shown by Kraus[6] to conduct the electric current in the same manner as solutions of salts in this solvent, the positive ion being identical with the alkali metal ion, the negative ion being the solvated negative electron (e^-). Just as silver nitrate and potassium iodide in water solution react to form potassium nitrate and silver iodide, so solutions of potassium chloride and metallic calcium in liquid ammonia react to form metallic potassium and the very sparingly soluble calcium chloride. The parallel metathetical reactions are represented by the equations, $Ag^+ + NO_3^- + K^+ + I^- = AgI + K^+ + NO_3^-$ and $2K^+ + 2Cl^- + Ca^{++} + 2e^- = CaCl_2 + 2K^+ + 2e^-$.[7] In a similar manner, when a sodium solution is added to a solution of potassium amide, sodium amide is precipitated: $KNH_2 + Na = NaNH_2 + K$. Under suitable conditions, both of these reactions may proceed from right to left, for neither calcium chloride nor sodium amide is entirely insoluble in liquid ammonia. In both of the above reactions, the less electropositive metal displaces the more electropositive metal from a solution of one of its salts, because the replacements do not depend upon the position of the metal in the electropotential series but rather upon the relative solubilities of the substances taking part in the reaction.

The author has found that the reaction represented by the equation, (1) $3NaNH_2 + Al \longrightarrow 3Na + Al(NH_2)_3$, takes place in the direction indicated because of the very low solubility of aluminum amide in liquid ammonia.[1a] The sodium thus set free reacts with the solvent, in the presence of metallic aluminum acting as a catalyst in accordance with the equation, (2) $2Na + 2NH_3 = 2NaNH_2 + H_2$. Aluminum amide dissolves in a solution of sodium amide in liquid ammonia to form sodium ammono-aluminate in the manner represented by the equation, (3) $NaNH_2 + Al(NH_2)_3 = Al(NH_2)_2NHNa{\cdot}NH_3$.

As a continuation of the investigation of reactions of this nature, a study has been made of the action of liquid ammonia solutions of a number of salts of potassium, sodium, lithium, calcium, barium and strontium upon magnesium.

The Action of Solutions of Salts in Ammonia upon Magnesium

In view of the fact that aluminum and magnesium react with potassium amide to form a solution of potassium,[1a] it is not surprising to find that sodium iodide and a number of other salts of the alkali and alkaline earth metals similarly react with magnesium to form solutions of the alkali or alkaline earth metal in accordance with the type equation, (4) $Mg + 2NaI \rightleftharpoons MgI_2 + 2Na$.[8] Now sodium in the presence of magnesium metal acting

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[6] Kraus, THIS JOURNAL, **43**, 749 (1921).

[7] Kraus, *ibid.*, **44**, 1224 (1922).

[8] This reaction is in reality a metathesis involving the ions Mg^{++}, Na^+, I^- and e^-, the negative electron which functions as anion in the solution of sodium and un-

as a catalyst reacts with the solvent to form hydrogen and sodium amide, which latter in turn reacts with magnesium iodide to form sodium iodide and the almost insoluble magnesium amide.[8a] The successive reactions are represented by the equations, (5) $2Na + 2NH_3 = 2NaNH_2 + H_2$ and (6) $MgI_2 + 2NaNH_2 = Mg(NH_2)_2 + 2NaI$. As magnesium amide is formed in quantities increasing with time, and as the sodium iodide is regenerated, this reaction may be regarded as a conversion of magnesium into magnesium amide under the catalytic influence of sodium iodide. Magnesium amide was likewise formed by the action of liquid ammonia solutions of sodium chloride, cyanide, bromide and iodide, of potassium iodide, cyanide and bromide and of lithium chloride upon magnesium.[9]

Magnesium in contact with a solution of sodium tetrasulfide becomes covered with a coat of difficultly soluble magnesium polysulfides, which prevents further action. Curiously enough, a 0.5 *N* solution of sodium nitrate has no appreciable action on magnesium. Barium and strontium iodides, which are very slightly soluble in liquid ammonia, react very slowly with magnesium to form deep blue solutions of the corresponding alkaline earth metal, while the almost insoluble cesium chloride does not react at all.

All of the salts mentioned above, excepting cesium chloride, sodium tetrasulfide, the iodides of strontium and barium and sodium nitrate, markedly catalyze the reaction between magnesium and the solvent to form magnesium amide, for it was found in a blank test that only a few milligrams of the latter substance resulted from the action of pure liquid ammonia for five months upon magnesium ribbon, the surface of which had been cleaned by the action of ammonium bromide solution.[10]

Preparation and Properties of Magnesium Amide.—The manipulations necessary for the preparation of magnesium amide by the action of salt solutions upon the metal will perhaps best be understood from the description of a typical experiment. In one leg of a two-legged reaction tube[11]

doubtedly also in the solution of magnesium. Magnesium metal is very slightly soluble in ammonia [Cottrell, *J. Phys. Chem.*, **18**, 96 (1914)], the saturated solution being a transparent blue. The solution resulting from Reaction 4 is opaque blue and on concentration to a small volume acquires the coppery luster characteristic of concentrated solutions of the alkali metals in liquid ammonia. The amount of sodium formed in the reaction depends upon the relative solubilities of the substances on the right- and left-hand sides of the equation. Magnesium iodide is only very slightly soluble in ammonia.

[8a] The reduction in concentration of Mg^{++} ions due to the formation of magnesium amide according to Equation 6 and the removal of sodium by action with the solvent in accordance with Equation 5 both cause a displacement of the equilibrium of Equation 4 toward the right.

[9] All of these salts are very soluble or moderately soluble in liquid ammonia with the exception of lithium chloride, which is only slightly soluble.

[10] Ammonium bromide is an acid in liquid ammonia solution.

[11] Franklin and co-workers, (a) This Journal, **27**, 831 (1905); (b) **29**, 1694 (1907); (c) **35**, 1460 (1913); (d) *J. Phys. Chem.*, **15**, 915 (1911); (e) **16**, 694 (1912); (f) **15**, 510 (1911).

was placed a few tenths of a gram each of clean magnesium ribbon and sodium iodide. Providing the materials used were perfectly dry, the resulting colorless liquid ammonia solution of the salt slowly became opaque blue as the result of the formation of free sodium in accordance with Equation 4. In the course of a day or two magnesium amide began to collect in noticeable quantities in the bottom of the reaction tube, and at the end of one or two weeks enough of this substance had been formed for an analysis. It was necessary from time to time in order to avoid danger of explosion, to open the stopcock of the reaction tube partially to allow accumulated hydrogen to escape. The more finely divided portions of the magnesium amide were transferred by repeated "flotations" to the other leg of the reaction tube and there thoroughly washed with liquid ammonia. The resulting preparation was dried in a vacuum, hydrolyzed by water[11g] and dissolved in dil. sulfuric acid. Magnesium was determined as pyrophosphate, while ammonia was estimated by distillation of a portion of the acid solution with sodium hydroxide into a standard solution of hydrochloric acid.

Analyses of a number of specimens of magnesium amide are given in Table I. Table II contains analytical data for a few preparations. Most of the preparations contain a small percentage of impurities derived from the alkali metal salt used in the reaction. Very thorough washing removes most of this impurity.

TABLE I

PREPARATIONS OF MAGNESIUM AMIDE

Preparation	1 NaCl	2* NaCl	3 NaI	4 NaI	5 NaI	6* NaI	7* NaCN	8 NaBr	9 KBr
Mg	42.1	43.2	43.0	40.5	41.8	42.2	42.8	42.8	41.6
N	49.2	49.6	49.0	50.6	49.3	50.0	48.5	49.0	48.5

Preparation	10 KCN	11* KCN	12* KI	13* LiCl	14[a] Na	15 $NaNH_2$	16 $NaNH_2$	17 $Na_2[Mg(NH_2)_4]$	Calcd. for $Mg(NH_2)_2$
Mg	40.7	41.7	42.0	42.0	41.8	42.0	43.3	42.3	43.15
N	48.2	48.9	49.6	48.8	49.3	49.0	49.5	48.1	49.72

[a] The reactions of Na, $NaNH_2$ and $Na_2[Mg(NH_2)_4]$ with magnesium to form magnesium amide are described later in this article. Sodium and sodium amide may in a sense be regarded as salts. Sodium ammonomagnesiate, $Na_2[Mg(NH_2)_4]$, is a true salt of the ammonia system.

TABLE II

ANALYTICAL DATA

No.	2 (140°)[a]	6 (20°)	12 (20°)	16 (20°)
Subs., g.	0.4501	0.2470	0.2605	0.1701
$Mg_2P_2O_7$	(½)[b] .4447	(½) .2388	(½) .2503	(½) .1688
N	(¼) .05585	(¼) .03091	(¼) .03227	(½) .04212

[a] Dried in a vacuum at (°).

[b] Refers to proportion of substance taken for analysis.

[11g] The reaction is vigorous.

The starred preparations were very thoroughly washed with liquid ammonia. All preparations were dried in a vacuum at room temperature or 100–160°, very little ammonia being given off at the higher temperatures. When magnesium amide was heated in a vacuum at 350–400°, light yellow deammonation products were formed, whose composition lay between those of the imide and the nitride.

Action of Solutions of Salts in Liquid Ammonia on Metals Other than Magnesium

It was found that solutions of sodium chloride or potassium cyanide in liquid ammonia at room temperatures have very little or no action upon metals less electropositive than magnesium. Thus, a saturated solution of potassium cyanide had no action on either zinc or amalgamated aluminum in five months, but did attack gold to a slight extent in half a year. A saturated solution of sodium chloride very slightly attacks tin, copper and impure lanthanum, but has no appreciable action on amalgamated aluminum. There is, therefore, very little tendency for the reaction $Al + 3NaCl \rightleftharpoons AlCl_3 + 3Na$ to take place in liquid ammonia.

Action of Solutions of Salts in Liquid Ammonia on Amalgams

In view of the observation of G. McP. Smith[12] that magnesium amalgam reacts with aqueous potassium hydroxide solution to form potassium amalgam and magnesium hydroxide, it was of interest to find that a large excess of potassium thiocyanate dissolved in liquid ammonia removes all but traces of magnesium from its amalgam with the formation of the readily soluble magnesium thiocyanate and potassium amalgam. In one experiment, the mercury of the amalgam after reaction with potassium thiocyanate solution in excess was found to contain 0.1852 g. of potassium, with only traces of magnesium, while the solution in contact with the amalgam contained 0.0574 g. of magnesium; that is, for every atom of magnesium going into solution, 2.01 atoms of potassium were liberated and dissolved by the mercury. A dilute magnesium amalgam reacts readily with sodium chloride solution to form a gray precipitate of magnesium chloride hexammonate mixed with finely divided mercury. Zinc and cadmium amalgams were not attacked by strong solutions of sodium chloride.

The Action of Potassium and Sodium Amides on Magnesium: The Preparation of Potassium and Sodium Ammonomagnesiates.—Potassium amide reacts with magnesium in accordance with the equation, $Mg + 2KNH_2 \rightleftharpoons Mg(NH_2)_2 + 2K$, to form an opaque blue solution containing potassium. This latter metal in turn reacts with solvent ammonia, in the presence of magnesium acting as a catalyst, to form potassium amide

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[12] Ref. 4 a, p. 541.

and hydrogen, as represented by the equation, $2K + 2NH_3 = 2KNH_2 + H_2$. Potassium amide then reacts with magnesium amide to form the sparingly soluble crystalline potassium ammonomagnesiate. This latter salt may also be formed by the action of a solution of metallic potassium upon magnesium.

Sodium amide similarly reacts with magnesium metal to form an opaque blue solution of sodium, which strangely enough does not change greatly in depth of color until nearly all of the magnesium has been converted to magnesium amide. Therefore, in order to prepare sodium ammonomagnesiate in a state of approximate purity, sodium amide or a solution of sodium in liquid ammonia is allowed to react with magnesium in a two-legged reaction tube until most of the latter metal has disappeared and the blue color of the sodium solution is no longer apparent. The precipitate of magnesium amide is then washed a number of times with liquid ammonia to remove the sodium ammonomagnesiate, which was found to be soluble to the extent of about 6 g. per liter at room temperatures. The sodium ammonomagnesiate so transferred to the clean leg of the reaction tube was submitted to analysis, after removal of liquid ammonia by evaporation, without further attempts at purification. Sodium ammonomagnesiate reacts very vigorously with water to form sodium and magnesium hydroxides and ammonia. Preparatory to analysis and after hydrolysis by water, the specimens were dissolved in dil. sulfuric acid. Magnesium and nitrogen were determined in the manner described previously in this article.

Anal. *Preparation 1:* Subs., (20°) 0.1831; (140°) 0.1796: (1/2) $Mg_2P_2O_7$, 0.0740; (1/2) N, 0.03613. *Preparation 2:* Subs., (20°) 0.2229: (1/2) MgO, 0.0336; (1/4) $Mg_2P_2O_7$, 0.0463; (1/4) N, 0.02384. Calcd. for $Mg(NHNa)_2{\cdot}2NH_3$: Mg, 18.1; N, 41.7. Found (dried in a vacuum at 20°): Mg, 17.7, 17.6; N, 41.0, 41.5.

The Action of Potassium and Sodium Ammonomagnesiates on Magnesium.—Franklin[13] assigned to potassium ammonomagnesiate the formula $Mg(NHK)_2{\cdot}2NH_3$ and regarded it as a salt analogous in constitution to the zincates and aluminates of the water system. Just as sodium iodide reacts with magnesium metal to form magnesium amide, so one might expect this latter substance also to be formed by the action of the ammono salts, potassium and sodium ammonomagnesiates, on magnesium.

The blue solution formed by the action of potassium amide upon magnesium becomes almost colorless within a day or two, leaving the magnesium covered with crystals of the sparingly soluble potassium ammonomagnesiate. This salt in turn reacts very slowly with magnesium to form a dilute solution of potassium, while magnesium amide is formed with lapse of time. On the other hand, sodium ammonomagnesiate reacts very readily with metallic magnesium to form a solution of sodium, and then magnesium amide, as shown by the following experiment.

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[13] Ref. 11 c, p. 1463.

A mixture of sodium ammonomagnesiate and magnesium amide was prepared in one leg of a two-legged reaction tube by the action of sodium amide on magnesium. When the magnesium had nearly all been converted to magnesium amide and the blue color of the sodium solution had disappeared, the precipitate formed was washed with liquid ammonia to transfer the sodium ammonomagnesiate to the other leg of the reaction tube, which contained a few pieces of fresh magnesium ribbon. An opaque blue solution of sodium formed within a few moments, and at the end of two weeks a sufficient quantity of magnesium amide had accumulated for an analysis. The magnesium amide which had been formed in the original reaction between the sodium amide and magnesium was then removed from the reaction tube in the manner described by Franklin,[11f] the liquid ammonia in the other leg having been cooled to —33° to reduce the pressure inside the tube to atmospheric. The leg from which the magnesium amide was removed was cleaned and resealed in a current of ammonia. The magnesium amide formed by the action of sodium ammonomagnesiate upon magnesium was transferred to this clean leg and washed thoroughly with liquid ammonia prior to analysis. (See Table I, No. 17.)

Metallic sodium and magnesium amide are formed by the action of sodium amide on magnesium, in accordance with the equation, $2NaNH_2 + Mg \rightleftharpoons Mg(NH_2)_2 + 2Na$. Sodium, in the presence of a metal which acts as a catalyst, slowly reacts with the solvent to form sodium amide and hydrogen. Sodium ammonomagnesiate may then be formed by the action of sodium amide on the amphoteric base magnesium amide, in the manner expressed by the equation, $2NaNH_2 + Mg(NH_2)_2 = Mg(NHNa)_2 \cdot 2NH_3$. One would expect this salt to react with magnesium in accordance with the equation, $Mg(NHNa)_2 \cdot 2NH_3 + Mg \rightleftharpoons 2Mg(NH_2)_2 + 2Na$. The sodium so formed is converted to sodium amide and this may further react with magnesium or magnesium amide.

The Action of Lithium and Calcium Amides on Magnesium.—Lithium amide reacts very slowly with magnesium in much the same manner that sodium does, that is, with the formation of a deep blue solution of lithium which does not disappear until most of the magnesium has been converted to magnesium amide. Calcium amide reacts even more slowly with magnesium to form magnesium amide, but the reaction is possibly to be attributed to impurities of alkali metal in the calcium used in the preparation of calcium amide. Both lithium and calcium amides were prepared by the action of liquid ammonia upon the corresponding metal in the presence of iron wire catalyst.

The Action of Aqueous Salt Solutions on Magnesium

Solutions of many salts of the alkali and alkaline earth metals in water attack magnesium metal with the formation of magnesium hydroxide or basic magnesium salts, and hydrogen.[14] The reaction of salt solutions with magnesium in the two solvents water and ammonia thus leads to the formation of entirely analogous products, for magnesium amide bears the same relation to ammonia that magnesium hydroxide does to water. In view of the fact that magnesium was found to react with a liquid ammonia solution of sodium iodide in the sense of Equations 4–6 to form a solution of sodium, it is probable that sodium is likewise formed by the action of an aqueous solution of sodium iodide on magnesium. In liquid ammonia this reaction proceeds fairly readily because of the low solubility of magnesium iodide; in water we should not expect this reaction to take place to so great an extent because of the high solubility of magnesium iodide. On the other hand, sodium reacts with ammonia rather slowly, even in the presence of a catalyst, to form sodium amide and hydrogen, while sodium is at once hydrolyzed by water to form sodium hydroxide and hydrogen. Sodium hydroxide then reacts with the magnesium iodide resulting from the first reaction between sodium iodide and magnesium to form magnesium hydroxide and sodium iodide. The sodium iodide may, therefore, be regarded as catalyzing an otherwise very slow reaction between magnesium and water. The corrosion of magnesium by salt solutions is due in part, of course, to electrochemical causes.

In support of this interpretation of the mechanism of the reaction between aqueous salt solutions and magnesium it was found that solutions of sodium polyselenides are readily formed around the anode of short-circuited cells of the type, Mg | alkali metal salt, aq. | Se. If the primary reaction of magnesium upon salt solutions results in the formation of hydrogen in accordance with the equation, $Mg + 2H_2O = Mg(OH)_2 + H_2$, one would expect only hydrogen to be liberated at the anode instead of sodium, and accordingly no alkali polyselenide would result.

In conclusion the author wishes to express his appreciation of Dr. Kraus' kind and helpful interest in this work, and to thank Dr. Franklin for looking over this manuscript prior to publication.

Summary

1. Magnesium slowly reacts with solutions of a number of salts of the alkali metals in liquid ammonia to form magnesium amide, $Mg(NH_2)_2$. It is shown that the reaction takes place in the following steps: $2NaI + Mg \rightleftharpoons MgI_2 + 2Na$; $2Na + 2NH_3 = 2NaNH_2 + H_2$; $2NaNH_2 + MgI_2 = Mg(NH_2)_2 + 2NaI$. The salt, in the above equations sodium iodide, may be regarded as catalyzing an otherwise extremely slow reaction between magnesium and ammonia, $Mg + 2NH_3 = Mg(NH_2)_2 + H_2$.

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[14] Kahlenberg, This Journal, **25**, 380 (1903). Getman, *ibid.*, **38**, 2594 (1916); **39**, 596 (1917). Hughes, *J. Chem. Soc.*, **115**, 272 (1919), to mention only a few of the numerous articles on this subject.

2. The ammono salts, sodium and potassium ammonomagnesiates, react with magnesium in a similar manner to form magnesium amide. This latter substance is likewise formed by the action of the amides of lithium and sodium and a solution of sodium in liquid ammonia on magnesium.

3. The preparation and properties of magnesium amide, $Mg(NH_2)_2$, and sodium ammonomagnesiate, $Mg(NHNa)_2 \cdot 2NH_3$ or $Na_2[Mg(NH_2)_4]$, are described.

4. It is well known that magnesium hydroxide is formed by the action of aqueous solutions of salts of the alkali metals upon magnesium. It is probable that the true mechanism of these reactions—in so far as they do not depend upon electrochemical influences—is the same as that by which magnesium amide—the magnesium hydroxide of the ammonia system—is formed by the action of liquid ammonia solutions of the same salts upon magnesium. For instance, the reaction between an aqueous solution of sodium iodide and magnesium may be represented by the equations, $2NaI + Mg \rightleftharpoons MgI_2 + 2Na; 2Na + 2H_2O = 2NaOH + H_2; 2NaOH + MgI_2 = Mg(OH)_2 + 2NaI$.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. IV. THE THERMAL DECOMPOSITION OF ANHYDROUS OXALIC ACID AND ITS RELATION TO THE PHOTOCHEMICAL DECOMPOSITION

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In a previous article[1] a report was made of a study of the photochemical decomposition of anhydrous oxalic acid. It was found that the anhydrous acid decomposes under the influence of radiation of wave length shorter than about 250 mμ. The presence of water was found to accelerate the reaction markedly. Mention was made of the fact that the wave length found for photochemical decomposition did not agree with that calculated from some rough measurements of the rate of thermal decomposition. Since the limits of the spectral regions used in this early study were only approximate, it was deemed advisable to repeat the work on photochemical decomposition with the aid of a monochromatic illuminator. At the same time, the study of the thermal decomposition has been carried out with more exact apparatus with the purpose of obtaining more direct evidence of the applicability or non-applicability of the radiation hypothesis to the decomposition of a solid body. A brief theoretical discussion will be given in which the question as to whether the radiation hypothesis should be applied to a system of this sort will be raised.

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[1] Noyes and Kouperman, THIS JOURNAL, **45**, 1398 (1923).