partial pressures of water vapor between 0.08% and 0.64%. The amount of oxygen retained by the catalyst is proportional to $\sqrt{P_{H_2O}/P_{H_2}}$. Very active catalysts are capable of retaining more oxygen than less active catalysts. The poisoning of both doubly and singly promoted catalysts by water vapor is almost entirely reversible, though a slight permanent injury to the catalyst results. A probable mechanism of ammonia synthesis consists in the reduction by hydrogen of surface Fe_4N formed by the reaction of nitrogen molecules with surface iron atoms having average free energies sufficiently in excess of those of normal iron atoms.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

ACETAMIDE AND FORMAMIDE AS SOLVENTS FOR THE ELECTRODEPOSITION OF METALS

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The possible application of formamide and acetamide as suitable media for the electrodeposition of metals from solutions of their salts has been suggested by various investigators,[1] but has thus far been given only little attention. That such a suggestion is based upon excellent theoretical considerations becomes evident from a survey of the physical and chemical properties of both of these substances. That such an investigation is highly desirable becomes increasingly apparent from the stress which has recently been laid upon solvent chemistry and solvents, in particular, non-aqueous ones.

Their differentiation on the basis of their acidity and basicity, as developed by Conant and Hall,[2] has thus far been limited to a consideration of liquid ammonia, water, alcohol and glacial acetic acid. Ammonia is regarded as the most basic of these in view of its great tendency to unite with the hydrogen ion or proton to form the ammonated hydrogen ion, the ammonium ion. Consequently, ammonium salts[3] and acid amides[4] act as acids in liquid ammonia. Glacial acetic acid, because of its tendency to part with the proton more readily, is considered the most acidic of the four above-mentioned solvents. This characteristic of acetic acid accounts for two of its most unexpected properties. Certain acids, such as perchloric acid, have been found to be "stronger" in acetic acid solution than in a less acidic solvent, such as water. On the other hand, compounds such as acetamide, which are usually considered as neutral substances re-

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[1] Walden, *Z. physik. Chem.*, **46**, 103 (1903); **54**, 129 (1905); **55**, 683 (1906).

[2] Conant and Hall, THIS JOURNAL, **49**, 3047, 3062 (1927).

[3] Franklin, *ibid.*, **27**, 820 (1905); Browne and Houlehan, *ibid.*, **33**, 1742 (1911).

[4] Franklin and co-workers, *J. Phys. Chem.*, **24**, 81 (1920); THIS JOURNAL, **44**, 486 (1922); **47**, 1485 (1925).

ferred to water, yield well-defined salts and may even be titrated by acids when dissolved in glacial acetic acid. The character of substances may change completely depending upon the solvent employed. Semicarbazide and guanidine are usually regarded as aquo-bases, but from their behavior in liquid ammonia may also be looked upon as ammono-acids.

These considerations concerning the nature of ionizing solvents and the behavior of dissolved solutes therein are all the more striking since such long accepted criteria as the dielectric constants find no place in such a classification.

Formamide and Acetamide as Parent Solvents.—The substitution of an amide group for the hydroxyl radical in formic and acetic acid affects very profoundly the chemical and physical properties of these substances. The dielectric constants are increased, and, as preliminary studies show, the solvent properties are accentuated. Applying the criteria suggested by Conant and Hall, it is obvious that the acidity of the resulting amides *as solvents* is less than that of the acids from which they are derived. That formamide is the more acidic of the two amides in so far as their solvent action is concerned, is indicated by the following chemical evidence: (1) metallic derivatives of formamide are more stable toward water than those of acetamide; (2) addition products or solvates are formed much more readily by acetamide; (3) the acid addition products of acetamide are the more stable.

That both of these substances may be considered as parent solvents seems evident (1) from the solvent properties which both exhibit, (2) from the fact that both yield conducting solutions, (3) since they enter into combination with various inorganic salts to form solvates. A large number of compounds has been prepared which bear a relationship to these two substances analogous to that existing between the ordinary acids and bases, and water.

Like water, formamide is miscible in all proportions with alcohol, and only very slightly soluble in ether. Metallic derivatives have been prepared which are related to formamide in much the same way as the metallic hydroxides are to water, even in such respects as solubilities in the corresponding solvents. It is an excellent dissociating solvent.[5] The conductivities[6] of salts in it indicate a behavior which parallels that observed in water. Molar conductivities are decidedly smaller. A study of the conductance of sodium formamide in formamide indicates the fact that the anion, $HCONH^-$, common to both solvent and solute, possesses an unexpectedly low ionic mobility,[7] only about one-tenth of that of the hydroxyl

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[5] Walden, *Bull. St. Petersburg Acad. Sci.*, **1911**; *cf. C. A.*, **6**, 1394 (1912).

[6] Davis, Putnam and Jones, *J. Franklin Inst.*, **180**, 567 (1915); *cf. C. A.*, **10**, 305 (1916); Davis and Johnson, *Carnegie Inst. Wash. Pub.*, **260**, 71 (1918); *cf. C. A.*, **13**, 3061 (1919).

[7] Röhler, *Z. Elektrochem.*, **16**, 419 (1910).

ion at similar concentrations in water. Formamide, like water, acts upon bismuth and antimony halides to produce solvo-basic compounds.[8]

Investigations concerning acetamide have been very much more prolific and extensive. Metallic derivatives of acetamide have been found to be unstable in water, but quite stable in liquid ammonia. In this connection it is interesting to note that their character varies from that of salts in liquid ammonia, by virtue of the behavior of acetamide as an ammono-acid, to what may formally be considered as bases in the parent solvent. Numerous addition compounds of salts with acetamide have been prepared. Their existence is all the more marked, because of the limited number of such solvates formed by formamide. Formamide has a more powerful "amidohydrolytic" effect, as evidenced by the fact that many metallic salts react directly with the solvent to yield the corresponding metallic formamides. Although observations are, as yet, far too limited to permit of any definite generalization, it would seem that the tendency toward the formation of solvates decreases as the acidity of the solvent increases. Acetic acid apparently forms few solvates.

The behavior of both amides as cryoscopic solvents has been investigated by Bruni and Manuelli.[9] Both solvents react with various mercury salts to give solvo-basic products.

In consideration of the above facts and in line with a series of investigations which are being conducted in this Laboratory,[10] the suitability of these substances as solvents for the electrodeposition of metals was believed to have sufficient theoretical background to warrant the experimental procedure outlined below.

Electrodeposition of Metals from Solutions of Their Salts in Formamide.—A preliminary study of this subject was made by Röhler,[7] who employed the following compounds as electrolytes for the deposition of the respective cations: $Pb(NO_3)_2$, $PbCl_2$, $CuSO_4$, Cu_2Cl_2, ZnO, $ZnCl_2$, $SnCl_2$. Metallic anodes composed of the metals to be deposited were used. Anodic losses were invariably found to be greater than the weight of the metal deposited. These differences were ascribed to the solvolysis of the respective electrolytes with the resultant formation of the metallic formamides and free acid. Subsequent chemical action of the acid thus formed upon the metallic anodes was postulated to account for these discrepancies. The character of the discharged metals was found to be influenced by dissolved oxygen, and by exposure of the solution to air, necessitating the use of a closed electrolytic vessel. Röhler made unsuccessful attempts to

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[8] Bruni and Manuelli, *Z. Elektrochem.*, **11**, 554 (1905).

[9] Bruni and Manuelli, *ibid.*, **10**, 601 (1904).

[10] The authors have studied the electrodeposition of metals from solutions of their salts in liquid ammonia and find that the results closely parallel those obtained in aqueous solution. The low temperature of deposition, however, does affect the character of the deposited metal.

deposit magnesium, aluminum, nickel, cobalt and iron from solutions of their respective chlorides.

These results were checked by the authors and supplemented by additional observations. For purposes of comparison all experiments were carried out at 100°. Fifteen cc. of formamide, purified by vacuum distillation, was placed in a closed electrolytic cell fitted with a platinum anode of one sq. cm. surface area and a copper cathode of varying size. A stirring device was employed to prevent impoverishment of the solution in the neighborhood of the electrodes. A 110-volt direct current, in series with a lamp-bank for variable resistance, was used. Results of typical runs are given in Table I.

TABLE I

ELECTRODEPOSITION OF METALS FROM FORMAMIDE AT 100°

Compound	Grams solute per 15 cc. solvent	Current density per sq. cm., amp.	Type of deposit
$Zn(CN)_2$	0.5	0.03	Adherent deposit. Continued electrolysis yielded spongy material
$Cd(CN)_2$	1.4	.02	Smooth, adherent deposit
$Pb(NO_3)_2$	3.0	.03	Non-adherent
		.06	Crystalline. Deposit is not uniform, but adheres only in spots
SnI_4	1.0	.04	Smooth, adherent
$(NH_4)_2SnCl_6$	2.0	.04	Excellent deposition
$Co(C_2H_3O_2)_2{\cdot}4H_2O$	2.0	.02	Poor deposit
		.05	Better deposition; adherent
$Ni(C_2H_3O_2)_2$	Satd.	.018	Fair, adherent deposit
$Ni(NH_3)_6Br_2$	2.0	.025	Good, adherent deposit

Where cyanides were used as electrolytes the odor of hydrogen cyanide soon became very apparent, indicative of the interaction of the solute with the solvent in accordance with the equation

$$Zn(CN)_2 + 2HCONH_2 = Zn(HCONH)_2 + 2HCN$$

This checks with previous observations made by Röhler, who noted that the solvolytic action of formamide upon dissolved metallic salts resulted in many cases in the formation of the free acid and the metallic formamide.

Cobalt and nickel plates were readily obtained. Even such complexes as nickel hexammino bromide were found to give very satisfactory results. The lesser stability of nickel complexes, noted previously from their behavior in aqueous solution, again differentiates these from the more stable cobalt complexes. In the hope that formamide might facilitate secondary dissociation of complex ions, such compounds as potassium cobaltic cyanide, potassium chromic chloride and potassium ferrocyanide were also investigated. No decisive results were obtained.[11]

[11] Preliminary experiments would seem to indicate that the stability of complex cations varies with the character of the solvent molecule which is associated. Franklin

Electrodeposition of Metals from Solutions of their Salts in Acetamide.—No work has been reported in which metals have been deposited from solutions of their compounds in fused acetamide. It has been shown by Bruni and Manuelli[9] that potassium iodide is almost completely dissociated in acetamide and that anhydrous manganous chloride, cobaltous chloride and cupric chloride are highly dissociated. When hydrated salts are dissolved, water is completely split off. Walker and Johnson[12] measured the electrical conductance of potassium chloride, iodide and cyanide and found them to be good conductors. Solutions of mercuric chloride were also found to conduct, but not as well as those of potassium chloride. Belladen[13] showed that the specific conductances of the halides of sodium, the chlorides of barium and calcium and potassium iodide bore the same general relationships to each other as in aqueous solution. In the case of cadmium iodide it was shown that stepwise dissociation took place with formation of the complex $CdI_4^{=}$ ion.

The electrolytic cell was the same as that described in the work with formamide. All the experiments were carried out at 100°. The acetamide was purified by vacuum distillation. Ten grams of acetamide and an amount of salt to make the solution approximately molar were used in each case. The average run was one or two minutes in duration.

TABLE II

ELECTRODEPOSITION OF METALS FROM ACETAMIDE AT 100°

Compound	Grams solute per 10 g. solvent	Current density per sq. cm., amp.	Type of deposit
$Zn(CN)_2$	0.117	0.05	Deposit localized
$Cd(CN)_2$	.164	.03	Smooth, adherent
SnI_4	.624	.05	Smooth, bright
$(NH_4)_2SnCl_6$	.368 (not completely soluble)	.04	Smooth, bright, "treeing" after two minutes
$PbCl_2$	.278	.037	Spongy, non-adherent
$Ni(NH_3)_6Br_2$	.320	.03	Good, adherent; higher current densities give a black powdery deposit
$Co(NH_3)_5Cl_3$	.250		No deposit
$K_3Co(CN)_6$	.332		No deposit
$CoCl_2$	....	.02	Smooth deposit; higher current densities give a black powdery deposit
$TlC_2H_3O_2$	.263	.025	Some adherent deposit, marked "treeing"

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has already shown that complex cations form much more readily in liquid ammonia than in water. Evidence already on hand in the chemical literature indicates that the more basic the donor molecule or solvent, the more stable the complex cation which is formed and the greater the tendency and the greater the number of such solvates probably capable of existence.

[12] Walker and Johnson, *J. Chem. Soc.*, **87**, 1597 (1905).

[13] Belladen, *Gazz. chim. ital.*, **57**, 407 (1907).

The solution of the nickel salt was an intense green and that of the cobalt a deep blue. In every case there was some evolution of gas at the cathode.

A number of experiments were performed using hydrated salts of the metals given in Table II and unpurified acetamide that contained considerable water. The deposition was good in each case. When 1 cc. of water was added to the solution of $Zn(CN)_2$ in the purified acetamide, an excellent deposit was obtained.

Summary

1. Zinc, cadmium, lead, tin, cobalt and nickel were deposited electrolytically from solutions of their salts in formamide. Current densities were of the order of 0.02 to 0.04 amp. sq. cm. The temperature was 100°.

2. Zinc, cadmium, tin, lead, cobalt, nickel and thallium were deposited from solutions of their salts in acetamide, under similar conditions.

3. Metals higher than zinc in the electromotive series were not deposited from solutions in either solvent.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE VOLUMETRIC DETERMINATION OF THIOCYANATE WITH IODINE AND WITH IODATE

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It has long been known that the quantitative oxidation of thiocyanate with iodine is extremely slow in neutral or in acid solution. The reaction is

$$NCS^- + 3I_2 + 4H_2O \longrightarrow SO_4^= + CN^- + 8H^+ + 6I^+ \qquad (A)$$

In slightly alkaline solution the above reaction is comparatively rapid, and a consecutive reaction occurs, $I_2 + CN^- \longrightarrow ICN + I^-$, giving the final quantitative relation

$$NCS^- + 4I_2 + 8OH^- \longrightarrow SO_4^= + 7I^- + 4H_2O + ICN \qquad (B)$$

Upon acidification the iodocyanogen again instantly and quantitatively reacts with iodide to form free iodine and cyanide. In the presence of a suitable buffer, Reaction B should go to completion rapidly with a moderate excess of iodine. Upon acidification the iodine in excess of that required for Reaction A may then be determined by back titration with standard thiosulfate, using starch as indicator.

During the past year we have investigated the iodimetric determination of zinc as zinc pyridine thiocyanate. Since pyridine interferes with the iodine titration it was hoped that a suitable non-volatile buffer might be found which would expel the pyridine on boiling and subsequently serve as a buffer for the oxidation reaction. Disodium hydrogen phosphate proved somewhat unsatisfactory, but borax served both purposes admirably. The suitability of borax as a buffer was studied with respect to time re-