zene have been determined and the results have been recorded as graphs and as empirical equations.

4. Each of the systems studied has been critically discussed, and an attempt made to explain the nature of the deviations between the molal heat capacities of the pure liquids and the partial molal heat capacities in solution. It is evident that the changes taking place on solution are intricate, and that dissociation phenomena are probably more important than has been recognized.

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THE ELECTRONEGATIVE POTENTIAL SERIES IN LIQUID AMMONIA

BY F. W. BERGSTROM[1]

Introduction

As has been pointed out by Kraus[2] the elements may be arranged in two electropotential series, or series of electro-affinity, depending upon whether the element functions as cation or as anion. In general, an element in the electropositive series will displace a less electropositive element from solutions of its salts; similarly, in the electronegative series, an element will in general displace a less electronegative element from solutions containing this latter as homo-atomic anion.[3] It is the purpose of the present investigation to establish the order of electro-affinities of the elements in the negative condition by means of a study of such replacement reactions.

The order of replacement of the elements in the electronegative state in water is but incompletely known, because salts of homo-atomic anions of many of the elements are unstable in this solvent. A few well-known reactions will serve for illustration:[4] $F_2 + 2KCl = 2KF + Cl_2$; $Cl_2 + 2NaBr = 2NaCl + Br_2$; $Br_2 + 2NaI = 2NaBr + 2I$; $2(Cl,Br)_2 + Na_2S = 2Na(Cl,Br) + S$.

Homo-atomic anions containing lead, tin, arsenic, antimony, bismuth and phosphorus, as well as the more electronegative elements tellurium, selenium, sulfur, iodine, bromine and chlorine are stable in liquid ammonia solution.[5] Accordingly, this solvent was chosen in order to make a more

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[1] National Research Fellow.

[2] Kraus, *Trans. Am. Electrochem. Soc.*, **45**, 175 (1924).

[3] Such as Br^-, I^-, S_5^{--}, Se_x^{--}, etc. (Nomenclature of Kraus.)

[4] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans and Co., London, **1922**, vol. II, pp. 13, 92, 93, 113. Friend, "Text Book of Inorganic Chemistry," Griffin and Co., London, vol. VIII, pp. 9, 28, 69, 205.

[5] Hugot, *Compt. rend.*, **121**, 206 (1895); **129**, 299, 388, 603 (1899). Joannis, *ibid.*, **113**, 795 (1891). Peck, THIS JOURNAL, **40**, 335 (1918). Smyth, *ibid.*, **39**, 1299 (1917). Kraus, *ibid.*, **29**, 1557 (1907); **44**, 1221 (1922).

complete study of replacement reactions involving elements in the negative state.

The Electronegative Replacement Series in Liquid Ammonia

In the following series, an element in general will replace any element on its left from solutions containing that element as a homo-atomic anion: lead, bismuth (?), tin, antimony, arsenic, phosphorus (?), tellurium, selenium, sulfur, iodine. As equilibria occasionally exist between adjacent elements in the series and solutions of salts containing them as anions, the order of replacement may be reversed by a proper change in concentration. For instance, the solution in equilibrium with selenium and tellurium contains a relatively large proportion of Se_x^{--} ions. Selenium is thus more electronegative than tellurium, and is therefore given a place to its right in the replacement series.

As the alkali metal hydrargides are insoluble in ammonia, mercury is not comparable with the other elements of the series, whose sodium and potassium salts are soluble. Accordingly, mercury cannot be assigned a place in the series on the basis of the present experimental work. Bismuth may not be correctly placed in the series, for the reactions in which bismuth or the polybismuthides of sodium and potassium took part were sluggish and not as definite as might be desired. Phosphorus is more negative than arsenic, but its exact position in the series is uncertain. Iodine is more negative than sulfur, judging from the rates of the reactions of these two elements with ammonia and with potassium amide.

Phosphorus, sulfur, iodine and possibly arsenic cannot be precipitated from solution by the action of other elements. It is probable that in these instances the element either dissolves[6] in liquid ammonia at the moment of its liberation, or forms hetero-atomic anions of the type of Cl_2I^-.

The replacement of one element by another was found to be the more definite and the more rapid the farther apart the elements were situated in the series. One may approximately predict the chemical reactivity of an element from its position in the potential series when, in one of the products of a reaction, that element is present as a homo-atomic anion. Thus, in general, the elements to the right in the series react the more vigorously with solutions of the alkali metals or potassium amide in liquid ammonia.[7] Lead, however, reacts more readily than bismuth, tin or antimony with solutions of sodium or potassium.

A current of dry air completely oxidizes liquid ammonia solutions containing homo-atomic anions formed from tellurium and elements to the

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[6] Iodine and sulfur, for instance, are known to react chemically with the solvent. (a) Ruff, *Ber.*, **33,** 305 (1900). (b) Ruff and Geisel, *Ber.*, **38,** 2659 (1905).

[7] The reactions between potassium amide and the elements in the table are all of the general type $Cl_2 + 2KOH = KClO + KCl + H_2O$. A complete discussion will appear in a forthcoming paper.

left of it in the series, but has little or no action on salts of anions containing elements to the right of tellurium.[8]

Experimental Work

All of the reactions to be described were carried out in liquid ammonia in the complete absence of air and, unless otherwise mentioned, at room temperatures. The methods of manipulation developed by Franklin and his co-workers have accordingly been used to a large extent.[9] In case of reactions requiring some time for completion, ammonia was distilled into the reaction tube maintained at a temperature of —40° by a bath of liquid ammonia, the small side-tube then immediately being sealed off. This enabled one to dispense with the stopcock customarily attached to the reaction tube.

Metallic alloys of the type of K_4Pb_9, soluble in liquid ammonia, may in general be prepared by the action of a solution of sodium or potassium upon an excess of the more electronegative element.[5] The polysulfides, -selenides, -tellurides, -arsenides and -phosphides were conveniently prepared in this manner. It was found that some potassium amide was formed in the reactions between solutions of potassium and lead, tin and bismuth. Accordingly, the alloys of the alkali metals with these three elements were made by fusion of the two reacting substances in closed, steel tubes. The alloys were broken up in a current of ammonia and preserved in sealed glass tubes of 15–20 mm. diameter, which had been drawn down at the ends to 6–8 mm. to facilitate introduction of material into the reaction vessels.

The reactions which served to determine the electronegative potential series are summarized in Table I. The potassium or sodium salt of one of the elements, A (in the upper horizontal column) (K_4Pb_9, K_3Bi_x, K_2Se_{4-5}, Na_2Te_4, K_3P_x, Na_4Sn_8, etc.) was allowed to react with an excess of one of the elements B. (In the vertical column on the left.) The reactions have been divided into a number of classes, designated by numerals, additional details of significance being described in footnotes. In certain instances, the experiments were repeated several times. In cases of a slow replacement, the sealed tubes containing the reacting substances frequently were under observations for six months or more.

It is of interest to note that many of these reactions are reversible. Thus, $K_2Te_4 + 5Se \rightleftharpoons K_2Se_5 + 4Te$. Some reactions, which under ordinary conditions, go almost to completion in one direction, may be reversed

[8] A more detailed discussion will appear in a forthcoming paper. The solutions were oxidized while cooled to —33°.

[9] Franklin and others, THIS JOURNAL, **27**, 832 (1905); **29**, 1694 (1907); **35**, 1460 (1913); *J. Phys. Chem.*, **15**, 915 (1911); **16**, 694 (1912). A modification of the reaction tube described by Kraus and Chiu [THIS JOURNAL, **44**, 2003 (1922)] was used in the experiments at —33°.

TABLE I

SODIUM OR POTASSIUM SALT OF HOMO-ATOMIC ANION A

Element B	Pb_9	Bi_x	Sn_8	Sb_x	As_x	P_x	Te_{4-4}	Se_{4-8}	S_4	I^-	Hg_x
Zn	5	..	..	..	..	..	..	..	..	..	..
Fe	4[a]	..	..	..	..	..	..	..	..	..	..
Cu	4[a]	..	5	..	..	..	..	..	..	..	..
Pb	..	4	4	..	..	..	..	..	..	..	..
Bi	3	..	4	..	..	..	..	..	..	..	..
Sn	1a[b]	3[c]	..	..	..	..	..	..	..	..	..
Sb	1a	3	1a	..	4a	..	..	..	..	..	3a
As	1a	..	..	3	..	4a	4a	7b[e]	7b[f]	..	1b
P	1a	..	..	1a	7a[g]	..	7	..	..	..	1b
Te	..	..	..	1a	7a	7a[h]	..	2	..	..	..
Se	..	..	..	..	..	..	2[i]	..	7a	5[l]	1b
S	1[j]	..	..	1[j]	..	..	..	2[k]	..	..	1b
I	..	..	..	..	..	..	..	1	7a	..	..
Hg	6[d]	6	6	5	5	..	..	..	..	..	..

1. Fairly rapid and complete or nearly complete replacement of A by B. A Na or K salt of a homo-atomic anion B_x is formed. Thus, $(2x + 2)$ S + K_4Pb_9 = 2 $K_2S.S_x$ + 9 Pb.

1a. Replacement of A by B is slow, due to the formation of a precipitate of A which diminishes the free surface of B. Replacement of A, in time, is nevertheless complete or nearly complete.

1b. Reaction readily takes place.

2. Replacement of A by B is fairly rapid, but not complete. An equilibrium is reached.

3. The reaction is slow and incomplete, and no definite conclusions can be drawn therefrom, owing perhaps to the formation of a coating of the precipitated element A on B.

3a. A slow reaction.

4. When B is treated with a very dilute solution of the K or Na salt of A_x, decolorization of the solution occurs with precipitation of a small amount of A. A larger quantity of this solution fails appreciably to react with B. (Successive small amounts of K_4Pb_9 soln. very slowly decolorize in contact with Cu or Fe.)

4a. A slight replacement of A by B.

5. No evidence of a definite reaction.

6. An alloy of this composition is removed from solution by metallic mercury.

7. B is dissolved, but A is not precipitated. (a) The element A at the moment of liberation from its salt may dissolve in the liquid ammonia. (b) Perhaps compounds of the nature of sodium thio-arsenite or seleno-arsenite are formed.

[a] Probably a very slow ammonolysis of K_4Pb_9 catalyzed by Cu or Fe.

[b] In most of the experiments performed, replacement of lead by tin was almost complete after a few months. A portion of the lead was frequently deposited upon the tin rod in well-defined metallic crystals.

[c] Tin and tin amalgam react much more rapidly with dilute solution of sodium or potassium amides than does bismuth or bismuth amalgam. This would indicate that tin is more electronegative than bismuth, a conclusion not in accord with the best available data on the free energy of formation of Na_3Bi_x and Na_4Sn_x. See Kraus and White, Ref. 2, p. 182.

[d] Mercury is even less electronegative than lead, judging from the relative low free energy of formation of the mercurides. See Gehrcke, THIS JOURNAL, 45, 2507 (1923). Ref. 2, p. 182.

e Judging from the amount of arsenic dissolved by a known weight of K_2Se_4, it is possible that potassium seleno-arsenite, $KAsSe_2$, is formed.

f The reaction product is extremely soluble in ammonia, and may be a potassium thio-arsenite or arsenate.

g Arsenic does not appear to be precipitated when a solution of sodium polyarsenide is electrolyzed at —33° with a mercury cathode (which dissolves the liberated sodium) and a platinum anode, the entire solution deepening very markedly in color. It is possible that the arsenic dissolves in ammonia, under these conditions. One modification of arsenic (yellow arsenic) is readily soluble in carbon disulfide. [Erdmann and Unruh, *Z. anorg. Chem.*, **32**, 437 (1902).]

h Yellow phosphorus is slowly dissolved by ammonia at room temperature. Franklin and Kraus, *Am. Chem. J.*, **20**, 828 (1898). Hugot, *Ann. chim. phys.*, **21** (7), 28 (1900). Stock, *Ber.*, **36**, 1120 (1903).

i A weighed stick of selenium was allowed to react with a solution of potassium ditelluride at —33°. Tellurium was precipitated. At equilibrium there was found in the solution between 2 and 2.5 mols. of K_2Se_5 per mol. of K_2Te_4. The solution was 0.07 N with respect to K.

j A solution of sulfur in liquid ammonia accomplishes the same result, but more rapidly.

k Most, but not all, of the selenium is precipitated from a solution of K_2Se_5 at —33° by solid sulfur. Subsequently a soluble sodium polysulfide is formed, in the presence of an excess of sulfur.

l This reaction is complicated by the fact that iodine reacts so readily with the solvent. Ref. 6.

under certain conditions. Thus, actually, $K_4Pb_9 + 8\text{--}9 \text{ Sn} \rightleftharpoons K_4Sn_{8\text{--}9} +$ 9Pb. Similar equilibria are of course well known in water. Thus, Smith[10] found that copper may even precipitate zinc and cadmium in small amounts from aqueous solution.

In conclusion, the author wishes to express his thanks to Dr. C. A. Kraus for suggesting this problem, and for his kind and helpful interest during the investigation.

Summary

1. The electronegative replacement series has been determined in liquid ammonia. In general, an element will displace any element to the left of it in the following series from solutions containing that element in a homo-atomic anion. As in the case of the electropositive series, the order of replacement in certain instances depends upon the concentration of the solution. Lead, bismuth (?), tin, antimony, arsenic, phosphorus (?), tellurium, selenium, sulfur, iodine.

2. The reactions which served to establish the above replacement series have been described. A few instances have been pointed out of a parallelism between the rates of chemical reactions in which the reacting element enters a homo-atomic anion, and the order of the electronegative potential series.

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10 Smith, THIS JOURNAL, **27**, 543 (1905).