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Semiannual Summary Report
Period Ending 31 August 1961
"STABLE DENSE COLD PLASMA"

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ABSTRACT

The first major objective of the program has been successfully achieved, namely, it has been established that metallic gaseous solutions with significant lifetimes may be synthesized at low temperatures. These plasmas are thermodynamically stable with respect to the ionization process, but unstable with respect to the chemical reaction between metal solute and gaseous solvent.

Cold dense gaseous plasmas have been prepared and maintained at 137°C for six minutes and at 149°C for seven minutes. In appearance these plasmas, contained in glass capillaries, look like gold-copper wires.

Normally, a material such as sodium is a metallic conductor in both the solid and liquid states, but an electrical insulator in the gaseous state. Use of a gaseous solvent produces a medium which provides a high dielectric constant (thus reducing the force between the ion and electron), and solvation (which stabilizes the positive ion). These effects permit the existence of gaseous sodium at high concentrations in highly ionized states at the relatively low temperatures of 133 to 200°C .

BRIEF REVIEW OF BACKGROUND

Before proceeding with a description of the experimental program itself, the background to this project will be reviewed briefly in this section.

The first objective of this program is to synthesize and maintain gaseous plasmas at low temperatures with electron densities comparable to those of the liquid metals. Present techniques for the preparation of gaseous plasmas are based on either fragmentation by particle bombardment or thermal dissociation at extremely high temperatures; in both cases, energy must continually be added to maintain the plasma. In the present program a chemical synthetic approach is taken. The basis of this approach is to use dielectric constant and solvation to produce thermodynamically stable, electrically conducting gaseous solutions at relatively low temperatures. Solubilization of solids in the gas phase, and their ionization, is adequately provided by the above; for example, NaCl dissolves readily to form an electrolytic solution in dense water gas above 370°C. In such instances the electrical conductivities are low, the conductivity mechanism being electrolytic rather than electronic.

In order to obtain gaseous plasmas with very high conductivities, metallic rather than electrolytic solutions are necessary. The proposed solution to this requirement is as follows: Metallic sodium dissolves in liquid ammonia with the formation of a true solution, the sodium being present as Na⁺ and electrons. Concentrated solutions have a metallic gold-copper reflectivity, the conductivity at room temperature being about half that of liquid mercury. Hence, sodium-ammonia solutions may have the requisite conductivity characteristics for gaseous plasmas. The sodium-ammonia solutions are stable with respect to ionization, i.e., the plasmas do not require energy input to produce high electron densities.

Unfortunately, there is a chemical reaction between sodium and ammonia, as follows:



At room temperature very pure solutions may last months before this reaction occurs appreciably. The reaction is catalyzed by impurities as well as by the product, NaNH_2

In 1880, the sodium-ammonia solution was produced in the gas phase for a few seconds before the above chemical reaction used up the sodium (this being visually observable by the disappearance of the characteristic color of the sodium-ammonia solution). The first objective of the present program was therefore centered around the problem of obtaining these metallic gaseous solutions for longer periods of time. As noted in the following sections, it has now been established that gaseous solutions can last for at least seven minutes with respect to the sodium-ammonia reaction

TECHNICAL FINDINGS

The principal technical findings to date have been as follows:

1. Gaseous plasma lifetimes of at least seven minutes are obtainable. As stated earlier, two gaseous solutions behaved as follows:
137°C for 6 minutes before visible reaction between Na and NH₃ started
149°C for 7 minutes without visible reaction--at which time the glass capillary ruptured.
2. Solubility of sodium in ammonia appears to increase markedly above 96°C near the melting point of sodium, which is 97.5°C. This is in contrast to the behavior at -105 to 0°C, in which range the solubility decreases slowly with temperature. About one volume of sodium dissolves in one volume of concentrated sodium-ammonia solution.
3. The critical points of sodium-ammonia solutions vary over at least the range 134°C to greater than 183°C.
4. It has been observed that a metallic phase which appears to be visually different from pure sodium is produced at the higher pressures and temperatures. This phase might consist of Na(NH₃)₄. When ammonia is pumped off the sodium-ammonia solution, only metallic sodium remains (plus any traces of impurities); whereas, in the case of calcium, metallic Ca(NH₃)₆ remains, this material being essentially a solvated or coordinated metal. It is possible that at the higher pressures encountered in this program, the decomposition pressure for a stable Na(NH₃)₄ complex is exceeded.
5. Rupture temperatures of the glass capillaries containing the gaseous plasma have been raised with continuing improvement in techniques. Thus, in the first quarter, 123°C was the maximum temperature reached before rupture. In the second quarter, there were a number of runs above 133°C, the critical temperature of pure ammonia, as follows:

134°C
155°C - without rupture
136°C
150°C - without rupture. $T_c = 134^\circ\text{C}$
149°C - critical temperature of this
solution, $T_c = 145^\circ\text{C}$
148°C
147°C
166°C
183°C - 13 minutes above 133°C.

Preparation of the solutions

The principal problem that must be solved in order to obtain long lifetime of the sodium-ammonia solution with respect to its decomposition is that of preparing these solutions in states of high purity.

In particular, both the sodium and the ammonia must be purified to a high state of purity. The transfer of these materials into the test container must be accomplished without introduction of impurities and in such a manner that the reaction of ammonia with sodium is not encouraged (such as by passage over catalytic walls). The test cell must be of such material as to introduce a minimum of impurities or catalytic materials. In the present technique, Pyrex capillary is used as the test cell, the sodium and ammonia being driven to the bottom end of a Pyrex capillary and the top sealed off in vacuo with the solution kept at liquid nitrogen temperatures. This seal-off technique undoubtedly produces contaminants; in particular, it has been observed that discolored materials are produced if any of the sodium or ammonia solution adheres to the glass in the neighborhood of the seal-off.

Ammonia

Ammonia is being processed as follows: tank ammonia (Matheson, purity 99.99% minimum) is condensed into a still pot containing metallic sodium which is used to remove water. While refluxing in a vacuum-jacketed fractionating column about 20" long and 25 mm i.d., packed with Raschig rings, the first ammonia fraction is transferred to a waste vessel, then the middle fraction to a second still pot, which again contains metallic sodium to ensure the drying of ammonia. Whereas the first fractionating column is operated at atmospheric pressure, the second is vacuum-operated. Again the first portion is transferred to a waste flask, then the middle portions to the test cells.

The ammonia purification system went through a number of stages before the present operational unit was arrived at. The following combination of problems was first resolved: (1) the boiling point of ammonia is -33°C (i.e., below room temperature); (2) vacuum fractionation is being used (in contrast to the more usual atmospheric pressure fractionations); and (3) greaseless valves are used to reduce contamination of the ammonia. Condensers operated at -35°C to -60°C are used above each purification stage as well as each test cell seal-off station.

The only additional feature that is planned for the near future on the ammonia purification system is the introduction of electrodes to measure the electrolytic conductivity of the purified liquid. This will provide quantitative information as to the degree of the purity of the ammonia.

At a later stage, if it becomes desirable to prepare ammonia of even greater purity, there are alternative techniques for preparing ammonia of high purity in small quantities. For example, a saturated solution of ammonium chloride is boiled with 1/10 of its volume of concentrated nitric acid until free from HCl, the solution is evaporated and ammonium chloride allowed to deposit. The ammonium chloride is further recrystallized to free it from ammonium nitrate. The chloride is mixed with soda lime and

gently heated in vacuo. The ammonia thus produced is dried and purified further by means of the fractionating process described earlier.

Metallic sodium

Originally it was planned to introduce pure sodium into the vacuum system by electrolysis through soda glass, this being a technique introduced by Burt. It would not only provide pure metallic sodium, but measurement of the current through the glass would provide a quantitative measure of the amount of sodium introduced. Because of the mobility of gaseous sodium in a vacuum system, this technique has not been adopted. Instead, metallic sodium is placed in a side arm and distilled in vacuum to the region of the test cell. Although results indicate that, for the time being, the simple distillation of sodium yields sodium of adequate purity, at a later stage it may become desirable to re-evaluate the sodium purification and introduction system.

FUTURE WORK

In the third quarter, materials studies will be carried out, and in the fourth quarter, preliminary conductivity studies.

Techniques and results are being evaluated to learn ways of obtaining additional experimental information. Analyses will be completed shortly on methods of measuring electron concentrations in the plasma contained in the capillary.

The pros and cons of the present capillary test cell, of an external pressurization on the glass capillary, and of a high-pressure system to be used instead of the capillary, will be evaluated when materials data have been established.

The principal difficulty with the use of the simple classical technique of filling a glass capillary with the solution and sealing off in vacuo is that internal pressures of 110 to 250 atmospheres are built up as the temperatures are raised above 133°C. These pressures frequently cause rupture of the capillary. In order to increase the reliability of these tests and to reduce the frequency of these ruptures, a glass strain gauge is used to check out the annealing procedure.

Until adequate information is obtained from the next phase of the program on materials that may be placed in contact with the sodium-ammonia solution with respect to low catalytic action, construction of pressure equipment is not practical.

An external pressurization system to prevent rupture of capillaries is less useful than a pressure system with the solution in direct contact with the container walls. In the long range, the question of the type of test container to be used, namely, a glass capillary or pressure vessel, is dependent on the type of data desired. The glass capillary is useful for visual aspects as well as for measurements of electron concentrations and electrical conductivity. The pressure vessel is useful for determining compositions; for example, the best way of determining the critical point is by analysis of the compositions of the gas and liquid phases.

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