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EQUIPMENT AND PROCEDURES FOR STUDYING THE EQUILIBRIUM SOLUBILITY OF IRON IN NaK

by

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ABSTRACT

This study of the equilibrium solubility of iron in NaK was part of a program to investigate the mechanisms whereby solid metals are attacked by liquid metals in engineering systems. Careful consideration was given to several experimental solubility methods and the equipment and procedures are described in detail. A trial run of the most promising method was made, and the equilibrium solubility of iron in NaK at 700°C was found to be 15 ± 3 ppm. The solubility methods that were devised made no provision for particles of iron that might remain suspended in NaK upon precipitation from saturated solutions on cooling. In tests that were performed to determine the degree to which this phenomenon occurred, little, if any, tendency for suspension was found.

This study was discontinued because of a shift in emphasis to other work.

I. INTRODUCTION

This study of the equilibrium solubility of iron in NaK was intended as one of a series of investigations aimed at providing accurate, fundamental data for the solution of materials of construction problems anticipated in the field of liquid metal cooled nuclear reactors. The mechanisms whereby solid metals are attacked by liquid metals in engineering systems are not understood. Numerous variables, some of which are time, temperature, impurities, and the presence of other metals, must be studied systematically before optimum operating conditions can be determined.

In this study it was proposed to determine the solubility of pure iron in NaK as a function of the following:

1. Composition of the NaK - from pure sodium to pure potassium
2. Temperature - up to 850°C
3. Time
4. Non-metallic impurities - especially oxygen
5. Some metallic alloying elements in steel.

This investigation was discontinued after careful consideration had been given to several experimental methods for determining solubility of iron in NaK and a trial test of the most promising method had been made. It was also necessary to make several tests to determine the tendency for iron to remain in suspension after it precipitates from NaK on cooling.

II. EXPERIMENTAL TECHNIQUE

A. Preliminary Considerations

The development of a solubility technique was complicated by the following considerations:

(1) The solubility of iron in NaK appears to be extremely low. A value of 19.5 ± 1.7 ppm in pure sodium is obtained by extrapolation to 700°C of the data of L. Epstein(1) and a value of 15 ± 3 ppm at 700°C in eutectic NaK was obtained in a preliminary test (see Part IV) by the authors.

(2) Iron is such a universally distributed element that a serious contamination problem arises when one has to deal with concentrations on the order of a few ppm.

(3) NaK, especially when hot, has a strong affinity for oxygen, water vapor, carbon dioxide, etc., in the atmosphere. Therefore, it must be handled in tight equipment under vacuum or inert gas.

(4) The vapor pressure of NaK becomes appreciable at higher temperatures. This means that unless the entire solubility apparatus is uniformly heated, fractional distillation of the NaK could occur, causing the composition of the solution to vary continuously during the course of the test.

(5) At elevated temperatures liquid NaK and NaK vapors are aggressive toward some common laboratory materials, which limits the choice of containers. Glass or quartz apparatus, for example, would have to be restricted to temperatures below 300°C.

A well-known technique for solubility studies consists in heating the solvent in a sealed, thin-walled iron capsule, then quickly quenching in oil, machining open the capsule, and drilling an analytical sample from the center of the frozen solvent. Such a sampling procedure would be difficult and involved for NaK alloys which freeze below room temperature. L. Epstein(1a) has utilized this method for Na and has found that heterogeneous segregation of the solute occurs during the segregation.

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Electrochemical concentration cells of the type M-pure/ M-ionic (fused salts)/M alloyed are often used for determining the activity of a metal in a binary alloy at elevated temperatures. This method is not feasible unless M is the more electropositive component and its concentration in the alloy is relatively low. Iron is much less electropositive than NaK.

Three techniques which appear feasible are described below. They are based on the obvious philosophy of using a small, hermetically sealed, all-metal system and sampling at test temperature in an iron-free crucible. The first method is probably the simplest and most versatile; it is presented in greater detail.

B. Materials of Construction

The metals recommended for the various components of the solubility unit are as follows:

(1) For the outer cartridge (including cover and capillary tube), 347 type stainless steel or nickel. Type 347 stainless steel had the advantage of being easier to weld. Nickel, on the other hand, is easier to clean and is relatively free of iron.

(2) For the iron component, high purity carbonyl iron or Westinghouse "Puron" iron. Welds are to be avoided.

(3) For the sampling crucible, tantalum, for want of something better. Tantalum has been used in preliminary solubility tests (see Part IV) and looks promising. It possesses several important virtues. It can be fabricated easily into crucibles by deep drawing (available from Fansteel Metallurgical Corporation). It is readily amenable to outgassing. It is resistant to attack by pure NaK or NaK vapors at elevated temperatures and to any cold acids (except HF) which may be employed in the chemical analysis procedure. In each of three leach tests on tantalum crucibles, less than 0.1 ppm of iron was picked up by 20% HCl standing for 15 hours. Possible disadvantages of tantalum are its cost, its rather high iron content (usually about 0.03%), and its susceptibility to attack by NaK containing oxygen and by even weak alkaline solutions.

(4) For the crucible spacer, nickel or tantalum. Contact of the sampling crucible with iron fosters contamination.

C. Method 1

The parts and assembly are illustrated in Figure 1.

The flange on the cartridge is made by spinning. The nickel or tantalum spacer centers the tantalum crucible and prevents it from touching the iron. The iron crucible cover prevents foreign matter from dropping into the NaK. The volumes of the iron and tantulum crucibles are 17 cc and 19 cc, respectively.

The sequence of operations in the experimental procedure is as follows:

The inside surfaces of the cartridge are acid etched to remove scale and then electropolished. The welds are tested for vacuum tightness with a helium mass spectrometer type leak detector.

The tantalum crucible is rinsed several times with hydrochloric acid. A leach test is performed on every tantalum crucible before it is used in an experiment.

The inside surfaces of the iron crucible and cover are electropolished, preferably, or cleaned with dilute HCl followed by passivation with NaOH solution.

All parts are thoroughly degreased in a trichloroethylene vapor degreaser, washed with distilled water, and dried with pure acetone or alcohol. Thereafter they are handled by means of tongs or rubber gloves.

The iron and nickel parts are heated in a stream of purified hydrogen at 500 - 600°C (see Part III) to reduce surface oxides and to promote outgassing.

All parts are thoroughly outgassed in high vacuum (see Part III) at 850°C or above.

Impurity specimens, if called for, are introduced into the iron crucible.

The parts are assembled and the unit is purged with purified argon or helium gas. The cartridge cover is firmly pressed against the flange and is welded along the circumference by an inert gas-arc or by induction welding. The weld is tested for vacuum tightness by use of a helium mass spectrometer type leak detector.

The unit is connected to the NaK dispenser (see Part III) and 8 cc of pure NaK is transferred into the iron crucible through the capillary tube. Oxygen impurity, if called for, is added and is followed by a small amount of purified helium gas (see Part III) (enough helium to make the final pressure atmospheric or a little above when the unit is heated to the test temperature).

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After the unit is charged, the capillary tube is squeezed vacuum-tight near the cover by means of a vise. (The practicability of this sealing process has been proven by a number of tests with annealed tubing.) The tube is then cut as closely as possible above the sealed point and the end is heli-arc welded shut. The weld is tested for vacuum tightness. If tight, the unit is ready for heating; otherwise, it is rejected.

The internal parts of the unit can be used in experiments repeatedly, the cartridge cover only once, and the body of the cartridge perhaps twice. Twelve of each of the internal parts should be sufficient for a comprehensive study.

Three duplicate units are prepared for each solubility determination. They are mounted in an invertible carriage shown in Figure 2. The loaded carriage is suspended in a large heating bath (oil, salt, lead) as indicated in Figure 3 and slowly rotated in opposite directions alternately or in one direction intermittently for the purpose of stirring the NaK. The bath temperature is set at the proper value before the carriage is immersed and accurately controlled and recorded throughout the duration of the test. After the units have been held at temperature for some time, the carriage is inverted so that the NaK solutions will pour from the iron crucibles into the tantalum crucibles. The carriage is locked in the inverted position, then carefully raised out of the bath and quenched into oil. Quenching is recommended to inhibit any reaction of the tantalum with the NaK solution and to minimize diffusion of iron into the tantalum crucible.

For determining the rate of solution at a given temperature, different triads are inverted after different time intervals. For obtaining the equilibrium solubility, a triad is held at the equilibrium temperature for a prolonged period of time prior to inverting and quenching.

The quenched units are dismounted from the carriage and placed in an inert-atmosphere glove box where they are opened by shearing or grinding off the flange weld. The tantalum crucibles containing the solubility samples are extracted, cleaned off exteriorly with alcohol, and weighed to the nearest one-hundredth of a gram, all inside the glove box. Finally, they are sealed in a desiccator and submitted for chemical analysis.

The analytical technique devised by Kenneth J. Jensen at ANL is described in Appendix I.

D. Method 2

The unit is diagrammatically represented in Figure 4. It constitutes a simple modification of the first design wherein the crucibles (reduced in diameter and increased in length) are set at right angles to each other instead of at 180 degrees. Therefore, up to the point where the NaK solution is emptied into the sampling crucible, the experimental procedure is essentially the same as that of Method 1. A larger quantity of NaK can be accommodated by this unit.

After the unit has been heated in the bath for the prescribed length of time in the lambda position, horizontal spinning is arrested, and it is rotated approximately 90 degrees vertically so that the NaK will pour into the sampling crucible. Then it is counter-rotated to its original position and withdrawn from the bath. The lower part of the leg containing the empty iron crucible is cooled by means of an air blower while the upper part and the entire sample-containing leg are uniformly heated by an auxiliary furnace at a temperature convenient for distillation (about 450° C). In this manner the NaK is distilled back into the iron crucible leaving the dissolved iron deposited as crystals in the sampling crucible. The cycle of dissolution, delivery, and distillation is repeated a large number of times until a substantial amount of iron is accumulated. Only one unit is required for each solubility determination. If desired, the cycling process can be made completely automatic.

The test is concluded with the NaK in the sampling crucible. The sample is extracted and analyzed as in Method 1. The actual solubility is derived by dividing the apparent solubility by the total number of cycles.

Quite obviously, closed-system cycling is not suitable for the study of such impurities as oxygen.

This method achieves a higher degree of accuracy at the expense of simplicity. It has greatest utility in the investigation of the lower solubilities encountered at the lower temperatures or in the early stages of dissolution (short time intervals of rate studies) at any temperature. Also, the method should permit a wider choice of sampling crucible from the standpoint of purity since iron contamination from that source is less critical.

E. Method 3

The unit is diagrammatically illustrated in Figure 5. The cleaning and filling procedures are essentially the same as in the previous methods. The operation of the unit consists simply of the NaK seeping by gravity from top to bottom through the column of powder into the sampling crucible. The extra-coarse sintered iron filter (or perforated disc) pressed in at the bottom of the column serves to prevent iron particles from dropping into the sampling crucible. The flow rate of the NaK through the powder could probably be controlled by regulating the porosity of the powder, which is a function of particle shape, size distribution, and degree of compactness. The maximum porosity must not permit infiltration by NaK at room temperature. Powdered impurities can be added as in the previous methods.

The following advantages may be cited for this method:

(1) Iron powder and small diameter iron rods of extremely high purity are readily available.

(2) The large contact area of the powder obviates stirring and reduces the time element in a test.

(3) Inversion and pouring are eliminated.

The main disadvantages are:

(1) The method is not convenient for studying rates of solution. Surface area measurements are difficult and tedious. Flow rate control is difficult and entails an extensive series of calibration tests.

(2) Outgassing the powder is time consuming.

F. Radioactive Tracer Technique

The radioactive tracer technique has been used widely in situations calling for the detection and estimation of minute quantities of material, difficult or impossible to accomplish by ordinary chemical means. The literature abounds in references to applications of radio-iron.

Radioactive iron can be exploited for the study of iron solubility in NaK. Any of the three methods described above can incorporate the radioactivity feature, although Method 2 would be more or less defeating its own purpose. It is not unreasonable to expect a thousand-fold increase in sensitivity by the employment of a radioiron indicator. Moreover, it could simplify the design of the solubility unit by making possible the use of any NaK resistant sampling crucible material including iron itself.

Iron has two radio-isotopes suitable for tracer work, Fe^{55} and Fe^{59}. They can be procured from the Isotopes Division of the Atomic Energy Commission at Oak Ridge, Tennessee.

Fe^{59} has a half-life of 46.3 days and decays with the production of two beta particles of 0.26 Mev and 0.46 Mev energies accompanied by gamma rays of 1.30 Mev and 1.10 Mev energies. Fe^{55} has a half-life of 2.91 years and decays by K-capture emitting only weak Mn X-radiation of 5.9 Kev energy. Mixtures of the two can be prepared by neutron bombardment of iron in a nuclear reator or by deuteron bombardment in a cyclotron: $Fe^{58}(n,\gamma)Fe^{59}$, $Fe^{54}(n,\gamma)Fe^{55}$, and $Fe^{58}(d,p)Fe^{59}$, $Fe^{54}(d,p)Fe^{55}$. The individual isotopes are generally prepared in a cyclotron by the following transformation reactions: $Co^{59}(d,2p)Fe^{59}$, $Co^{59}(n,p)Fe^{59}$, $Cu(A-6, Z-3)Fe^{59}$ and and $Mn^{55}(p, n)Fe^{55}$, $Mn^{55}(p, n)Fe^{55}$, $Ni^{58}(n, \alpha)Fe^{55}$.

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Fe^{59} supplied by the AEC is recommended for the iron-NaK study. Fe^{59} is easier to detect than Fe^{55} because of its beta radiations and more energetic gammas.

Iron test surfaces can be activated conveniently by electroplating from a labeled iron solution or by a metal-ion exchange reaction with such a solution. The exchange reaction affords a means of determining true surface area.

III. SERVICE EQUIPMENT

A. NaK Purifier and Dispenser

Filtration is an effective and convenient way of removing from NaK dispersed solid particles such as oxides, hydroxides, hydrides, metals, etc.(2) The efficiency of particle removal is increased by repeated recirculation through the same filter.

A Pyrex glass, combination filtering-dispensing apparatus is illustrated in Figure 6. It operates as follows:

(1) Filtering - NaK is introduced into the top reservoir under vacuum through the filling tube which is then sealed off. Valve 2 and stopcocks 4 and 5 are closed during charging; valve 1 and stopcocks 1, 2, and 3 are open. Stopcocks 2 and 3 are then closed and the top reservoir is pressurized with purified helium through stopcock 1. The NaK is forced through the ultra-fine filters ($1.2\,\mu$) by the pressure difference and flows by gravity through the middle reservoir into the bottom reservoir. When almost all of the NaK has passed, stopcock 2 is carefully opened and filtration ceases. Then valve 1 is closed and valve 2 is opened. The top and middle reservoirs are evacuated slowly, causing the NaK to rise through the connecting tube from the lower to the top reservoir. When almost all of the NaK has been transferred, valve 2 is closed and stopcocks 2 and 3 opened. Then valve 1 is opened, stopcock 1 closed, and the middle and bottom reservoirs evacuated, resulting in filtration again. If more pressure is needed, stopcocks 2 and 3 are closed and gas is added to the top reservoir. In this manner the filtration cycle can be repeated any desired number of times.

The apparatus is cleaned prior to the addition of a new NaK alloy. For those alloys that melt above room temperature, the system may be heated by means of infrared lamps.

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If argon is used instead of helium, the cycling can be accomplished without replenishment of the gas and without the use of a vacuum pump. Alternate pressurizing and evacuating can be effected by freezing out and boiling off the argon in a trap situated in the gas-vacuum manifold. This is done simply by raising and lowering a flask of liquid nitrogen around the trap.

(2) Dispensing - The solubility unit (or a glass ampoule) is connected to the dispenser by means of a standard adaptor containing a thin-walled, nickel tube-funnel. The unit is evacuated through stopcock 4 while all other stopcocks are closed. It is purged several times with pure helium, then heated under high vacuum to a temperature above 100°C for final outgassing and drying.

With the NaK in the top reservoir, filtration is initiated as described above, but now valve 1 is closed as well as valve 2. This permits the NaK to accumulate in the middle reservoir until it rises above the level of the dispenser and pours into it. When the dispenser is full, valve 1 is opened and the excess NaK runs by gravity into the bottom reservoir.

Stopcock 5 is now opened and the nickel funnel is raised through the large bore by means of a magnet and slipped around the nozzle inside. In order to avoid contact with the grease in the stopcock, the funnel is centered by a thickened section in the sampler's female adaptor. The funnel is long enough to extend from the nozzle down into the male adaptor. The volume of the male adaptor is greater than 8 cc.

Stopcocks 1, 2, and 3 are opened. This simultaneously stops the filtration and drives the NaK from the dispenser into the solubility unit. Next, the funnel is lowered by means of the magnet and stopcock 5 is closed. The pressure in the solubility unit is adjusted through stopcock 4. The capillary is sealed and cut as described in Experimental Method 1 and another unit with clean adaptor and funnel are inserted for filling. One or two glass ampoules are filled for blank chemical analyses.

If a unit is designated to receive oxygen impurity, it is not sealed up immediately after charging with NaK. It is evacuated through stopcock 4. Then stopcock 4 is closed and the appropriate amount of pure oxygen is admitted through stopcock 6 from a measuring flask or burette. It is usually necessary to agitate the NaK and to heat it to about 70°C in order to insure complete reaction with the oxygen. A manometer should be provided in the oxygen manifold to indicate when the reaction is complete. Next, stopcock 6 is closed, helium is introduced, and the unit is sealed.

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The solubility of oxygen in sodium, potassium and NaK has been determined by several investigators, and the data is summarized in the Liquid Metals Handbook.(2)

B. NaK Purification by Distillation or Gettering

If filtration does not prove adequate, it can be supplemented by distillation and/or gettering. However, there is no concrete evidence that these methods are more effective.

For distillation, nickel stills are recommended. One still for sodium and one for potassium should be sufficient. NaK alloys can then be prepared easily in small quantities as needed.

For gettering oxygen in NaK, some success has been reported with the use of uranium, calcium, beryllium, or magnesium at elevated temperatures. Any of the following metals, which are capable of reducing sodium or potassium monoxide, might serve as well: Cr, Al, Zr, Ti, Ta, and Mo. The NaK should be intimately mixed with the getter for best results.

C. Vacuum-Gas Manifold

A satisfactory vacuum-gas manifold is illustrated in Figure 7. It contains a minimum of stopcocks and waxed joints and only one rubber connection (to the roughing pump). "Apiezon-M" grease is recommended for the stopcocks, "Apiezon-W" wax for the joints, and "Octoil-S" oil for the diffusion pump. The ultimate vacuum attainable with a system of this type is at least 10^{-7} mm of Hg.

D. Gas-Purifiers

Helium, hydrogen, and oxygen gases of very high purity are commercially available. However, further purification is necessary for NaK work.

"Lectrodryers" (activated alumina) are recommended for removing moisture from the gases. These dehumidifiers are capable of being reactivated.

Eutectic NaK alloy is convenient and effective for purifying helium and hydrogen. A temperature of 100° - 150°C is recommended for hydrogen. NaK reacts with hydrogen only to a very limited extent below 150°C. Tests have shown that oxygen is practically completely removed from helium by bubbling through NaK at room temperature. However, higher temperatures increase the propensity of NaK for scavenging such impurities as CO_2, H_2, organic compounds, etc. A temperature of 250° - 300°C is recommended.

Two practical, NaK gas purifier designs which have been used successfully at ANL for the purification of argon and helium gases are represented schematically in Figure 8.

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Needless to say, there are many other good gettering materials that can be used instead of or in conjunction with NaK. NaK will not react with nitrogen and is, at best, a very poor getter for hydrogen. Should it become necessary to remove nitrogen from the helium, molten lithium activated charcoal at liquid nitrogen temperature, or any of the following metals at about 750° - 800°C: uranium, titanium, zirconium, calcium, barium, and magnesium, can be used. For hydrogen removal, the following getters are recommended: uranium powder (prepared by the thermal decomposition of UH_3) at room temperature, molten lithium, palladium black at room temperature, and zirconium, calcium, barium or magnesium at about 450° C.

IV. PRELIMINARY EXPERIMENTS

A. Solubility Determination by Method 1

A complete solubility determination was made based on Method 1 to evaluate the practicability of this method.

Only one solubility unit was tested. Armco iron was used for the iron crucible and cover. The cartridge was of Type 347 stainless steel and the crucible spacer of nickel. Instead of using a heating bath, the unit was placed in a heavy Type 347 stainless steel block and heated in an invertible resistance tube furnace. The block was mounted on a shaft and rotated in opposite directions alternately every three revolutions at a rate of 30 R.P.M. by means of a small D-C motor. The NaK was purified by filtering twice through different ultra-fine (1.2μ) fritted Pyrex filters instead of by recirculation through the same filter. The duration of the test was 5 days and the temperature 700° C. Every operation proceeded smoothly.

Unfortunately, about one half of the sample was accidentally spilled and lost during the chemical analysis. The remaining portion analyzed 4.7 ppm of iron.

B. Suspension and Solubility Experiments

1. Preliminary Considerations

Certain facts gave rise to the suspicion that iron has a tendency to remain suspended in NaK when saturated solutions are cooled. For example, mass transfer, i.e., solution in a high temperature zone followed by deposition in a lower temperature zone, occurs to only a limited extent in dynamic NaK - iron systems.(1) On the other hand, drastic mass transfer has occurred in comparable mercury systems, even though the solubility of iron in mercury is considerably lower (0.96 ppm at 700° C) than it appears to be in NaK.(3)

The solubility methods described herein make no provision for suspended particles.

Suspensions might be avoided if the equilibrium temperature is approached from below and held "constant." However, if iron is highly prone to suspension, it is conceivable that small fluctuations in the equilibrium temperature would lead to the formation of suspensions.

Consequently, several experiments were performed to verify the phenomenon of suspension and to determine some properties of the particles.

2. Experiment I

This was a composite experiment to check the suspension-forming tendency under conditions of slow cooling and to determine the efficacy of low temperature filtration and distillation in the separation of the dispersed particle.

Twenty-five ml of M.S.A. eutectic NaK were heated under argon in a small Armco iron container (3/4" I.D. and 5" long, with low-carbon steel inlet tube, 1/4" diameter and 15" long) by means of a lead bath for 33 hours at 700°C. Before testing, the container was cleaned with dilute HCl, NaOH, and distilled water, and dried with acetone and by gentle heating under vacuum. After 33 hours at 700°C the furnace failed and the lead bath cooled very slowly to room temperature. This necessitated reheating the bath to its melting point in order to extract the test container, after which the container was allowed to cool slowly to room temperature under powdered asbestos.

At room temperature the container was inverted and four samples (approximately 5 ml each) were drawn under vacuum. The first sample was a blank; the second was filtered at room temperature through a medium (14μ) fritted Pyrex filter; and the fourth was partially distilled in Pyrex glass at 300° under vacuum.

The results of the chemical analysis were as follows:

(a)	M.S.A. NaK before heating	8.8 ppm
(b)	Test blank NaK (Sample 1)	3.2 ppm
(c)	Filtered NaK - medium filter (Sample 3)	2.6 ppm
(d)	Filtered NaK - fine filter (Sample 2)	1.2 ppm
(e)	Distilled NaK - (Sample 4)	1.9 ppm

A second sample of M.S.A. - NaK, taken from the same reservoir under similar sampling conditions, analyzed only 1.14 ppm of iron, thus throwing some question on the source of iron in sample (a). The iron content of this sample was slightly decreased (to 0.82 ppm) by filtering through a fine (5 μ) fritted Pyrex filter.

The data are a real indication that iron particles were present in a state of suspension and that filtration and distillation are promising methods of separation.

The iron in the distilled sample (e) may have been picked up from the Pyrex glass which was somewhat discolored, indicating attack by the NaK. Incidentally, the vacuum distillation at 300° C proceeded very slowly; the distillate was solid at room temperature.

It should be pointed out that the procedure used for cleaning the container may not have eliminated all of the iron oxide and that the container may not have been outgassed sufficiently. Also, the NaK used was not filtered or treated in any way to remove impurities.

3. Experiment II

This experiment was made as a recheck on the tendency of iron to become suspended under conditions of slow cooling and to observe the influence of time on the settling of the particles.

A large, Armco iron container (2" I.D. and 10" tall) which had 3 large low-carbon steel inlet tubes (3/8" I.D. and 14" long) symmetrically arranged at the top was used. Prior to using, the inside surfaces of the container were cleaned as in the first experiment and, in addition, by firing at 550° - 600°C for 4 hours in purified hydrogen (activated charcoal - liquid air purifier). The container was outgassed by heating under vacuum at a temperature of about 350°C for 2 hours. Six hundred and sixty ml of filtered NaK (coarse fritted Pyrex glass) were then introduced, followed by argon at atmospheric pressure, and the unit was heated in a lead bath at 700°C for 3 days. It was allowed to cool slowly to room temperature over a period of 8 hours, first in the lead bath and subsequently under powdered asbestos.

At room temperature 3 glass sampling pipettes filled with argon were inserted through the steel tubes to different levels in the 8" column of NaK: 1" below the surface, 4-1/2" below the surface, and 1/4" from the bottom. This arrangement was allowed to stand undisturbed for 4 days. At the end of this time, part of the gas in the pipettes was exhausted, permitting the NaK to rise into them for sampling. A fourth sample was taken after the pipettes were removed and the NaK in the container was thoroughly shaken. The samples were approximately 7 ml each.

The results of the chemical analysis were as follows:

(a)	Top	0.4 ppm
(b)	Middle	1.0 ppm
(c)	Bottom	0.5 ppm
(d)	Mixed	0.7 ppm

In a similar manner, samples were taken from the top and bottom of the large M.S.A. reservoir (15" column of NaK) after it had stood undisturbed for several weeks. (M.S.A. tanks are originally filled through steel pipes with NaK at elevated temperatures.) Some of these samples were filtered through medium fritted Pyrex filters. Every sample analyzed less than 0.7 ppm of iron and all values agreed within the accuracy of the analytical technique.

4. Experiment III

This experiment was made to get an estimate of the equilibrium solubility of iron in eutectic NaK at 700° C and to confirm the presence of suspended particles at an elevated equilibrium temperature (700° C).

The technique consisted of obtaining at 700° C two identical samples of the solution and filtering one through a fine porosity (less than 5μ) sintered iron filter at that temperature.

The apparatus is diagrammatically illustrated in Figure 9. The Armco iron container is that of Experiment 2 but with a different top. The sampler is of Armco iron and the sampling crucibles are of tantalum. The tantalum crucibles passed the HCl leach test. The volume of the region in the sampler above the filter surrounding the small tantalum crucible is equal to the volume of that crucible (8.5 ml).

The tantalum crucibles were cleaned by the procedure outlined in Method 1. Before insertion of the tantalum crucibles, the sampler was cleaned in the same manner as the container in Experiment 2. The container was received clean from Experiment 2 and required final rinsing only with distilled water and acetone. The parts were assembled and the necessary welds were made in an argon atmosphere. Then, with the sampler drawn up into the top of the container, 400 cc of filtered NaK (fine fritted Pyrex glass) were added under vacuum. The unit was pressurized with argon and immersed in a lead bath at 700° C for 3 days. At that time the sampler was pushed down and completely submerged in the solution which, of course, filled the top tantalum crucible and the space surrounding it above the filter. The loaded sampler was promptly raised above the surface of the solution and the chamber below the filter was partially evacuated causing the solution surrounding the top tantalum crucible to pass through the filter into the bottom tantalum crucible. The lead bath was then allowed to cool about 100° C and the unit was carefully lifted out and cooled to room temperature by means of a fan. The container and sampler were machined open in an argon atmosphere and the samples were extracted.

The concentration of iron in each sample was 15 ± 3 ppm.

5. Conclusions

On the basis of the foregoing experiments, static, saturated NaK solutions of iron can hardly be characterized as suspension prone under conditions of slow cooling. Therefore, little or no apprehension should be felt about using the solubility methods described herein. An investigation of the influence of impurities on the formation of suspensions would be very worth while but was not undertaken.

The equilibrium solubility of iron in eutectic NaK at 700°C is 15 ± 3 ppm.

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APPENDIX I

The Determination of Micro Amounts of Iron in NaK

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The sample is dissolved in methyl alcohol, neutralized with hydrochloric acid and finally evaporated to dryness, yielding sodium and potassium chlorides. The salts are dissolved in water, made slightly acid with hydrochloric acid and the iron is determined colorimetrically using ortho-phenanthroline.

PROCEDURE

1. The sample is dissolved in a known excess volume of cooled, distilled methyl alcohol in a very carefully cleaned glass or quartz container.
2. After dissolution, a known excess of distilled hydrochloric acid is added, and the solution is evaporated to dryness.
3. Twenty five ml water plus a few drops of hydrochloric acid are added and the solution is transferred to a 50 ml volumetric flask.
4. Five drops 10% hydroxylamine hydrochloride are added and the solution is heated to near boiling on a water bath.
5. The solution is cooled, five drops 10% hydroxylamine hydrochloride and 10 drops 0.1% ortho-phenanthroline are added.
6. The pH of the solution is brought to ca. 6 by the addition of a few drops ammonium hydroxide and the solution is diluted to 50 ml with water.
7. The transmittance of the solution is read at 510 mμ against a blank on the reagents used to develop the color. Five cm cells are used.
8. The amount of iron present is obtained from a previously prepared transmittance-concentration curve and corrected for a previously determined iron blank on the reagents used to dissolve the samples.

NOTES

It was found necessary to distill reagent grade methyl alcohol in order to obtain a low blank. In one experiment, for example, the iron content of the methyl alcohol was reduced from 0.096 γ Fe/ml to 0.028 γ Fe/ml by a single distillation. (We use 50-100 ml methyl alcohol to dissolve a sample.) Distilled hydrochloric acid, prepared by the spectrographic laboratory, was also used to help bring down the blank on the dissolution reagents.

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Some typical data obtained on various blanks at different times is shown:

Blank No.	Contained	γ Fe/Blank
1, 2, 3	60 ml methyl alcohol, 20 ml HCl, 50 ml H_2O	1.50, 2.25, 1.30
4, 5, 6, 7	30 ml methyl alcohol, 10 ml HCl, 30 ml H_2O	0.75, 0.75, 0.35, 0.80
8, 9, 10	75 ml methyl alcohol, 50 ml HCl, 50 ml H_2O	0.60, 0.35

ACCURACY OF THE DETERMINATION

The accuracy of a result obtained by the above procedure depends mainly on two factors: (1) the actual iron determination, and (2) the correction due to the iron blank on the dissolution reagents. Regarding the iron determination it is estimated that the amount of iron present can be determined to ±0.15 γ Fe in the range 1-20 γ Fe. Thus the accuracy of the iron determination depends upon the amount of iron being determined. One microgram of iron can be determined with an accuracy of ±15% while 10 micrograms of iron can be determined with an accuracy of ±1.5%.

As can be seen from the data given above, variable results were obtained on duplicate blank determinations. These variations are believed to be due to the fact that the amounts of iron being determined are small with resulting relatively large errors as described above and also possibly due to a slight contamination while the solutions are being evaporated to dryness in order to get rid of the methyl alcohol and hydrochloric acid. If one estimates the error involved in the blank determination to be of the order of ±0.25 γ Fe then the total error in the determination is ±0.4 γ Fe. Thus the estimated error in the determination of 1-10 micrograms of iron under the conditions described above ranges from ±40 to ±4% depending upon the amount of iron being determined.

All this assumes, of course, that the sample is submitted in such a manner that there is no question about getting the iron out of the sample as in the case of a known weight of NaK sealed in a glass tube. In the case of NaK submitted in a tantalum crucible there is the question of some of the iron having diffused into the crucible, and one would have to devise a procedure to assure complete removal of the iron from the crucible to keep the error of the determination within the limits given above. This sampling phase of the determination of iron in NaK hasn't been completely worked out. The indications are that leaching two or three times with hot, distilled 6N hydrochloric acid is effective in removing any iron which may have diffused into the crucible.

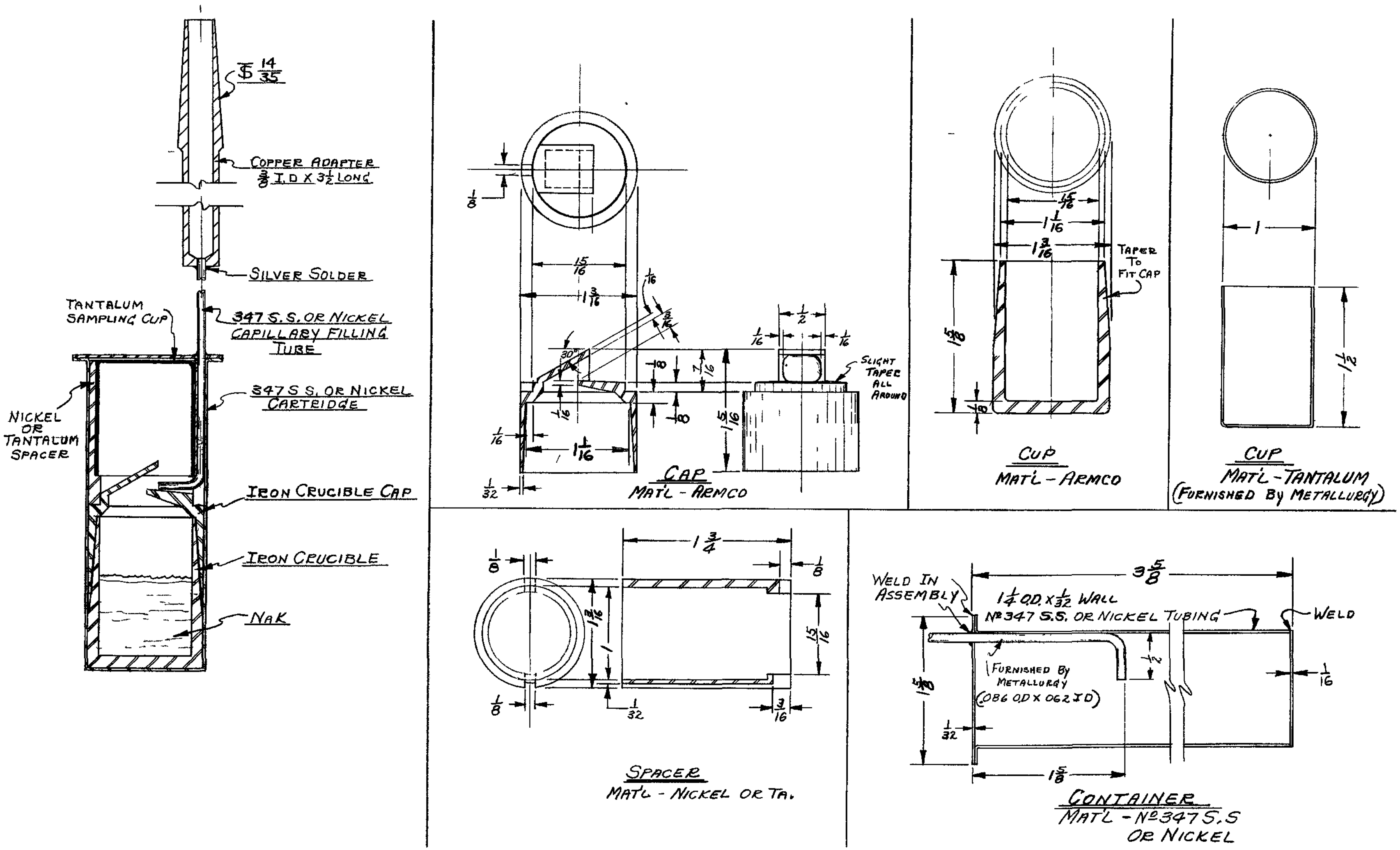

Figure 1

Solubility Unit for Method 1

22

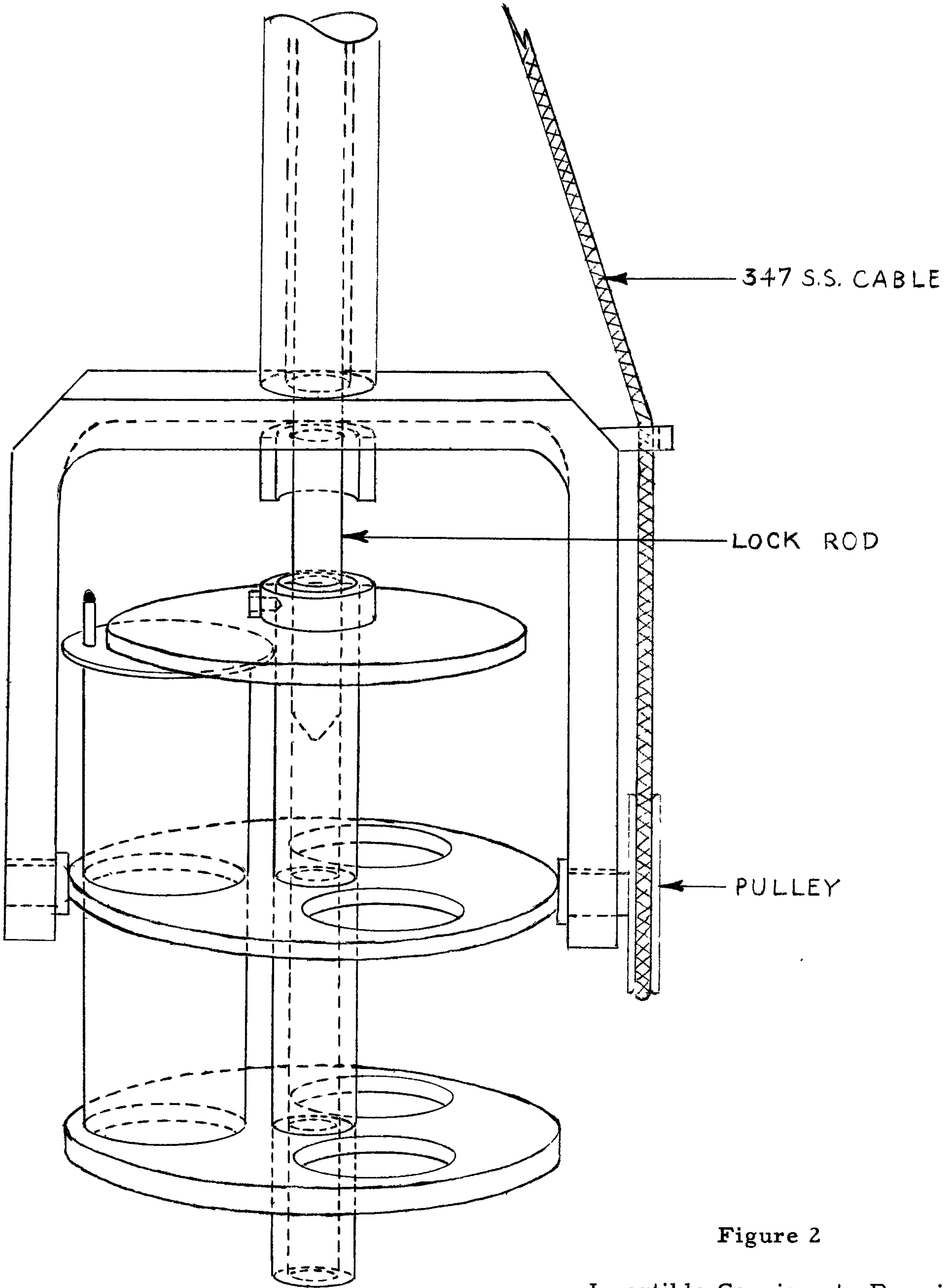

Figure 2

Invertible Carriage to Permit
Sampling at Temperature

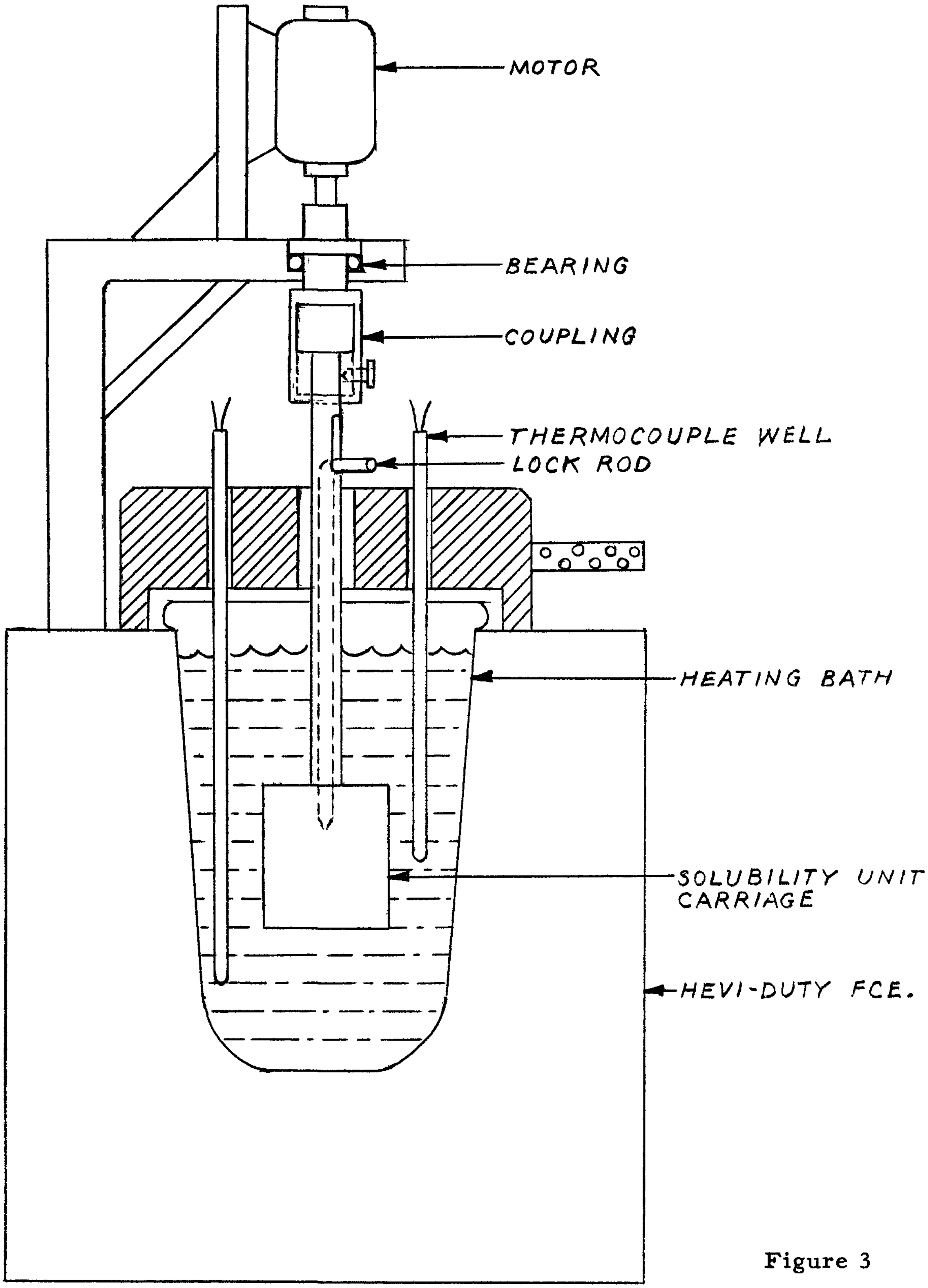

Figure 3

Solubility Apparatus
Assembled in Heating Bath

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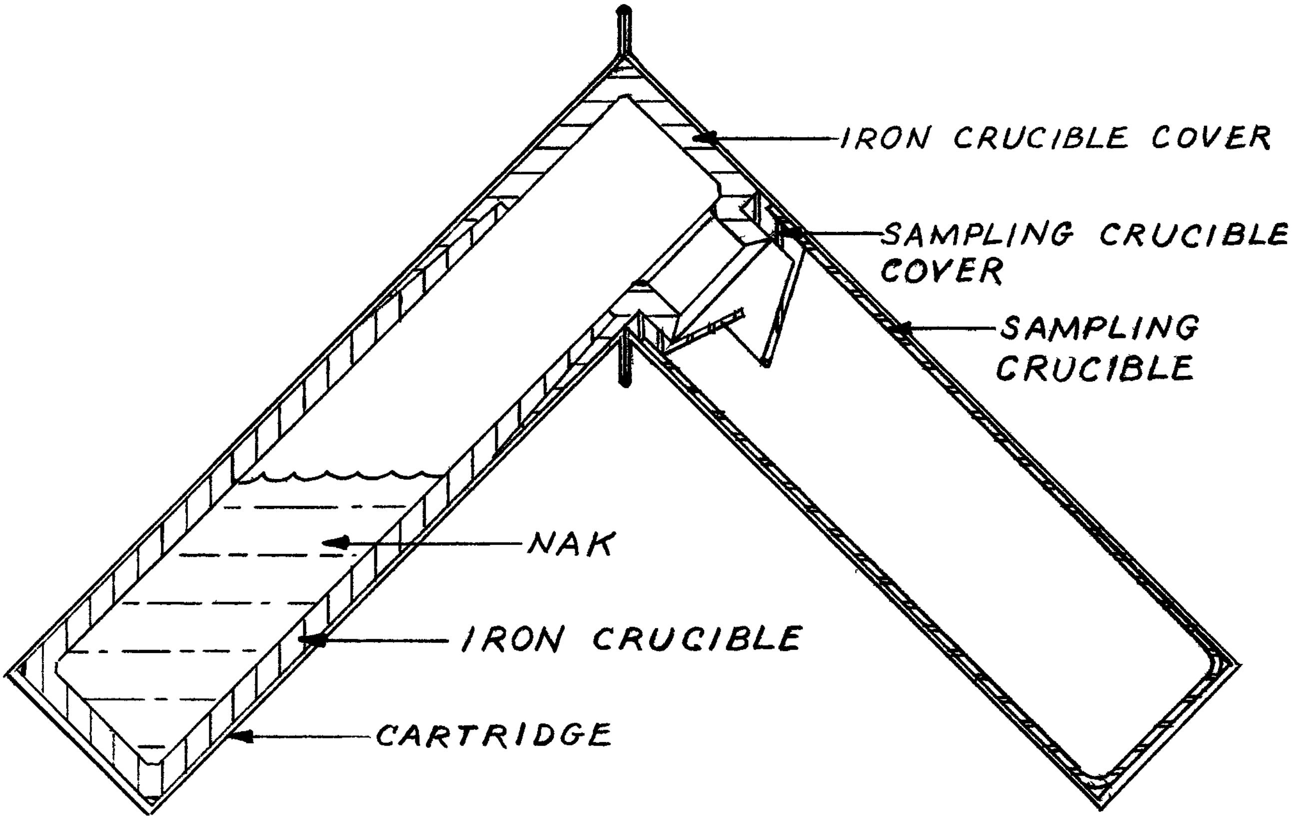

Figure 4

Solubility Unit for Method 2

25

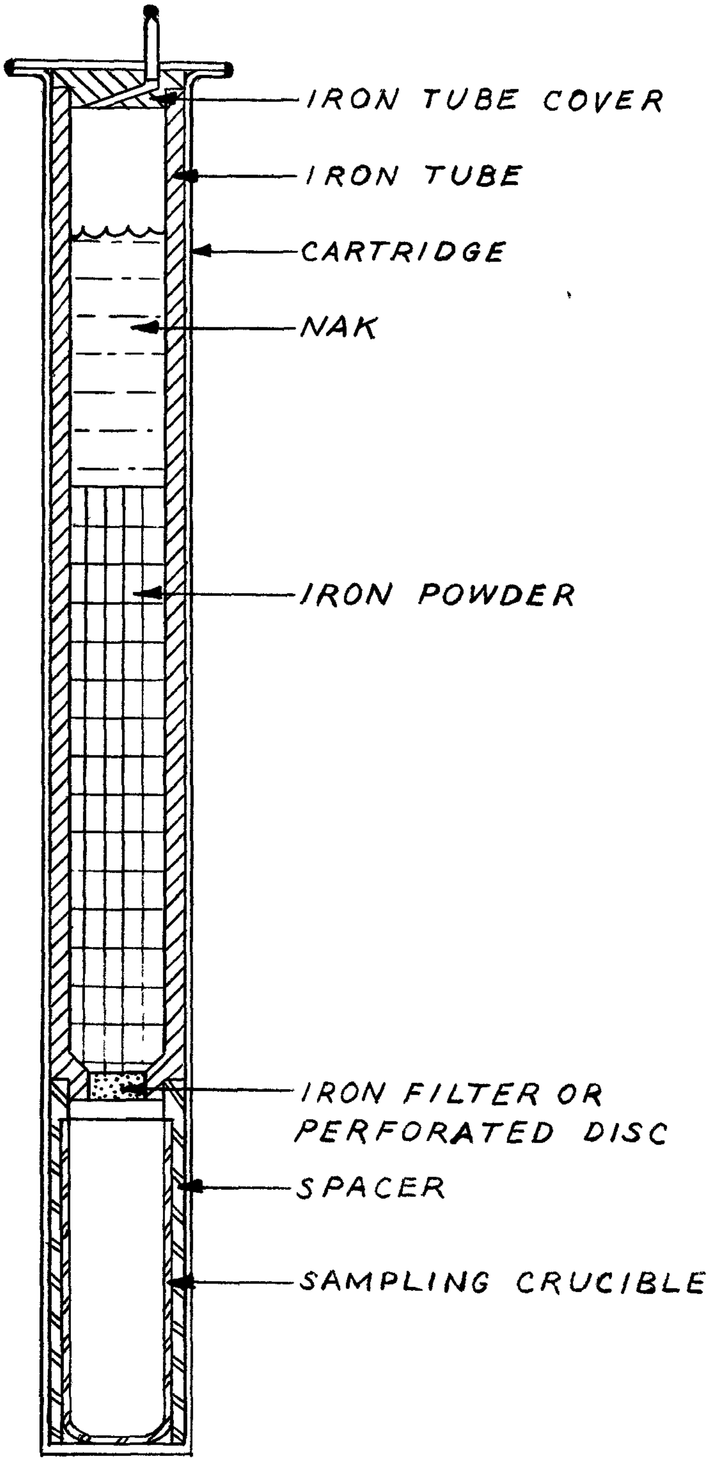

Figure 5

Solubility Unit for Method 3

26

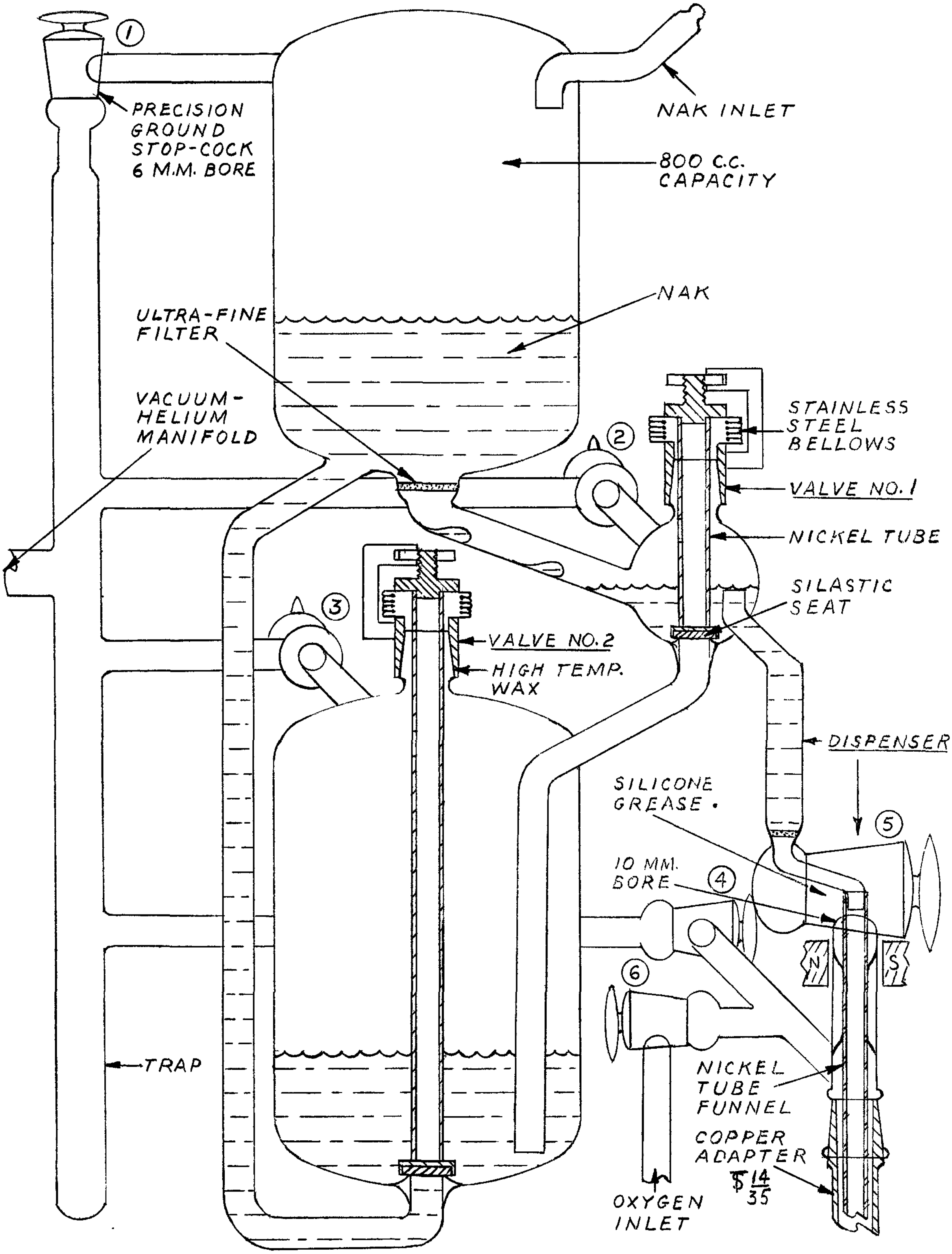

Figure 6

NaK Purifier and
Dispenser

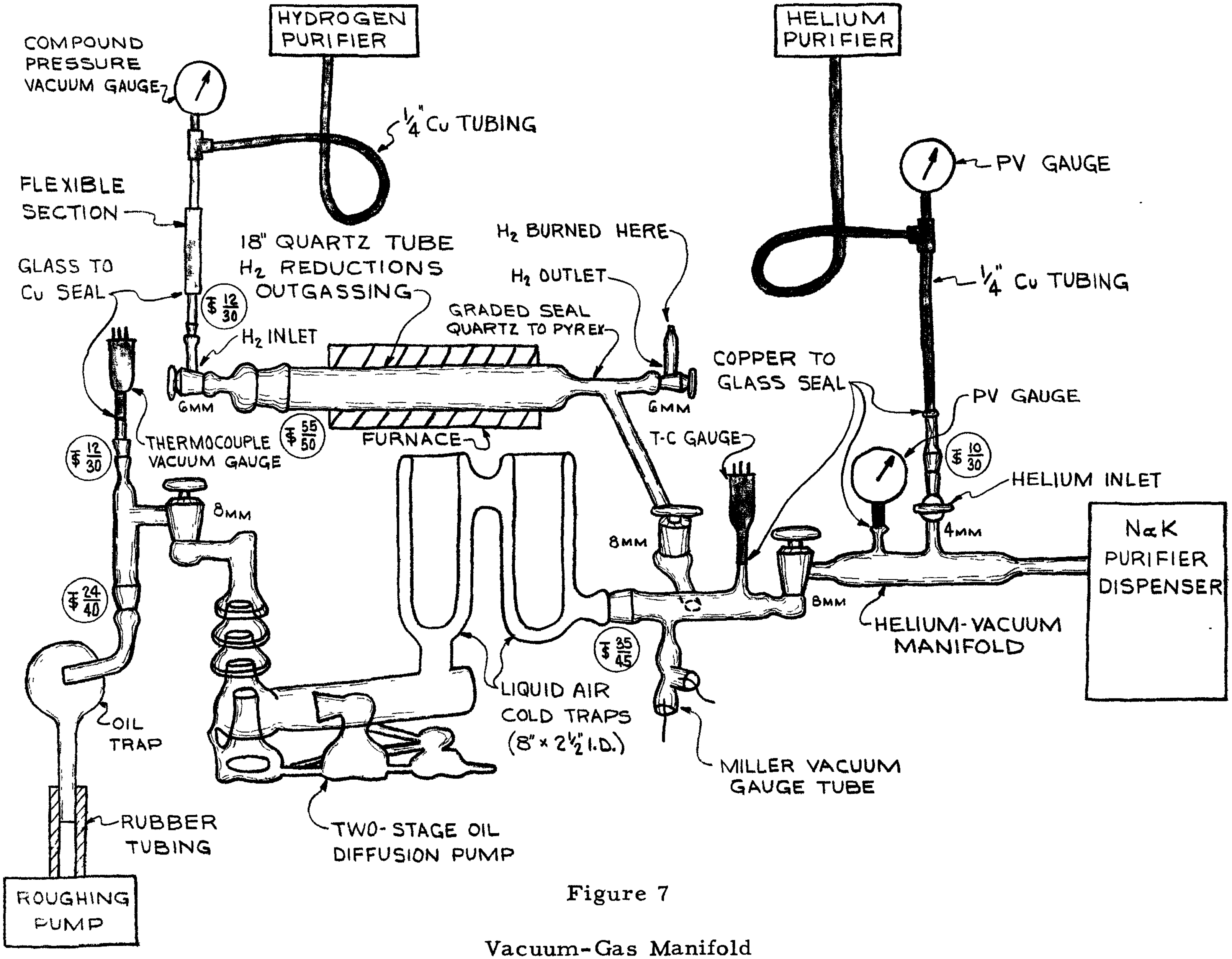

Figure 7

Vacuum-Gas Manifold

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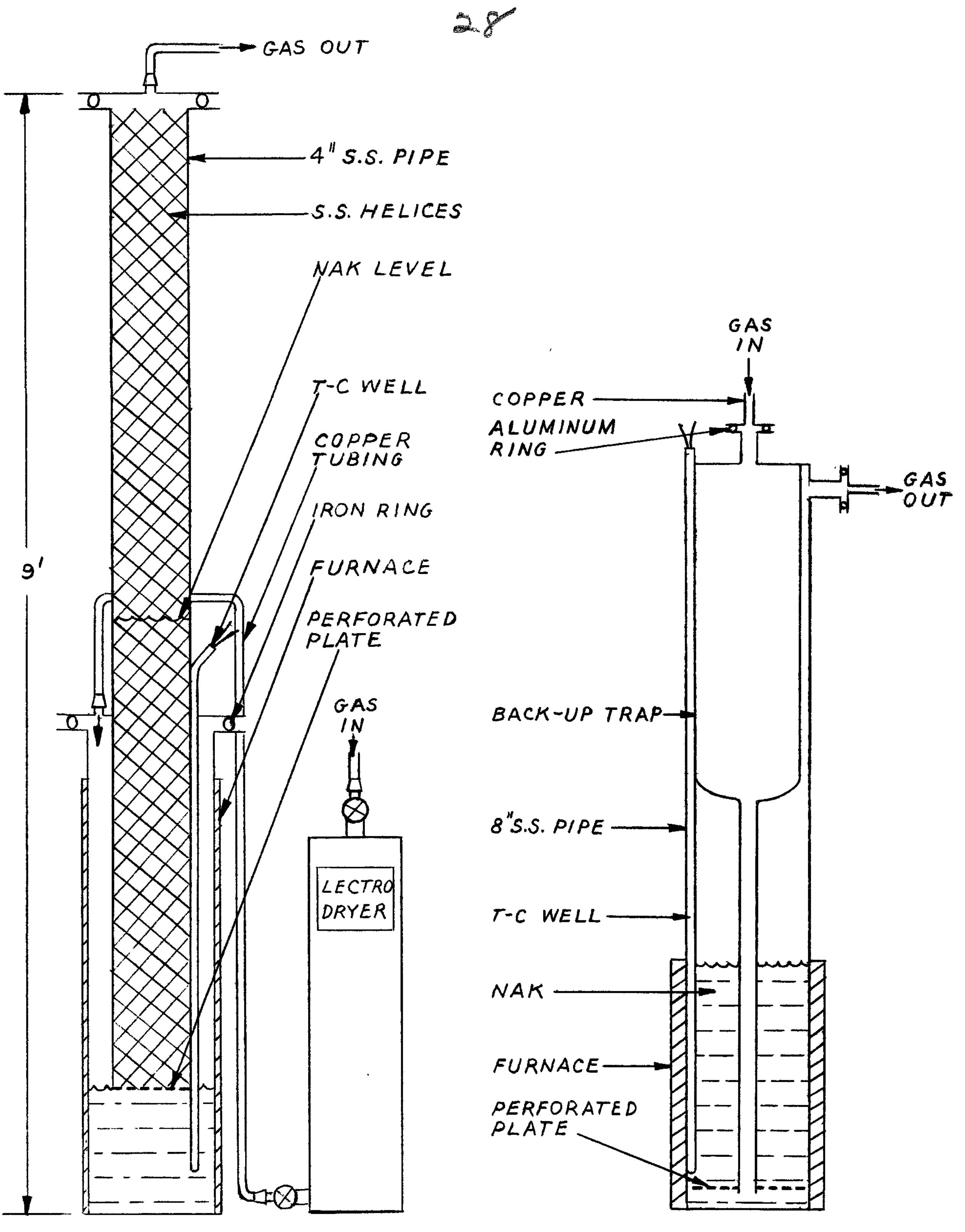

Figure 8

NaK Gas Purifiers

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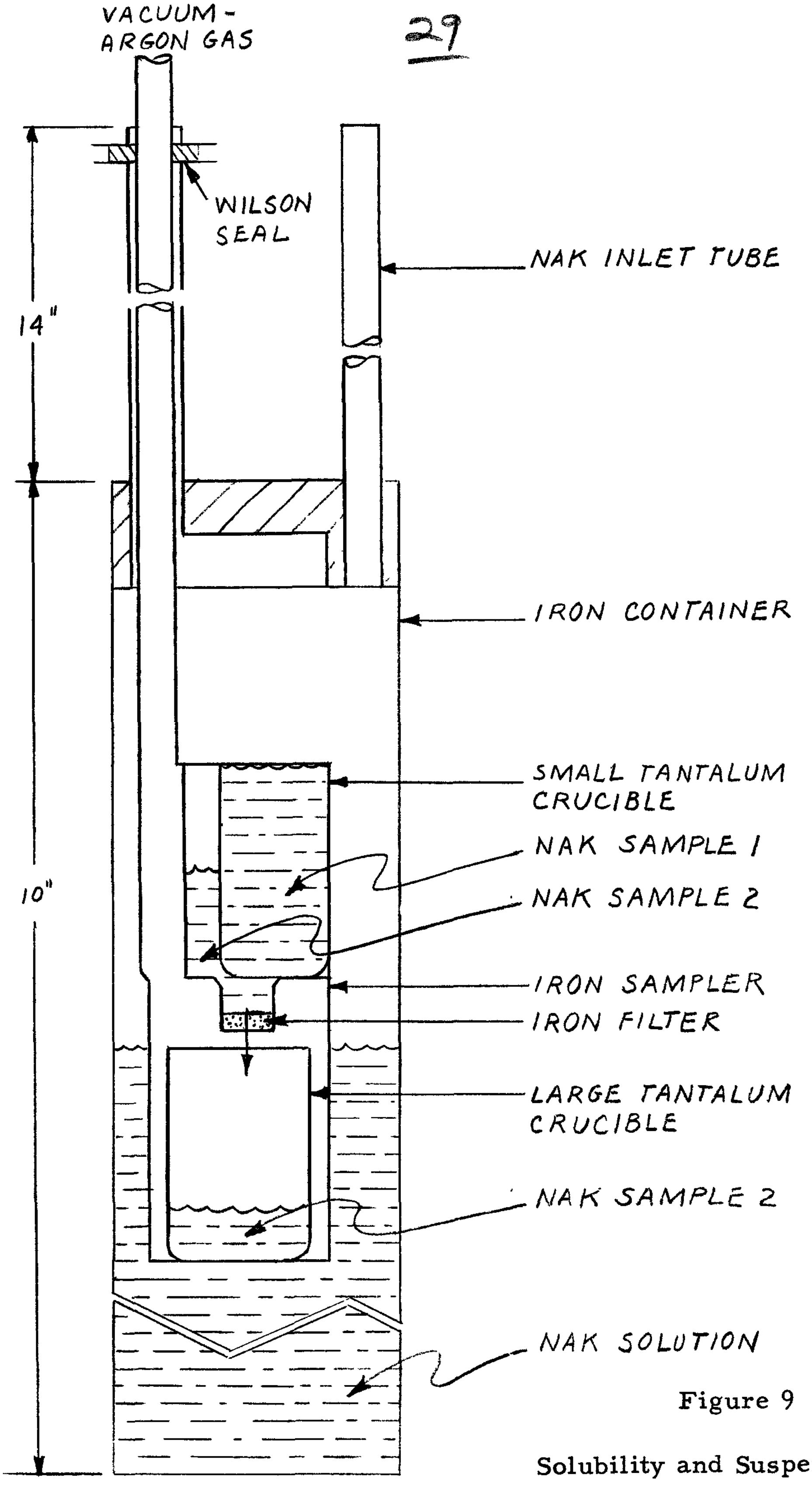

Figure 9

Solubility and Suspension Test
Equipment for Experiment III