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QUARTERLY PROGRESS REPORT No. 3 ON THE MEASUREMENT OF THE PHYSICAL AND CHEMICAL PROPERTIES OF THE SODIUM-POTASSIUM ALLOY

by

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ABSTRACT

The alloys of potassium and sodium are under study as a heat-transfer medium. Physical and chemical properties, together with measurements of heat-transfer coefficients on an engineering scale, are being investigated. The status of active property measurements and all measured results obtained since the last Quarterly Report (NRL Report P-3057) are presented. Included are recent results on viscosity, boiling temperatures, freezing temperatures, phase separation, handling, and other pertinent data. Where results are given on the property, a description of the current apparatus and methods is also presented. Changes in both apparatus and methods are necessary as dictated by experience.

AUTHORIZATION

The study of the physical and chemical properties of Sodium-Potassium Alloy was authorized by BuShips Project 990/46 and NRL Problem Number C01-06.

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STATEMENT OF PROBLEM

The program of study presented and discussed with personnel of the Bureau of Ships has been followed with respect to the phases of the problem being investigated by the Naval Research Laboratory and contracted to the Mine Safety Appliances Company, Pittsburgh, Pennsylvania. This report combines the results obtained by the two groups since the preceding quarterly Report,[1] and covers the period from 1 January to 1 April 1947.

The Laboratory has designed and constructed apparatus to measure some of the physical properties of the alloys of sodium and potassium. The properties to be measured immediately were viscosity, thermal conductivity, specific heat, and the determination of the liquid-solid phase diagram. Other properties such as densities, heat-transfer coefficients, and a study of the handling of the alloys are being conducted under a Laboratory contract with the Mine Safety Appliances Company, Pittsburgh, Pa. (MSA Preliminary Report No. 3. entitled "Methods of Handling, Storing, Shipping and Transferring Liquid KNa Alloys" is presented in the Appendix of this report.) Other properties and characteristics which appear to deserve study will be determined to the extent justified by the project. Certain of the unforeseen difficulties are being solved. They are problems inherent in purification, transferring, and maintaining the alloy in suitably pure condition.

VISCOSITY

KNOWN FACTS BEARING ON VISCOSITY

Technical aspects, together with the time-consuming nature of the investigations with the large nickel apparatus, dictated the need for more precise measurements with a standard Ostwald-type viscometer in the lower temperature range. A Fenske modification of the Ostwald viscometer, of pyrex glass, has been used successfully to obtain measurements up to 200°C. Preliminary measurements with a quartz viscometer were unsuccessful. The metals were found to adhere to the roughened inside surface of the quartz, particularly in the vicinity of seals. An attempt is now being made to obtain a quartz viscometer blown from a single piece of capillary, such that no joints will be necessary in the critical portion of the viscometer.

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1 C. T. Ewing and R. S. Hartman, NRL Report P-3057, "Quarterly Progress Report on the Measurement of the Physical and Chemical Properties of the Sodium-Potassium Alloy, No. 2," January 1947.

The properties of the metals under study impose many conditions on measurements with a capillary viscometer, requiring elaborate attachments to the viscometer and unusual methods. The most important factors influencing results with the Ostwald-type viscometer, their influence on the present measurements, and how each was dealt with, are presented in the ensuing paragraphs.

Effective Head and Surface Tension

The determination of mean effective head in the capillary viscometer for relative measurements is normally side-stepped by the introduction of equal working volumes and the use of hydrostatic heads. Thus, with suitable correction factors for any change in liquid levels with temperature, the mean effective head approaches a constant and may be supplanted by a density factor. The substitution of density for mean effective head, however, is applicable only with the assumption that the head is independent of surface tension. One should select, if possible, a calibration fluid similar in properties to that of the unknown. In which case, the effect of any difference in surface tension on the mean effective head is negligible. However, in the present measurements, the only calibrating fluid available in any way comparable to the mobile alloys was water. Thus, metals which do not appear to wet pyrex glass in the lower temperature range (here we assume that any apparent wetting in the high-sodium composition range is due to impurities present in the alloy), and have surface tension values from 200-400 dynes/cm, are referred to water which does wet glass and has surface tension values from 60-72 dynes/cm. It can then be concluded that surface effects assume important proportions and that the determination of mean effective heads with extreme accuracy is required.

To obtain an accurate value of the mean effective head at any temperature, it is necessary to resort to experiment. The mean effective head can be determined by (1) noting the actual hydrostatic pressure, as registered by an attached manometer, corresponding with successive positions of the menisci between the upper and lower extremes, and (2) noting the times required for these positions to be reached when the liquid runs out under its own head. Now from a plot of the experimental heads at successive positions of the falling menisci against the fraction of total time required to reach each position during the run, a mean hydrostatic head can be determined by graphical integration. The mean head so obtained differs from that calculated from the difference of level at mean time due to surface effects. The use of this experimental method for mean head determinations up to the present has been applied successfully only to water, but, barring difficulties, should be adaptable shortly to accurate determinations on the alloys.

The mean effective heads for the results presented in this report were obtained by a method fashioned after that used by Kuenen and Visser.[2] The values of capillary effect for any given temperature at successive positions of the menisci between the upper and lower extremes were calculated from measurements made on the diameters at those positions. The effective head at each position of the menisci was then obtained by applying the surface tension correction to the observed difference in level. Now by plotting effective head against fractional time required to reach successive positions during runs at the same temperature, the mean effective head could be determined by graphical integration. Mean head values were determined over the temperature range as dictated by the required accuracy.

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2 Kuenen and Visser, Comm. Univ., Leiden, 1913, 13, No. 136.

Calibration and Kinetic Energy

A discussion of the capillary-flow method was presented in the last Quarterly Report.[3] It was shown that for a viscometer of the capillary-type, the Poiseuille equation for absolute viscosity including the correction for any gain in kinetic energy was:

$$\eta = \frac{\pi P t r^4}{8 V l} - \frac{m V d}{8 \pi l t}$$

where

η = absolute viscosity

P = mean effective pressure

t = time

V = volume

r = capillary radius

l = capillary length

m = kinetic energy constant

d = density

Now, when relative measurements are to be made by calibration of the viscometer with a fluid of known viscosity, all of the terms in the equation above which are constant for a given viscometer can be determined experimentally. Grouping all these constant terms, the equation then reduces to:

$$\eta = APt - \frac{Bd}{t}$$

To determine the viscometer constants A and B, a graphical method was employed. The time of flow and the mean effective head was determined for water at several temperatures. Then by plotting η/Pt against d/Pt^2, a straight line was obtained, the intercept and the slope of which determine the values of A and B, respectively. The absolute viscosity of the alloy at any temperature was then calculable from a knowledge of its density, the time of transpiration, and the mean effective pressure. An apparent advantage in the above method of calibration is that any expansion in the pyrex viscometer, though slight, will be included in the empirical constants.

METHODS

Apparatus

The pyrex viscometer and the attached glass system are diagramed in Figure 1. An arrangement of stopcocks provided that the entire system could be alternately evacuated and filled with purified helium. The high-vacuum system, consisting of the usual high-vacuum pump, mercury-diffusion pump, and McLeod gage, consistently maintained pressures of less than one micron. Highly purified helium was furnished to the system from

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3 C. T. Ewing and R. S. Hartman op. cit.

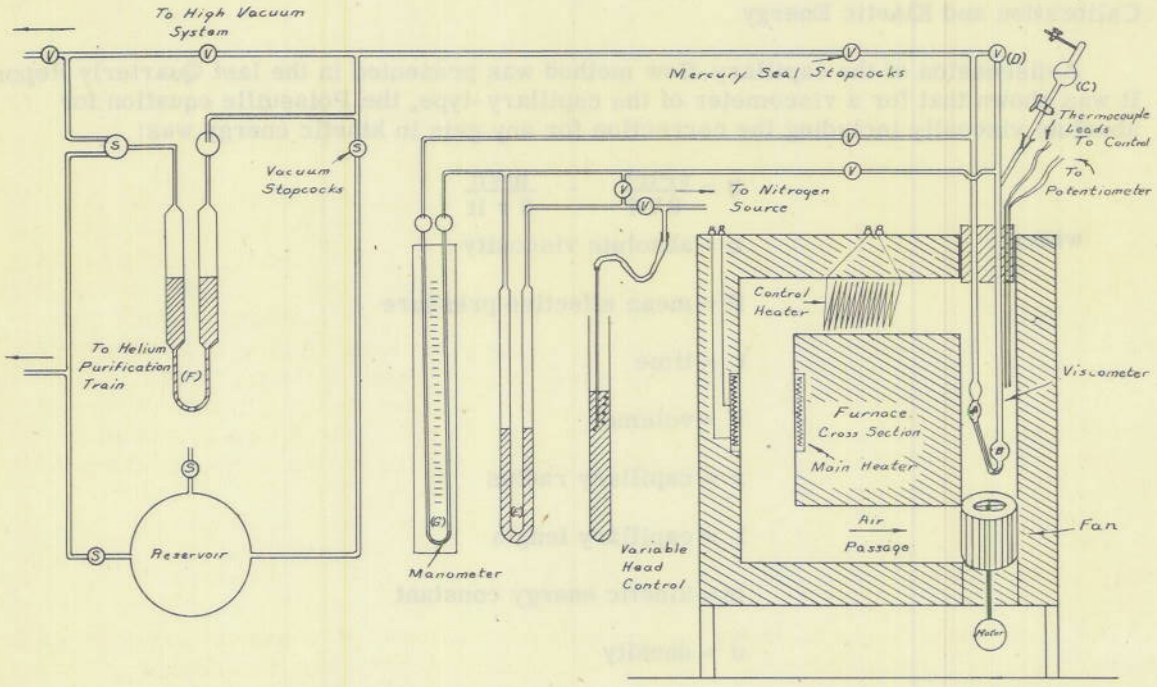

Figure 1 Viscometer Assembly

a train comprised of copper turnings at 450 °C, potassium hydroxide, silica gel, and activated charcoal at the temperature of liquid nitrogen.

The viscometer was housed in an electrically heated furnace. The furnace make-up consisted of four large alundum tubes, mitred to form a square passage, with one tube extended at the top to provide entrance for the viscometer. A motor-driven fan was shafted into the alundum tunnel to recirculate the heated air continuously. Two heaters were employed; one 900-watt heater around one alundum tube, and a 300-watt control heater exposed inside the air passage. This complete assembly was supported inside a metal framework with insulation materials. Two quartz windows on opposite sides of the furnace were provided for viewing the viscometer.

Very sensitive temperature control was supplied with a galvanometer-relay assembly. In short, a variable source of bucking emf was supplied to balance the emf furnished to a sensitive galvanometer by a Pt-PtRh thermocouple in the furnace. With the galvanometer balanced at the emf equivalent to the desired temperature in the furnace, the control heater was turned on and off by two relays, which were activated by a pointer moving in conjunction with the galvanometer beam. Temperature readings were noted with a Leeds and Northrup, type K, potentiometer using another Pt-PtRh thermocouple which was calibrated up to 350 °C against a Bureau of Standards thermocouple and against the freezing temperature and boiling temperature of water. Temperatures could be controlled and known to at least 0.1° C.

Operation

The wetting characteristics of the liquid metals necessitated extreme cleanliness of the viscometer in order to obtain workable conditions. This required that before each group of runs, the viscometer be completely detached from the system and subjected to the following tedious cleaning steps: (1) chromic acid cleaning solution; (2) distilled water; (3) absolute ethyl alcohol; (4) distilled water; (5) concentrated nitric acid; and finally (6) distilled water. The viscometer was then sealed onto the system, and the sample of freshly distilled alloy placed in position at (C). Now before the introduction of purified helium, evacuation of the system to pressures below one micron with the viscometer at 300°C was required to remove adsorbed oxygen from the surfaces of the glass. The working volume of alloy could then be drawn into the viscometer at (C). Manipulation of the liquid into the measuring bulb was accomplished by closing the stopcock at (D) and either compressing the gas in bulb (B) at (E), or by expanding the gas in bulb (A) at (F). Then to observe the time of transpiration between the two marks on bulb (A), it was necessary only to open the stopcock at (D) to equalize the pressures of gas in the two limbs of the viscometer.

EXPERIMENTAL RESULTS

This report presents viscosity measurements on two alloys of sodium and potassium, 52.0 and 93.9 percent by weight potassium. Each composition value represents an analysis on the alloy as removed from the viscometer at the conclusion of the runs.

The method for calibration of the viscometer by preliminary experiments with water has already been described. The calibration constants, determined by graphical solution of the water results, were $A = .439 \times 10^{-8}$ and $B = 1.23 \times 10^{-2}$ using cgs units. The viscosity values for all measurements made on the two alloys are presented in Tables I and II.

The viscosity results presented for the two alloys are intended only as preliminary results to indicate a trend. Several factors of uncertainty, particularly in the estimation of capillary effects, gave rise to possible error. These factors were: (1) estimation of surface tension values for the alloys from uncertain literature values for the pure metals; (2) the use of tables prepared for water[4] in estimating the effect of diameter on the capillary effect; and (3) the effect of drainage and shape of delivery bulb on the meniscus. However, the maximum capillary effect was found to amount to only 9 percent of the total head. Thus, any error in final results due to surface effects should not be greater than 2 percent, provided there was no radical change in the non-wetting meniscus. Another source of error was in observing the difference of level in the two limbs of the viscometer. Although these levels were read with a cathetometer, an error of 2 millimeters in the total head was possible or approximately 2 percent in the final viscosity result. Experimental determination of alloy heads in future experiments should eliminate all these sources of possible error.

The shape of the meniscus in the measuring bulb for the 52.0 weight-percent alloy indicated what might have been a partial wetting, and the results are therefore somewhat less reliable than those for the other alloy. Surface effects for both alloys were figured on a non-wetting basis.

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4 Kuenen and Visser, op. cit.

TABLE I

VISCOSITY OF SODIUM - POTASSIUM ALLOY

(52.0 Weight-Percent Potassium)
(38.9 Mol-Percent Potassium)

Temperature (°C)	Density (gm/cc)	Absolute Viscosity (Centipoises)
53.8	.900	.842
53.8	.900	.814
54.2	.900	.812
54.2	.900	.814
73.6	.894	.696
73.5	.894	.697
98.3	.887	.595
98.3	.887	.595
98.0	.887	.597
127.0	.879	.513
126.5	.879	.510
126.3	.879	.511
154.0	.872	.454
170.5	.867	.423
170.2	.867	.423
201.0	.859	.377
201.0	.859	.377

TABLE II

VISCOSITY OF SODIUM - POTASSIUM ALLOY

(93.9 Weight-Percent Potassium)
(89.9 Mol-Percent Potassium)

Temperature (°C)	Density (gm/cc)	Absolute Viscosity (Centipoises)
40.5	.844	.691
42.5	.844	.687
43.4	.844	.685
43.4	.844	.685
42.7	.844	.690
43.1	.844	.691
45.9	.843	.673
46.7	.842	.670
46.5	.842	.669
54.8	.840	.630
55.1	.840	.629
59.8	.839	.608
60.2	.839	.606
61.0	.839	.603
70.5	.836	.567
70.6	.836	.565
94.3	.830	.494
94.5	.830	.499
94.5	.830	.499
114.0	.826	.456
114.0	.826	.455
136.2	.823	.421
136.2	.823	.421
142.4	.821	.402
142.5	.821	.400
161.0	.819	.380
160.8	.819	.380

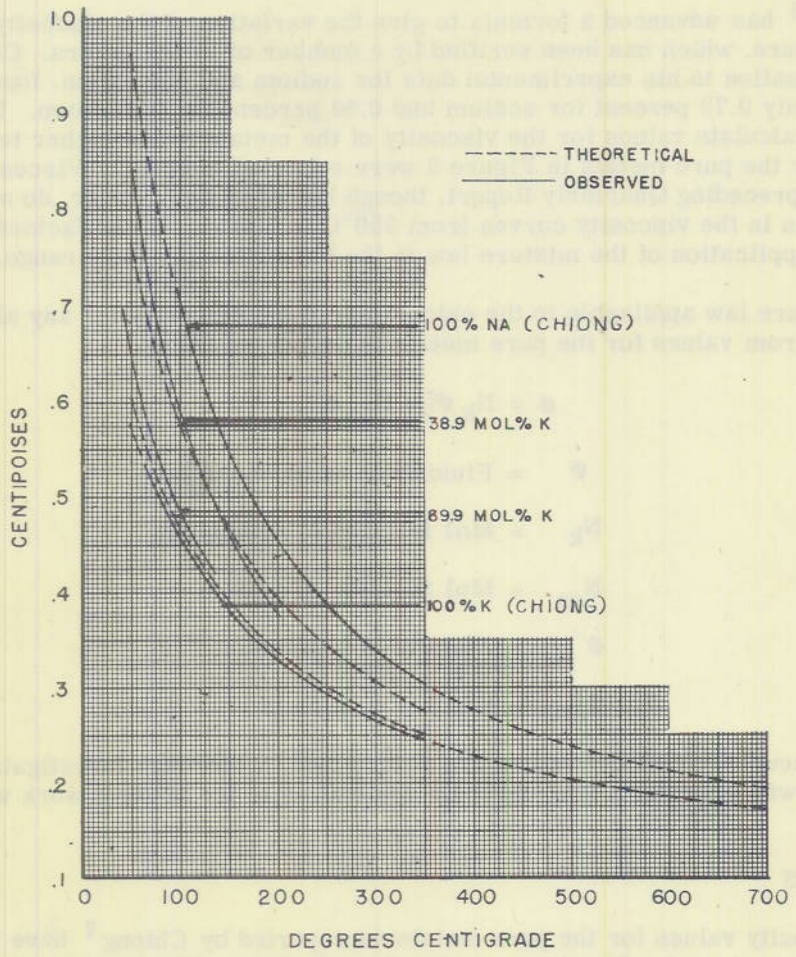

Figure 2 Viscosity vs Temperature for Na-K Alloys

With two chemically similar elements such as sodium and potassium, one could reasonably expect solutions of the two to approach ideal behavior, barring strong deviations due to compound formation, association, etc. Approximate additivity of volumes and only slight deviations from Raoult's law (Figure 4, p. 12) over the composition range provide evidence that the two metals unite to approach a perfect solution. Such reasoning justified an approach to viscosity values through mixture laws. Assuming additivity of fluidity, viscosity values for the two alloys studied were calculated up to 350°C from the values for the pure metals advanced by Y. S. Chiong.[5] These calculated values are plotted in Figure 2, together with the experimental values. The good agreement between the experimental and calculated values justifies the conclusion that viscosity values for any composition and at any temperature up to 350°C (the extent of data by Andrade and Chiong) may

5 Y. S. Chiong, Proc. Roy. Soc. London, A 157, 264 (1936)

be calculated by a simple mixture law to give an accuracy of better than ±5 percent.

Andrade[6] has advanced a formula to give the variation of the viscosity of a liquid with temperature, which has been verified by a number of investigators. Chiong, in fitting this equation to his experimental data for sodium and potassium, found a maximum deviation of only 0.72 percent for sodium and 0.59 percent for potassium. Using these equations to calculate values for the viscosity of the metals in the higher temperature range the curves for the pure metals in Figure 2 were extended to 700°C. Viscosity values reported in the preceding Quarterly Report, though known to be in error, do not show any obvious breaks in the viscosity curves from 350°C to 700°C. These factors accumulate to justify an application of the mixture law in the higher temperature range, also.

The mixture law applicable to the calculation of the viscosity for any alloy at any temperature from values for the pure metals is presented below.

$$\phi = N_k \phi^\circ_k + N_{na} \phi^\circ_{na}$$

where

ϕ = Fluidity of Alloy = $\frac{1}{\text{viscosity}}$

N_k = Mol fraction of potassium

N_{na} = Mol fraction of sodium

ϕ°_k = Fluidity of potassium

ϕ°_{na} = Fluidity of sodium

When more accurate viscosity values are determined, a thorough investigation of available mixture laws will be undertaken, and their application to the present work will be presented.

CONCLUSIONS

The viscosity values for the pure metals as reported by Chiong[7] have been corroborated by the present work. Densities used in the calculation of results by Chiong, though differing slightly from those reported by MSA, do not appreciably affect the results.

Application of a simple mixture law, to estimate the viscosity of an alloy from the corresponding values for the pure metals, was found to give viscosity values with less than 5 percent error. For engineering data the values so obtained should be well within the required accuracy.

Results obtained with a large nickel viscometer and reported in NRL Report P-3057 are known to be in error at the higher temperatures due to turbulent flow. Turbulent eddies are also believed to exist in the lower temperature range.

Barring difficulties, viscosity measurements up to 350°C should be obtained in the near future with a pyrex or quartz viscometer and should contain less than 1 percent error.

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6 E. N. Andradé, Da C., Phil. Mag., Ser. 7, 17, 698 (March 1934) Part II.

7 Y. S. Chiong, op. cit.

BOILING TEMPERATURES AT HIGHER PRESSURES

KNOWN FACTS BEARING ON BOILING TEMPERATURES

Some few investigators[8] have studied the boiling temperatures of sodium and potassium metal at atmospheric pressure, and Kistiakowsky[9] has investigated the boiling point of alloys at atmospheric pressure, but there seems to be no available data for boiling temperatures under pressure.

Some theoretical consideration can be given to this problem by assuming simple laws. The vapor pressure of pure sodium has been found[10] to be

$$\log p_{(mm)} = \frac{-5400.0}{T} + 7.5510 = R$$

or

$$p_{(mm)} = 10^{R}$$

and the vapor pressure of potassium[11] was found to be

$$\log p_{(mm)} = \frac{-4433}{T} + 7.1830 = S$$

by Raoult's law:

$$p_{(na)} = p^{\circ}_{(na)} \, X_{(na)}$$

where $p_{(na)}$ = vapor pressure Na above a perfect solution

$p^{\circ}_{(na)}$ = vapor pressure Na in a pure state

$X_{(na)}$ = mol fraction Na in liquid phase

If the same law is considered to be valid for potassium also, the addition $p_{(na)}$ and $p_{(k)}$ gives the total pressure or

$$p_{(mm)} = (1 - N)\, 10^{R} + N\, 10^{S}$$

where N is the mol fraction of potassium in the liquid.

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8 International Critical Tables

9 G. B. Kistiakowsky, NDRC-Division B, NRL Report P-2958, "Report on Vapor-Liquid Equilibria for Mixtures of Alkali Metals (Sodium-Potassium)," 10 April 1941.

10 W. H. Rodebush and E. G. Walters, JACS, 52, 2654 (1930).

11 W. H. Rodebush and E. F. Fiock, JACS, 48, 2522 (1926).

METHODS

Apparatus

A 1 1/2-inch stainless-steel pipe 24 inches long was fixed with a pipe cap containing 2 thermocouple wells; one 15 inches long, one 22 inches long; a 1/4-inch stainless-steel bubbler tube, 23 1/2 inches long; an opening for filling; and an outlet tube (Figure 3). The outlet tube was arranged so that the system could be used either for atmospheric-pressure runs, or the gas could be bled into a large tank of six-cubic-feet capacity which could be adjusted to any desired pressure, and because of its large volume, remain essentially constant throughout the entire run. The bubbling of helium through the alloy was used for stirring and to prevent the ever-present danger of superheating. The flow indicator was used to show that helium was flowing through the system when making runs at elevated pressures.

Operation

The tube was filled with approximately five or six inches of alloy and placed in a nine-inch-high electric furnace, with a six-inch-high heating element, purified helium flowing constantly. The furnace temperature was then adjusted by means of a variac. Temperatures were recorded at ten-minute intervals by two chromel-alumel couples. The No. 2 thermocouple was supposed to read the same temperature as No. 1 thermocouple when equilibrium

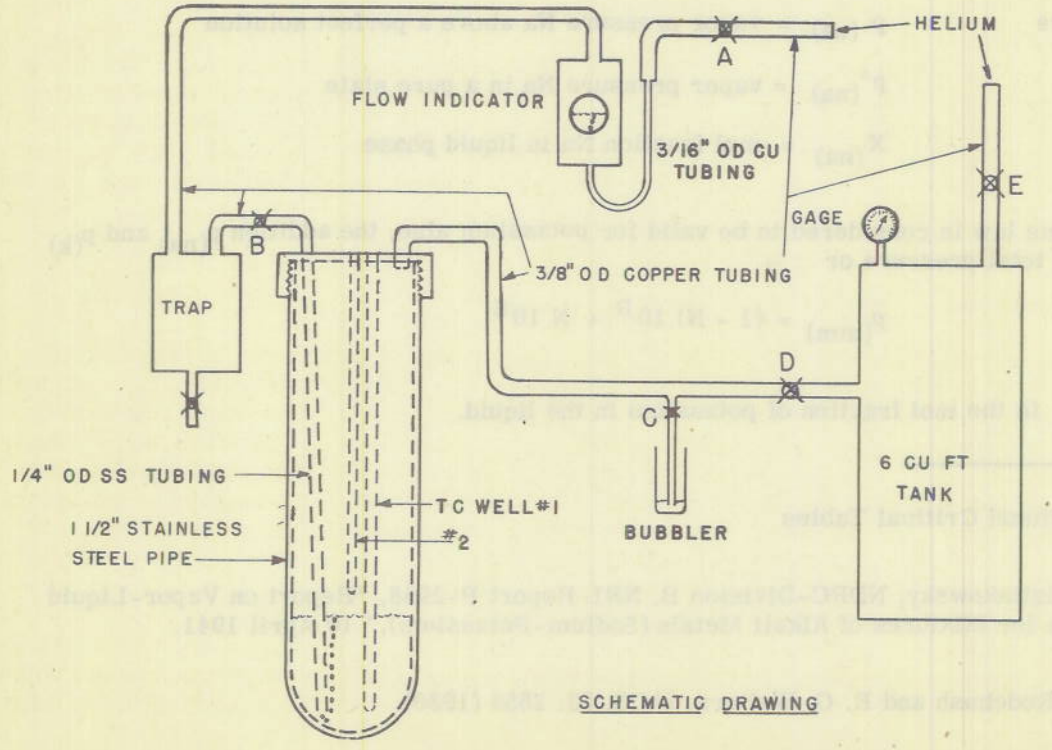

Figure 3 Apparatus for Boiling Point Determinations

TABLE III

BOILING TEMPERATURES OF SODIUM - POTASSIUM ALLOYS

Composition (mol % K)	Pressure (mm)	Boiling Temperature Observed (°C)	Boiling Temperature Theoretical (°C)	% Deviation
7.8	700	859	867	- .9
	2000	980	985	- .5
28.1	743	825	833	-1.0
	2000	945	950	- .5
34.7	760	819	824	- .6
48.0	762	804	806	- .2
	2000	918	923	- .5
66.9	758	783	785	- .3
	2000	901	900	+ .1
			Average % deviation -.5	

was reached, but this was unsuccessful in all but one run. Two reasons are given for this: (1) the furnace could not be heated high enough for the vapors to reach No. 2 thermocouple, or more likely, (2) the ease of fractionation kept a lower-boiling composition refluxing off the end of the well. However, in all cases, when a constant temperature was recorded for one hour with No. 1 thermocouple, this was taken as the boiling point. For runs under pressure, the tank was first filled to the desired pressure and the same procedure followed, valve C being closed.

EXPERIMENTAL RESULTS

Two runs were made on each alloy, one at atmospheric pressure and one at a gage pressure of 24 psi, (2,000 mm absolute pressure). The results are presented in table III. These observed temperatures are plotted in circles on Figure 4 and compared to the theoretical curves. The points not encircled were those found by Kistiakowsky.[12] Better agreement may be noted between the results of this investigation and the points of Kistiakowsky than with the theoretical curve at 760 mm. However, as pointed out before, the discrepancy is small and probably no greater than experimental error.

CONCLUSIONS

A theoretical equation relating pressure to composition and temperature was evolved, using the best available data of vapor-pressure measurements and assuming the validity

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12 Kistiakowsky, op. cit.

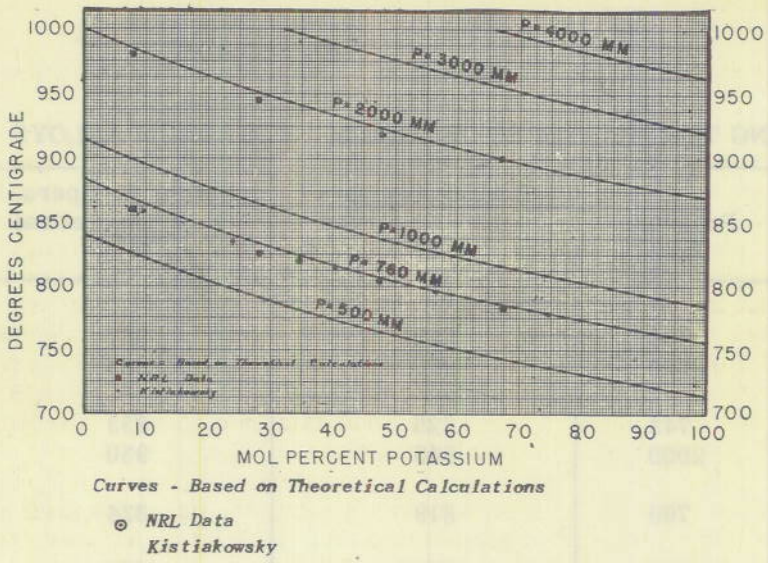

Figure 4 Boiling Point vs Composition for Na-K Alloys at Various Pressures

of Raoult's law over the entire range of composition. This equation was checked experimentally and gave values correct to .5 percent for the temperature. The equation which was derived follows:

$$P_{(mm)} = (1 - N)\, 10^{\left[-\frac{5400.0}{T} + 7.5510\right]} + N \times 10^{\left[-\frac{4433}{T} + 7.1830\right]}$$

where $P_{(mm)}$ = total pressure in mm

N = mol fraction K in the liquid

T = °Kelvin

PHASE DIAGRAM

KNOWN FACTS BEARING ON PHASE DIAGRAM

Several previous investigators [13,14] have determined freezing points and have constructed liquid-solid phase diagrams for sodium and potassium alloys. Since the results of these investigators check each other very closely, the data presented is in the nature of a check on the previous work done. The purity of the alloys used and the improved technique

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13 Bornemann, Die binaren Metallegierungen, Halle (1905), p. 7; N. S. Kurnakow, and N. A. Puschin, Zeitschrift fur Anorganische Chemie, 30, 109 (1902); E. Rinck, Comptes Rendus, 197, 49 (1933); C. H. Kean, Physical Review, 55, 750 (April 1939); and Joannis, Ann. Chim. Phys., (6) 12 (1887), 358.

14 G. L. C. M. Van R. H. Van Bleiswijk, Zeitschrift fur Anorganische Chemie, 74 Band S, 152 (1912).

in handling and analysis of samples may all contribute to improved and more accurate data.

The alloys of sodium and potassium form a compound which is indicated by a break in the phase diagram at approximately 42 mol-percent potassium, at which point the reaction takes place. Van Bleiswijk[15] has presented data indicating that the compound formed is Na_2K. This seems to agree with the results of the other investigators. Bornemann[16] states that there are three species of mixed crystals between the two pure components and that the metals form solid solutions when they separate from the melt. According to Bornemann, the presence of a strongly dissociated compound of the type Na_nK must be admitted. Rinck[16] in 1933, checked the results of Van Bleiswijk (1912) and presented results which were "in complete accord with those found by Van Bleiswijk". No attempt has been made here to check previous data on compound formation other than to verify the break at 42 mol-percent potassium.

Very few previous investigators presented any tabulated data with their reports, presenting instead, only their completed phase diagrams. The latest available tabulated data is that of Van Bleiswijk which has been plotted and the phase diagram is included in this report (Figure 5) as a comparison with the NRL data.

METHODS

Apparatus

The most important part of the apparatus was the temperature-measuring device. It consisted of a five-junction thermel constructed of five iron-constantan thermocouples arranged in series. By this arrangement very small electromotive-force differences were enlarged five times and made more easily and more accurately read. The emf was measured on a Rubicon high-precision potentiometer, type B, using a cold junction at 0° C. Each junction of the thermel was welded in an atmosphere of N_2 by means of an electric arc to avoid oxidation. The thermel was calibrated using the following standard temperature reference points:

ice + NaCl	-21.10°C
ice	0°C
transition of $Na_2CrO_4.10H_2O$	19.53°C
transition of $Na_2SO_4.10H_2O$	32.38°C
boiling point of H_2O at 757.6 mm	99.91°C
boiling point of C_2H_5OH at 756.1 mm	78.13°C

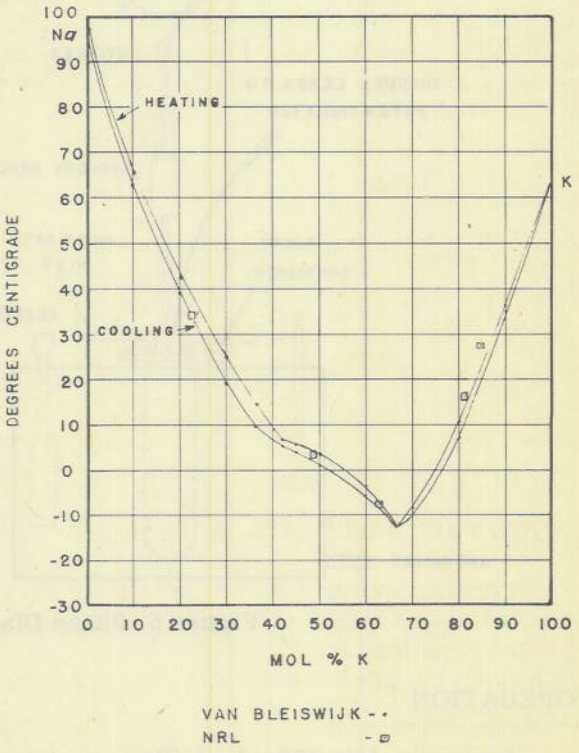

Figure 5 Sodium-Potassium Liquid-Solid Phase Diagram

15 G. L. C. M. Van R. H. Van Bleiswijk, op. cit.

16 Bornemann, E. Rinck, op. cit.

A calibration curve using these points was constructed and was used to convert millivolt readings to degrees centigrade. The thermel had an equivalent of 5 single iron-constantan thermocouples.

The alloy was contained in a 1 1/2-inch standard stainless-steel tube fitted with a flanged top (Figure 6). A soft copper gasket served as a seal when the top flange plate was bolted down. The alloy was stirred with a vertical stirrer having a mercury seal to prevent the entrance of air. Argon, purified by passage over calcium at 450°C and through a coil in a dry-ice-acetone bath to condense water vapor, was passed over the alloy, then through a mercury bubbler, at all times during a run. The cooling was carried out by inserting the stainless-steel tube containing the sample into a mineral oil bath in a copper tank, which was equipped with a cooling coil, heater, and stirrer. Compressed air was blown through a vertical column packed with dry ice and through the cooling coil. The rate of cooling was controlled by varying the rate of air flow. The electrical heating unit was installed in the mineral oil bath for heating alloys whose freezing points were above room temperature.

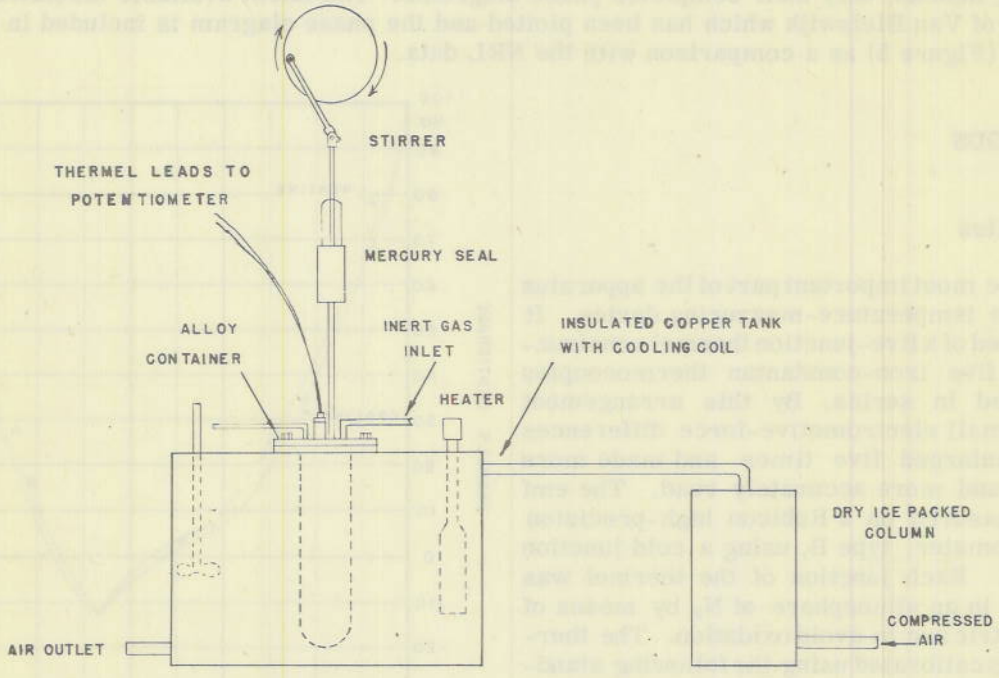

Figure 6 Phase Diagram Apparatus

OPERATION

Approximately 180 ml of alloy was introduced into the container and the stirrer was started. Cooling air was admitted to the oil bath and millivolt readings were recorded every minute. By plotting the data (millivolt vs. time), a cooling curve was obtained. The curve was smooth without breaks until the freezing point was reached where a sudden change in slope occurred. The thermel calibration curve was used to convert millivolts to degrees centigrade. By cooling to a low enough point, the eutectic temperature was reached and the cooling curve stayed horizontal for a short period before cooling lower. Both freezing point and eutectic were obtained on heating as well as cooling curves.

EXPERIMENTAL RESULTS

Table IV includes the results of freezing-point studies of five different alloys. As the work was done as a check on previous investigators, it was not considered necessary to study more than the five reported.

Theoretically, a heating and cooling curve should give a break at the same point but actually this does not often occur due to thermometer lag or other cause. The results obtained, both heating and cooling, check each other to within 0.2°C due to the use of the fine wire thermel, and the results reported are averages of the heating and cooling values. The plot of Van Bleiswijk's (Figure 5) data indicates a maximum difference as much as 5°C between the heating and cooling values, due, quite possibly, to his use of a mercury thermometer. The NRL points are plotted on the same curve for comparison.

TABLE IV

FREEZING POINT DATA

Composition		Freezing Point Data	Eutectic Point
Weight-% K	Mol-% K	(°C)	(°C)
32.5	22.1	34.5	-12.3
61.5	48.5	3.2	-12.3
74.2	62.9	-7.3	-12.3
87.8	81.0	16.2	---
90.5	84.8	27.8	---

CONCLUSIONS

Comparison of the data obtained with that previously presented seems to indicate that the phase diagram of Van Bleiswijk needs little modification. The fact that two more recent investigators [17] have also indicated agreement with Van Bleiswijk helps to establish that his data is reasonably correct.

Van Bleiswijk's eutectic of 66.6 mol-percent K at -12.6°C does not agree with the data here presented which indicates a eutectic at -12.3°C. The fact that Rinck [17] found the eutectic to be 66.0 mol-percent K at -12.5°C indicates that there may be some disagreement about this. It is possible that the improved techniques and purity of the alloys used may account for the differences noted.

Previous work at NRL [18] indicates that the freezing point of pure potassium is 63.7°C rather than 62.5°C as commonly reported.

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17 E. Rinck and C. H. Kean, op. cit.

18 R. R. Miller and S. L. Walters, Ind. Eng. Chem.(Anal. Ed.) 18, 8. 468, 16 August 1946.

WETTING TEMPERATURES

The temperatures at which alloys of sodium and potassium were found to wet some of the common metals were reported in the first Quarterly Report.[19] As only a brief description of the apparatus and methods was presented at that time, a more complete picture is presented here, together with results for sodium with nickel and steel.

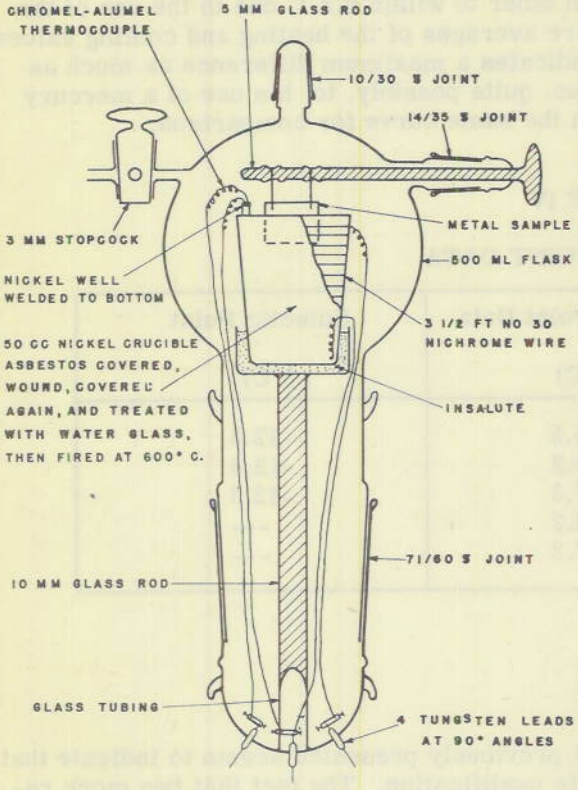

Figure 7 Apparatus for Wetting Point Determinations

A diagram of the apparatus in which the wetting determinations were made is presented in Figure 7. The metal was introduced into the nickel crucible through the top joint under an atmosphere of nitrogen, purified in the usual manner. The heating coil wound around the crucible was used to raise the temperature of the alloy. A chromel-alumel junction extending below the surface of the liquid alloy was used to record temperatures. To determine the wetting temperature, a one-inch-square metal plate, suspended by wires from the glass rod, was alternately raised and lowered into the alloy as the temperature was gradually changing. The liquid alloy was said to be "wetting the metal" at the temperature where the alloy was observed to climb the metal surface as the metal sample was lowered into the liquid alloy.

The results of the tests with sodium are tabulated below:

Alloy	100% Sodium
Metal Sample	Nickel
Wetting Temperature	355 ± 5°C
Alloy	100% Sodium
Metal Sample	Steel (Low Carbon)
Wetting Temperature	370 ± 5°C

With wetting determinations, there is always the possibility that undetected small amounts of dissolved impurities will affect results. At present, work is in progress in an attempt to learn more regarding the wetting characteristics of the liquid metals. Some difficulty was experienced in obtaining alloy samples free from contamination, but the samples reported were free from surface impurities. One source of error in the present apparatus would appear to be any difference in temperature between the surface of the alloy and that recorded by the thermocouple. The results reported, however, are believed to be within ± 5°C.

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19 C. T. Ewing and R. R. Miller, NRL Report P-3010, "Quarterly Progress Report on the Measurement of the Physical and Chemical Properties of the Sodium-Potassium Alloy, No. 1," 30 September 1946.

PHASE SEPARATION IN THE ALLOY ON STORAGE

Samples of alloy removed from the same container have been reported to vary in composition. This might questionably be attributed to a phase separation in the alloy upon standing. It was, therefore, the purpose of this investigation to determine if there is any evidence of the so-called phase separation.

As a complete description of apparatus and methods was presented in NRL Report P-3057, this section shall be confined to experimental results and their analysis. Storage tests were made on two alloys under varying conditions. The results of these tests are tabulated in Table V. The analytical values reported for No. 1 storage test in Report P-3057 were slightly in error.

TABLE V

DATA ON PHASE SEPARATION STUDY

Alloy	Time of Storage Between Sampling (Hours)	Storage Temperature (°C)	Composition After Storage (Mol-% K)		Preliminary Treatment
			from top	from bottom	
No. 1 (F. P. 0°C)	146	145	54.7	54.5	none
	433	145	-	54.8	none
No. 2 (F. P. 53°C)	52	80	16.5	17.2	Alloy cooled to 20°C and heated to 80°C
	52	110	-	16.3	Alloy mixed
	72	110	-	17.3	Alloy cooled to 20°C and heated to 110°C

These experiments should indicate conclusively that no phase separation occurs. However, a case of improper mixing might easily be construed as phase separation. It is noted from the table above that if an alloy is cooled below its melting point, separation of the solid from the liquid phase can occur, and complete mixing does not take place when the alloy is reheated to 110°C for 72 hours. It seems probable, then, that reports of settling out may have originated from similar conditions.

THERMAL CONDUCTIVITY

Professor Bidwell of Lehigh University is under contract to furnish data on thermal conductivity. Measurements will be conducted on the pure metals and on

four alloys covering the composition range. No attempt was made to duplicate master samples in these four alloys. The stainless steel containers for these measurements were made here at the Laboratory, filled with freshly distilled metals, and shipped to Lehigh University. The report from Professor Bidwell should be available for the next Quarterly Report and should furnish complete particulars.

CONCLUSIONS

A study of the properties of the sodium-potassium alloys is being continued.

APPENDIX

PRELIMINARY REPORT NO. 3

METHODS OF HANDLING, STORING, SHIPPING AND TRANSFERRING LIQUID KNA ALLOYS

by

R. E. Lee
R. C. Werner and R. A. Tidball

Mine Safety Appliances Company
Callery, Pennsylvania

January 28, 1947

CONTENTS

ABSTRACT

Information on handling, storing, shipping, and transferring KNa as a liquid metallic alloy has been compiled from experience obtained in the manufacture of tonnage quantities of KNa over the past six years

INTRODUCTION

A. Authorization

This project was authorized by Contract No. N6 ori-146

B. Statement of Problem

This project covers collection and compilation of information on methods of handling, storing, shipping, and transferring KNa alloys. Material for this report was gathered from research and production experience in the manufacture of K and KNa alloys. As further information on these methods is obtained, it will be compiled and issued as supplements to this report.

C. Known Facts Bearing on the Problem

Because of the relatively recent importance which has been attached to the use of KNa alloys, little has been known of methods of handling, storing, shipping, and transferring it in quantity. Since Mine Safety Appliances Company has been engaged in large scale production of these alloys for the past six years, considerable experience in these methods has been acquired. This report is designed to present these methods.

METHODS

A. General

KNa is an alloy of potassium and sodium having chemical and physical properties similar to the two elements. On exposure to air at room temperature, an oxide coating will be formed on the surface and, with water vapor from the air, the reaction will form a coating of hydroxide. After this initial reaction, which is very rapid, the reaction rate slows considerably and, if not disturbed, the reaction will continue slowly until all the KNa has reacted. If, however, the KNa is disturbed so that the moist hydroxide comes in contact with fresh metal, the reaction rate is increased and a fire may result which will spread rapidly.

KNa reacts violently with water, releasing hydrogen. Sufficient heat is liberated to cause the hydrogen to react explosively with oxygen in the air. However, in the absence of oxygen there can be expected only a rapid generation of hydrogen.

B. Means of Moving

KNa can be pumped intermittently with standard pumps at temperatures up to 350°F. Worthington GI 1/2 gear pumps have been used with some degree of success pumping KNa intermittently at temperatures as high as 350°F. However, for continuous operation, these pumps cannot be recommended for use at temperatures greater than 250°F. Viking Model EC H2 gear pumps, Hills-McCanna Type RM 1FD, Milton Roy, and Bump pumps have all been used at temperatures under 200° F.and have all given excellent service at these temperatures. None of these have, however, been tested at higher temperatures. In all these pumps, standard mild steel and cast iron construction was used and no noticeable corrosive effects have been found.

The principal problem encountered in any of these pumps is that of packing. This problem is present even in pumps operating at room temperature and, becomes more acute as the temperature is increased. The Hills-McCanna and Milton Roy pumps used were operated at temperatures under 200°F. For these pumps, John Crane #811 SP packing was used which gave very satisfactory performance. In the Worthington pumps, Cutno (for Caustic Soda), Pelro (for gasoline, naptha, etc.) and Garlock 1700 RG were tried at temperatures up to 350°F. Of these, the Cutno was by far the most satisfactory though it did not give nearly as good service as the Crane #811 SP which was used in the Hills-McCanna. No metallic packings were tried though some of these might prove more satisfactory than those used.

For movement of KNa from a tank, pressure of an inert atmosphere in the tank can be used as the motivating force. Wherever its use is possible, this method is probably the best for moving KNa as it provides none of the difficulties inherent in the use of pumps.

Natural circulation can be used to transfer KNa due to the great variation in density with temperature changes. The system must be a closed one before this effect can be achieved. However, in many applications of heating or cooling this method could be used to great advantage. The only requirements for this type system are that the KNa be cooled at the upper level and heated at the lower level.

NOTE: When samples of alloy are being drawn from a container, it is advisable to insure homogeneous mass by warming to 200°F, and agitating. Agitation may be accomplished by rocking the container.

C. Permissable Atmospheres over KNa

Any gas is permissable for use over KNa which will not react with the KNa or with the materials of construction at the temperatures being used. Nitrogen, helium and argon have been used apparently with no detrimental effects either on the KNa or on the metals used for containers. Nitrogen has been used extensively and, while complete data is not available, it seems that nitrogen neither dissolves in the KNa nor reacts with it. There is some basis for belief that nitrogen, in the presence of KNa, at elevated temperatures does react with certain steels producing brittleness. Also, although some references warn of reaction between nitrogen and KNa, no definite proof of this has been obtained in our extensive use of nitrogen. Metallographic and chemical analyses were made of samples of wrought iron in contact with boiling KNa for 500 hours. This investigation showed no evidence of nitrogen absorption by the iron.

D. Purification of Atmosphere

The gas to be used for atmosphere over KNa must be purified to remove any impurities that might react with it. For the most part, these consist of water vapor and oxygen. These impurities will give oxides and hydroxides of K and Na. Oxides and hydroxides, if present, will plug pipes, meters and pumps. Since commercial nitrogen may have as much as 0.3% oxygen present and some water, it is important that a good method for deoxidizing and drying the gas be employed.

Any of several deoxidizers can be used. However, one of the simplest is a tower packed with copper turnings. The tower is heated to 600-800° F and the gas is passed through it over the hot copper. The hot copper forms copper-oxide with the oxygen from the gas. To reactivate, hydrogen is passed through the tank reducing the copper-oxide again to copper and, after flushing out the hydrogen, the deoxidizer is again ready for use. If continuous use is required, a bank of two deoxidizers can be used, reactivating one while using the other. The degree of purification obtained by the method is not accurately known. However, oxygen analyses have been run and concentrations as low as 0.03% oxygen by volume have been recorded. If further purification is required, a KNa deoxidizer can be set up wherein the gas is bubbled through KNa in a packed tower. If copper and KNa deoxidizers are used in series the highest degree of purification should be obtained.

For removal of water vapor from gases to be used, a system could contain any good drying agent. One that has been used quite successfully is a unit made by Pittsburgh Lectrodryer Corp. This unit contains activated alumina which absorbs water from the gas. It is reactivated by heating, with a blast of air passing through the alumina bed to remove the water. A lectrodryer contains two units so that one can be reactivated while using the other. If further drying is required, the gas can be passed through a KNa bubbling tower for final purification. However, dew points of -40° F have been recorded with no drying other than the Lectrodryer.

Thus, gas to be used for atmosphere over KNa should be passed through a deoxidizer, then through a dryer and, if desired, finally through a KNa bubbling tower.

E. Materials of Construction

Corrosion tests have been run at 1400-1500 °F on samples of standard black iron pipe, type 304 stainless steel and are in the process of being run on nickel, inconel and type 25-20 stainless steel. Results of these tests show that the wrought iron pipe was severely attacked under the conditions of the test. These test conditions include bubbling

nitrogen through the KNa throughout the life of the test to prevent excessive super-heating of the KNa. The tests on stainless steel showed that it withstood attack well. The test pieces that were immersed in boiling KNa were not attacked at all. However, test pieces suspended in KNa vapor had a light metallic deposit on the lower end.

In our production equipment, stainless steels have been used exclusively for all installations operating at temperatures in excess of 400°F. Most failures in stainless steel high temperature equipment have been at welded joints, generally at points where considerable strain was exerted on the weld. These failures are of two forms: cracks through the weld probably due to excessive stresses; and pin holes through the welds from faulty welding.

Where a leak occurs in a system containing KNa, it is difficult to make a good weld. This is due to the oxide of KNa which forms in and around the failure. Our practice, which has given satisfactory results, has been to wash the section with 3% acetic acid and clean with a wire brush. In some cases, it is necessary to polish with a grind wheel. This is particularly true where the equipment has been in use at 1400-1600°F for some time because, after being heated to these temperatures, an extremely hard scale is formed over the outside of the steel. This scale makes welding very difficult, causing the weld to spatter and preventing the weld from burning into the parent metal. We are at the present time experimenting with acetylene welding of stainless steel with the possibility of having better success in prevention of small cracks and pin holes in welds.

In none of our equipment have we noticed any undue pitting or corrosion from the inside. Almost without exception, failures have been from the outside. After a leak has occurred, if the oxides and hydroxides of K and Na are not completely removed from the outside of the equipment and from the furnace, corrosion from the outside is very rapid with deep pitting, and failure occurs soon. It is very important, where the equipment is contained in a furnace, that care be taken to remove the hydroxides and oxides of K and Na because, in the case of porous insulating bricks, these oxides will saturate the pores of the bricks and, on subsequent firing, be volatilized and corrode the equipment.

As far as low temperature (Under 250°F) operations are concerned, it has been our practice to use standard black iron pipe and fittings, standard mild steel, cast steel, or cast iron pump construction, and mild steel tank construction for storage. Standard cast iron plug valves are currently being used where valving is necessary. Some investigators believe that KNa will decarburize cast iron. If this is true, plugging of a system due to this carbon, which would be carried along by the KNa, could easily result. In one system containing three pumps and piping to three pieces of equipment, the entire pumping system has been in use for over two years and shows no visible signs of corrosion. This system has been operated at temperatures under 100°F. The pumps used in the system are Milton Roy and Hills-McCanna with standard cast iron stuffing box and mild steel check valve system.

There is a possibility that nitrogen, in the presence of KNa at elevated temperatures, may have a detrimental effect on steels. However, we have had no failures which we felt could be attributed directly to this cause. As stated previously chemical analysis showed no absorption of nitrogen by wrought iron in contact with boiling KNa for 500 hours.

F. Liquid Level Indicators

Liquid level indicating presents one of the more difficult problems in the handling and storing of KNa. Several methods have been developed and employed.

Floats can be used and give good service where remote indicating is not necessary. It is necessary to have a packing gland on the indicator arm so that the vessel can be kept under pressure. However, a float system is easily mounted on any tank and little difficulty is experienced in their use. It is possible to set up a system using micro-switches which will complete an electrical circuit at various levels in the tank. By means of a system such as this, remote indicating of various levels is possible.

Liquid levels can also be determined by means of the pressure drop between the bottom of the vessel and the top. This system is installed by placing one pipe to the bottom and one to the top of the container. Nitrogen, or any other inert gas, is then flowed slowly through both lines. From the difference in pressure required to force gas through the two lines, and the density of the KNa, the depth of liquid is easily determined. Pressure gages can be placed in each line and the pressure differential observed; or a commercial liquid level indicator can be used which will show directly the pressure differential and can be calibrated to read inches of water or inches of KNa at any desired temperature.

Since KNa is an electrical conductor, liquid levels can be determined using this property. By this method, the KNa is used to complete an electrical circuit from batteries through an adjustable rod, the KNa, to the sides of the metal container and back to the battery. A light or buzzer may be included in the circuit, to serve as an indicator when the circuit is closed. In using this method, it is important that the tip of the rod be clean and free from KNa oxides or hydroxides. More accurate measurements are obtained by lowering the rod into, rather than raising it from, the liquid. If an adjustable rod is not desirable, fixed rods may be placed at various critical levels to determine the approximate level.

If it is possible to place the tank in which the KNa is to be stored on scales, accurate weight measurements can be made by making connections to the tank with a flexible tube. In this manner continuous weights can be obtained and the amount of KNa in the container at any time can be determined. Using a long copper tube 5/16 inches O. D. for the connecting pipe, the weight can be determined to an accuracy of ± one ounce. By using a 4 ft flexible steel tube, 1-1/4 in. I. D., weights to ± one pound can be made.

Another method which might prove useful for certain applications involves measurement of the pressure of gas over the KNa at two pressures and the volume of gas added to or removed from the container to obtain the different pressure. From these data the volume of the tank occupied by gas can be determined and by subtraction, the volume of the KNa. This method might be useful in some cases where none of the above-mentioned measurements are practicable.

G. Measurement of Flow

KNa flow can be measured by any means that is suitable for any other fluid at the temperatures desired. Calibrated orifice, standard flow meter, rotometer, or positive displacement pump are some of the methods which could be used. With the possible exception of the orifice meter and rotometer, it is necessary that the KNa be clean and free from solid particles which might clog the meter being used. Most flow meters are built with very close tolerances between the rotating disc and the meter body and very small particles of solid material are sufficient to jam the disc. Generally, it is recommended that close tolerance meters be avoided.

H. Preparation of Equipment

Before charging a system with KNa, the entire system must be thoroughly cleaned, dried, and purged of oxygen. Equipment can be cleaned by sand blasting, pickling, or buffing, depending on the surface condition, followed by thorough washing with water. After the original treatment to remove oxide and scale, an inert atmosphere should be kept in contact with the container at all times to prevent rusting. If rusting does occur, it can be removed by heating in an atmosphere of hydrogen.

After cleaning, the equipment must be thoroughly dried before introducing KNa into the system. Extreme care must be exercised in drying the system, particularly at any points where there is a possibility of having a water pocket. Some materials of construction, stainless steel for example, are very poor conductors of heat so that the entire apparatus should be well heated since one portion could be hot enough to evaporate water while an adjacent section would receive very little heat. While heating to dry, a stream of dry gas should be passed through the apparatus to remove the water vapor.

The final step is thorough purging with an inert gas to insure removal of all oxygen from the system.

When filling equipment with KNa for high temperature operation, ample expansion tanks must be provided as some of the alloys may expand as much as 25% on heating from 60°F to 1300°F.

I. Cleaning Equipment Containing KNa

When it is desired to clean equipment containing KNa, the KNa should be drained as completely as possible from the apparatus. The KNa left clinging to the walls of the equipment can then be removed by reacting with steam, butyl alcohol, wet air, or methyl alcohol - xylene mixture. Any of the above-mentioned reagents will react non-violently with the KNa provided an inert atmosphere is kept in the equipment. Steam is rather rapid while wet air would be rather slow in reacting. The reaction rate with methyl alcohol-xylene can be controlled by varying the ratio of the two.. When all the KNa has been reacted, the equipment can be washed with water and dried. It is essential that all the KNa be reacted before the addition of water for rinsing. It is also important that no oxygen be admitted to the equipment until after it has been thoroughly rinsed with water to prevent the possibility of a violent reaction between oxygen and hydrogen.

J. Means of Heating KNa

KNa can be heated by any of the means used ordinarily for heating liquids. Gas fired boilers, have been extensively used and this method is especially suited for heating large quantities. External electrical heating elements have also been used to some extent in smaller installations. Perhaps the most suitable method, however, is immersion heaters. Chromalox heaters, manufactured by Wiegand Co., have been used and have proven satisfactory at temperatures up to 1500°F. Due to the high heat transfer coefficient of KNa, there is little danger of overheating the elements as is the case with oils.

K. Extinguishing KNa Fires

When a fire occurs with KNa, it is likely to spread rapidly if an appreciable surface is exposed. Few commercial fire extinguishers are suitable for use on these fires as most contain either water or carbon tetrachloride, both of which react violently with KNa.

One commercial extinguisher that can be used is the liquid CO_2 type wherein CO_2 gas and snow are sprayed on the fire. The method most commonly used for extinguishing KNa fires is smothering with dry sand or salt. After the fire has been extinguished, the salt - KNa mixture can be shoveled up and disposed of.

L. Removal of KNa from Skin and Clothing

In the handling of KNa in quantity, it is possible that at times some KNa will be spattered on the person or clothing of the workers. Ample personal protective clothing should be employed. At low temperatures, under 200°F, it is seldom that small amounts of it spattered on clothing or skin will burn. In these cases involving small amounts, KNa can best be removed by scraping it off with a knife or other sharp instrument. In no case should an attempt be made to brush it off as this will ignite the KNa and cause it to burn. This applies both to clothing and to skin. After removal by scraping, the last traces can be removed by washing with 3% solution of acetic acid which will neutralize the alkali formed.

If a person should be covered with large amounts of KNa on his clothing, the clothing should, of course, be removed quickly. If, however, KNa contacts exposed parts of the body, the best treatment is the removal of it as quickly as possible. This can best be accomplished by flooding with large quantitites of water or 3% acetic acid. A quick-opening safety shower should be provided for such a contingency.

It is seldom, if ever, that this latter threatment for large amounts of KNa will be necessary but the possibility must be considered and provided for.

M. Shipping of KNa

At the present time KNa is shipped in 1 pound, 2 pound, and 225 pound containers. The one pound and two pound containers are fitted with two 1/4 inch pipes, one of which is flush with the top of the container for pressurizing and the other extending to the bottom of the container for removal of the KNa. The pipe extending to the bottom is marked with a tag for identification.

The 225 pound containers are fitted with three 1/2 inch pipe connections on the top. Two of these are flush for pressurizing and the third, which is painted with aluminum paint and labeled, extends to the bottom for removal of contents.

In all shipping containers, a minimum of 15% void space is allowed for expansion of the KNa. The tank is shipped with an atmosphere of dry, oxygen-free nitrogen over the KNa. When removing the KNa from the containers, care must be taken that no oxygen be admitted into the container. Nitrogen, argon, or helium are all permissable atmospheres for use over KNa. When empty, the container should be pressurized and returned to shipper.