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TECHNICAL MEMORANDUM

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TITLE: Oxides in NaK

ABSTRACT

The eutectic alloy of sodium and potassium (NaK) is very oxygen-reactive. A review was made of how the NaK and the SNAP-8 system are affected; the sources of oxygen contamination in a NaK system; the solubility of the oxide; the effects of the oxide in respect to the system and on the NaK; and oxide control methods.

KEY WORDS: cold trapping, crystallization, hot trapping, mass transfer, NaK, oxides, potassium superoxide, sodium monoxide, solubility

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NOTE: The information in this document is subject to revision as analysis progresses and additional data are acquired.

AEROJET-GENERAL CORPORATION

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I. SUMMARY

NaK has a high chemical affinity for oxygen with the resulting product being Na_2O; sodium monoxide, because it is the most thermodynamically stable oxide. Principal source of oxygen is from opening a sealed system. Other sources can be from the cover gas impurities, residual oxygen and moisture when first filling a loop; and from oxides that are less thermodynamically stable than Na_2O.

Uncontrolled oxide can cause loop plugging in cooler areas; acceleration of corrosion of iron-base alloys; damage to oxygen-sensitive materials and changes in NaK physical properties. The oxide can be controlled by starting with and assuring a tight system; use care when cutting into a loop; and removal of oxides by a purification system. Methods are available for monitoring oxide content to assure high purity.

II. INTRODUCTION

NaK, the primary loop heat transfer fluid for the SNAP-8 system, is an eutectic mixture of two alkali metals, sodium and potassium. The basic reasons for selection of this alloy system was because of its relatively low melting point, high boiling point, low vapor pressure, thermal stability, and high heat transfer coefficients.

The alkali metals are very reactive toward moisture and oxygen, and thus special handling is required. If these contaminants are present, the chemical reaction results in the formation of alkali metal oxide, which can have adverse effects on the system. This technical memorandum describes the reaction of NaK with these impurities, the effects of the oxide on system operation and methods for removal.

III. ALKALI METAL OXIDES

The alkali metals are assigned Group 1 position in the periodic chart of elements, Fig. 1. As the atomic number increases, so does reactivity. Lithium is less reactive than sodium; sodium is less reactive than potassium. However, the combination of sodium and potassium in the eutectic alloy

NaK, Fig. 2, is more reactive than is the potassium, because it is a liquid and thus it has greater internal energy due to the added heat of fusion. The reason that the activity increases with the atomic number is that as the lone electron in the outer circle becomes further distant from the nucleus, the binding energy decreases. On the opposite side of the table oxygen in Group 6A is a strong electron acceptor. The reactivity of the elements in this group decreases as the atomic number increases because the nucleus has more attraction power in the lower atomic number than the higher atomic number of the same group.

Various oxides of the individual alkali metals can exist in equilibrium with the metal. The presence of a particular compound is contingent on the availability of the oxygen and the temperature.

The several oxides of sodium and potassium and selected physical properties are shown in Table 1. Some of the properties of these oxides were not available. The table shows that the stable oxide for potassium at room temperature is the KO_2 but for the sodium, it is the Na_2O_2. This means that if an excess of oxygen exists, the compound that will form with the individual alkali metal will be that which is stable at room temperature.

The normal oxide that is present in the NaK systems is the Na_2O, sodium monoxide.

Potassium super oxide, KO_2 the stable oxide for K at room temperature, a very strong oxidizing agent, is used as a source of oxygen in Kemox Gas Masks, Ref. 1. This oxide reportedly will explode if it comes in contact with organics or with unoxidized K or NaK. Shortly after World War II in England two men were killed when an oxidized potassium ingot - probably with some of the protective oil on it - was cut, see Appendix I.

While it is true that oxygen is preferentially attached to the sodium in the NaK alloy system, oxidation of potassium to KO_2 may occur on the walls of equipment where static NaK is not in direct contact with the bulk of the liquid metal and there is a source of oxygen. This condition would also exist in the expansion reservoir above the liquid line where concentration of the potassium is greater. The pressurizing cover gas will supply finite amounts of moisture and oxygen which will oxidize the liquid metals in this area. Oxidation of potassium is also possible on the surface of a pool of NaK where an oxide layer is formed preventing direct contact between the NaK and the top of the oxide layer. Under these conditions, when KO_2 is present an explosive reaction may occur in a NaK system if hydrocarbons are used for cleaning the equipment. In several instances where explosions have occurred in NaK systems, there was the possibility that both super oxides and hydrocarbons existed. However, there have been no difficulties encountered with KO_2 formation in equipment operated in the proper manner.

Deposited oxides from sodium are reported to be silvery and brittle, Ref. 2. The silvery color may have been sodium metal contamination. Hardness values of the oxides would be very difficult to measure because of potential presence of the metal.

The NaK oxide is heavier than the NaK. On initial exposure to air, the oxide is on the surface because of surface tension. There is no information on the settling rate of the oxide, as it grows on top of the NaK.

From the reactivity of potassium and the amount of potassium in the NaK it would be assumed that the potassium oxides preferentially exist but this is not true. Figure 3, the free-energy of formation of various oxides from Ref. 3, solves this anomaly. Free energy of formation is a thermodynamic function that defines the stability of a compound. Stability increases as the free-energy value becomes more negative. Note, however, the free-energy does not define the kinetics of the system, i.e., it does not say when the reaction will occur, only that it has the potential to occur. Na_2O, sodium monoxide is more negative than the potassium monoxide, see Fig. 3. Thus, when a system of sodium and potassium occur with oxygen, the stable oxide will be the sodium monoxide. Potassium monoxide probably forms but does not remain because it is less thermodynamically stable than the sodium monoxide. It has been shown that the sodium in the potassium system as an impurity, can be removed by reacting it with oxygen, Ref. 4.

A. SOURCES OF OXYGEN

The table below lists the sources of oxygen in a liquid metal system.

SOURCES FOR OXYGEN PICKUP BY ALKALI METAL SYSTEMS

1. Opening a system to remove or replace a component, or a leak.
2. Residual O_2 and moisture in a loop when first filling
3. Cover gas impurities.
4. Scavenging of oxide from compounds less thermodynamically stable than Na_2O

The primary source occurs when a system is opened. Extreme care must be taken because both air and its included moisture react to produce oxide. The main precautions are to not have a vacuum in the system and to seal the open line as soon as possible after removing the item of interest. Expandable rubber plugs (i.e., similar to those used for Thermos bottles) are recommended for sealing because of their utilization ease and sealing ability.

Another source of oxide is the cover gas which as-procured for SNAP-8 use is guaranteed to have no more than 20 ppm (by wt) gaseous impurities and 2 grains of moisture per 1000 ft.^{3} If it were assumed that oxygen was the only impurity and its level were 20 ppm, there would be enough oxygen in 1000 ft^3 at STP to generate approximately .009 lb sodium monoxide, a quantity sufficient to plug a 0.6 in. dia. line if it were to deposit in one place. The moisture in the same gas quantity would produce approx. 10^{-4} lbs. sodium monoxide. See Appendix 2 Section 1 and 2 for calculations.

The other sources are minor and with good operating procedure can be controlled or circumvented as problem areas.

B. SOLUBILITY AND CRYSTALLIZATION

Many liquids are capable of selectively dispersing solids by dissolving, such that the liquid and the solid become a homogeneous solution. The solvent action is postulated to result from attractive force between the liquid and a specific solid. Thermal forces aid solvation forces of the liquid to break apart the structure of the solid and disperse the molecules. This is analgous to vaporization of a liquid to a gas. The dispersed solid in the solution is defined as a solute; the dispersing liquid is defined as the solvent.

The solute, in the solvent as molecules or ions, moves around the system due to its kinetic energy of translation. Some particles will thus continue to return to the surface of undissolved solid. Particles from the solid having the composition of the solute will continue to disperse into the liquid. When the return rate equals the dispersing rate at a specific temperature, equilibrium is established and this can be plotted. The equilibrium solubility curve has been defined for the sodium monoxide in NaK, see Fig. 4. This is also known as a plugging curve. The figure shows that the sodium monoxide concentration increases as temperature increases, but since it is an equilibrium condition, it is time-dependent.

If a solution is saturated - that is, it cannot hold any more solute at that temperature - the concentration of the solute is on the curve of the equilibrium diagram at that specific temperature. For example, at 600°F, the equilibrium quantity of Na_2O in a NaK system is 100 ppm, as oxygen, see Figure 4.

It is theorized that as the equilibrium solubility level is approached the attractive forces between some of the solute molecules begin to overcome the forces of solvation. When the temperature is decreased below the saturation level, the molecular attractive forces are the dominating ones and enough solid will be formed to re-establish equilibrium.

In solute/solvent systems supersaturation can occur, that is the retention of solute beyond the solubility values. This phenomenon occurs because of the high solubility of small crystals. Supersaturation is aided by careful exclusion of crystallized particles; by slow changes in temperature; and by quiescent conditions in the liquid. Conversely precipitation or crystallization is aided by: moderately fast changes in temperature; the flowing system; the existence of crystals of the solids that act as seeds; and rough surfaces. The conditions for super saturation do not exist in the SNAP-8 system.

Crystallization is utilized by SNAP-8 to purify NaK. This is known as cold-trapping and will be described later.

C. THE EFFECT OF OXYGEN ON A LIQUID ALKALI METAL SYSTEM

The table below lists the effects of alkali metal oxides on a liquid metal system.

EFFECTS OF ALKALI METAL OXIDES ON A SYSTEM

1. Plugging by crystallization in cooler portions of the loop, especially small diameter lines.
2. Acceleration of mass transfer corrosion of iron base alloys.
3. Oxidation of materials more thermodynamically stable than sodium monoxide.
4. Depletion of sodium from NaK alloy, which will change the physical property of NaK.

Each of these are considered below.

1. PLUGGING

If the NaK system is saturated with Na_2O at a particular temperature the oxide will crystallize in cooler areas, for example transducer lines and smaller clearance areas. Redissolving is very difficult because solvation is controlled by temperature and concentration of the oxide in the NaK at that location. If a line is plugged, the oxide removal would be controlled by thermal convection and diffusion. Removal by melting is difficult because of the oxide melting point, approximately 1700°F.

2. MASS TRANSFER

Na_2O accelerates corrosion of iron-based alloy if the concentration as oxygen is 50 ppm or greater (200 ppm Na_2O). It is postulated that the following chemical formula defines the mass transfer corrosion in NaK/iron base alloy system when the concentration of Na_2O is above a 50 ppm as oxygen:

In the hot leg, (approximately 1300°F):

$$y\,Fe + (x + y)\,Na_2O \longrightarrow (Na_2O)_x(FeO)_y + 2yNa$$

In the cold leg (approximately 1100°)

$$(Na_2O)_x\,(FeO)_y + 2y\,NaK \longrightarrow yFe + (x + y)\,Na_2O + 2yK \text{ (Ref. 5)}$$

As can be seen, the Na_2O) recycles and picks up additional iron in the hot leg, but the oxide is never depleted. As the iron precipitates in the cooler leg, it gradually builds up and can eventually close a line.

3. OXIDES OF MATERIALS MORE THERMODYNAMICALLY STABLE

If materials exist in the system that have oxides that are more thermodynamically stable than the Na_2O, see Fig. 4, the Na_2O can react to give the oxide of that metal and regenerate the sodium. If the metal is a material that is sensitive to oxygen, its physical properties can be affected. This principle is employed when zirconium is utilized in hot traps to getter oxygen from liquid alkali metal system.

4. DEPLETION OF SODIUM

Table 2 summarizes the properties that could be affected by depletion of sodium from the NaK, Ref. 6. If the oxygen were continually present to deplete sodium, enough would eventually be removed that could change the physical properties. By definition, 83% potassium NaK has been defined as the maximum utilizable composition for SNAP-8 that will not sacrifice system performance. This limit gives wide latitude, however, since 27 ft.^{3} of oxygen per 100 lbs. NaK would be required, see Appendix 2, Section 3 for calculations.

IV. CONTROL OF ALKALI METAL OXIDES

A. OPERATIONAL PROCEDURES TO PREVENT CONTAMINATION

During the developmental days of the liquid metal cooled nuclear reactor, realization of the adverse effect of oxide in liquid alkali metals led to the development of handling and purification techniques that were capable of achieving and maintaining high purity. Among the techniques were the following:

1. Assure that the system is leak tight since liquid alkali metals can leak through very small holes particularly at elevated temperature. Joints should be welded and helium leak checked.

2. Sub-assemblies must be cleaned and dried prior to incorporation in a loop. (It is recommended that cleaning be done in the simplest configuration and the item prevented from subsequent re-contamination). If cleaning solutions or water remain, NaK will react, causing oxide or a potential explosive condition depending on the fluid remaining.

3. Adequate control of oxygen and moisture in the cover gas must be maintained.

4. Minimize the time a system is open to the air. An open system is the biggest source of oxygen contamination in a liquid alkali metal system. If an open system is subjected to continuous atmospheric conditions, excessive oxygen will be absorbed by the system because of residual NaK. NaK on the wall and any that does not drain will react with oxygen and moisture in the air. As this reaction proceeds a partial vacuum results as the O_2 and moisture are depleted. The vacuum continues to such in additional air with its moisture and oxygen. The NaK would then be converted to sodium and potassium hydroxides, which are very hydroscopic, they would continue to absorb the oxygen from the air and eventually a sodium and potassium hydroxide solution would be present*.

5. Perform hot and/or cold dumps as necessary if the system becomes grossly contaminated. The purpose of a hot or cold dump is to prevent gross contamination of the cold trap, which can trap limited quantities of oxide. Hot or cold dumping can be economical if gross contamination exists.

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* Carbon monoxide from the air will also react forming carbonates.

B. PURIFICATION TECHNIQUES DURING LOOP OPERATION

1. Cold Trapping

Cold trapping, a purification technique developed to remove sodium monoxide, Ref. 7, utilizes the principles of solubility and crystallization (see IIIB). The technique consists of by-passing approximately 1-3% of the main loop fluid, cooling it below the oxide crystallization temperature, passing it through a bed of stainless steel mesh of approximately 20-24 lbs/in^3 density, reheating and returning it to the main flow. Figure 5 is a schematic of a typical purification system.

The oxide level at any time is determined by performing a "plugging run," i.e., a test to determine the crystallization temperature of the sodium monoxide. For this test, a small flow of NaK is passed through a closed valve with a serrated seat, see Fig. 5, as the temperature is slowly decreased. The flow rate and temperature are monitored by an X-Y plotter. When the slope of the curve suddenly drops, the value is taken as the plugging temperature. The Na_2O content - as PPM oxygen - can then be determined by referring to the equilibrium solubility curve, Fig. 4. For example, if the plugging temperature is 600°F, the NaK contains 100 ppm Na_2O as oxygen.

2. Hot Trapping

Alkali metal oxides can be removed from the alkali metal by reacting with a metal whose oxide has greater thermodynamic stability than the oxide being removed, see Figure 3. It is noted that elements such as zirconium, titanium, hafnium, tantalum, tungsten, boron are among the materials that can be used. These materials are used at elevated temperatures because the kinetics of reaction and diffusion of the oxides into the trapping metal are such that the low temperatures are not kinetically feasible and thus, the reduction of Na_2O by this method is called "hot trapping." Zirconium has been found to be one of the most effective hot trapping materials because it forms an adherent oxide and the oxygen readily diffuses into the base zirconium metal. For the zirconium to be effective, it must be heated to approximately 1100 to 1500°F.

Prior to hot-trapping as much oxide as possible must be removed by cold-trapping for economic reasons. The cold trap then is valved out of the system because the oxide from the cold trap would be continuously redissolved to satisfy equilibrium conditions and be transferred to the hot trap. Hot traps are utilized principally when an oxygen sensitive component is in the system.

3. Soluble Getters

A material-like barium which is soluble in NaK and which has oxides that are more thermodynamically stable than sodium monoxide, can theoretically be used to purify a system. The advantage of such a system is that the getter is continuously in intimate contact with the NaK and thus is readily available for reaction with oxygen wherever it exists in the system. Potential problems would be the solubility of the barium oxide in the NaK and the reaction of the barium and/or barium oxide with the materials of construction. Little work has been performed to define the parameters of the technique.

C. OTHER INLINE MONITORING DEVICES

In addition to the plugging valve previously described, there are two in-line monitoring devices being developed. An electrochemical cell has been developed for Na systems with a range of detection of from one to 100 parts per million of oxygen and an operational temperature of 650°F, Ref. 8. Although it has never been tested in NaK, it is claimed that it can be adapted for NaK systems also. The apparatus consists of a solid electrolyte separating an inner reference electrode from the alkali metal. This combination forms a galvanic cell which develops a voltage proportional to the content of the oxygen in the alkali metal. The advantage of an in-line monitoring device is that continuous monitoring can be achieved.

A resistivity meter (RHOMETER) is being developed, Ref. 9, 10, which measures the resistance increase of the alkali metals with increase in impurities. However, this instrument is not selective, that is, not only oxygen but carbon and hydrogen can influence it.

References:

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9. "Evaluation of the Blake Sodium Resistivity Meter," APDA-149, Atomic Power Development Associates, Oct. 15, 1962, (NSA 17-6382).

10. "Operation of the Sodium Technology Loop For Contamination Meters Evaluation," APDA-163, Atomic Power Development Associates, Mar. 25, 1964 (NSA 18-17973).

TABLE I

OXIDES OF SODIUM AND POTASSIUM

POTASSIUM	MELTING TEMP. °F	DENSITY g/cc	COLOR	COMMENTS
K_2O	945	-	White	-
K_2O_2	914	-	Orange	-
K_2O_3	806	-	Chocolate Brown	Dissociates at 1335°F
KO_2	716	2.14	Deep Orange	Stable Oxide at Room Temperature
KO_3	171	-	Red	-
SODIUM				
Na_2O	1688	2.39	White	
Na_2O_2	960	2.6	Yellow White	Stable Oxide at Room Temperature; Starts Decomposing Approx. 960°F
NaO_2	1026	2.8	Bright Yellow	Starts Decomposing Approx. 210°F.
NaO_3	-	-	Dark Red	-

NaK Density at Room Temperature 0.87

TABLE II

CHANGE OF PHYSICAL PROPERTIES OF EUTECTIC NaK CAUSED BY SODIUM DEPLETION

PROPERTY	VALUE FOR EUTECTIC NaK (78%K)		PERCENT CHANGE FOR 83%K NaK	
	600°F	1400°F	600°F	1400°F
Density (Lb/Ft^3)	49.6	43.0	-1.2	-0.93
Specific Heat (BTU/Lb-°F)	0.2117	0.2122	-0.65	-0.62
Viscosity, Abs. (Lb/Hr-Ft)	0.58	0.31	+0.12	+0.84
Prandl Number ($C \mu / K$)	0.0082	0.00475	-6.7	-5.5

NOTE: 83% K NaK has been defined as the maximum utilizable composition for SNAP-8 that will not sacrifice system performance.

PERIODIC TABLE OF THE ELEMENTS

KEY TO CHART
Atomic Number → 50 +2 +4 ← Oxidation States
Symbol → Sn
Atomic Weight → 118.69
-18-18-4 ← Electron Configuration

Transition Elements
Group 8

1a	2a	3b	4b	5b	6b	7b	8			1b	2b	3a	4a	5a	6a	7a	0	Orbit
1 +1 −1 H 1.00797 1																	2 0 He 4.0026 2	K
3 +1 Li 6.939 2-1	4 +2 Be 9.0122 2-2											5 +3 B 10.811 2-3	6 +2 +4 −4 C 12.01115 2-4	7 +1 +2 +3 +4 +5 −1 −2 −3 N 14.0067 2-5	8 −2 O 15.9994 2-6	9 −1 F 18.9984 2-7	10 0 Ne 20.183 2-8	K-L
11 +1 Na 22.9898 2-8-1	12 +2 Mg 24.312 2-8-2											13 +3 Al 26.9815 2-8-3	14 +2 +4 −4 Si 28.086 2-8-4	15 +3 +5 −3 P 30.9738 2-8-5	16 +4 +6 −2 S 32.064 2-8-6	17 +1 +5 +7 −1 Cl 35.453 2-8-7	18 0 Ar 39.948 2-8-8	K-L-M
19 +1 K 39.102 -8-8-1	20 +2 Ca 40.08 -8-8-2	21 +3 Sc 44.956 -8-9-2	22 +2 +3 +4 Ti 47.90 -8-10-2	23 +2 +3 +4 +5 V 50.942 -8-11-2	24 +2 +3 +6 Cr 51.996 -8-13-1	25 +2 +3 +4 +7 Mn 54.9380 -8-13-2	26 +2 +3 Fe 55.847 -8-14-2	27 +2 +3 Co 58.9332 -8-15-2	28 +2 +3 Ni 58.71 -8-16-2	29 +1 +2 Cu 63.546 -8-18-1	30 +2 Zn 65.37 -8-18-2	31 +3 Ga 69.72 -8-18-3	32 +2 +4 Ge 72.59 -8-18-4	33 +3 +5 −3 As 74.9216 -8-18-5	34 +4 +6 −2 Se 78.96 -8-18-6	35 +1 +5 −1 Br 79.904 -8-18-7	36 0 Kr 83.80 -8-18-8	-L-M-N
37 +1 Rb 85.47 -18-8-1	38 +2 Sr 87.62 -18-8-2	39 +3 Y 88.905 -18-9-2	40 +4 Zr 91.22 -18-10-2	41 +3 +5 Nb 92.906 -18-12-1	42 +6 Mo 95.94 -18-13-1	43 +4 +6 +7 Tc (97) -18-13-2	44 +3 Ru 101.07 -18-15-1	45 +3 Rh 102.905 -18-16-1	46 +2 +4 Pd 106.4 -18-18-0	47 +1 Ag 107.868 -18-18-1	48 +2 Cd 112.40 -18-18-2	49 +3 In 114.82 -18-18-3	50 +2 +4 Sn 118.69 -18-18-4	51 +3 +5 −3 Sb 121.75 -18-18-5	52 +4 +6 −2 Te 127.60 -18-18-6	53 +1 +5 +7 −1 I 126.9044 -18-18-7	54 0 Xe 131.30 -18-18-8	-M-N-O
55 +1 Cs 132.905 -18-8-1	56 +2 Ba 137.34 -18-8-2	57* +3 La 138.91 -18-9-2	72 +4 Hf 178.49 -32-10-2	73 +5 Ta 180.948 -32-11-2	74 +6 W 183.85 -32-12-2	75 +4 +6 +7 Re 186.2 -32-13-2	76 +3 +4 Os 190.2 -32-14-2	77 +3 +4 Ir 192.2 -32-15-2	78 +2 +4 Pt 195.09 -32-16-2	79 +1 +3 Au 196.967 -32-18-1	80 +1 +2 Hg 200.59 -32-18-2	81 +1 +3 Tl 204.37 -32-18-3	82 +2 +4 Pb 207.19 -32-18-4	83 +3 +5 Bi 208.980 -32-18-5	84 +2 +4 Po (209) -32-18-6	85 At (210) -32-18-7	86 0 Rn (222) -32-18-8	-N-O-P
87 +1 Fr (223) -18-8-1	88 +2 Ra (226) -18-8-2	89** +3 Ac (227) -18-9-2																-O-P-Q

*Lanthanides	58 +3 +4 Ce 140.12 -19-9-2	59 +3 Pr 140.907 -20-9-2	60 +3 Nd 144.24 -22-8-2	61 +3 Pm (145) -23-8-2	62 +2 +3 Sm 150.35 -24-8-2	63 +2 +3 Eu 151.96 -25-8-2	64 +3 Gd 157.25 -25-9-2	65 +3 Tb 158.924 -26-9-2	66 +3 Dy 162.50 -28-8-2	67 +3 Ho 164.930 -29-8-2	68 +3 Er 167.26 -30-8-2	69 +3 Tm 168.934 -31-8-2	70 +2 +3 Yb 173.04 -32-8-2	71 +3 Lu 174.97 -32-9-2	-N-O-P
**Actinides	90 +4 Th 232.038 -19-9-2	91 +5 +4 Pa (231) -20-9-2	92 +3 +4 +5 +6 U 238.03 -21-9-2	93 +3 +4 +5 +6 Np (237) -22-9-2	94 +3 +4 +5 +6 Pu (244) -23-9-2	95 +3 +4 +5 +6 Am (243) -24-9-2	96 +3 Cm (247) -25-9-2	97 +3 +4 Bk (247) -26-9-2	98 +3 Cf (251) -28-8-2	99 Es (254) -29-8-2	100 Fm (257) -30-8-2	101 Md (256) -31-8-2	102 (254) -32-8-2	103 Lw	-O-P-Q

Numbers in parentheses are mass numbers of most stable isotope of that element.

Figure 1

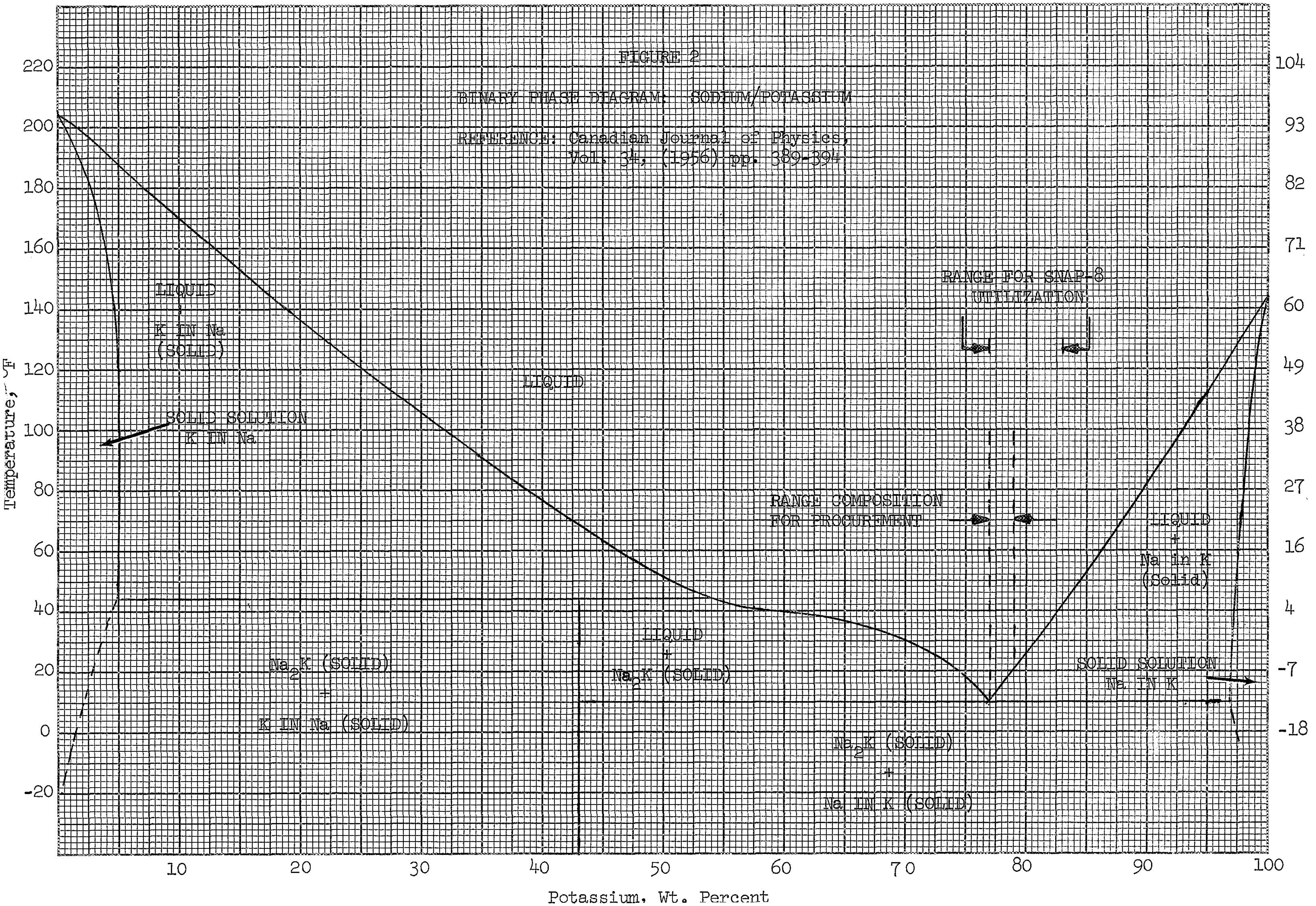


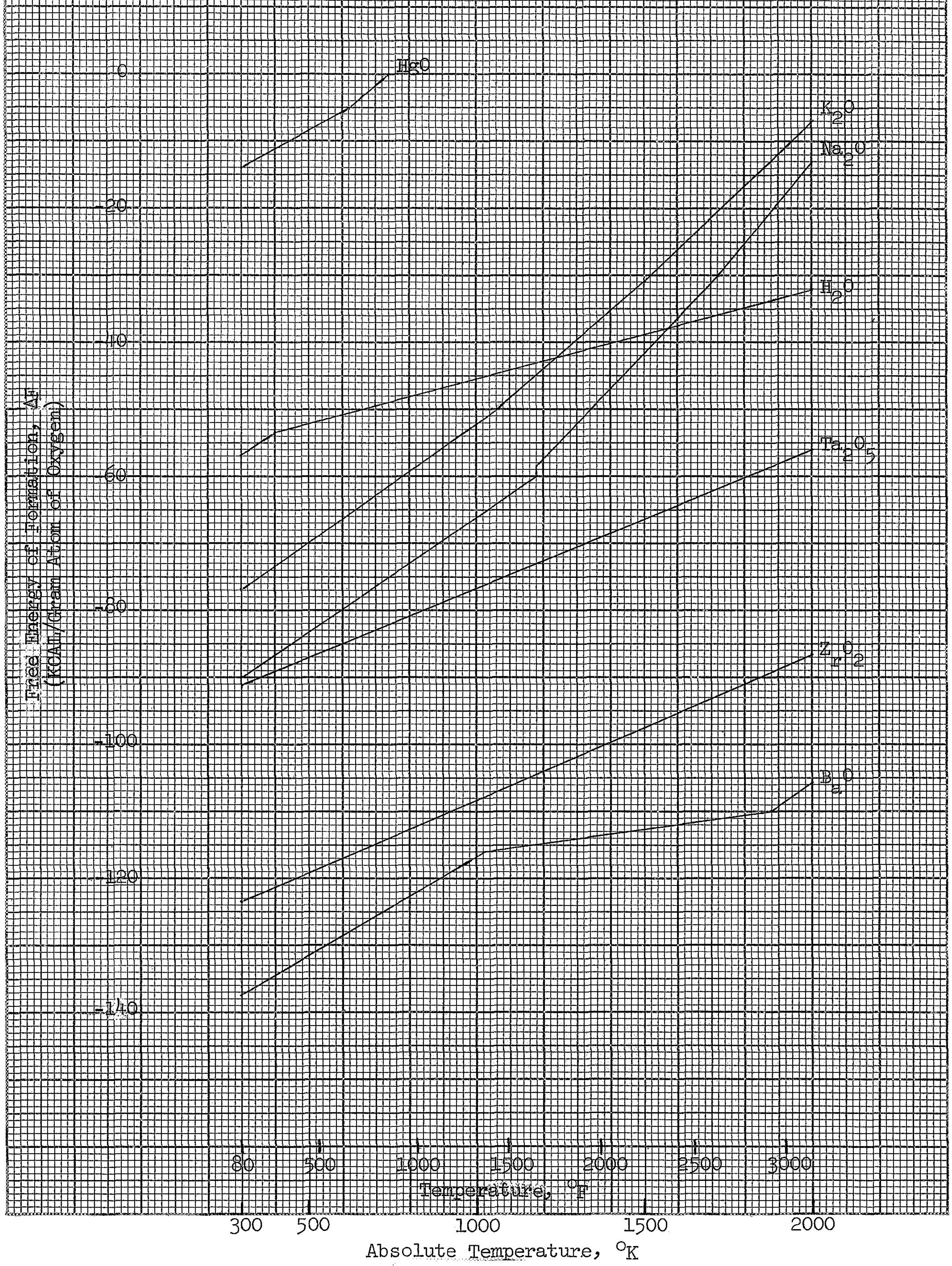
FIGURE 2

BINARY PHASE DIAGRAM: SODIUM/POTASSIUM

REFERENCE: Canadian Journal of Physics,
Vol. 34, (1956) pp. 389-394

FIGURE 3

FREE ENERGY OF FORMATION VS TEMPERATURE FOR SELECTED OXIDES (FROM ANL-5750)



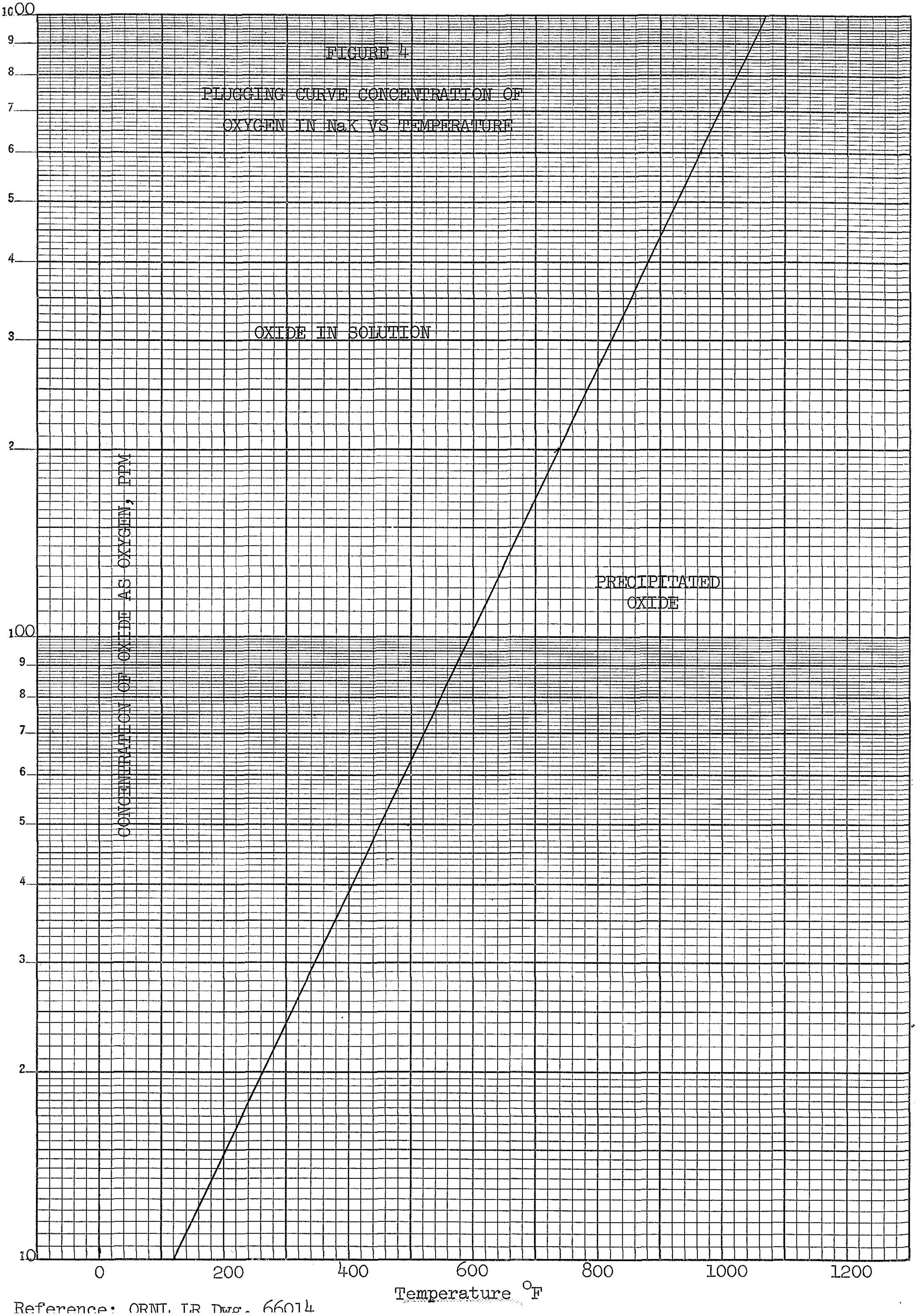
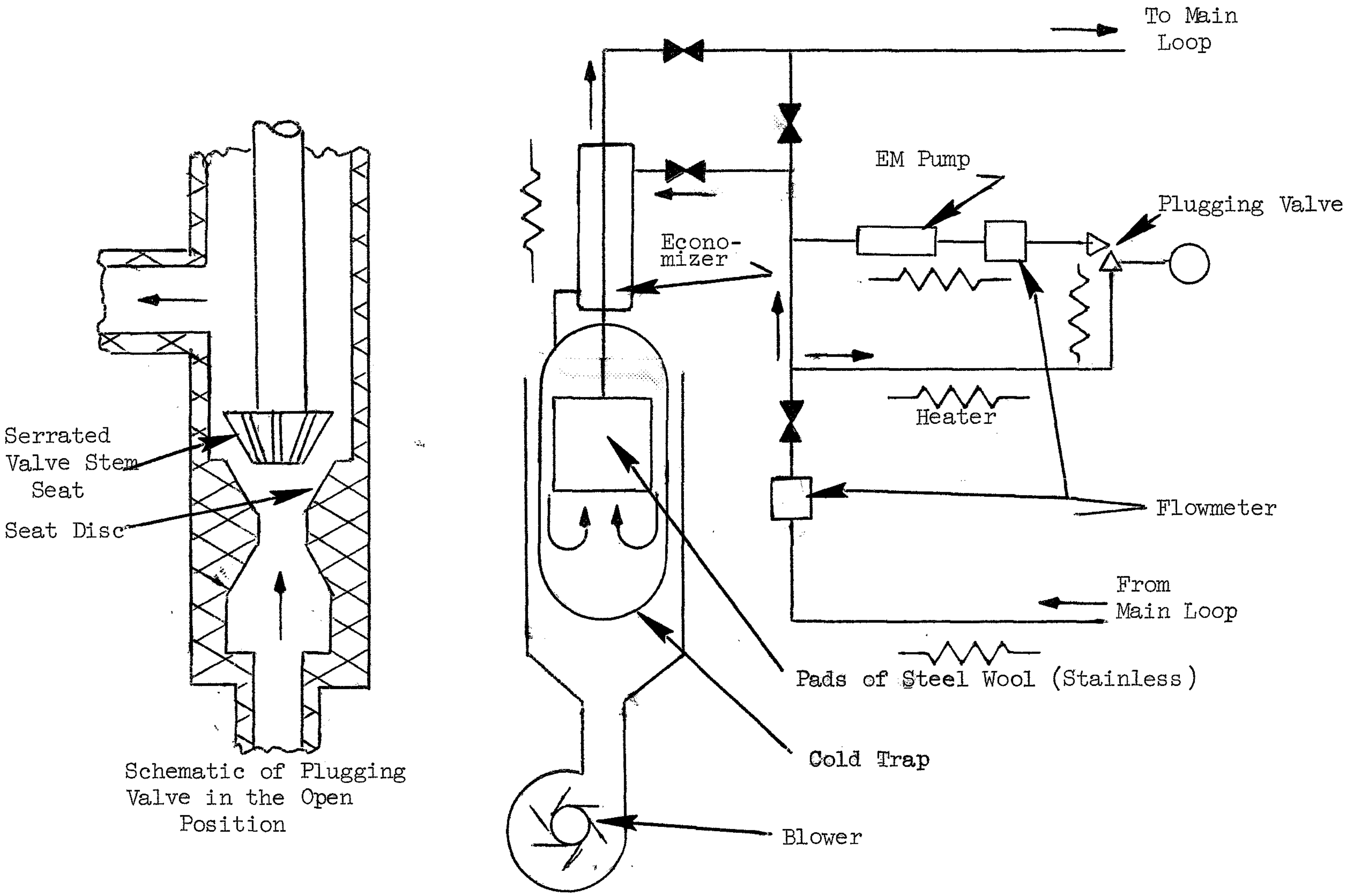


FIGURE 4

PLUGGING CURVE CONCENTRATION OF OXYGEN IN NaK VS TEMPERATURE

Reference: ORNL LR Dwg. 66014



Schematic of Plugging Valve in the Open Position

FIGURE 5

SCHEMATIC OF PURIFICATION SYSTEM

PLUGGING LOOP AND PLUGGING VALVE

APPENDIX A

ARMED SERVICES EXPLOSIVES SAFETY BOARD
Nassif Building
Washington, D. C. 20315

Explosives Incident Report No. 209

Explosion of Potassium Metal

DESCRIPTION

From the time of World War II, several drums of potassium metal (in brick form) had been left in stock. It was decided to dispose of them and sell the potassium for laboratory use. A special bench, covered with a thick steel plate, was set up in the open yard and two operators were assigned to removing one brick at a time, putting it on the bench without delay, cutting it with a knife into cubes as quickly as possible, and finally placing the cubes into smaller bottles filled with an inert solvent. The operation, which was of an emergency character only and not intended as a standard procedure, was performed on a sunny, dry day and usual precautions, as when working with sodium metal, were taken. During the handling, a terrible, unexpected explosion took place. As a result, two operators lost their lives on the spot before help could arrive. The steel plate and bench were scattered all over the yard, and a deep hole was blasted in the ground.

CAUSE:

The exact development of the accident could never be established for lack of witnesses. The concensus of chemists was that an oxide or peroxide of potassium was formed during the long storage under the protecting liquid, which then initiated the ignition.

It has been reported that hitting the potassium with a hammer is dangerous and results in its ignition, and that dry potassium ignites spontaneously on longer exposure in the air due to the oxidative formation of an easily flammable mixture of metallic potassium with its oxides. It has also been mentioned that old, oxidized potassium metal is to be handled with the greatest precaution due to its oxidation to KO_2, which is a very strong oxidizing agent reacting, e.g. vehemently also with potassium metal itself.

Cutting even small amounts of potassium in the air on filter paper or destroying scraps of it with commercial alcohol should be avoided. Experience shows that it is better stored and handled in dry xylene (minimal surface oxidation and discoloration) than in kerosene (petroleum, naphtha). It should always be cut under a layer of xylene in a porcelain dish or mortar, the oxidized surface cuttoff, the scraps transferred without delay into a beaker containing xylene, the freshly-cut potassium removed by forceps into a tared beaker containing xylene, and the weighed potassium then introduced into the reaction mixture. Scraps of potassium, covered with xylene, should be immediately decomposed in a hood by adding tert.-butyl alcohol (not methyl or ethyl alcohol) gradually, at such a rate as to keep the reaction under control and until all the potassium has reacted. A sheet of asbestos or steel to cover the beaker in case the liquid catches fire should always be kept at hand.

Why does the "explosion" of potassium occur with greater ease and violence than that of sodium? We may assume that an ignition, whatever its origin, breaks up the adjacent area of the hot, liquid potassium metal and scatters it as a spray in the surrounding atmosphere, where the metal evaporates, mixes with atmospheric oxygen, and detonates. All these steps occur in a minute fraction of a second and the phenomenon is somewhat similar to the gasoline explosion in an automobile motor. Also, because potassium has a lower m.p. (63·5-97·5°C) and b.p. (779°-892°C) than sodium, it is consequently evaporated and atomized faster than the latter.

(REPORTED BY THE MANUFACTURING CHEMISTS'ASSOCIATION, INC.
FROM THE QUARTERLY SAFETY SUMMARY OF THE BRITISH CHEMICAL
INDUSTRY SAFETY COUNCIL)

Reference Number of this Report: EI-209
Duplication of this Report is Authorized.

APPENDIX B

CALCULATIONS

A. AMOUNT OF OXYGEN FROM ARGON COVER GAS

ASSUMPTIONS:

1. Argon is as pure as require i.e. 99.998% pure (gaseous)
2. All impurities (gaseous) are O_2 = 20 PPM = 2×10^{-3}%

CALCULATIONS:

1. For 1000 Ft.^{3} at STP, there are $\frac{1000 \text{ ft}^3}{359 \text{ Ft}^3/\text{lb-mole}} = 2.78$ lb-moles Argon

2. Oxygen Impurity:

$$(2.78 \text{ lb-Mole A}) \left(39.95 \frac{\text{lb A}}{\text{lb-mole}}\right) \left(2 \times 10^{-5} \frac{\text{lb } O_2}{\text{lb Argon}}\right) = 2.21 \times 10^{-3} \text{ lbs. } O_2/1000 \text{ ft}^3 \text{ of Argon}$$

3. $$\frac{2.21 \times 10^{-3} \text{ lbs } O_2}{32 \text{ lbs/lb-mole}} = 6.95 \times 10^{-5} \text{ lb-moles } O_2$$

4. $4 \text{ Na} + O_2 \longrightarrow 2 \text{ Na}_2O$

Thus, 1 lb-mole O_2 causes 2 lb-moles of Na_2O to be formed.

or $(6.95 \times 10^{-5} \text{ lb-moles } O_2)(2) = 13.9 \times 10^{-5}$ lb-moles Na_2O

$$(13.9 \times 10^{-5}) \text{ lb-moles } Na_2O \times 62 \frac{\text{lb } Na_2O}{\text{lb-mole } Na_2O} = 8.6 \times 10^{-3} \frac{\text{lbs } Na_2O}{1000 \text{ ft}^3 A}$$

5. Volume of Na_2O generated per 1000 ft.^{3} of Argon.

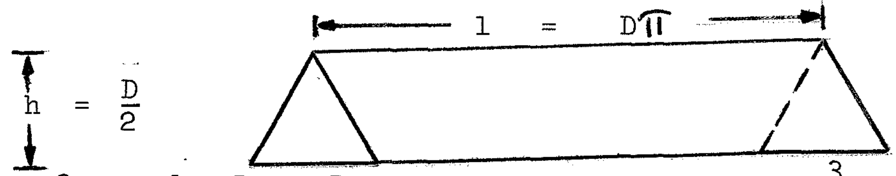
a. Density of Na_2O - 2.39 g/cc.

$$\text{or } \frac{2.39 g}{cc} \times 16.4 \frac{cc.}{in^3} \times \frac{lb}{454 \text{ g}} = 8.6 \times 10^{-2} \frac{lb}{in^3}$$

b. $$\frac{8.6 \times 10^{-3} \quad \frac{\text{lbs } Na_2O}{1000 \text{ ft}^3 \text{Argon}}}{8.6 \times 10^{-2} \quad \frac{lb}{in^3}} = 1 \times 10^{-1} \text{ in.}^3 \text{ of } Na_2O/1000 \text{ ft}^3 \text{ Argon}$$

6. Line Size Pluggable By 0.1 in^3 Na$_2$O.

Assume all the Na$_2$O deposits in one spot to make a plug as an equilateral triangle. Then approximate value would be



$$V = 0.1 \text{ in}^3 = \frac{1}{2}\left(\frac{D}{2}\right)\left(\frac{D}{\tan 60^\circ}\right)(\pi D) = \frac{D^3}{4 \tan 60^\circ}$$

$$\tan 60^\circ = \sqrt{3} = 1.732$$

$$D = \left[\frac{(0.1)(4)(1.732)}{\quad}\right]^{\frac{1}{3}} = .6 \text{ in.}$$

B. MOISTURE IN ARGON GAS: REACTION WITH NaK

The procurement specification requires that argon as procured cannot contain more than 2 grains moisture per 1000 ft^3 argon.

1. $\left(\frac{2 \text{ grains}}{1000 \text{ ft}^3}\right) \left(1.429 \times 10^{-4} \frac{\text{lbs}}{\text{grain}}\right) = 2.86 \times 10^{-4}$ lbs H$_2$O/1000 ft^3

2. $4 \text{ Na} + H_2O \longrightarrow \text{NaOH} + 1/2 \; H_2 + 3 \text{ Na} \xrightarrow{\text{Heat}} \text{Na}_2O + 2\text{NaH}$

3. Thus, for every lb - mole H$_2$O, 4 lb = moles Na required

4.. $\frac{2.86 \times 10^{-4} \text{ lbs } H_2O}{18 \text{ lbs/lb - mole}} = 1.59 \times 10^{-6}$ lb. moles H$_2$O/10^3 ft^3 of A

5. The amount of Na$_2$O generated by moisture in 1000 ft^3 argon:
From (2): 1 lb-mole H$_2$O will generate 1 lb-mole Na$_2$O
Therefore, from (4): 1.59 x 10^{-6} lb. mole Na$_2$O generated by H$_2$O in 1000 ft^3 argon:

$$\left(62 \frac{\text{lb Na}_2\text{O}}{\text{lb-mole Na}_2\text{O}}\right) 1.59 \times 10^{-6} \text{ lb-mole Na}_2\text{O} = 9.9 \times 10^{-5} \text{ lb of Na}_2\text{O}/1000 \text{ ft}^3 \text{ Argon}$$

C. AMOUNT OF Na THAT MUST BE REMOVED FROM NaK TO GET TO 83% K and AMOUNT OXYGEN REQUIRED.

1. Condition: NaK = 0.228 wt. fraction of Na in new material

2. Amount of Na to be removed to give 83% K.

   Let X = amount of Na to be removed then .228 - X = new amount of Na.

   New weight fraction of Na = $\frac{.228 - x}{.772 + (.228-x)} = 1 - .83 = .17$

   X = .07 weight fraction of Na removable

   or: 7 lbs. of <u>Na</u> per <u>100</u> lbs. <u>of</u> <u>NaK</u> may be removable.

3. Weight of Oxygen Required:

   7 lbs. ÷ 23 lbs/lb-mole = 0.304 lb - moles of Na

   $4\ Na + O_2 \rightarrow 2\ Na_2O$, or 1 lb-mole O_2 per 4 lb moles Na

   thus, amount of oxygen required will be $\frac{0.304}{4}$ lb - moles = .076

4. Volume of Oxygen Required:

   $(.076 \text{ lb-moles})\ (359 \frac{\text{cu ft}}{\text{lb mole at STP}}) = 27 \text{ ft}^3 \text{ of } O_2$

   per 100 lbs. of NaK.