

~~SECRET~~

UCRL-1241 Revised
C.2

UNIVERSITY OF
CALIFORNIA

DECLASSIFIED

*Radiation
Laboratory*

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

BERKELEY, CALIFORNIA

SECRET

UCRL-1241 Rev.
C.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

~~SECRET~~

UCRL-1241 Revised
Oak Ridge Declassification

Classification cancelled by
authority of the Office of
Classification 1-4-84
Date

UNIVERSITY OF CALIFORNIA
Radiation Laboratory
Contract No. W-7405-eng-48

DECLASSIFIED

ON THE REMOVAL OF Na_2O FROM Na BY DISTILLATION

Leo Brewer and John L. Margrave

June 13, 1951

~~RESTRICTED DATA~~

This document contains restricted data as defined in the Atomic Energy Act of 1946. Its transmittal or disclosure of its contents in any manner to an unauthorized person is prohibited.

Berkeley, California

SECRET

DECLASSIFIED

-2-

UCRL-1241 Revised
Oak Ridge Declassification

Standard Distribution: Series C

Copy Nos.

Declassification Officer

1-6

Publication Officer

7

Patent Department

8-9

Information Division

10

~~SECRET~~

DECLASSIFIED

-3-

UCRL-1241 Revised
Oak Ridge Declassification

ON THE REMOVAL OF Na₂O FROM Na BY DISTILLATION

Leo Brewer and John L. Margrave

Radiation Laboratory, Department of Chemistry
University of California, Berkeley, California

June 13, 1951

Lee¹ of MSA has presented data indicating that in the atmospheric pressure distillation of Na (filtered at 150-175° C.), the Na₂O passes off first, so that the still-pot residue is leaner in oxygen than the initial feed or the distillate and that the distillate uniformly contains 0.01 - 0.03 wt. percent oxygen. Epstein and Weber² have considered this behavior on the basis of the simple solution laws and find (assuming that an unsaturated solution of Na₂O in Na follows Henry's Law) that for an n-plate distillation of a Na-Na₂O solution,

$$W' = \left(\frac{Z}{W_s} \right)^n W$$

where W' = wt. percent oxygen in the distillate

W = wt. percent oxygen in the original sample

W_s = wt. percent oxygen in saturated solution

Z = wt. percent oxygen in vapor.

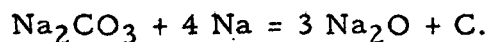
Thus, for removal of oxygen from the still-pot, W' must be greater than W or $\frac{Z}{W_s} > 1$.

Values for Z may be calculated if the vapor pressures of Na and Na₂O are known using Dalton's law. Epstein and Weber have used 13.7 mm. of Hg as the vapor pressure of Na₂O at the normal boiling point of Na (1187° K.). Calculations by Brewer and Mastick³ for the gaseous alkali metal oxides indicated that the vapor pressure of Na₂O at 1000° K. is not over 5 x 10⁻⁷ atm. and is due almost completely to decomposition to the gaseous elements.

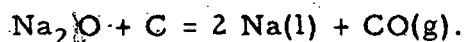
~~SECRET~~

Bunzel and Kohlmeyer⁴ have studied Na₂O at high temperatures and found its melting point to be 920° C. They state that at temperatures up to 1350° C. practically no vaporization of Na₂O occurs. These data make it seem very unlikely that the vapor pressure of Na₂O is large enough to account for any vaporization from boiling Na. Also, the requirement that $Z > W_s$ to get fractionation of the Na-Na₂O melt with the Na₂O appearing in the distillate requires some sort of maximum in the boiling point curve for the liquid solutions of Na-Na₂O. This maximum has not been observed.

A more plausible explanation for the removal of oxygen from the melt seems to be that arrived at by considering the carbon impurity present in the Na either as organic material, or Na₂CO₃. Available data indicate that at temperatures where the rate is appreciable, this reaction will occur:



The free carbon available might then react as shown below:



The free energy change and equilibrium pressure of CO for this reaction have been calculated at four temperatures:

<u>Temperature</u>	<u>ΔF</u>	<u>P_{CO}</u>
298° K.	57.0 kcal	10 ^{-41.8} atm.
500° K.	46.2 kcal	10 ^{-20.2} atm.
1000° K.	19.5 kcal	10 ^{-4.3} atm.
1187° K.	10.5 kcal	10 ^{-1.9} atm.

The low stability of Na₂C₂ makes its consideration of minor importance in these calculations.⁵ On this basis, the high equilibrium pressure of CO could well account for the removal of oxygen from the still-pot to the distillate in fractionations carried out at atmospheric pressure.

~~SECRET~~

-5-

UCRL-1241 Revised

It seems very unlikely that Lee has actually observed fractional distillation of Na_2O from a Na- Na_2O solution. Our interpretation can easily be checked experimentally. Due to the very endothermic nature of the reaction between Na_2O and C, the CO partial pressure will drop off rapidly with drop in temperature. Thus a low pressure distillation should show little oxygen removal. Also our interpretation can easily be verified by distilling sodium containing an excess of oxide. After removal of the CO, no more oxide should be removable from the still-pot.

REFERENCES

1. R. C. Werner and C. B. Jackson, MSA, Report on Research with Sodium and Sodium-Potassium Alloys from July 1, 1948 to May 31, 1949, Confidential, May 31, 1949.
2. L. F. Epstein and C. E. Weber, J. Metallurgy and Ceramics, Issue No. 6, pp. 80-82, January, 1951. (Secret).
3. L. Brewer and D. Mastick, J. Amer. Chem. Soc. 73, 2045 (1951).
4. E. Bunzel and E. Kohlmeyer, Z. anorg. Chemie 254: 1-30 (1947).
5. L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, "Thermodynamic and Physical Properties of the Carbides, Sulfides, Silicides, and Phosphides", National Nuclear Energy Series Vol. 19B, pp. 40-59, 1951. McGraw-Hill.

~~SECRET~~

~~SECRET~~

DECLASSIFIED

~~SECRET~~