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ON THE REMOVAL OF Na₂O FROM Na BY DISTILLATION

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ON THE REMOVAL OF Na_2O FROM Na BY DISTILLATION

Leo Brewer and John L. Margrave

June 13, 1951

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ON THE REMOVAL OF Na_2O FROM Na BY DISTILLATION

Leo Brewer and John L. Margrave

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June 13, 1951

Lee¹ of MSA has presented data indicating that in the atmospheric pressure distillation of Na (filtered at 150-175° C.), the Na_2O 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 Na_2O in Na follows Henry's Law) that for an n-plate distillation of a Na- Na_2O 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.

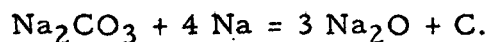
Thus, for removal of oxygen from the still-pot, W' must be greater than W or $\frac{Z}{W_s} > 1$.

Values for Z may be calculated if the vapor pressures of Na and Na_2O are known using Dalton's law. Epstein and Weber have used 13.7 mm. of Hg as the vapor pressure of Na_2O 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 Na_2O at 1000° K. is not over 5×10^{-7} atm. and is due almost completely to decomposition to the gaseous elements.

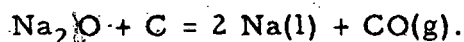
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Bunzel and Kohlmeyer⁴ have studied Na₂O at high temperatures and found its melting point to be 920° C. They state that at temperatures up to 1350° C. practically no vaporization of Na₂O occurs. These data make it seem very unlikely that the vapor pressure 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.

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It seems very unlikely that Lee has actually observed fractional distillation of Na_2O from a $\text{Na-Na}_2\text{O}$ 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.

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