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of Oxygen in Sodium
by Vacuum Distillation

by

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DETERMINATION OF THE SOLUBILITY OF OXYGEN IN SODIUM BY VACUUM DISTILLATION

V. J. Rutkauskas

ABSTRACT

The solubility of oxygen in sodium was determined over the range 125 to 300°C by vacuum distillation. The temperature range was covered in increments of 10 to 25°C with a minimum of three separate determinations at each temperature level. A least-squares fit of the experimental data yielded a correlating equation of $\log_{10} \gamma = 4.25 - 3499/T$, where γ = wt % oxygen. The expression gives a value for ΔH of 16,000 cal-mole⁻¹. The reproducibility of results obtained at each of the equilibrium temperature conditions was excellent, with an apparent standard deviation of 0.5 ppm in the oxygen concentration range of 1 to 10 ppm and 5% above 10 ppm. The internal consistency of the solubility results is better than that of previously published data, and the values are considerably less in the low temperature range than those shown on other solubility curves.

INTRODUCTION

The characterization and control of impurities in high-temperature sodium systems is a basic requirement for the successful operation of a sodium-cooled, fast-breeder reactor. Oxygen is one of the principal impurities which can significantly affect system performance; metallic oxides can strongly influence the corrosion resistance of structural and cladding materials. Therefore, it is necessary to control the concentration of this impurity at acceptable levels over the operating life of a system. To ensure the effectiveness of purification methods, provisions must be made for the routine analysis of oxygen in sodium. The vacuum distillation analytical technique is readily adaptable to this type of operation.

Accurate solubility data are also required for the delineation of system operating parameters and the interpretation of materials compatibility data. The conclusions of Claxton's¹ review are that none of the solubility data currently available accurately represents the solubility of oxygen in sodium (Na₂O) as a function of temperature. The discrepancies are primarily attributed to errors introduced during sampling and analysis.

In the original application of vacuum distillation techniques² for impurity analysis in high-temperature dynamic sodium systems, a sample of sodium was removed from the system and the sodium metal was separated from the nonvolatile residue under vacuum from 350 to 400°C. The residue, assumed to be primarily sodium oxide, was then dissolved in water and determined by acid titration.

Although this method is simple and straightforward compared to some more widely accepted, e.g., mercury amalgamation, it has had limited acceptance, especially by U. S. investigators, because sodium monoxide (Na_2O) can be lost during distillation. It has been reported^{3,4} that Na_2O is thermodynamically stable at temperatures well above the distillation temperatures normally employed. The "proof of method" on the validity of using vacuum distillation for the analysis of oxygen in sodium was reported by Bergstresser et al.⁵ In that investigation, trace amounts of oxygen (3 to 10 μg) were added to 3-g samples of sodium, and the recovery following distillation was quantitative. It was also concluded that the method was sensitive to 0.5 ppm over the range of 1 to 10 ppm of oxygen in sodium. Walker et al.⁶ also reported the satisfactory recovery of oxygen from sodium following distillation over the concentration range from 0 to 100 ppm.

In this investigation, the solubility of oxygen in sodium was determined over the temperature range 125 to 300°C. This was considered to be a practical saturation temperature range for most engineering applications, and any extension of the data beyond 300°C would have been of academic interest only. System equilibrium conditions were established with a forced-circulation crystallization chamber (cold trap) on a dynamic basis as compared to the more classical laboratory methods employed by previous investigators. The vacuum distillation sampling system was constructed of Type 304 stainless steel and was incorporated as an integral part of the facility. Sodium samples were removed from the system, after sufficient flushing to ensure the retention of a representative sample, and introduced into a nickel sampling cup where the sodium metal was separated from its nonvolatile impurities. The distillation was conducted under a dynamic vacuum of $< 10^{-4}$ torr using an induction furnace as a heat source. The residue remaining in the sample cup following the separation was dissolved in dilute hydrochloric acid and analyzed with a flame emission spectrophotometer for sodium as an indirect measurement of the oxygen concentration, assuming the residue to be Na_2O .

EXPERIMENTAL APPARATUS

The general configuration of the experimental facility is shown schematically in Fig. 1. A

Fig. 1. Sodium experimental facility.

forced-circulation sodium loop and an integral vacuum distillation sampling system are the principal features of this facility. All components which were contacted by sodium were constructed of Type 304 stainless steel.

Sodium Analytical Loop

A schematic of the sodium loop is shown in Fig. 2. The salient features of the loop are a bulk sodium reservoir, heat economizer, crystallizer tank, and dc electromagnetic pump. The volume of sodium in the reservoir was approximately 1 ft³ (7.5 gal), and the total system inventory was ~8.6 gal. The bulk sodium reservoir, constructed from a section of 12-in., schedule 10 pipe, was divided along its centerline by a weir which provided a means for mechanical separation of insoluble materials. The sodium flow from the pump was directed into the reservoir through an internal baffle

Fig. 2. Sodium loop.

which provided a tortuous flow path to promote mixing. After going over the weir, the sodium passed through the heat economizer, into the crystallizer, and back into the reservoir. Flow rates of up to 3 gpm could be obtained by regulating the current input to the pump from a 750-A dc rectifier. The sodium sample line was located on the discharge side of the crystallizer tank and upstream of the pump. Calrod heaters around the periphery of the reservoir made temperature control to 500°C possible. Temperature sensors were located in the thermocouple wells positioned on either side of the weir. The pressure above the free surface of the sodium could be regulated from full vacuum to +5 psig of helium. A view port and an access chamber were provided on the top of the reservoir and were isolated from the sodium environment with 2-in. sliding gate valves. The access chamber, located directly above the pump discharge side of the weir, was used for the introduction of contaminants and the removal of sodium samples for spectrographic analysis.

The forced-circulation crystallizer tank used

for controlling system oxygen concentrations, which was fabricated from 5-1/2-in.-o.d. x 0.125-in.-wall tubing, 12-in. long, contained approximately 1 gal of sodium. Counterflow within the tank was provided by a baffle which divided the cylinder into central and annular zones of equal volumes, producing uniform sodium flow velocity and residence time. The baffle was fastened to the top plate and terminated 1 in. from the bottom; sodium flow was directed down through the annulus and up through the center column. With the exception of 1-in.-long header sections at the top and bottom of the tank, the entire volume was filled with Type 304 stainless steel wire mesh. The mesh offered little resistance to flow while providing the additional surface area needed to produce nucleation and precipitation of impurities within the crystallizer tank. Heaters and a coolant manifold for temperature control were located around the periphery of the tank. Temperature sensing points in the form of thermocouple wells were located in the center and in the annulus. This provided the capability for sensing the lowest temperature within the tank for control purposes. The crystallizer tank could be controlled at any desired temperature independent of the bulk sodium temperature. This temperature control provided an effective method for rapidly achieving and maintaining system equilibrium on a dynamic basis over the temperature range of interest.

Vacuum Distillation Sampling System

The vacuum distillation sampling system shown schematically in Fig. 3 was incorporated as an integral part of the dynamic facility. It consisted of a sampling chamber, an intermittent siphon chamber for removing known aliquots of sodium from the dynamic system, an overflow reservoir, a distillation section, and a vacuum/inert gas manifold. The installation is shown in Fig. 4.

During the sampling operation, the nickel sampling cup was positioned in the sampling head, and sodium from the loop flowed through the sample line into the cup. The sodium was allowed to overflow into the intermittent siphon chamber and then into the overflow reservoir. A diametrical clearance of 0.005 in. between the cup and a locating collar in the sampler head allowed the cup to be inserted into the sampling head, but the cup design

Fig. 3. Schematic of vacuum distillation sampling system.

Fig. 4. Vacuum distillation sampling system.

produced a cascade effect for the flowing sodium which prevented metal from entering and/or spilling past the annulus. Sodium flow was terminated when a signal was received from an electromagnetic flowmeter that sodium was flowing from the siphon chamber to the reservoir. The siphon chamber contained sufficient sodium to flush the sample lines six times and the sample cup 15 times. This was considered to be adequate for obtaining a representative sample of system sodium in the sampling cup for analysis. After the sample was obtained, the cup was lowered into a 2-in.-diam Pyrex glass distillation section and isolated from the sampling head with a 2-in. sliding seal gate valve. The cup was positioned in the work coil of a 1-kW, high frequency induction generator which was used as the heat source for distillation. A thermocouple located in the 1/4-in.-diam stainless steel sample cup support tube provided temperature sensing during operations and allowed distillation rate data to be compiled.

The sample line was fabricated from 0.250-in. x 0.035-in. wall tubing and was trace-heated along its entire length to eliminate temperature gradients. The sample line and its isolation valve located above the sampling head were maintained at or slightly above the system bulk sodium temperature. A short section of line between the valve and the sample head was chilled to temperatures below the melting point of sodium when the distillation system was not in use. This feature provided an immediate freeze seal of the line following a sampling operation as well as a safety backup for the valve. When the overflow reservoir (1-liter capacity) became full, it was drained back into the bulk sodium reservoir by pressurizing the sampling head with helium. All sampling and distillation operations were conducted under a dynamic vacuum of $< 10^{-4}$ torr using a mechanical pump.

Trace heaters on the sampling head top plate and overflow line, in addition to internal baffles and cooling coils around the periphery of the head, prevented sodium vapor from entering the vacuum/inert gas line and eliminated the retention of sodium in the head, except for a few occasional droplets. The gate valve isolated the distillation section from the sampling head so that the sampling head was always maintained under vacuum or at a

positive helium pressure. It was not exposed to atmospheric contamination during normal system operation.

On the completion of distillation, the entire distillation section was removed from the system and replaced. This was accomplished by backfilling the system below the sliding valve with ~ 2 psig helium and disconnecting the glass section at the upper metal-to-glass joint visible in Fig. 4. The equipment exchange required ~ 10 to 15 sec, and the flow of helium under pressure during this period minimized the introduction of atmospheric contaminants. Following the exchange, the distillation section was evacuated, and the sample cup was heated to 500 to 525°C prior to receiving another sample.

EXPERIMENTAL PROCEDURE

After the sodium loop was helium mass spectrometer leak tested, the system was vacuum outgassed at 200 to 225°C. It was then cooled to 125°C and charged with reactor-grade sodium at 110 to 115°C. After flow was established, the system temperature was raised to 400°C isothermally and maintained at this level, with the gas phase under vacuum, for several hours. The temperature of the bulk sodium reservoir was then lowered to 150°C, and that of the crystallizer tank was reduced to 125°C. These conditions were maintained for approximately 2-1/2 months while the vacuum distillation sampling system was being assembled and readied for operation. During this preliminary checkout period, many sodium samples were removed from the system; several were analyzed before the system was charged with oxygen. The purpose was to compare samples obtained with the initial sodium loading and purification procedures with samples taken later under the same equilibrium conditions.

The sodium was seeded with oxygen in the form of anhydrous sodium hydroxide (NaOH) while the system was maintained under isothermal temperature conditions at slightly above 400°C with the gas phase evacuated to $< 10^{-2}$ torr. The sodium hydroxide was loaded under inert gas into a holder fabricated from a section of very fine Type 304 stainless steel screen supported by a fixture and introduced into the sodium system through the access chamber on the bulk sodium reservoir. The reaction,

$\text{Na} + \text{NaOH} \rightarrow \text{Na}_2\text{O} + 1/2 \text{H}_2$, is extremely rapid and goes to completion under the conditions described.⁷ Maintenance of the reduced pressure above the free surface of the sodium prevented the buildup of a partial pressure of hydrogen. This, coupled with a system temperature high enough to decompose sodium hydride,⁸ eliminated the possibility of system contamination by a compound other than sodium monoxide. The view port on the top of the bulk sodium reservoir allowed observation of the sodium hydroxide introduction into the sodium pool. The reaction, which began on contact, was accompanied by the vigorous evolution of hydrogen gas and was terminated within 2 to 3 min. At this time, the sodium hydroxide support fixture was withdrawn into the access chamber, and a visual inspection confirmed complete reaction of the hydroxide. Helium was introduced into the gas space, and a gauge pressure of -3 to -5 in. of mercury was maintained during the rest of the experiment.

Following the introduction of oxygen into the sodium system, the solubility of oxygen in sodium was determined by the incremental lowering of system temperatures to establish crystallizer tank equilibrium temperature conditions at 300, 275, 250, 225, 200, 185, 175, 150, and 125°C. The crystallizer tank was controlled to $\pm 1^\circ\text{C}$ of the desired set point and maintained as the lowest temperature zone in the system. A temperature differential of 50 to 175°C normally existed between the bulk sodium reservoir and the crystallizer tank. Flow rates of 0.5 to 1.2 gpm were used to maintain system equilibrium conditions. This resulted in 7 to 14 system turnovers per hour through the crystallizer tank with a residence time of 1 to 2 min within the tank for the precipitation and dissolution of Na_2O . The system was operated for 2 to 3 days to ensure equilibration before samples were taken for oxygen analysis. A minimum of three separate determinations was made at each temperature. After each determination, the system equilibrium conditions were perturbed by changing the flow rate and temperature. Additional measurements were taken, usually at a slightly different flow rate and bulk sodium temperature, to ensure that the system was at equilibrium. Equilibrium was attained a minimum of three times per temperature point by the precipitation and dissolution of oxygen within the crystallizer

tank. Perturbations also included variations in system turnover rates and residence times within the crystallizer tank. After additional data were obtained at 125°C to confirm the point obtained during preliminary system operation, additional determinations of oxygen solubility were made at 165, 215, and 265°C to obtain supplementary data in this important region.

Sodium samples were periodically removed for analysis for dissolved interstitials, other than oxygen, and spectrochemical analysis. A typical analysis of the system sodium is given in Table I.

Table I
Typical System Sodium Analysis

Element	Concentration (ppm)	Element	Concentration (ppm)
Li	< 1	Rb	< 20
Be	< 1	Sr	< 1
B	< 5	Zr	< 20
Mg	1	Mo	< 2
Al	< 2	Ag	< 2
Si	< 10	Cd	< 5
P	<200	In	< 2
K	100	Sn	< 5
Ca	< 10	Ba	< 2
Ti	< 10	Ta	<200
V	< 2	W	<200
Cr	< 2	Au	< 5
Mn	1	Hg	<500
Fe	< 2	Pb	< 5
Co	< 5	Bi	< 5
Ni	< 5	H ₂	≤ 5
Cu	< 1	N ₂	≤ 3
Zn	<200	C	≤ 10

Note: Symbol < represents limit of detection.

The values shown for hydrogen, nitrogen, and carbon represent the limits of sensitivity for the analytical methods^{9,10,11} used. The concentrations of these impurities were below the limits of detectability for all of the samples analyzed during the investigation. In addition, no significant changes were observed in concentrations of the trace metallic elements present as tramp impurities in the sodium.

The nickel sample cup was machined with a 0.500-in. hemispherical radius and had a volume of 4.3 cm³. With a normal meniscus, it was expected

that it would contain ~ 5 g of sodium. However, during the initial checkout to establish the operating parameters of the system, it was discovered that up to 65% more sodium than the nominal sample size could be retained. This was remedied to yield samples of 5.0 ± 0.5 g by means of an abrasive and chemical cleaning after each use in conjunction with a preheating procedure which consisted of heating the sample cup to 500 to 525°C under vacuum and maintaining a minimum cup temperature of 250°C prior to sampling.

When not in use, the sampling system was maintained at a pressure of < 10⁻⁴ torr at ambient temperature, with the exception of the sampling line. Normally this line temperature was controlled at or slightly above the sodium loop bulk sodium temperature for its entire length, except for the short frozen section between the isolation valve and sampling head. A thermocouple welded to the sample line at this point provided a reliable and rapid temperature sensing capability.

When a clean glass distillation section had been inserted into the system following completion of the previous sampling operation, it was isolated from the rest of the system and evacuated to < 10⁻⁴ torr to remove any trace moisture and other volatile impurities. This was a precautionary measure against contaminating any active sodium film remaining on the surfaces of the sampling head. Preheating of the sample cup also helped to prevent contamination.

While the sample cup was being preheated, the sampler head, overflow line, and overflow reservoir were also being raised to operating temperatures. The overflow line and reservoir were heated to 225 ± 25°C, and the top of the sampler head was maintained at ~ 325°C. After the sample cup reached 500°C, the sliding valve was opened and the cup was raised to the sampling position within the sampler head. The coolant flow to the sampler head and the sample line freeze seal was then shut off to enable the rest of the system to reach the required temperatures. The sodium loop was ready for sampling when the sample line equilibrated to the control temperature along its entire length and the bottom of the unheated section of the sampler head reached a minimum of 100°C. During this system preheat

cycle, the sample cup temperature normally dropped to 275 to 350°C as a result of the time lapse and lack of further heat input. System pressure prior to sampling ranged from 10^{-3} to $< 10^{-4}$ torr. The sample valve was opened, and sodium flowed through the sample cup and into the intermittent siphon chamber until an indication of flow to the overflow reservoir was observed. Then the sample line isolation valve was closed and coolant flow was re-established.

After the 15 to 20 sec required to freeze the sample line, the cup was lowered into position within the heater coils surrounding the distillation section. The sampler head was isolated from this portion of the system, and the distillation was conducted under a dynamic vacuum of $< 10^{-4}$ torr. A chilled-water condenser located around the periphery of the distillation tube, shown in Fig. 4, collected 95% of the distillate, and the rest was deposited on the lower portion of the tube. Slight heating of the glass with a torch in the region above the liquid level of the sample afforded a window for visual observation of the distillation process. The distillations always proceeded smoothly and without surface perturbations which could be attributed to gas entrainment, gas evolution, or superheating. The power input to the cup was adjusted to maintain a temperature of $355 \pm 5^\circ\text{C}$ throughout the distillation period of approximately 14 min. This resulted in a distillation rate of 0.35 ± 0.02 g/min, based on the recovery of the distillate. A sharp increase in temperature without a change in power input to the cup marked the termination of the separation process. The cup temperature was then raised to 400 to 410°C, and heating was discontinued. The sample cup was cooled to ambient temperature while under vacuum. The distillation section was then backfilled with helium, removed from the system, and replaced.

The sample cup was removed from the thermocouple support rod, and the residue was dissolved in 5 ml of 0.01 *N* hydrochloric acid. Mixing to ensure homogeneity was accomplished by repeatedly withdrawing the solution into the transfer pipette and draining it back into the sample cup. The sodium concentration in the solution was determined by flame-emission spectrophotometry using a Beckman Model DB spectrophotometer. This spectrophotometer

had been calibrated using standard solutions which were prepared by dissolving sodium chloride in 0.01 *N* hydrochloric acid. The standards were also used as control samples during analysis of the unknown samples. The oxygen equivalent of the sample was calculated on the basis that the distillation residue was entirely in the form of sodium monoxide (Na_2O). The sodium distillate was recovered and titrated with 1.0 *N* hydrochloric acid to determine the total inventory of sodium initially present in the sample.

At the conclusion of the analysis, the sample cup was cleaned with a mild abrasive. After the abrasive was thoroughly removed, the cup was rinsed with dilute acid, distilled water, and ethyl alcohol. The rest of the distillation section was cleaned and rinsed with distilled water and ethyl alcohol. All parts were thoroughly dried prior to reassembly for replacement into the system.

DISCUSSION OF RESULTS

The experimental solubility data are presented in Table II. The reproducibility of the results obtained at each temperature was excellent. The apparent standard deviation in the oxygen concentration range of 1 to 10 ppm was 0.5 ppm; above 10 ppm it was 5%. No blank corrections were required because the method yielded a zero blank. The internal consistency of the solubility results at each temperature is notable because each determination represents the solubility value obtained after the system had been re-equilibrated under a different set of conditions. Exceptions to this are the six determinations made while the system was held in a state of equilibrium during the preliminary system checkout. Therefore, the 52 determinations made at the 12 temperature levels represent a total of 47 independent sets of system equilibrium conditions.

A minimum time of 2 days was allotted for the system to attain equilibrium before samples were taken for analysis. This was sufficient time to reach equilibrium, and no effort was made to determine the minimum time needed. The large number of system turnovers through the crystallizer tank in a given time ensured that equilibrium conditions were attained very rapidly for both the precipitation and dissolution approaches to equilibrium. To establish that representative sodium samples were

Table II
Solubility of Oxygen in Sodium

	Temperature (°C)											
	125	150	165	175	185	200	215	225	250	265	275	300
Oxygen concentration (ppm)	1.7 ^a	2.3	4.0	4.9	6.8	8.1	10.6	21.9	37.1	46.5	74.4	145.9
	1.7 ^a	2.5	4.6	4.9	6.8	9.0	11.6	20.1	40.1	48.7	72.3	134.5
	2.3 ^a	2.3	3.3	5.0	7.2	7.9	11.2	18.5	37.8	49.2	74.3	145.3
	2.5 ^a	2.0	3.7	4.6	7.5	9.5	13.1					
	2.2 ^a			5.4	6.3							
	1.7 ^a				6.7							
	1.7											
	1.4											
	1.4											
	1.2											
Average concentration (ppm)	1.8	2.3	3.9	5.0	6.9	8.6	11.6	20	38	48	74	142
Standard deviation (ppm)	0.4	0.2	0.5	0.3	0.4	0.8	1.0	2	2	1	1	6
Relative standard deviation (%)	22	9	13	6	6	9	9	10	5	2	1	4

^aInitial samples taken during preliminary system checkout.

being removed from the system for analysis, several samples were taken after extended flushing of the sample line and sample cup. No anomalous results were obtained; therefore, flushing with the amount of sodium necessary to fill the sampler siphon chamber was adequate for the obtaining of a representative sample.

The experimental data, plotted as ppm oxygen vs t °C, are shown in Fig. 5. The data points yielded a smooth curve which extrapolates to a solubility of approximately 1 ppm oxygen at the melting point of sodium. It is of interest to note that the slope of the curve yields a "rule of thumb" solubility relationship of a factor of two change in the oxygen concentration for a 25°C temperature change.

The original intent of this experiment was to extend the solubility data to 350°C. After the system was charged with oxygen, attempts were made to equilibrate the system at 350, 325, and 315°C, but the analyses at these temperatures yielded oxygen concentrations which were considered to be much too high for continuous operation of the loop. Although only one determination was made at each of these temperatures, which leaves some doubt as to the confidence in the values obtained, the solubility values fell on the curve shown in Fig. 5.

Fig. 5. Solubility of oxygen in liquid sodium, ppm oxygen vs t °C.

The experimental data were also plotted as ppm oxygen vs $1/T^{\circ}K$, as shown in Fig. 6. A least-squares

Fig. 6. Solubility of oxygen in liquid sodium, ppm oxygen vs $1/T^\circ K$.

fit¹² of the data, in which unity weighting was given to each of the data points, yielded the correlating equation:

$$\log_{10} y = 4.25 - 3499/T,$$

where y = wt % oxygen.

This expression gives a differential heat of solution of 16 kcal-mole⁻¹ for sodium monoxide (Na_2O) in sodium.

Comparison of the data plotted in Figs. 5 and 6 indicates a slight discrepancy of approximately 1 ppm in the concentration range below 10 ppm. The data plotted in Fig. 6 extrapolate to ~ 0.1 ppm solubility at the melting point. This discrepancy is considered to be insignificant, and is within the limits of experimental error.

CONCLUSIONS

The experimental results for the solubility of oxygen in sodium obtained from this investigation yielded a correlating equation of

$$\log_{10} y = 4.25 - 3499/T,$$

where y = wt % oxygen.

The expression gives a differential heat of solution of 16,000 cal-mole⁻¹ for sodium monoxide in sodium. In the oxygen concentration range of 1 to 10 ppm, the standard deviation was 0.5 ppm, and above the 10-ppm level it was 5%.

The consistency of the solubility data obtained at each temperature and the lower than previously published results obtained in the low temperature range are attributed to the analytical technique and the method of establishing and maintaining dynamic system equilibrium. The vacuum distillation sampling system described in this paper provided representative sodium samples for analysis on a routine basis, and the total time required for a completed analysis was approximately 2 hours. The equipment design eliminated the need for sample transfer, thus eliminating the probability of sample contamination by atmospheric impurities. No blank corrections were required because the method yielded a zero blank. The use of the high frequency induction generator as a heat source in lieu of resistance heating provided excellent control of the distillation process. The sharp rise in cup temperature which marks the complete separation of sodium from the nonvolatile impurities and the distillation rate data generated during this experiment provide reliable information for estimating sample sizes with reasonable accuracy. Therefore, the equipment can be adapted for remote operation with the same level of precision obtained in this investigation.

Because of the low solubility of oxygen in sodium at 125°C, the cold-trap mode of quality control can be used as a practical means of purifying and maintaining sodium system oxygen concentrations in the range of 1 to 2 ppm. Many investigators in the field of sodium technology have felt that low oxygen concentrations could be maintained in dynamic sodium systems containing cold traps, operating near the freezing point of sodium, but the available solubility data were inadequate to support these intuitive feelings.

Most of the cold-trapped systems currently in use are designed to operate with a minimum crystallizer-tank¹³ residence time of approximately 5 min. However, in this investigation the residence times used for the precipitation and dissolution of Na_2O

ranged from 1 to 2 min, and from 7 to 14 system turnovers per hour were passed through the crystallizer tank. Very rapid equilibrations of system oxygen concentrations with respect to the crystallizer tank temperatures were obtained as a result of this mode of system operation.

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REFERENCES

1. K. T. Claxton, "Review of Solubility Data for the Liquid Sodium-Oxygen System," Report AERE-R-4897, United Kingdom Atomic Energy Authority, April 1965.
2. J. R. Humphreys, "Sampling and Analysis for Impurities in Liquid Sodium Systems," Chemical Engineering Progress Symposium Series, 53, No. 20, 7 (1957).
3. E. Bunzel and E. Kohlmeier, "The Thermal Behavior of Sodium Compounds Especially Sodium Oxide and Sodium Sulfide and Their Reactions with Metals," Z. Anorg. Allgem. Chem. 254, 1 (1947).
4. L. Brewer and J. Margrave, "Vaporization of Alkali Metal Oxides," Report UCRL-1864, University of California Radiation Laboratory, July 1952.
5. K. S. Bergstresser, G. R. Waterbury, and C. F. Metz, "Determination of Trace Amounts of Oxygen Added to Metallic Sodium," Report LA-3343, Los Alamos Scientific Laboratory, August 1965.
6. J. A. J. Walker, E. D. France, and W. T. Edwards, "The Determination of Oxygen in Sodium," The Analyst 90, No. 1077, 727-731 (December 1965).
7. L. P. Pepkowitz and E. R. Proud, "Determination of Hydrogen," Anal. Chem. 21, No. 8, 1000-1003 (August 1949).
8. G. W. Horsely, "The Purification of Sodium by Vacuum Distillation," Report AERE M/R-1152, United Kingdom Atomic Energy Authority, May 1953.
9. R. D. Gardner and W. H. Ashley, "The Gravimetric Determination of Trace Amounts of Hydrogen in Sodium Metal," Report LA-3049, Los Alamos Scientific Laboratory, April 1964.
10. C. H. Ward, R. D. Gardner, W. H. Ashley, and A. Zerwekh, "The Titrimetric Determination of Traces of Nitride Nitrogen in Sodium Metal," Report LA-2892, Los Alamos Scientific Laboratory, June 1963.
11. R. D. Gardner and W. H. Ashley, "The Gravimetric Determination of Trace Amounts of Carbon in Sodium Metal," Report LA-3035, Los Alamos Scientific Laboratory, January 1964.
12. R. H. Moore and R. K. Zeigler, "The Solution of the General Least Squares Problem with Special Reference to High Speed Computers," Report LA-2367, Los Alamos Scientific Laboratory, March 1960.
13. N. H. Bruggeman, "Purity Control in Sodium-Cooled Reactor Systems," Chemical Engineering Progress Symposium Series, 53, 20 (1957).