11/27
228 Oct
120 2nd Run
AS
MASTER

THE SOLUBILITY OF OXYGEN IN LIQUID SODIUM:
A RECOMMENDED EXPRESSION

AEC Research and Development Report

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or 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 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. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THE SOLUBILITY OF OXYGEN IN LIQUID SODIUM:
A RECOMMENDED EXPRESSION

BY

R. L. EICHELBERGER

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION

CONTRACT: AT(04-3)-701
ISSUED: NOVEMBER 1, 1968

RESTRICTION OF THIS DOCUMENT IS UNLIMITED

DISTRIBUTION

This report has been distributed according to the category "Metals, Ceramics, and Materials," as given in the Standard Distribution for Unclassified Scientific and Technical Reports.

CONTENTS

	Page
Abstract	4
I. Introduction.	5
II. Bases for Data Selection	7
III. Discussion	9
Appendix: Tabulated Solubility Data	14
References	20

TABLES

1. Sources of Data for Oxygen Solubility Curve	10
--	----

FIGURES

1. The Solubility of Oxygen in Sodium: All Data	11
2. The Solubility of Oxygen in Sodium: Recommended Curve	12
3. The Solubility of Oxygen in Sodium: Plotted Linearly	13

ABSTRACT

The solubility of oxygen in sodium as reported in nine publications from eight laboratories was reviewed, and criteria established for the selection of data to be used to derive a recommended solubility curve. The recommended curve, based on 107 solubility determinations from five laboratories, is described by the equation

$$\log S(\text{wppm O}) = 6.239 - 2447/T(^{\circ}\text{K}).$$

I. INTRODUCTION

Liquid sodium has been used as a heat-transfer medium for a number of years, particularly in the high-temperature applications required by nuclear power reactors. With the currently increased potential use of sodium as the heat-transfer fluid for fast-breeder reactors, the importance of understanding the interactions of sodium with its environment is strongly emphasized. Without a doubt the greatest potential problem in the operation of any sodium system is in the measurement and control of the concentration of the oxygen in the sodium. Cold traps are often used as a means of controlling the oxygen level, and the interactions observed in a system are related to the oxygen concentration corresponding to the solubility of oxygen at the cold-trap temperature. The problem in this, however, is in knowing the solubility for a given temperature. The literature shows a serious lack of agreement, and individual workers needing to use solubility data have had to make a choice among the published solubility expressions.

The solubility of oxygen (or of Na_2O , since solid Na_2O is the phase in equilibrium with liquid sodium saturated with oxygen) in sodium has been measured by Salmon and Cashman,^{(1)*} Walters,⁽²⁾ Bogard and Williams,⁽³⁾ Noden and Bagley,⁽⁴⁾ Jahns and Weidmann,⁽⁵⁾ Thorley,⁽⁶⁾ Dorner,⁽⁷⁾ Bergstresser et al.,⁽⁸⁾ and Rutkauskas and Meadows.⁽⁹⁾ The various determinations of oxygen solubility are not in good agreement. Smith⁽¹⁰⁾ has reviewed the work reported in References 1, 2, 3, and 4. He concluded that there were systematic errors in the work reported, particularly in the mercury amalgamation methods used for oxygen determination. Claxton⁽¹¹⁾ reviewed the same four papers, and in addition Reference 6. He correlated all the data in several ways, concluding that the best expression for oxygen solubility is in the form $\log S = A + B/T$, in which S is oxygen solubility, A and B are constants, and T is absolute temperature. In a second report⁽¹²⁾ Claxton includes data from Reference 9 and recorrelates all the data using an expression in the form $\log S = K(1/T - 1/T_m)$, in which K is a constant and T_m is the melting point of Na_2O , and suggests that the solubility curve consists of a low-temperature portion and a high-temperature

*Superscript numbers in parentheses are for References at the back of this report.

portion, intersecting somewhere between 215 and 315°C. Dorner⁽⁷⁾ includes a short discussion of References 1, 2, 3, 4, 5, and 11, and argues against the two-line representation for the solubility. A generalized expression for oxygen solubility is also given by Subbotin et al.,⁽¹³⁾ based on a "generalization of the data of several papers and the results of our experiments," but they do not discuss the data from which they derived the expression. Kassner and Smith⁽¹⁴⁾ have used the data of Rutkauskas and Meadows⁽⁹⁾ and the high-temperature points of Noden and Bagley⁽⁴⁾ to derive a solubility expression. Mausteller, Tepper, and Rodgers⁽¹⁵⁾ have calculated a solubility expression from that data of Walters⁽²⁾ which was obtained at temperatures above 300°C.

Because of the lack of agreement among those who have measured the solubility of oxygen in sodium and the difficulty in choosing a solubility expression from among those published, the decision was made to review all of the published data to attempt to develop criteria for assembling a set of consistent pooled data from which a solubility expression could be derived.

II. BASES FOR DATA SELECTION

A determination of the solubility of oxygen in sodium consists basically in carrying out three procedures: equilibration, sampling, and analysis. Equilibration has been accomplished in static capsules and in flowing loops. Sampling has been carried out with both glass and metal devices, and samples have either been removed from the equilibration system or analyzed directly in apparatus which is a part of the equilibration system. Analysis has been by either the distillation method or the mercury amalgamation method.

It is considered that all groups reporting oxygen solubility have done careful work, with proper attention to contamination from the atmosphere, accurate measurement of temperature, etc. It then seems that reliable data could be obtained in experiments using either equilibration technique, provided that the sodium did not interact with the container.

Sodium reacts with glass, the rate and extent of reaction being determined by the temperature and the nature of the glass. Naud⁽¹⁶⁾ presents data which indicate that the attack on Pyrex is appreciable at 150°C. Because of this reaction with glass, solubility experiments in which either the equilibration or the sampling were carried out in glass apparatus may give rise to high solubility values.

The need for analyses of sodium for oxygen levels below 20 or 30 wppm was not present until the middle 1960's. Therefore there was no strong impetus to refine the amalgamation method for accurate analyses at low oxygen levels. Smith⁽¹⁰⁾ concluded that the method, as used in the 1950's, was of doubtful accuracy below 400 wppm. Subsequent study of the method by Scarborough and DeVries⁽¹⁷⁾ has shown that there is a blank associated with the method, and that the blank originates primarily in moisture adsorbed on the surface of the glassware used, with some contribution from the glass itself. In routine work the blank can range from 4 to 10 micrograms of oxygen equivalent, even when the glassware is vacuum dried at 150°C before use. More recently Prach et al.⁽¹⁸⁾ have confirmed both the presence and magnitude of the blank. In the earlier applications of the method the blank was undoubtedly higher and more variable. By vacuum drying overnight at 300°C, and transferring the glassware to the analytical station in an evacuated container, Scarborough and DeVries⁽¹⁷⁾

were able to reduce the blank to 1.3 ± 0.3 micrograms. It is evident from the results of these studies of the amalgamation method that earlier determinations of dissolved oxygen in sodium must include a sizeable blank. While a blank of 5 or 10 micrograms in a one-gram sample will go unnoticed at high oxygen levels, it may not be neglected at lower concentrations of oxygen. The presence of such a blank provides a reasonable explanation for the apparent change in slope for the oxygen solubility curve proposed by Claxton and others. The distillation method has been developed to a point where it seems to be reasonably free from systematic errors or variable blank phenomena. In a study of analytical methods for oxygen in sodium, Prach⁽¹⁹⁾ reports a zero blank for the distillation analysis.

In light of the discussion above, the following criteria were developed as the basis for selection of solubility data to be used in the derivation of a recommended solubility expression.

- 1) Data from experiments in which the sodium was equilibrated or sampled in glass apparatus should be excluded, because of the high probability of errors introduced by the sodium-glass reaction.
- 2) Data from experiments which used mercury amalgamation analysis, and which were equilibrated at temperatures below 250°C , should be excluded, because the analytical blank becomes too great a proportion of the solubility, which is about 35 wppm at this temperature. No attempt to correct for this blank can be made, since it is variable and very much dependent on the details of the analytical procedure employed.
- 3) Data which have been presented only as averaged curves instead of as individual data points should not be included.

III. DISCUSSION

Table 1 shows the sources of data used in deriving the recommended solubility curve. The individual data points are listed in the Appendix. In the seven references which give individual data points the results of 212 solubility determinations are reported. These points are plotted in Figure 1. Applying the criteria described at the end of Section II for the selection of data, 107 of these points are not excluded; they are plotted in Figure 2. These data have been used to derive the best straight line in the form $\log_{10} S(\text{wppm}) = A + B/T$ using a "least-squares" procedure. This treatment of the data implies that the heat of solution (in the term "B") is constant over the temperature range. Although it is probable that the heat of solution will not be strictly constant over such a wide range, the change will be slow and continuous, making the straight line a better representation than one showing an abrupt change in slope at some temperature. The heat of solution derived from the line shown in Figure 2 is 11,200 cal-mole⁻¹. The equation of the recommended solubility curve is

$$\log S(\text{wppm } 0) = 6.239 - 2447/T(^{\circ}\text{K})$$

The portion of the curve below 220°C is replotted on linear coordinates in Figure 3 for easy reference.

A comparison of Figures 1 and 2 shows that there are many data points which were excluded which nevertheless fall close to the derived line. The previously mentioned criteria for the inclusion of data points were held rigorously, however. It is interesting to note that inclusion of the 21 points above 240°C from the work of Jahns and Weidmann⁽⁵⁾ would not appreciably alter the recommended line even though the work was done in glass apparatus. On the other hand many of the Noden and Bagley⁽⁴⁾ experiments in glass are much above the line. The four points from Bogard and Williams⁽³⁾ for which stainless steel apparatus was used are included, although they fall much below the derived line.

TABLE 1
SOURCES OF DATA FOR OXYGEN SOLUBILITY CURVE

Reference	Laboratory	Total Data Points	Temperature Range of Points (°C)	Number of Data Points Used	Reason for Exclusion of Some Points
Bergstresser et al. ⁽⁸⁾	Los Alamos Scientific Laboratory	22	155 to 340	22	Analytical blank <250°C
Rutkauskas and Meadows ⁽⁹⁾		52	125 to 300	52	
Walters ⁽²⁾	Mine Safety Appliances Corporation	25	152 to 549	17	
Noden and Bagley ⁽⁴⁾	U. K. Atomic Energy Authority, Culcheth	46	127 to 540	7	Glass solubility apparatus
Bogard and Williams ⁽³⁾	Naval Research Laboratory, Washington	10	110 to 555	4	Glass solubility apparatus
Dorner ⁽⁷⁾	Kernforschungszentrum, Karlsruhe	30	130 to 480	5	Glass samplers
Jahns and Weidmann ⁽⁵⁾	Siemens-Schuckertwerke A. G., Erlangen	27	156 to 406	None	All glass apparatus
Salmon and Cashman ⁽¹⁾	Knolls Atomic Power Laboratory	Not Known	115 to 495	None	Only average data reported
Thorley ⁽⁶⁾	U. K. Atomic Energy Authority, Culcheth	Not Known	114 to 292	None	Only average data reported

8-7694-202-51A

Figure 1. The Solubility of Oxygen in Sodium: All Data

8-7694-202-49B

Figure 2. The Solubility of Oxygen in Sodium: Recommended Curve

8-7694-202-50C

Figure 3. The Solubility of Oxygen in Sodium: Plotted Linearly

APPENDIX

TABULATED SOLUBILITY DATA

Walters⁽²⁾ sampled a flowing-sodium loop to which Na_2O_2 had been added and the temperature adjusted. He tabulated many more points than are listed here, but from the operating information on the loop the points chosen appear to represent samples taken at oxygen saturation. The analytical technique used was mercury amalgamation.

Temperature (°C)	Oxygen Solubility (wppm)	Temperature (°C)	Oxygen Solubility (wppm)
152*	10	341	170
157*	10	343	150
160*	30	377	340
166*	10	404	520
213*	40	413	490
232*	50	421	800
232*	50	457	1130
238*	50	502	1500
252	30	535	1760
277	80	538	1980
279	60	538	2000
296	50	549	2250
332	180		

*Points excluded by criteria discussed in text.

Bogard and Williams⁽³⁾ equilibrated in a static apparatus, using Pyrex below 400°C and stainless steel above. Analysis was by the mercury amalgamation method.

Temperature (°C)	Oxygen Solubility (wppm)	Temperature (°C)	Oxygen Solubility (wppm)
110*	20	390*	190
225*	60	440	250
275*	100	490	430
300*	120	515	610
350*	130	555	920

*Points excluded by criteria discussed in text.

Noden and Bagley⁽⁴⁾ used both glass and steel apparatus, equilibrating in static apparatus. Analysis was by the mercury amalgamation method.

Temperature (°C)	Oxygen Solubility (wppm)	Temperature (°C)	Oxygen Solubility (wppm)
127*	32	288*	132
152*	15	290*	86
168*	28	292*	90
177*	40	299*	70
191*	40	300*	248
210*	28	301*	92
218*	44	302*	167
220*	45	302*	230
220*	42	302*	240
221*	41	303*	168
234*	28	306*	100
240*	45	309*	165
250*	58	320*	132
251*	39	321*	138
260*	69	325	99
263*	105	332*	188
270*	57	332*	188
278*	44	380	412
278*	51	400	716
280*	54	416	873
281*	68	470	1365
282*	61	511	2408
284*	187	540	2742

*Points excluded by criteria discussed in text.

Jahns and Weidmann⁽⁵⁾ used glass apparatus for static equilibration, and analyzed by the mercury amalgamation method.*

Temperature (°C)	Oxygen Solubility (wppm)	Temperature (°C)	Oxygen Solubility (wppm)
156	12	306	116
194	36	306	139
194	21	306	141
194	32	306	153
200	30	356	201
201	49	356	238
240	39	356	276
244	71	356	225
246	50	406	384
256	55	406	383
256	65	406	373
276	95	406	389
306	134	406	379
306	135		

*All points are excluded by criteria discussed in text.

Dorner⁽⁷⁾ did some sampling in glass but also took some samples directly into the mercury used for the amalgamation analytical procedure. Those points not excluded were from the latter.

Temperature (°C)	Oxygen Solubility (wppm)	Temperature (°C)	Oxygen Solubility (wppm)
130*	6.5	204*	40
140*	10	204*	42
150*	13	221*	31
160*	20	250*	54
161*	24	250	54
175*	9.4	260*	68
179*	17	300*	79
180*	19	300	116
187*	28	315*	153
187*	33	318*	177
187*	13	319*	174
187*	21	400*	312
200*	21	400	335
200*	8.2	440	362
204*	48	480	649

*Points excluded by criteria discussed in text.

Bergstresser et al.⁽⁸⁾ were studying the distillation method of analysis. The solubility data arose from experiments in which the experimental system appeared to have been saturated with oxygen.

Temperature (°C)	Oxygen Solubility (wppm)	Temperature (°C)	Oxygen Solubility (wppm)
155	3.8	240	38
155	4.3	240	37
155	1.6	240	42
155	2.1	240	34
155	4.8	340	176
155	2.1	340	176
155	3.7	340	184
155	3.0	340	168
240	45	340	160
240	35	340	172
240	35	340	168

Rutkauskas and Meadows⁽⁹⁾ used the analytical method developed by Bergstresser et al.⁽⁸⁾ to obtain the solubility data presented.

Temperature (°C)	Oxygen Solubility (wppm)	Temperature (°C)	Oxygen Solubility (wppm)
125	1.7	185	7.5
125	1.7	185	6.3
125	2.3	185	6.7
125	2.5	200	8.1
125	2.2	200	9.0
125	1.7	200	7.9
125	1.7	200	9.5
125	1.4	215	10.6
125	1.4	215	11.6
125	1.2	215	11.2
150	2.3	215	13.1
150	2.5	225	21.9
150	2.3	225	20.1
150	2.0	225	18.5
165	4.0	250	37.1
165	4.6	250	40.1
165	3.3	250	37.8
165	3.7	265	46.5
175	4.9	265	48.7
175	4.9	265	49.2
175	5.0	275	74.4
175	4.6	275	72.3
175	5.4	275	74.3
185	6.8	300	145.9
185	6.8	300	134.5
185	7.2	300	145.3

REFERENCES

1. O. N. Salmon and T. J. Cashman, Jr., "The Solubility of Sodium Monoxide in Liquid Sodium," KAPL-1653 (1956)
2. S. L. Walters, "The Effects of Adding Oxygen to Sodium Flowing in a Stainless Steel System," NP-1955 (1950)
3. A. D. Bogard and D. D. Williams, "Solubility of Sodium Monoxide and of Sodium Hydroxide in Metallic Sodium," NRL-3865 (1951)
4. J. D. Noden and K. Q. Bagley, "The Solubility of Oxygen in Sodium and Sodium-Potassium Alloy," RDB(C)-TN-80 (1954)
5. W. Jahns and G. Weidmann, "The Determination of Low Oxygen Concentrations in Sodium," Nukleonik 1, 189 (1959)
6. A. W. Thorley, as quoted in Reference 11
7. S. Dorner, "Solubility of Oxygen in Sodium," EURFNR-179P (English translation of Projekt Schneller Bruter (PSB) Report 195/66 [1966])
8. K. S. Bergstresser, G. R. Waterbury, and C. F. Metz, "Determination of Trace Amounts of Oxygen Added to Metallic Sodium," LA-3343 (1965)
9. V. J. Rutkauskas and G. E. Meadows ("Measurement of Impurities and Development of Quality Control Techniques for High Temperature Sodium Coolant Systems") in "Quarterly Status Report on the Advanced Plutonium Fuels Program, April 1 - June 30, 1967," LA-3745-MS (1967), p 10. A more detailed discussion of the work described in this reference, including a few additional data points, is being published by V. J. Rutkauskas, "Determination of the Solubility of Oxygen in Sodium Using the Vacuum Distillation Analytical Technique," LA-3879 (1968), which was not available when this report was written.
10. C. R. F. Smith, "The Determination of Oxygen in Sodium - A Critical Review of Analytical Methods," NAA-SR-Memo-2061 (1960)
11. K. T. Claxton, "Review of Solubility Data for the Liquid Sodium-Oxygen System," J. Nuclear Energy 19, 849 (1965); also AERE-R4897
12. K. T. Claxton, "Contribution on the Solubility of Oxygen in Liquid Sodium," J. Nuclear Energy 21, 351 (1967)
13. V. I. Subbotin, P. L. Kirillov, and F. A. Kozlov, "Removal of Oxygen from Sodium and Monitoring of Oxygen in Sodium," USSR-701 (in Russian); Translation: Inf. Series 10(r) (1964), p 6; CA62:15799 g
14. T. F. Kassner and D. L. Smith, "Calculations on the Kinetics of Oxygen Solution in Tantalum and Niobium in a Liquid-Sodium Environment," ANL-7335 (1967)

15. J. W. Mausteller, F. Tepper, and S. J. Rodgers, Alkali Metal Handling and Systems Operating Techniques (Gordon and Breach, Science Publishers, New York, 1967)
16. G. Naud, "Contribution to the Study of the Impurities Hydrogen and Oxygen in Sodium," CEA-R 2853 (EURFNR-30F) 1964; English Translation: AEC-tr-6582
17. J. M. Scarborough and P. F. DeVries, "Characterization of Blank Correction in Determination of Oxygen in Sodium by the Amalgamation Method," Anal. Chem. 39, 826 (1967)
18. T. F. Prach, L. Newman, and C. Auerbach, "The Determination of Oxygen in Sodium by the Amalgamation Method," BNL-50118 (1968)
19. T. F. Prach ("Determination of Oxygen in Sodium") in "Annual Progress Report of Work Sponsored by the Fuels and Materials Branch, January 1 - December 31, 1967," BNL-50092 (1968), p 45