300
Fast Reactor + C-25
6-30-70
H+B
Formal.
C.H.H.

SOLUBILITY STUDIES
OF
Cr, Co, Mn, Mo, Ni, Nb, Ti, V, AND Zr
IN
LIQUID SODIUM

AEC Research and Development Report

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY J.H. Kahn and
DATE 6/29/70

Atomics International
North American Rockwell

P.O. Box 309
Canoga Park, California 91304

P5708

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Released to Herman

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.

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, express 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 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.

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

SOLUBILITY STUDIES
OF
Cr, Co, Mn, Mo, Ni, Nb, Ti, V, AND Zr
IN
LIQUID SODIUM

By

R. L. EICHELBERGER
R. L. McKISSON

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
North American Rockwell

P.O. Box 309
Canoga Park, California 91304

CONTRACT: AT(04-3)-701
ISSUED: MAY 25, 1970

P5708

DISTRIBUTION 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, TID-4500.

ACKNOWLEDGMENT

The authors gratefully acknowledge the indispensable contributions of V. C. Davis, R. J. Sullivan, and J. Renteria in carrying out the experiments described. Dr. D. C. Gehri contributed helpful suggestions and discussions. The analytical chemistry was carried out by Mrs. Mary Maseda, Mrs. Betty Johnson, T. B. Crockett, and Dr. D. R. Kendall.

CONTENTS

	Page
Abstract	5
I. Introduction	7
II. Methods and Materials	9
III. Results	13
A. Chromium	13
B. Cobalt	16
C. Manganese	18
D. Molybdenum	19
E. Nickel	19
F. Niobium	20
G. Titanium	23
H. Vanadium	23
I. Zirconium	26
IV. Summary and Evaluation	28
References	30

TABLES

1. Manufacturers' Typical Analyses of Solute Materials	8
2. Metal Solute Description and Treatment	10
3. Analysis of Purified Sodium	11
4. Results of Chromium Solubility Experiments	12
5. Results of Cobalt Solubility Experiments	16
6. Results of Manganese Solubility Experiments	17
7. Results of Molybdenum Solubility Experiments	17
8. Results of Nickel Solubility Experiments	20
9. Results of Niobium Solubility Experiments	23
10. Results of Titanium Solubility Experiments	24
11. Results of Vanadium Solubility Experiments	24
12. Results of Zirconium Solubility Experiments	26

FIGURES

	Page
1. Chromium Concentration in Sodium	15
2. Nickel Concentration in Sodium.	21
3. Niobium Concentration in Sodium	22
4. Titanium Concentration in Sodium	25
5. Zirconium Concentration in Sodium	27

ABSTRACT

Solubility experiments with solid refractory metals and iron group metals in liquid sodium were conducted in the temperature range of 600 to 1000°C. All materials used were the highest purity available, and procedures stressed the prevention of contamination from the environment.

Equations were derived for four solutes as follows:

$$\begin{aligned}\text{Cr)} \quad \log_{10} S(\text{wppm Cr in Na}) &= 5.876 - 5362/T(^{\circ}\text{K}) & S_{700^{\circ}\text{C}} &= 2.3 \text{ wppm} \\ \text{Ni)} \quad \log_{10} S(\text{wppm Ni in Na}) &= 1.594 - 1087/T(^{\circ}\text{K}) & S_{700^{\circ}\text{C}} &= 3 \text{ wppm} \\ \text{Nb)} \quad \log_{10} S(\text{wppm Nb in Na}) &= 2.20 - 654/T(^{\circ}\text{K}) & S_{700^{\circ}\text{C}} &= 34 \text{ wppm} \\ \text{Zr)} \quad \log_{10} S(\text{wppm Zr in Na}) &= 5.429 - 3464/T(^{\circ}\text{K}) & S_{700^{\circ}\text{C}} &= 74 \text{ wppm}\end{aligned}$$

Limitations in analytical methods, and experimental scatter precluded the derivation of similar equations for the other five solutes investigated. In the temperature range studied, the results for these metals are summarized as follows:

Solute	Concentration in Sodium (wppm)
Co	<5
Mn	<5
Mo	<2
Ti	10 ± 5
V	<2

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

I. INTRODUCTION

Because sodium is the most promising coolant for the present generation of fast breeder reactors, a knowledge of the solubility of construction metals in sodium has seemed to be of practical importance as well as of theoretical interest. Of the nine solutes discussed in this report, no solubility-in-sodium data have previously been reported for manganese, molybdenum, titanium, vanadium, and zirconium. The previously reported work on the other solutes is discussed in relation to the present results later in this report. A comprehensive compilation of solubility data may be found in the latest edition of the Sodium-NaK Supplement to the Liquid Metal Handbook (Gordon and Breach Science Publishers, in press 1970).

The approach to measuring solubilities which is described here stresses the purity of the solvent and solute materials. The presence of impurities, especially those originating from the nonmetallic elements oxygen, carbon, nitrogen, and hydrogen has appeared to be detrimental to the measurement of solubilities in liquid alkali metal systems. Therefore, the care taken to procure the solutes in "pure" form, and to purify the sodium solvent, was as extensive as was practical within the limits of the work.

This report does not attempt to present a generalized discussion of the solubility of metals in liquid sodium, but is mainly a description of experimental results. However, generalizations are invoked in the discussion where appropriate.

TABLE 1
MANUFACTURERS' TYPICAL ANALYSES OF SOLUTE MATERIALS

Material	Chromium	Titanium	Molybdenum	Nickel	Niobium	Cobalt	Manganese	Vanadium	Zirconium
Nominal Purity (%)	99.996	99.97	99.992	99.995	99.98	99.99	99.96	99.94	99.99
Impurity Element	Content (wppm)*								
C	6	78	10	37	8	40	40	57	20
H	<0.1	4	0.9	0.2	0.4	1.6	7.5	3	3
O	7	63	4.3	18	23.4	50	-	250	200
N	1.3	6	0.5	3	4	9	-	3	2
Ag	<0.1	<0.1	<0.7	<0.002	<0.3	<0.04	-	<0.02	<0.4
Al	<1	15	<0.03	0.3	0.15	2	<10	0.1	3
As	<0.1	1	<0.01	<0.04	<0.01	<0.08	-	<0.05	<0.01
Au	<1	<0.02	<0.02	<0.15	<0.03	<0.3	-	0.6	<0.2
Bi	<0.1	<0.02	<0.02	<0.01	<0.01	<0.01	-	<0.02	<0.007
Ca	0.2	0.08	0.04	0.1	0.02	0.7	<10	0.1	0.04
Cd	<0.1	<0.4	<1.0	<0.08	<0.5	<0.07	-	<0.03	<0.5
Cl	10	0.1	0.4	0.1	0.03	8	-	0.1	2
Co	<0.3	0.4	<0.06	<0.1	<0.01	-	<10	<0.15	<0.007
Cr	-	12	0.1	1.5	0.05	0.2	<10	<50	0.5
Cu	<0.5	8	<0.02	<0.04	<0.01	0.5	<10	<0.3	0.01
Fe	10	30	12	12	0.12	20	10	200	30
Ga	<0.6	<0.1	<0.02	0.4	<0.01	<0.3	-	<20	<0.02
Ge	<0.1	<0.15	<0.02	<0.7	<0.01	<1.2	-	<0.6	<0.03
Hf	<0.1	12	<0.03	<0.03	<0.02	<0.03	-	<0.03	40
In	<0.1	<0.05	<1	<1	<0.07	<0.1	-	<0.03	<0.08
Ir	<0.1	<2	<0.03	<0.02	<0.01	<0.05	-	<0.06	<0.03
K	<0.2	0.08	1	0.2	<0.04	0.8	-	0.4	0.004
Li	<0.1	<0.001	<0.02	<0.02	<0.01	0.001	-	<0.02	<0.001
Mg	0.5	<15	<0.25	0.02	<0.05	0.3	<10	<0.25	<0.05
Mn	<1	1.2	0.06	0.03	0.03	<0.03	-	<0.15	<0.03
Mo	<0.1	<5	-	0.5	<0.7	<0.3	20	0.08	<0.6
Na	<0.1	<1	<1	<0.04	<0.03	0.4	-	<0.05	<1
Nb	<0.2	2	1	<0.02	-	<0.05	-	0.8	<0.5
Ni	<1	2	0.1	-	0.15	65	<10	12	1.5
P	<0.2	0.15	<0.03	<2	<30	0.5	10	0.2	0.1
Pb	<1	<0.03	<0.03	<0.02	<0.02	0.02	<10	<0.03	<0.015
Pd	<0.1	<0.15	<1	<0.03	<0.5	<0.08	-	15	<0.8
Pt	<0.1	<0.04	<0.06	<0.03	0.02	<0.03	-	<0.04	<0.2
Re	<0.1	<0.08	<0.4	<0.02	<0.02	<0.02	-	<0.5	<0.3
Rh	<0.1	<0.05	<0.1	<0.01	<0.06	<0.02	-	<0.5	<0.2
Ru	<0.1	0.12	<0.3	<0.03	<0.4	<0.02	-	<0.5	<0.6
S	2	1.5	1	<0.12	<0.07	0.6	300	0.1	<1
Sb	<0.1	0.1	<0.2	<2	<0.04	<0.04	-	<0.02	<0.15
Si	1	3.5	0.08	0.2	0.6	5	10	20	1.5
Sn	<0.6	3.5	<0.4	<4	<0.3	<0.06	<10	<0.03	<0.25
Ta	<1	<0.04	2	<0.5	100	<0.3	-	<0.3	<0.2
Ti	<0.1	-	<1	0.15	<0.02	0.3	<10	6	1
V	1	1	<0.02	<0.01	<0.8	<0.03	<10	-	0.05
W	<0.1	<0.04	50	1.5	6.4	0.6	-	7	<0.7
Zn	<3	<0.25	0.02	<0.4	<0.02	<0.6	<10	<0.4	<0.5
Zr	<0.1	20	<0.04	<0.15	<0.3	<0.1	<10	<0.12	-
Rare Earths	<2	<2	<1	<0.5	<0.5	<0.5	-	<1	<0.5

- Not analyzed

* Mass spectrometer analysis, except for Mn, for which the method is not stated

AI-AEC-12955

II. METHODS AND MATERIALS

The experimental method for determining solubility has been previously described in some detail.⁽¹⁾ It consists of contacting the solute under study with sodium at the desired temperature for 6 hours (this time period has been previously shown to be adequate to attain equilibrium) and then removing the sodium from the solute material. The entire sample of sodium is analyzed for the solute after it has solidified. The sodium is purified before use by a process combining hot gettering and fractional distillation,⁽²⁾ and is dispensed by extruding it into an ion-pumped high vacuum system. The crucible-collector assemblies are loaded and sealed by welding, and the outer pressure capsules are welded, in the vacuum system, without exposing any components or materials to any environment except high vacuum (10^{-7} to 10^{-8} torr) after purification or final outgassing. After the capsules are loaded, they are removed from the vacuum system and equilibrated at temperature in a furnace installed in a purified argon atmosphere glove box, as previously described.⁽¹⁾ Separation of the solvent from the solute is accomplished by inverting the equilibration furnace at the test temperature, causing the sodium to flow by gravity away from the solute end of the assembly into the collector.

Table 1 shows the analyses of the solute materials used in these studies. Specific information relating to these solutes is summarized in Table 2. Three different configurations of solute specimens were used for the several solutes. Where the physical properties and availability of the solute permitted, crucibles of the material were machined and electron-beam welded to the collectors. In some cases, rods were machined from the solute materials, threaded on one end, and screwed into mating threads in the bottom of a crucible made of the collector material. In the case of manganese, the only form available was an electrolytic deposit about 2 mm thick. Samples of manganese were formed in small plates and mounted with niobium wire onto threaded Cb-1 Zr plugs which were then installed similarly to the rod specimens. Information on the solute configuration used for each material studied is included in Table 2.

Table 3 shows the analysis of one batch of the purified sodium used in the solubility experiments. The values shown are typical of the product of the purification system, except perhaps for the oxygen level, which was as high as 4 wppm in some batches.

TABLE 2
METAL SOLUTE DESCRIPTION AND TREATMENT

Solute	Source	Solute Configuration	Cleaning Process	Collector Material	Crucible-Collector Degassing	Analysis Method
Co	MRC* "MARZ Grade" (E-B zone refined)	Rods	5:3:2, HNO ₃ :H ₂ SO ₄ :H ₂ O + few drops HF, followed by H ₂ O and acetone wash	Cb - 1 Zr	350°C, 2 hours	Atomic absorption spectrometry
Cr	MRC "MARZ Grade" (Vapor deposit from iodide)	Rods	2:1, HCl:H ₂ O, followed by H ₂ O and acetone wash	Cb - 1 Zr	350°C, 2 hours	Radiochemistry
Mn	American Potash and Chemical Corp. "Tronamang Extra Low-Hy" (Electrolytic deposit)	Plates	SiC grit blast, acetone wash	Cb - 1 Zr	350°C, 2 hours	Atomic absorption spectrometry
Mo	MRC "MARZ Grade" (E-B zone refined)	Crucibles	1:1, HNO ₃ :H ₂ O, followed by H ₂ O and acetone wash	Cb - 1 Zr	750°C, 2 hours	Spectrophotometry
Nb	MRC "MARZ Grade" (E-B zone refined)	Crucibles	2:3, HCl:H ₂ O, followed by H ₂ O and acetone wash	MARZ Grade Ti	900°C, 2 hours	Spectrophotometry
Ni	MRC "MARZ Grade" (E-B zone refined)	Crucibles	1:1, HNO ₃ :H ₂ O, followed by H ₂ O and acetone wash. Collector cleaned with HNO ₃ after welding to crucible	MARZ Grade Ti	400°C, 2 hours	Atomic absorption
Ti	MRC "MARZ Grade" (E-B zone refined)	Crucibles	HNO ₃ - 3% HF, followed by H ₂ O and acetone wash. Collector reamed after welding	Fe	350°C, 2 hours	Spectrophotometry
V	MRC "MARZ Grade" (E-B zone refined)	Rods	5:3:2, HNO ₃ :H ₂ SO ₄ :H ₂ O + few drops HF, followed by H ₂ O and acetone wash	Cb - 1 Zr	350°C, 2 hours	Spectrophotometry
Zr	MRC "MARZ Grade" (E-B zone refined)	Crucibles	1:3:4, HF:HNO ₃ :H ₂ O, followed by H ₂ O and acetone wash	Fe, with Nb transition piece	350°C, 2 hours	X-ray fluorescence

*MRC = Materials Research Corporation, Orangeburg, New York

TABLE 3
ANALYSIS OF PURIFIED SODIUM

Element	Level in Na (wppm)	Element	Level in Na (wppm)
Ag	<1 D*	Li	<1 ND
Al	<1 ND†	Mg	<5 ND
B	<1 ND	Mn	<1 ND
Ba	<5 ND	Mo	<1 ND
Be	<1 ND	Ni	<5 ND
Bi	<5 ND	O	0.6
C	8	Pb	<1 ND
Ca	<10 D	Rb	<5 ND
Cd	<1 ND	Si	<10 D
Co	<5 ND	Sn	<5 ND
Cr	1	Ta	<1 ND
Cs	<10 ND	Ti	<5 ND
Cu	<5 D	V	<1 ND
Fe	<1 ND	Zn	<100 ND
H	-	Zr	<10 ND
K	<10 D		

*D = Detected

†ND = Not detected

To permit the radiochemical determination of chromium in the experiments with this solute, the chromium rods were irradiated in the Shield Test Irradiation Reactor (STIR) to a level of about 500 dpm/ μ g Cr. The cleaning and degassing noted in Table 2 was done after the irradiation.

TABLE 4
RESULTS OF CHROMIUM SOLUBILITY EXPERIMENTS

Experiment No.	T (°C)	$\frac{10^3}{T(^{\circ}\text{K})}$	Na (g)	Cr γ -S* (μg)	Cr AAS (μg)	Cr γ -S* (wppm)	Cr AAS (wppm)	Remarks
525	700	1.027	1.119	6	10			Series I, solute rods came loose from crucible
526	800	0.932	1.20	43	16			
527	900	0.853	1.21	208	9			
528	1000	0.786	1.2	10	7			
531	700	1.027	1.97	2.3		1.2		Series II
532	800	0.932	1.94	19.4		10		
533	900	0.853	1.89	6.5		3.4		
534	1000	0.786	2.42	16.6		6.9		
537	700	1.027	1.96	1.6		0.8		Series III
538	800	0.932	1.82	19.9		11		
539	900	0.853	1.80	206		114		
540	1000	0.786	1.90	24.4		12.8		
544	800	0.932	2.88	43	14	15	4.9	Series IV
545	800	0.932	1.56	44	19	28	18	
546	900	0.853	1.55	282	4	182	117	
13B	700	1.027	1.50	1.7	14	0.7	9.5	Series V
14A	800	0.932	1.58	51	48	32	30	
14B	900	0.853	1.86	50	73	27	39	
15A	1000	0.786	1.83	93	125	51	68	
36A	900	0.853	1.87	267	25	142	13	Series VI
36B	1000	0.786	1.31	10	6	7.6	4.6	
37A	700	1.027	1.72	198	<2	115	<1	
37B	600	1.145	1.20	1	2	0.8	1.6	
16B	700	1.027	1.77	0	1.5	0	0.8	"No solute" blanks
17A	800	0.932	1.69	0	1.7	0	1.0	
17B	900	0.853	1.65	0	2.4	0	1.4	
18A	1000	0.786	1.72	0	2.3	0	1.3	

*Gamma-spectrometer results (plotted in Figure 1). AAS results are tabulated to permit comparison.

III. RESULTS

The results of the solubility-in-sodium experiments for the nine solutes included in this report are presented below in alphabetical order. Results from other laboratories are included and discussed where this is possible.

A. CHROMIUM

The first four experiments with chromium rod solute which had not been irradiated all gave chromium concentrations in the sodium of less than 4 wppm, when analyzed by atomic absorption spectrometry (AAS). However, subsequent experience showed that there was a high probability that the technique used to prepare the aqueous solution for analysis caused volatilization of an appreciable amount of chromium; therefore, these first experiments must be disregarded.

For the next series of experiments, the same high purity Cr rods were irradiated in the Shield Test and Irradiation Reactor (STIR) to an activity level of approximately 500 dpm/ μ g. Six sets of experiments using the irradiated Cr rods were completed. In the first group of experiments, equilibrated at 700 to 1000°C, the sodium was found to have small radioactive particles on the surface, and the Cr rods had all come loose from the threaded crucible during the opening of the outer capsule and the sample collector. Therefore, it was necessary to cut the collectors again, below the surface of the sodium, and to cut through the sodium, discarding the surface. The results for these four samples (Series I) showed the presence of 6, 43, 208, and 10 μ g Cr. The high values are perhaps the result of particulate Cr in the "pipe" formed in the center of the collector as the sodium solidified. Nevertheless, the results showed the feasibility of the radiochemical technique for chromium solubility studies.

Results of five subsequent series (II through VI) of chromium solubility runs, using the same irradiated rods, but with refinements in technique which prevented the rods from coming loose from the crucibles, are shown in Table 4. The sodium from Series I, IV, and V experiments was submitted for chromium analysis by atomic absorption spectrometry. The results from Series I were very low, as with the group of experiments run with unirradiated solute rods, with only about 1 μ g chromium found, although gamma-spectrometry had

indicated as much as 200 μg . Volatilization of chromium during the preparation for analysis is the probable cause for the difference.

The chromium solute rods were reirradiated between the Series IV and Series V experiments. Four blank experiments were conducted in which capsules were identical to those used to obtain the results in Table 4 except that no solute rod was included. They were treated in exactly the same manner as the solubility runs reported. Analysis of these was also by gamma-spectrometer examination of the sodium in the sample collector, followed by dissolution and analysis for chromium by AAS. Gamma-spectrometry showed no ^{51}Cr detected. AAS analysis showed about 1 wppm of chromium in the sodium. This latter result compares with a result of ≤ 1 wppm of Cr in the original sodium.

Although the chromium found by gamma-spectrometry in Series I experiments was not seen on subsequent dissolution and AAS analysis, the results of Series V show reasonable correspondence between the spectrometer and AAS results. Minor changes in the analytical procedure and sample preparation for AAS analysis are probably responsible for the improved agreement between the analysis techniques. The agreement between techniques is seen to be lacking in Series VI, however. While there are plausible explanations for this (e. g., external radioactive contamination on the sample collector) there is no evidence to explain the discrepancies.

The only other experimental work on the solubility of chromium in sodium has been conducted at Brookhaven National Laboratory (BNL), and has not been published. A preliminary result indicates a solubility of about 0.4 wppm at 650°C ,⁽³⁾ using irradiated chromium as solute and determining the amount dissolved by radiochemistry. This point, with the radiochemical results from Table 4, is shown in Figure 1. The curve was calculated by a least squares procedure from the AI data, with the exception of Experiment Number 37A, which result is an order of magnitude greater than the other results at the same temperature. The equation for the curve shown is

$$\log_{10} S(\text{wppm Cr in Na}) = 5.876 - 5362/T(^{\circ}\text{K}) \quad \dots (1)$$

The value of ΔH (solution) calculated from Equation 1 is 24,670 cal/mole.

Figure 1. Chromium Concentration in Sodium

These experiments have not unequivocally defined the solubility of chromium in sodium. They are, however, the first to be reported on the subject, and show that chromium is similar in solubility to the other major constituents of stainless steel, nickel, and iron. It also appears that reasonable agreement may be obtained between AAS and radiochemical analyses, provided extreme care is exercised in the analytical procedures.

B. COBALT

The results of four experiments with cobalt solute are shown in Table 5. No explanation is offered for the very high result found in Experiment Number 49A. The other three results are near the limit of analytical sensitivity, and cannot be interpreted beyond indicating that there is detectable cobalt in the sodium, whereas none is detected in the purified sodium which was loaded into the crucible. Lee and Berkey⁽⁴⁾ have reported the results of solubility experiments with cobalt, in which spark source mass spectrometry was used as the analytical method. The temperature range of their experiments was 289 to 544°C. Their results showed no consistency in temperature dependence, but ranged from about 0.1 to 14 wppm in 28 analyses from four equilibrated samples, with most of the analyses falling between 0.1 and 1.0 wppm. Grand, et al.⁽⁵⁾ measured the solubility of cobalt in sodium by irradiating cobalt-saturated sodium and determining the cobalt concentration by radioactivity measurements. They reported 1.00 wppm at 525°C, 0.021 wppm at 425°C, and 0.028 wppm at 365°C. The results from the three laboratories are not inconsistent, although they do not serve to define the solubility of cobalt in sodium except within rather broad limits.

TABLE 5
RESULTS OF COBALT SOLUBILITY EXPERIMENTS

Experiment Number	T (°C)	$\frac{10^3}{T(^{\circ}K)}$	Na (g)	Co (μg)	Co (wppm)	Co in Crucible Etch (μg)
49A	600	1.148	1.86	175	94	86
49B	700	1.027	2.01	8	4	13
50A	800	0.932	1.53	3	2	12
50B	900	0.786	1.61	3	2	11

TABLE 6
RESULTS OF MANGANESE SOLUBILITY EXPERIMENTS

Experiment Number	T (°C)	$\frac{10^3}{T(^{\circ}\text{K})}$	Na (g)	Mn (μg)	Mn (wppm)	Mn in Crucible Etch (μg)
42B *	800	0.932	1.55	312	201	Not analyzed
43A †	900	0.853	0.93	50	54	Not analyzed
43B *	700	1.027	1.62	100	62	Not analyzed
44B	600	1.145	1.56	6.3	4	485
45A	700	1.027	2.13	3	1.3	120
46A	900	0.853	1.55	3	1.9	280

*Manganese solute embedded about 1/8 in. in sodium.

†Much sodium had escaped to outer capsule.

TABLE 7
RESULTS OF MOLYBDENUM SOLUBILITY EXPERIMENTS

Experiment Number	T (°C)	$\frac{10^3}{T(^{\circ}\text{K})}$	Na (g)	Mo (μg)	Mo (wppm)
282	1000	0.786	2.10	<1	<1
283	1000	0.786	2.30	<1	<1
284	900	0.853	2.15	<2	<1
285	800	0.932	1.45	<2	<1.5
286	700	1.027	2.00	2.4	1.2
505	800	0.932	1.43	2.0	1.4
506	850	0.890	1.47	0.77	0.5
507	900	0.853	1.26	1.1	0.9
508	950	0.817	1.58	1.95	1.2
511	1005	0.783	1.65	2.2	1.3

In addition to analyzing the sodium in the collector and the collector washings for cobalt, the walls of the crucibles were acid etched to remove any cobalt that may have entered the metal of the wall. The etch solutions were analyzed; the results are shown in Table 5. An appreciable amount of cobalt transferred through the sodium into the surface of the Cb - 1 Zr crucible. The crucible apparently acts as a sink for the isothermal transfer of cobalt, and very possibly affects the amount of cobalt found in the sodium. Solution-deposition kinetics, about which there is no information, are of importance here. It is notable that Experiment Number 49A, which showed a large amount of cobalt in the sodium sample, relative to the amount in the other experiments, also showed a markedly greater amount of transfer to the crucible.

C. MANGANESE

The first three experiments with manganese solute did not give satisfactory results. In Experiments 42B and 43B the solute specimen had broken loose from the mounting wire during opening and imbedded about 1/8 in. in the sodium, and in Experiment 43A a leak in the crucible-collector assembly permitted a substantial amount of sodium to transfer into the outer capsule. The samples were submitted for analysis to confirm that the analytical method would determine manganese when it was present in a reasonable amount. The results are shown in Table 6, which includes results of all experiments with manganese solute. As with cobalt, the results indicate that a detectable amount of solute is present in the equilibrated samples, whereas none was detected in the sodium before loading. No previous report of solubility of manganese in sodium was found.

The walls of the crucibles were etched to remove any manganese that may have transferred, and the etch solutions were analyzed. Results are shown in Table 6. It is seen that very much more manganese has transferred to the Cb - 1 Zr crucible than was present in the sodium at the termination of the experiments. As with cobalt, the crucible is a sink for the isothermal transfer of manganese through sodium. If the rate of deposition on the Cb - 1 Zr is fast compared to the rate of solution from the manganese, the values in Table 6 do not represent the solubility of manganese in sodium.

D. MOLYBDENUM

The results of 10 experiments completed with molybdenum crucible solutes are shown in Table 7. The molybdenum concentration found was less than 2 wppm for the 10 experiments. All experiments were in the temperature range of 700 to 1005°C. More precise work is dependent on overcoming the apparent limitation in the analytical method. No other work on the solubility of molybdenum in sodium has been found in the available literature.

E. NICKEL

The solubility of nickel in sodium has been studied by Rodgers, Mausteller, and Batutis,⁽⁶⁾ Singer and Weeks,⁽⁷⁾ and Lee and Berkey,⁽⁴⁾ by conventional techniques, and by Kovacina and Miller⁽⁸⁾ using a radioactive tracer technique. The results from this latter work are below 0.01 wppm at 600°C, whereas all the other work showed apparent solubilities in the ppm range, or at least 100 times greater. The solubilities reported by Rodgers, et al.⁽⁶⁾ are generally higher than the others obtained by conventional techniques. The results reported by Singer and Weeks,⁽²⁾ by Lee and Berkey,⁽⁴⁾ and the present work all lie in between these earlier results, although the higher slope of Lee and Berkey's results makes an extrapolation of their work yield very large numbers. The results of the current experiments are shown in Table 8, and plotted in Figure 2, together with the data from References 4 and 7.

The solubility curve shown in Figure 2 was derived by a least squares treatment of seven of the points in Table 8, the values reported by Singer and Weeks (which are averages of from 2 to 11 determinations), and the average of the values at each temperature reported by Lee and Berkey. Four of the AI experimental points have been excluded on the basis of being unreasonably high, from one to two orders of magnitude above the other data. The equation for the curve is

$$\log_{10} S(\text{wppm Ni in Na}) = 1.594 - 1087/T(^{\circ}\text{K}) \quad \dots(2)$$

The ΔH (solution) calculated from Equation 2 is 5000 cal/mole.

TABLE 8
RESULTS OF NICKEL SOLUBILITY EXPERIMENTS

Experiment Number	T (°C)	$\frac{10^3}{T(^{\circ}\text{K})}$	Na (g)	Ni (μg)	Ni (wppm)
273	1000	0.786	1.45	30.5	21
274	700	1.027	2.75	180	65
275	800	0.932	0.80	91	114
276	900	0.853	2.05	940	459
299	700	1.027	1.95	5.9	3.0
300	800	0.932	2.03	8.2	4.0
501	900	0.853	1.50	7.3	4.9
519	600	1.145	2.08	216	104
22A	650	1.083	1.95	5	2.6
22B	750	0.976	1.89	2	1.1
23A	850	0.890	2.04	5	2.5

F. NIOBIUM

The results of eight experiments completed with niobium crucible solutes are shown in Table 9, and together with the data reported by Kovacina and Miller⁽⁹⁾ are plotted in Figure 3. Neither the AI data nor the NRL data shows very good internal agreement, but the two sets of data are reasonably consistent, as seen, and can be represented by

$$\log_{10} S(\text{wppm Nb in Na}) = 2.20 - 654/T(^{\circ}\text{K}) \quad \dots (3)$$

The ΔH (solution) derived from Equation 3 is 3000 cal/mole.

A radioactive tracer technique was used to determine the niobium concentration in the NRL work, and their solute was an alloy of niobium containing 1% zirconium. The sodium used in both sets of experiments reportedly contained less than 10 wppm O₂. The solubility values measured seem to be high, compared to those for other similar metals which dissolve in sodium by a simple solution process, but there is not enough oxygen available to explain the measured values in terms of oxide formation. Until more definitive work which

Figure 2. Nickel Concentration in Sodium

Figure 3. Niobium Concentration in Sodium

TABLE 9
RESULTS OF NIOBIUM SOLUBILITY EXPERIMENTS

Experiment Number	T (°C)	$\frac{10^3}{T(^{\circ}\text{K})}$	Na (g)	Nb (μg)	Nb (wppm)
521	600	1.145	1.87	53	28
547	700	1.027	1.67	120	72
548	800	0.932	1.58	138	88
522	800	0.932	1.75	55	31
549	900	0.853	1.95	173	88
19B	750	0.976	1.75	50	28.5
20A	850	0.890	1.78	108	66.3
20B	950	0.817	1.81	52	28.6
21A	150		1.76	39	22.2

shows otherwise is done on this system, it must be assumed that niobium is more soluble in sodium than are iron, nickel, chromium, molybdenum, titanium, cobalt, manganese, vanadium, and zirconium.

G. TITANIUM

The results of eight experiments completed with titanium crucible solutes are shown in Table 10. These results are plotted in Figure 4, although there is no foundation for drawing a "solubility curve" on the basis of the data. It is indeterminate if the values presented represent a solution equilibrium, or if there is some other phenomenon to explain the presence of titanium in the sodium after equilibration. The iron tubing from which the collectors were made contained less than 5 wppm Ti by emission spectrography, and 1.1 wppm Ti by spark source mass spectroscopy. Because the usual acid etch of the collector removed much less than 100 mg of iron, this process added an insignificant amount of titanium to the solution. No reports of other attempts to measure the solubility of titanium in sodium have been found in available literature.

H. VANADIUM

The results of five experiments with vanadium solute rods are shown in Table 11. The spectrophotometric method used for analyzing for vanadium is

TABLE 10
RESULTS OF TITANIUM SOLUBILITY EXPERIMENTS

Experiment Number	T (°C)	$\frac{10^3}{T(^{\circ}K)}$	Na (g)	Ti (μg)	Ti (wppm)
27B	900	0.853	2.04	17	8.3
28A	800	0.932	2.00	16	8
28B	700	1.027	1.97	12	6.1
29A	600	1.145	1.71	22	12.9
38-1	600	1.145	1.50	20	13
38-3	900	0.853	1.40	10	7.2
38-8	900	0.853	1.30	21	16
39-11	750	0.976	1.49	10	7

TABLE 11
RESULTS OF VANADIUM SOLUBILITY EXPERIMENTS

Experiment Number	T (°C)	$\frac{1000}{T(^{\circ}K)}$	Na (g)	V (μg)	V (wppm)	V in Crucible Etch (μg)
46B	600	1.145	1.58	4	2	4
47A	700	1.027	2.07	2	1	0
47B	800	0.932	1.72	2	1	0
48A	900	0.853	1.85	0	0	0
48B	700	1.027	2.50	6	2	0

not satisfactorily sensitive. In four of the five experiments vanadium was detected in the sodium, but just at the threshold of detectability, which is perhaps 5 wppm in the samples prepared.

The walls of the crucibles which contained the vanadium solute rods were etched, and the solution was analyzed for vanadium. From the results shown in Table 11, vanadium apparently did not transfer through the sodium from the solute rod to the Cb - 1 Zr crucible wall.

Figure 4. Titanium Concentration in Sodium

I. ZIRCONIUM

The results of four experiments with zirconium solute crucibles are shown in Table 12 and plotted in Figure 5. It is notable that the concentration of zirconium is significantly higher than that of the other refractory metals and iron group metals reported, with the exception of niobium. The curve shown in Figure 5 was calculated from the three points shown, and fits the equation

$$\log_{10} S(\text{wppm Zr in Na}) = 5.429 - 3464/T(^{\circ}\text{K}) \quad \dots (4)$$

The ΔH (solution) indicated by Equation 4 is 16,000 cal/mole.

Although this work is not extensive, and the curve is based on only three points, it does provide a valid comparison with the results obtained with the other solutes studied.

TABLE 12
RESULTS OF ZIRCONIUM SOLUBILITY EXPERIMENTS

Experiment Number	T ($^{\circ}\text{C}$)	$\frac{10^3}{T(^{\circ}\text{K})}$	Na (g)	Zr (μg)	Zr (wppm)
39A-2	750	0.976	1.35	104	77
39A-3	900	0.853	1.46	538	370
39B-1	600	1.145	1.70	58	34
39B-2	800	0.932	*	54	*

*Crucible-collector weld cracked, allowing sodium to escape into outer capsule during test.

Figure 5. Zirconium Concentration in Sodium

IV. SUMMARY AND EVALUATION

The work described resulted in analytical expressions for the solubility in sodium of chromium, nickel, niobium, and zirconium. These expressions, and the solubility values calculated from them at 700°C are as follows:

$$\begin{array}{ll} \text{Cr)} & \log_{10} S(\text{wppm Cr in Na}) = 5.876 - 5362/T(^{\circ}\text{K}) \quad S_{700^{\circ}\text{C}} = 2.3 \text{ wppm} \\ \text{Ni)} & \log_{10} S(\text{wppm Ni in Na}) = 1.594 - 1087/T(^{\circ}\text{K}) \quad S_{700^{\circ}\text{C}} = 3 \text{ wppm} \\ \text{Nb)} & \log_{10} S(\text{wppm Nb in Na}) = 2.20 - 654/T(^{\circ}\text{K}) \quad S_{700^{\circ}\text{C}} = 34 \text{ wppm} \\ \text{Zr)} & \log_{10} S(\text{wppm Zr in Na}) = 5.429 - 3464/T(^{\circ}\text{K}) \quad S_{700^{\circ}\text{C}} = 74 \text{ wppm} \end{array}$$

The equations were developed from data obtained over the temperature range of 600 to 1000°C. Results for the other solutes investigated, over the same temperature range, are summarized as follows:

Solute	Concentration in Sodium (wppm)
Co	<5
Mn	<5
Mo	<2
Ti	10 ± 5
V	<2

For these metals, with the probable exception of titanium, the amount of solute found in the sodium was near the limit of detection of the analytical method. It is almost certain that the quantity of solute found represents an increase over that present in the sodium originally, but the uncertainty in the analysis and the scatter of data prevent a more quantitative evaluation.

Other solubility-in-sodium experiments with metal solutes reported from this laboratory include similar work with bismuth,⁽¹⁰⁾ iron,^(1b) and copper.^(1a) The solubility of bismuth is several orders of magnitude greater than that of the other metals examined, and that of copper is intermediate, measuring approximately 300 wppm at 700°C. An estimate for iron is between 1 and 3 wppm at the same temperature.

It is not the purpose of this report to provide an exhaustive discussion of metal solubility in sodium and the factors affecting the reported measurements. It is appropriate, however, to extract a few generalizations from the work discussed above.

It has been possible to develop satisfactory solubility expressions for metals that are relatively soluble in sodium, such as bismuth and copper. These latter two metals also have oxides that are significantly less stable than those of the other metals listed. Although a rather successful effort was made to prevent oxygen contamination in the present experiments, it may be conjectured that the solubilities of the oxygenated species (metal oxides, or double oxides such as sodium chromite, ferrite, zirconate, etc.) may be a significant factor in the success of this type of solubility experiment. Detailed knowledge of the relative thermodynamic stabilities of the species known and postulated to be important in the various metal-sodium-oxygen systems would be helpful in interpreting the data. Experimental and chemical analysis techniques which would provide more specific information on the oxygen inventory, for example, are needed to obtain unequivocal solubility data for oxygen-reactive and/or very slightly soluble metals.

REFERENCES

- 1a. R. L. Eichelberger and R. L. McKisson, "Solubility of Copper in Sodium," AI-AEC-12671 (May 1968)
- 1b. R. L. Eichelberger and R. L. McKisson, "Studies of the Solubility of Iron in Sodium," AI-AEC-12834 (July 1969)
2. R. L. McKisson, R. L. Eichelberger, and J. B. Ott, "The Construction and Operation of a Sodium Purification Apparatus," NAA-SR-12444 (July 1967)
3. H. S. Isaacs, Brookhaven National Laboratory, Personal Communication
4. P. K. Lee and E. Berkey, "Solubility of Cobalt and Nickel in Sodium," in Proceedings of the International Conference on Sodium Technology and Large Fast Reactor Design, November 7-9, 1968, ANL-7520, Part I, p 299
5. J. A. Grand et al., "The Solubility of Tantalum and Cobalt in Sodium by Activation Analysis," J. Phys. Chem. 63, 1192 (1959)
6. S. J. Rodgers, J. W. Mausteller, and E. F. Batutis, "Iron and Nickel Concentrations in Sodium," MSA-TR-27 (June 1954)
7. R. M. Singer and J. R. Weeks, "On the Solubilities of Cu, Ni, and Fe in Liquid Sodium," in Proceedings of the International Conference on Sodium Technology and Large Fast Reactor Design, November 7-9, 1968, ANL-7520, Part I, p 309
8. T. A. Kovacina and R. R. Miller, "The Solubility of Nickel in Sodium by a Tracer Technique," Nucl. Sci. and Eng. 10, 1963 (1961)
9. T. A. Kovacina and R. R. Miller, "The Solubility of Columbium - 1% Zirconium in Sodium by Activation Analysis," NRL-6051 (March 1964)