

THE UNIVERSITY OF MICHIGAN  
INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

THIRD COMPONENT INTERACTIONS WITH  
THE URANIUM-BISMUTH SYSTEM

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A dissertation submitted in partial fulfillment  
of the requirements for the degree of  
Doctor of Philosophy in The  
University of Michigan  
1960

October, 1960

IP-471

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JMR0198

## ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Professor David V. Ragone who ignited and nurtured the motivation necessary to initiate and complete this program. His technical guidance and encouragement have been most gratefully appreciated throughout the course of this investigation. The author is also deeply indebted to Professor E. E. Hucke for serving as Chairman in the absence of Professor Ragone and for his liberal contribution of time and advice. Appreciation is also expressed to Professor Philip Elving, Professor Kenneth Gordon, Professor Joseph Martin and Professor Maurice Sinnott for their contributions. Sincere appreciation is also expressed to the analytical group for their efforts throughout this program and to Mr. John Verhoeven whose skill as an experimentalist is unsurpassed.

The author wishes to express his thanks to Professor Donald L. Katz and the Department of Chemical and Metallurgical Engineering for the opportunity of serving as a member of the staff during his enrollment in Graduate School. Acknowledgement is also made of the financial aid afforded by the Atomic Energy Commission through their Contract No. AT(11-1)543.

## TABLE OF CONTENTS

	Page
INTRODUCTION.....	1
REVIEW OF THE LITERATURE.....	4
Studies of Uranium-Bismuth Systems.....	4
Interaction Studies.....	17
EXPERIMENTAL PROGRAM.....	35
Theoretical Considerations.....	35
Equipment.....	41
Materials.....	45
1. Crucibles.....	45
2. Uranium.....	47
3. Bismuth.....	47
4. Palladium.....	48
5. Copper.....	48
6. Uranium Dicarbide.....	48
7. Flux.....	49
Procedure .....	49
1. Solubility Studies.....	49
2. Decomposition Studies.....	51
RESULTS.....	53
DISCUSSION OF RESULTS.....	64
APPENDICES.....	72
BIBLIOGRAPHY.....	108

## LIST OF TABLES

	Page
I. Summary of Solubility Relationships	5
II. Summary of Solubility Effects Induced by Third Components	15
III. Summary of Proposed Interaction Parameters	34

## LIST OF FIGURES

	Page
1. Summary of Solubility Data for Uranium in Bismuth	7
2. Valve Arrangement on Equipment	42
3. Filter Type Crucible	42
4. Furnace Assembly for Equilibrium Study	44
5. Solubility of Uranium in Bismuth	54
6. Effect of Copper on Uranium-Bismuth Liquidus at 600°C	55
7. Evaluation of $\epsilon_U^{(Cu)}$ at 600°C	56
8. Suggested Bismuth Corner of Bismuth-Copper-Uranium Ternary at 600°C	57
9. Effect of Palladium on Uranium-Bismuth Liquidus at 600°C	59
10. Effect of Copper on $UC_2$ Decomposition at 800°C	61
11. Effect of Palladium on $UC_2$ Decomposition at 800°C	62
12. Evaluation of $\epsilon_U^{(Pd)}$ at 800°C	63

## LIST OF APPENDICES

	Page
Appendix A - Data	72
Solubility of Uranium in Bismuth	72
Effect of Copper on Uranium-Bismuth Liquidus	74
Effect of Palladium on Uranium-Bismuth Liquidus	75
Effect of Sodium on Uranium-Bismuth Liquidus	76
Effect of Various Third Components on Uranium-Bismuth Liquidus	77
Determination of Equilibrium Uranium Concentration for Carbide Decomposition in Bismuth at 800°C	78
Effect of Copper on Carbide Decomposition	80
Effect of Palladium on Carbide Decomposition	81
Appendix B - Calculations	82
Calculation of Activity Coefficient of Uranium in Bismuth	82
Partial Molar Enthalpy Change of Uranium for Dissolution of $UBi_2$	82
Determination of Uninvestigated Portion of Cu-U-Bi Liquidus	83
Appendix C - Phase Diagrams	85
Uranium-Bismuth Phase Diagram	85
Copper-Bismuth Phase Diagram	86
Copper-Uranium Phase Diagram	87
Palladium-Uranium Phase Diagram	88
Palladium-Bismuth Phase Diagram	89

	Page
Uranium-Carbon Phase Diagram	90
Lead-Uranium-Bismuth Phase Diagram	91
Tin-Uranium-Bismuth Phase Diagram	92
Appendix D - Analytical Procedures	93
Spectrophotometric Determination of Uranium in Bismuth	93
Spectrophotometric Determination of Copper in Bismuth	98
Spectrophotometric Determination of Palladium in Bismuth	102



## NOMENCLATURE

$\Delta G^\circ$	free energy of formation
$\gamma_i$	activity coefficient of component i
$N_i$	mole fraction of component i
$a_i$	thermodynamic activity of component i
$\mu_i$	chemical potential of component i
R	gas constant
T	temperature $^\circ\text{K}$
$\epsilon_i^{(j)}$	Wagner's interaction parameter
$Q_{(i)}^{(j)}$	interaction parameter of Turkdogan
$P_{(i)}^{(j)}$	interaction parameter of Turkdogan
$\gamma_i^{(j)}$	ratio of $\gamma_i$ in ternary containing j to $\gamma_i$ in binary
$\lambda_i^{(j)}$	interaction parameter of Ohtani and Gokcen
$\alpha_i^{(j)}$	interaction parameter of Ohtani and Gokcen
$\bar{H}_i$	partial molar enthalpy, cal/gm. mole
$\bar{S}$	partial molar entropy, cal/gm. mole $^\circ\text{K}$
K	equilibrium constant
E	electronegativity

### Subscripts

e - electron	o standard state
$\text{H}^+$ hydrogen ion	j component
i component	

## INTRODUCTION

The present status of metallic solution technology does not permit one to predict with any assurance the behavior of a particular solute in a solvent containing other solute species. Exploratory studies have shown that in many instances significant effects are produced by extremely small concentrations of foreign elements. Consequently much of the available information on binary systems can not be used with confidence when additional components are present. Unfortunately many practical metallurgical operations involve multicomponent systems. Iron-base systems afford an excellent example of one such family in which a number of alloying elements and/or impurities are present in small but significant quantities. Their presence produces interactions which are of considerable interest to the steel-making industry. The magnitude of this industry and the possible importance of the effects has stimulated investigators to explore in detail many iron alloy systems. These studies have yielded much information in recent years, the significance of which will be discussed in a subsequent section of this report.

Although bismuth solutions of uranium are of less commercial importance at the present time, they are also subject to such effects. The proposed use of these solutions as nuclear fuels has created a need for better understanding the nature of the possible interactions. Small quantities of magnesium and zirconium have proven advantageous in minimizing corrosion problems. Since the uranium concentration is extremely critical in this instance, it was necessary to investigate experimentally the effects of these two elements.

However, corrosion as well as the fission process will continuously introduce many foreign elements to the solution which, if permitted to accumulate, could change appreciably the behavior of the uranium solute. The need for this type of information supplied much of the motivation for the investigation. Further impetus was derived from the anticipation that systematic investigations supplementing the iron-base alloy data might be more revealing from a mechanistic point of view. Although bismuth as a solid exhibits many non-metallic tendencies, a transition toward metallic properties is observed in the melting process. Thus, work on liquid bismuth systems should contribute to the overall goal of better understanding and predicting behavior in the liquid metallic state.

In this study attention was focused on the interaction of third components with a molten solution of uranium in bismuth. Two specific reactions were utilized to evaluate the interaction parameters. The first involved the equilibria occurring along the liquidus at the bismuth-rich end of the system. At temperatures above the melting point of bismuth the two phase equilibrium involves a liquid solution of uranium in bismuth and the compound  $UBi_2$ . The second reaction consisted of the decomposition of  $UC_2$  in a bismuth-rich medium according to the reaction  $UC_2 \rightarrow U + 2C$ . This decomposition proceeds until the activity of uranium in solution reaches its equilibrium value.

The first of these reactions determines the maximum concentration of uranium which can be maintained in solution. Any factor which tends to alter this value is of significance in criticality calculations for nuclear fuel purposes. Consequently investigations were conducted at the Brookhaven National Laboratories to determine the significance of small concentrations

of additives and impurities on the position of the liquidus. Their results (to be discussed later) indicated that certain elements produce pronounced effects on this equilibrium. However, the studies were not extensive enough to warrant generalizations regarding effects of the other solute elements. A literature search revealed that although much effort had been expended in determining phase diagrams and thermodynamic properties of binary systems, relatively little work has been performed on ternary and higher systems. Thus, this program was initiated with the purpose of exploring the bismuth corner of several carefully selected ternaries to obtain additional knowledge of the interaction phenomena. The results are discussed in terms of structural considerations, electron effects and thermodynamic behavior for the different alloys. Comparisons are made with the conclusions and correlations developed by previous investigators.

## REVIEW OF LITERATURE

### Studies of Uranium-Bismuth Systems

The original study of the uranium-bismuth system was performed by Ahmann and Baldwin (1). Subsequent revisions by Teitel (50) and Ferro (20) produced the presently accepted phase diagram shown in Appendix C. Because of its importance as a liquid-metal, nuclear fuel the liquidus at the bismuth end of the diagram has been carefully studied in several additional investigations. The original studies by Bareis (4) covered the range from 271<sup>o</sup> to 700<sup>o</sup>C and yielded the equation listed in Table I. His values were later confirmed by Teitel's work which extended the upper temperature to 900<sup>o</sup>C. However, Teitel's results above 600<sup>o</sup>C were approximately 10% higher than the previous work of Greenwood (23). At lower temperatures Greenwood's results agreed well with those of Bareis. Cotterill and Axon (14) employed differential thermal analysis techniques to study the system from 0-35 atomic percent uranium. Their work also confirmed Bareis's earlier results obtained using filtration and settling methods.

Later studies by Schweitzer and Weeks (47) at Brookhaven disagreed with these results. Their data produced two linear segments when plotted as the natural logarithm of weight percentage vs 1/T. The temperature range from 300<sup>o</sup>C - 725<sup>o</sup>C was explored with the discontinuity in slope occurring at 480<sup>o</sup>C. The equations representing these two segments can be found in Table I. Their expressions yield values which fall below those observed by previous investigators for this temperature region. Filtration techniques utilizing Vycor, Graphitite "G" and molybdenum samplers were employed for their

TABLE I

Summary of Solubility Relationships

<u>Investigator</u>	<u>Equation</u>	<u>Range</u>	<u>Predicted Values wt%</u>		
			<u>400°C</u>	<u>600°C</u>	<u>800°C</u>
Bareis	$\log \frac{w}{o}U = 3.13 - \frac{2550}{T^{\circ}K}$	271°-700°C	0.251%	1.78%	--
Greenwood	$\log \frac{w}{o}U = 3.00 - \frac{2440}{T^{\circ}K}$	515°-960°C	--	1.62%	5.37%
Schweitzer and Weeks	$\log \frac{w}{o}U = 2.585 - \frac{2240}{T^{\circ}K}$	300°-480°C	0.182%	--	--
Schweitzer and Weeks	$\log \frac{w}{o}U = 3.263 - \frac{2744}{T^{\circ}K}$	480°-725°C	--	1.32%	5.13%
Armour		350°-600°C	0.140%	1.65%	--
Barton		400°-800°C	0.165%	1.30%	5.9%
Author	$\log \frac{w}{o}U = 3.272 - \frac{2690}{T^{\circ}K}$	400°-800°C	0.190%	1.55%	5.9%

studies. No differences were observed in the results for the three different types of samplers and crucibles. This factor was also checked by other investigators, all of whom concurred with the Brookhaven findings. Recent work by P. J. Barton (5) produced values for the uranium solubility at 400°, 600° and 800°C. His values at lower temperatures approximate those of Schweitzer and Weeks reasonably well. His value at 800°C, of 5.9 weight percent, was below the values reported by Greenwood but in fair agreement with the work of Cotterill and Axon.

An even more pronounced effect at 470°C was observed by investigators at Armour Research Foundation (3). Their solubility curve below 560°C was considerably lower than those obtained in other studies. The maximum deviation occurred at 470°C where Armour reported a value of 2600 ppm compared to values of 4000 ppm and 4700 ppm predicted by Weeks and Bareis respectively. Sampling techniques similar to those used at Brookhaven were employed to obtain this data. A resistivity change which occurs when crystallization begins in the melt was used to confirm the results. For a melt of known composition resistivity was determined as a function of temperature. A discontinuity in the slope of the curve was used to determine the liquidus temperature for a particular concentration.

Bareis's data was corroborated by Teitel, Greenwood and Cotterill between 400° and 600°C, whereas the data of Barton, Schweitzer and Weeks and that from Armour deviated considerably to the lower side (see Figure 1). Results are known to be sensitive to certain impurities which might account for the discrepancies. Analytical problems could also generate such deviations.

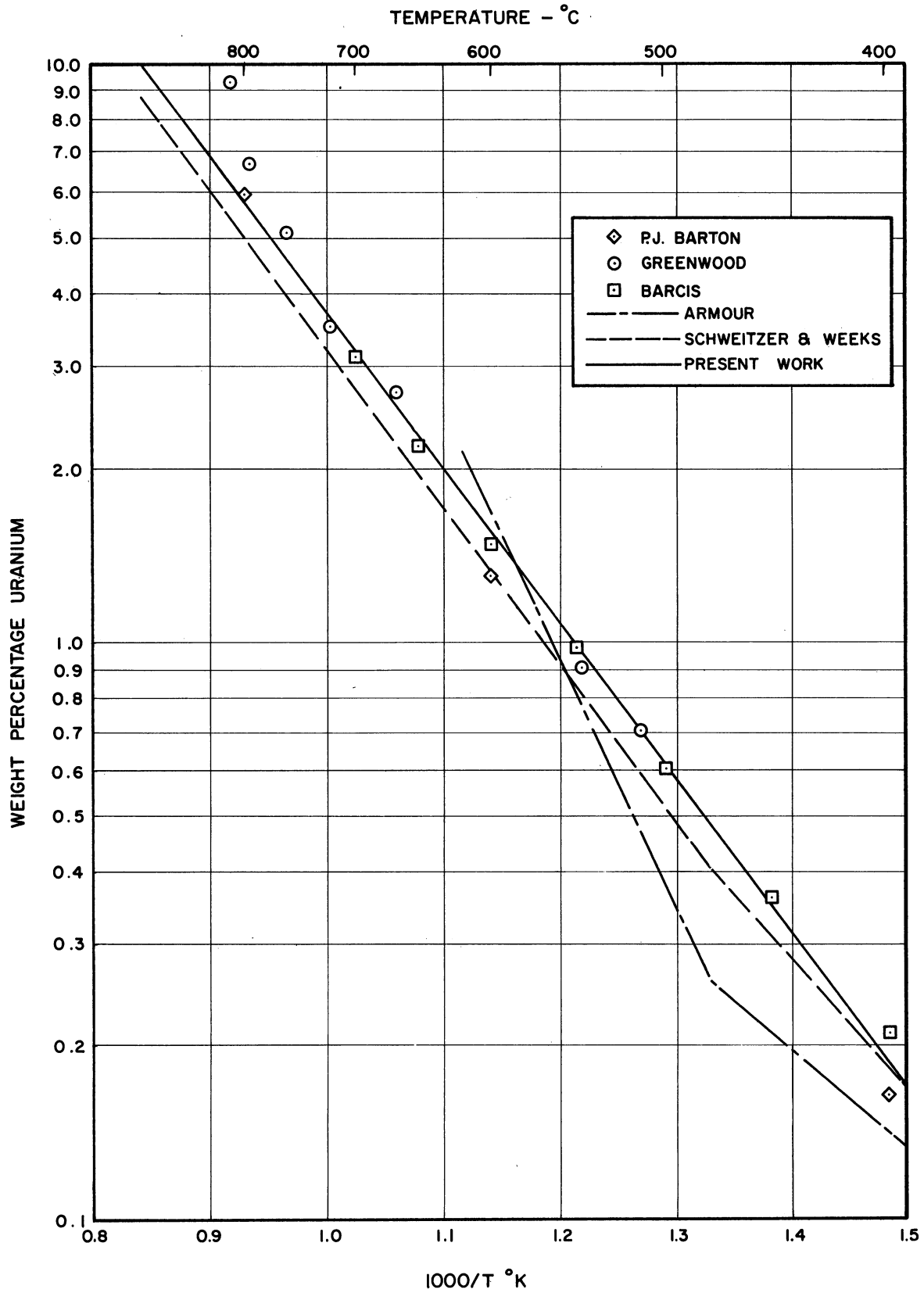


Figure 1. Summary of Solubility Data for Uranium in Bismuth.



The thermodynamics of the binary system, uranium-bismuth, has been the subject of several recent investigations. Egan's emf measurements (18) using a  $U_S/KiCl-KCl_{eut}-5\%UCl_3/UBi_1$  cell estimated the activity coefficient of uranium in bismuth to be  $10^{-5}$  at  $500^\circ C$ . His measurements also suggested that the system exhibits regular solution behavior in the liquid region. More recent investigations by Cosgarea (12) and Gross, Levi and Lewin (25) have revised Egan's initial estimate upward. Gross et al. used effusion measurements to determine the bismuth vapor pressure over alloys of different compositions. They assumed bismuth obeyed Raoult's law in the liquid region and used the Gibbs-Duhem equation to calculate uranium activities. Their measurements were made at  $742^\circ C$  and yielded an activity of  $2.7 \times 10^{-4}$  for a saturated solution of uranium in bismuth. Using Greenwood's solubility data the activity coefficient at saturation would equal approximately  $5 \times 10^{-3}$ .

Cosgarea also measured bismuth vapor pressures across the binary using optical absorption methods. He reported activities for uranium from  $745^\circ C$  to  $842^\circ C$ . At  $745^\circ C$  the activity of uranium in the saturated solution was  $2.19 \times 10^{-3}$ . Assuming the solubility to be approximately 5 atomic percent, this value produces an activity coefficient of  $4.38 \times 10^{-2}$  which is an order of magnitude above the value reported by Gross, Levi and Lewin. His data also displayed a very pronounced temperature effect. The Henry's law parameter at  $745^\circ C$  was estimated to be about  $10^{-3}$ . This is an order of magnitude greater than Egan's corrected value of  $1.6 \times 10^{-4}$  at  $742^\circ C$ . A correction of Gross's et al. data using Cosgarea's measurements in the liquid region to establish the deviation from ideality yielded a value of  $2.5 \times 10^{-4}$  which agrees well with Egan's extrapolated value. These measurements all concur in the fact that the system exhibits strong negative deviations from ideality.

Gross, Levi and Lewin also reported free energies of formation for the compounds in the U-Bi systems. Cosgarea calculated partial and integral molar enthalpies and entropies for the various regions of the diagram. He also concludes from the non-linear behavior of the regular solution parameter that the system does not conform to regular solution behavior, even in the very dilute region.

Grieverson and Alcock (24) have determined the thermodynamics for the Au-U system by measuring the vapor pressure of gold. The Gibbs-Duhem equation was applied to obtain uranium activities for the system. This information permitted the calculation of the free energy of the formation of  $UC_2$  and UC from carbide decomposition studies conducted in gold. They reported the following values in cal/gm mole:

For UC

$$\Delta G^{\circ}(\text{U as solid}) = - 22,200 + 1.5 T$$

$$\Delta G^{\circ}(\text{U as liquid}) = - 25,200 + 3.6 T$$

For  $UC_2$

$$\Delta G^{\circ}(\text{U as solid}) = - 29,610 + 1.5 T$$

$$\Delta G^{\circ}(\text{U as liquid}) = - 32,610 + 3.6 T$$

These values compare favorably with the best values previously available in the literature. Bowman (7) measured by combustion the heat of formation of UC to be  $-21,300 \pm 1000$  cal/gm mol. An accurate value for the free energy of formation of  $UC_2$  is essential to the evaluation of  $\gamma_U$  to be made in this program.

Third element interactions with the bismuth-uranium system have been investigated recently by several groups. In 1953 Bryner (58) studied the effect of iron, chromium and nickel on the uranium solubility at 450°C using a filtration technique. Neither iron nor chromium produced measurable changes in the binary liquidus at that temperature. Both of these elements are virtually insoluble in bismuth. However, nickel which readily dissolves in bismuth at 450°C effected drastic reductions in the solubility. The filtrate contained 0.012% uranium and 1.8% nickel. This corresponded to a 30 to 1 reduction in uranium solubility.  $U Ni_2$  and  $U Ni_5$  were both detected in the residue but  $UBi_2$  was apparently absent.  $NiBi_3$  was found in both the filtrate and residue after cooling. Weisman (58) studied the effect of nickel concentration on the observed solubility depression. His studies were conducted at 350°C and 500°C. At both temperatures the solubility was reduced by a factor of 10 for 1% additions of nickel. Marked effects were observed with additions of only 0.01% nickel in his studies.

Weisman also studied the effect of magnesium on the liquidus composition at 500°C. He reported a slight depression for concentrations greater than 0.01% (0.087 atomic percent). In 1955 Weeks et al. (58) studied the effect of magnesium as a function of temperature over the range 300°-635°C. For 1275 ppm magnesium a definite reduction was observed. The addition of 400 ppm zirconium to the above solution produced no further solubility changes. These tests contained approximately 10 ppm chromium and iron at its normal saturation.

Schweitzer and Weeks (46) studied the Zr-U-Bi ternary liquidus in considerable detail at 350°, 375°, 400° and 425°C. Their studies indicated a negligible decrease in uranium solubility at low zirconium concentrations

over this temperature range. A very sharp reduction was shown to occur for zirconium: uranium ratios above 0.125. However above this ratio the liquid was no longer in equilibrium with  $UBi_2$ , but with a ternary field of varying composition. Thus the sharp reduction in solubility can not be interpreted in terms of the  $U + 2Bi \rightarrow UBi_2$  reaction. For zirconium concentrations below the 0.125 ratio the zirconium appears to have no effect on the preceding equilibrium. Although magnesium additions of 1% had not affected the Zr-Bi and U-Bi binary liquiduses in earlier studies, Schweitzer and Weeks reported an increased solubility of both uranium and zirconium along the U-Zr-Bi ternary liquidus for magnesium additions.

The Armour investigators (3) also studied interaction effects of various solutes. Their results for zirconium confirmed the sharp decrease at certain zirconium concentrations. However, the liquidus curves at 370°C and 400°C which they determined differed considerably from the Brookhaven family of curves. Particular inconsistency was observed at low zirconium concentrations. Additions of magnesium to the ternary melts produced an increased uranium solubility. Magnesium effects on the uranium-bismuth binary were not studied. Sodium additions to a quaternary composed of bismuth-uranium-magnesium-zirconium produced little effect on uranium solubility at lower temperatures. However, an increased solubility was observed at higher temperatures for 5000 ppm sodium additions.

Brookhaven investigators (59) studied the entire alkali metal group. Their results showed lithium and rubidium to have little or no effect on the binary uranium-bismuth liquidus. Sodium increased uranium solubilities up to 30%. The maximum effect was observed at 500°C for 0.5% sodium. Potassium (3000-6000 ppm) approximately doubled the uranium solubility over the temperature range investigated. 1.5% cesium increased the solubility about 30% at 450°C.

Solubility determinations were also performed on a uranium-bismuth alloy containing 250 ppm zirconium, 350 ppm magnesium, and 120 ppm of mixed fission products (60 ppm neodymium, 15 ppm samarium, 15 ppm strontium, 10 ppm cesium and 8 ppm ruthenium). Values slightly below those obtained for the U-Bi + 250 ppm zirconium curve were observed. Of the elements present both magnesium and cesium had been shown to exert positive effects, if any. Hence, the solubility was fairly sensitive to one or more of the remaining elements. Studies in our laboratories have shown cerium to exert a depressing effect. One might expect, therefore, that both neodymium and samarium would behave similarly.

Barton's interaction studies (5) included many of the transition elements which had not been previously investigated. His studies were conducted at 450°C, 600°C and 750°C for varying third component concentrations. Manganese was observed to increase the uranium solubility slightly. The effect appeared to be more pronounced at higher temperatures where increases of approximately 25% were observed for 3.5% (atomic) manganese. At 450°C the effect appeared difficult to distinguish. The increase appeared to be directly proportional to the manganese concentration for the conditions investigated.

Rhodium was studied at 400°, 600° and 800°C. At 600°C two tests yielded rather inconclusive data. One determination for 0.5% (atomic) produced a 20% increase, whereas a second test containing 0.45% (atomic) showed no change. These were the only two points reported at that temperature so it is difficult to evaluate the actual behavior. At 800°C a very definite suppression of about 20% seemed to occur for 1.7% and 2.0% (atomic) rhodium,

but at 400°C 0.18% (atomic) rhodium increased the solubility by a factor of three. Cobalt from the same group produced 20% reductions in solubility for both 6.7% and 20% (atomic) cobalt at 800°C and 10% reductions for 2.0% and 5.4% (atomic) cobalt at 600°C. At 400°C 1% (atomic) produced no detectable change in the liquidus composition.

Nickel was studied at 350°, 500° and 600°C with a definite depression occurring over this entire temperature range. At 600°C 325 ppm nickel reduced the solubility almost 50%. These results agreed reasonably well with Weisman's earlier determinations.

The copper group was examined by Barton at 450°, 600° and 750°C. The data for copper additions produced considerable scatter at 800°C. However, at both 450°C and 600°C no significant effects were detected for copper concentrations up to 4.5% (atomic). Silver which lies immediately below copper in the periodic chart produced a slight increase in the uranium concentration. The results at 750°C showed a 10% increase for 2% (atomic) silver. The effect at 600°C seemed to confirm this tendency. Deviations at 450°C were difficult to detect on the available plot. Gold, the third member of the copper group, displayed the most pronounced effect. A 10% increase was effected by 1.2% (atomic) gold at 800°C. An increase of close to 50% was produced by 1% (atomic) gold at 600°C. Even the lower temperature deviations were distinguishable for 0.8% (atomic) gold.

Teitel has studied the Sn-U-Bi and the Pb-U-Bi ternary diagrams (51). His work produced no evidence of a U-Pb-Bi intermetallic compound at 800°C. The phase diagram (Appendix C ) indicates a decreasing uranium solubility

as the lead content increases with the liquid solution remaining in equilibrium with  $UBi_2$ . This behavior would necessitate a compensating increase in  $\gamma_U$  as  $N_U$  decreases. Support for such an increase was provided by earlier Brookhaven carbide-formation studies (58). Their attempts to form uranium carbide on the walls of graphite crucibles from uranium-bismuth solutions were unsuccessful until uranium concentrations reached 4.7% uranium at  $1100^\circ C$ . 120 hour runs at  $1000^\circ C$  for 1% uranium solutions in bismuth were unsuccessful in producing a detectable carbide layer at the interface. Later carbide decomposition studies (54) performed by the author showed this concentration to be well below the necessary concentration at  $1000^\circ C$ . However, lead-bismuth eutectic solutions containing 1% uranium formed a detectable uranium carbide layer after only 96 hours. A kinetic explanation for the results seemed unsatisfactory since conditions in the two runs were essentially the same. However, an increased  $\gamma_U$  resulting from the presence of lead could increase the  $a_U$  for 1% to that required for the formation of the carbide.

The  $350^\circ C$  section of the Sn-U-Bi ternary (Appendix C) was also studied. Tin was shown to decrease the solubility of uranium and bismuth. The bismuth-rich, liquid solution was found to be in equilibrium with  $UBi_2$  as in the preceding diagram. Thus one would expect similar behavior in this system as the  $\gamma_U$  must increase to compensate for the decreasing uranium concentration. The decreasing solubility of uranium in this system was confirmed by Barton's work.

The results of interaction phenomena in bismuth-uranium systems have been summarized in Table II. With the exception of Barton's recent work all

Table II

SUMMARY OF SOLUBILITY EFFECTS INDUCED BY THIRD COMPONENTS

<u>Element</u>	<u>Investigator</u>	<u>Temperature</u>	<u>Effect</u>	<u>Magnitude*</u>
Na	Brookhaven	500°C	Increase	Weak
	Author	600°C	Increase	Weak
K	Brookhaven	500°C	Increase	Strong
Li	Brookhaven	500°C	None	
Rb	Brookhaven	500°C	None	
Cs	Brookhaven	450°C	Increase	Moderate
Mg	Weisman	500°C	Decrease	Weak
	Weeks	300-635°C	None	
	Author	600°C	None	
Zr	Schweitzer&Weeks	350-425°C	Decrease	Strong
	Armour	370-420°C	Decrease	Strong
	Author	400-600°C	Decrease	Strong
Ce	Author	600°C	Decrease	Weak
Fe & Cr	Brookhaven	450°C	None	
Ni	Weisman	450°C	Decrease	Strong
Ni	Barton	350-600°C	Decrease	Strong
	Author	600°C	Decrease	Strong
Mn	Barton	450,600&750°C	Increase	Moderate
Co	Barton	400,600&800°C	Decrease	Moderate
Rh	Barton	400,600&800°C	Decrease	Moderate
Cu	Barton	450,600&750°C	None	
	Author	600°C	Decrease	Moderate
Ag	Barton	450,600&750°C	Increase	Moderate
Au	Barton	450,600&750°C	Increase	Mod-Strong
Pb	Teitel	800°C	Decrease	
	Author	600°C	Decrease	
	Hayes&Gordon	600°C	Decrease	
Sn	Teitel	350°C	Decrease	
	Hayes&Gordon	350°C	Decrease	
Pd	Author	600°C	Decrease	Moderate

\* Slight corresponds to a change of 5% or less for 1 atom percent  
 Moderate corresponds to a change of 5-25% per 1 atom percent  
 Strong corresponds to a change of 30% or more per 1 atom percent.



of the previous interaction studies on bismuth-uranium systems were performed in conjunction with nuclear fuel development. The third component elements studied were determined primarily by the anticipated fuel composition, with little concern given to a systematic control of variables such as valence, size or electronegativity, which are known to have an effect on the extent of interaction. Only the study by Schweitzer and Weeks of Bi-U-Zr interactions possessed the depth required to evaluate the interaction process parameters. The Brookhaven investigation of the effect of alkali metals furnished a semi-quantitative indication of the behavior within a group (or of the size effect), but the available information was insufficient to permit definite conclusions.

Barton's work when completed should shed considerably more light on the nature of the interaction phenomena. His selection of the elements should permit an evaluation of the relative importance of the parameters cited above. His preliminary results seem to suggest a definite size effect in the copper and cobalt group. Likewise, his data permits evaluation of valence effects for the fourth period transition elements manganese, cobalt, nickel and copper. Each element was studied at three temperatures thus permitting assessment of this effect. In most cases the difference in solubilities remained about constant at the two upper temperatures, 600°-800°C. At the lower temperatures, 350° and 400°C, the effects appeared much less apparent.

Solubility results can not be used to calculate activity coefficient changes without first establishing the activity of uranium in the solid phase. If a ternary field does not replace the  $UBi_2$ , then the activity of uranium remains unchanged in the presence of the third component and the activity

coefficient change is proportional to the reciprocal of the solubility change. However the formation of a ternary field will likely change the value of the uranium activity along the liquidus, and thus necessitate additional measurements.

### Interaction Studies

Despite recent contributions from X-ray and neutron diffraction experiments, the structural aspects of the liquid state still remain uncertain. Recent work (19,21,36,42,55) has confirmed the existence of short range order and has yielded the coordination number of most low melting liquid metals. Liquid alloys have also been studied by several investigators and the results suggest that a type of micro-inhomogeneity may occur among clusters in certain liquid alloy systems. X-ray diffraction work by Danilov and Danilova (15) on lead-bismuth and tin-lead eutectics demonstrates a foregrounding of the solid eutectic at temperatures just above the liquidus. The radial distribution curves for these systems produce certain peaks which correspond to those obtained from the pure tin and bismuth liquids. Examination of these phase diagrams shows that in each case the eutectic mixture is composed of a lead solution and essentially the pure constituent, tin or bismuth. Thus, the formation of tin and bismuth clusters in the respective systems at temperatures just above the liquidus seems quite probable.

Hendus (28) in his studies of the gold-tin system observed a doubling of the main peak for compositions near that of the intermetallic compound. He concluded that clusters possessing a coordination similar to that exhibited

by the compound were present along with clusters of gold and tin randomly arranged. However, the validity of this model has not been established. Gingrich and Henderson (22) have explored the sodium-potassium system for different compositions at  $115^{\circ}\text{C}$ . A systematic shift in breadth and main peak positions was observed for different compositions. Recent work in this field has been voluminous and future efforts seem certain to disclose many enlightening features pertaining to the coordination and structure in molten media.

Evidence suggests that in many respects the liquid state differs only slightly from that of the solid. Physical properties of true metals undergo only a slight change during the melting process and hence the bonding forces cannot change radically. However at the melting point a very definite stability transition occurs which produces fluidity at the expense of long range order. Despite these changes, which are also characteristic of the gaseous state, proximity of the atoms is maintained such that a definite density is assured. Numerous theories have been proposed to account for this behavior, but each possesses apparent shortcomings. Consequently, one can only conjecture as to the actual structure and type of forces persisting in liquid metallic media.

Evidence to date suggests a sea of electrons containing charged atoms migrating continuously from cluster to cluster. These clusters or cybotactic groups possess orderly structures very similar to the solid state. Densities of these groups are imagined as being equal to or greater than densities in the solid state. However the free volume between clusters

contributes to the overall reduction in density observed for most metals upon melting. Some investigators have postulated that these micro-groups possess five fold axes of symmetry. This would certainly explain the absence of long range order in the liquid structure.

Solution of a metallic constituent appears to involve a transfer of electrons between solvent and solute. Certain elements with relatively free peripheral electrons (conduction electrons) contribute them to the sea, whereas others extract electrons to fill lower energy levels. Consequently these atoms become charged particles which may attract or repel one another as ordinary charged bodies. The electron sea maintains electro-neutrality by adjusting to the fluctuating local charge.

Hume-Rothery (30), Raynor (43), Jones (31) and others have demonstrated the significance of the electron/atom ratio for phase diagrams. Sieverts and Krumbhaar (48) have shown that the solubility of hydrogen in copper is decreased considerably by tin and aluminum additions, but is increased by additions of nickel and platinum. Bever and Floe (6) have likewise confirmed the results for tin. Himmler (29) observed a decrease of the hydrogen solubility in solid copper for zinc additions and confirmed the increases for nickel and platinum cited above. These results have been interpreted by ascribing a chemical potential,  $\mu_e$ , to the free electrons. The condition of thermodynamic equilibrium may be stated by the following equation:

$$\mu_{H_2}^{1/2} = \mu_{H^+} + \mu_e \quad (1)$$

Elements such as aluminum, tin and zinc possess electron/atom ratios greater than that of copper. Their dissolution in a copper solvent results in an increase in the free electron concentration. This increases  $\mu_e$  and necessitates a corresponding decrease in  $\mu_{H^+}$  at a given hydrogen activity. Both nickel and platinum have been shown by magnetic measurements to dissolve in copper as essentially neutral atoms. This produces a decrease in the electron concentration which reduces  $\mu_e$ . The equilibrium requires an increase in  $\mu_{H^+}$  which necessitates an increased solubility.

Although the systems considered in the present study are far more complex than hydrogen and copper, the foregoing considerations provide a possible interpretation of the results. Hargreaves (27) has shown that additions of aluminum, which contribute three valence electrons per atom to  $\alpha$  brass, produce a decrease in the zinc vapor pressure; whereas nickel with no effective valence electrons produces an increase. Wagner (57) has concluded from the foregoing studies that the activity of a solute metal, 2, will be increased by a third component, 3, if 2 and 3 change the electron/atom ratio in the same direction. Conversely if the electron/atom ratios differ from that of the solvent in opposite directions, a decrease in the activity coefficient of 2 is to be expected.

Wagner points out that the preceding considerations have neglected the interdependence of  $\mu_{H^+}$  and  $\mu_e$ . Since the electron concentration is likely to influence  $\mu_{H^+}$ , this factor must be considered when utilizing this concept. Opie and Grant (40) have shown that the behavior of copper additions to an aluminum solution containing hydrogen contradicts this theory. Further study will likely explain the apparent discrepancies.

Wagner (57), with consideration to the chemical potential of the electrons, derived a quantitative relationship expressing the effect of one solute on the activity coefficient of a second. The derivation neglected direct interaction between ions of like charge and ascribed all deviations from ideality to electronic effects. Hence for his assumptions

$$d(RT \ln \gamma_i) = 0 \quad \text{if} \quad d\mu_e = 0$$

The following expression relating behavior in the binary systems 1-2 and 1-3 to that in the ternary resulted:

$$\frac{\partial \ln \gamma_2}{\partial N_3} = \frac{\partial \ln \gamma_3}{\partial N_2} = \pm \left[ \frac{\partial \ln \gamma_2}{\partial N_2} \frac{\partial \ln \gamma_3}{\partial N_3} \right]^{1/2} \quad (2)$$

Qualitative considerations described previously must be utilized to evaluate the sign. Wagner proceeds to show that for a system in which ion interactions can be neglected,  $\frac{\partial \gamma_i}{\partial N_i}$  for any solute in a given solvent must have the same sign. Hence, the expression appearing to the 1/2 power should always be positive. This supposition is contradicted in mercury systems where bismuth, lead, tin and zinc are known to produce negative values while cadmium, thallium, lithium, sodium and potassium yield positive expressions. This demonstrates the limitations of the derivation and of the underlying assumption of negligible ionic interaction. Since these interactions generally occur, this expression is probably valid only for systems where the binaries exhibit pronounced deviations from ideality. Wagner obtained experimental data for the effect of thallium on the activity coefficient of potassium, sodium and lithium amalgams. His observed values agreed remarkably well with values predicted from his expression.

The most extensive studies of interaction phenomena have been performed on iron-base systems. The actual values obtained for interaction parameters are of secondary interest for purposes of this study, but the models and correlations used in presenting and discussing the data are quite pertinent to the problem at hand. Wagner (56) using a Taylor series expansion for the excess partial molar free energies (or the logarithm of the solute activity coefficients) developed the following expression:

$$\ln \gamma_2(N_2, N_3, N_4 \dots) = \ln \gamma_2^0 + N_2 \frac{\partial \ln \gamma_2}{\partial N_2} + N_3 \frac{\partial \ln \gamma_2}{\partial N_3} + N_4 \frac{\partial \ln \gamma_2}{\partial N_4} \quad (3)$$

This expression neglects second and higher order derivatives which seems reasonable for dilute solutions. He defined the interaction coefficients as

$$\epsilon_i^{(j)} = \frac{\partial \ln \gamma_i}{\partial N_j}$$

and evaluated them for the limiting condition of zero concentration for all solutes. Wagner has also shown a simple proof of the reciprocity of solute effects on one another such that  $\epsilon_2^{(3)} = \epsilon_3^{(2)}$ . This equation, or a simple modification permitting the direct use of weight percentage and common logarithm, has been used with fair success by many investigators to correlate their results. The elimination of second order terms implies that different solutes will have a negligible influence on the effect exerted by other solutes. If both solutes are in the dilute range, the probability of interaction should be small and the assumption valid.

Chipman (11), Turkdogan (52), and Ohtani and Gokcen (39) have all published summary articles concerning interactions in iron-base systems.

Chipman lists values for the parameter,  $\epsilon_{\text{Y}}^{(\text{X})}$ , for cases where "X" represents C, Al, Si, P, S, V, Cr, Mn, Ni, Cu and Mo, and "Y" signifies H, C, N, O, Si and S. The values for carbon and silicon substantiated Wagner's reciprocity relationship. Chipman also discusses the parameter values in terms of interatomic attraction. He suggests that negative values can be explained using a simple model. He considers the Fe-Cr-O system as an example where  $\epsilon_{\text{O}}^{(\text{Cr})} = -8.8$ . He pictures chromium atoms replacing iron atoms as the nearest neighbors of oxygen. The greater bonding energy for chromium-oxygen than for iron-oxygen results in the oxygen atoms being held more firmly by the solution. This decreases its activity and hence its activity coefficient. Vanadium has a greater effect than chromium and manganese a lesser effect. Aluminum yields a very large negative coefficient  $\epsilon_{\text{O}}^{(\text{Al})} = -1340$ . Although this value is subject to considerable experimental uncertainty, it is definitely indicative of a large aluminum-oxygen bonding energy.

Chipman has postulated that nickel which has little affinity for oxygen atoms associates itself with iron atoms in the solution. This competition with oxygen to coordinate iron results in weaker oxygen bonding and an increased oxygen activity coefficient. Carbon, silicon, aluminum and phosphorous react similarly in iron-sulfur melts thus producing an increased activity coefficient for sulfur.

Chipman evaluated Wagner's expression for interaction effects between positive metal ions and electrons. In the Fe-C-Si system the values for  $\epsilon_{\text{C}}^{(\text{Si})}$  and  $\epsilon_{\text{S}}^{(\text{C})}$  were equal as predicted, but their magnitude was considerably



greater than that predicted by Equation 2. The Fe-O-S system yielded an exceptionally large value for  $\epsilon_0^{(S)}$  of + 130 which Chipman attributed to a combination of ion interactions and electron competition. Both atoms would apparently diminish the electron chemical potential thereby raising the activity coefficients.

Turkdogan (52), recognizing the limitations of very dilute solutions for Wagner's derivation, developed a correlation which he felt was applicable over greater concentration ranges. Wagner's expression (Equation 3) for the effect of different solutes on the activity coefficient of a particular solute can be written as:

$$\gamma_2 = \gamma_2^{(2)} \gamma_2^{(3)} \gamma_2^{(4)} \quad (4)$$

where  $\gamma_2^{(2)}$  represents activity coefficient of 2 at some concentration.

$\gamma_2^{(3)}$  represents the effect of 3 on  $\gamma_2^{(2)}$

or  $\frac{\gamma_2}{\gamma_2^{(2)}}$  for  $N_3 = 0, N_4 = 0$

From Equation 3 and 4 it can be seen that  $\ln \gamma_2^{(3)} = N_3 \frac{\partial \ln \gamma_2}{\partial N_3} = N_3 \epsilon_2^{(3)}$ .

$\epsilon_2^{(3)}$  was evaluated at zero concentration for all solutes. Consequently,  $\ln \gamma_2^{(3)}$  is seen to be a linear function of the atom fractions in this expression. Turkdogan's examination of data from the Fe-Si-C, Fe-Mn-C and Fe-Cr-O systems indicates that the individual coefficients  $\gamma_2^{(3)}, \gamma_2^{(4)}$  etc. may also vary with the concentration of component 2. The variation is generally not as great as with the third components themselves, particularly at low concentrations, but it does restrict the composition range over which the relationship is valid.

To overcome this difficulty Turkdogan has suggested plotting the data as

$$\frac{\Delta N_Y^X}{N_Y^Y} \text{ vs } N_X \quad \text{where} \quad \Delta N_Y^X = N_Y^X - N_Y^Y$$

$N_Y$  represents the atom fraction of component Y in the Z-rich ternary, X-Y-Z, and  $N_Y^Y$  the atom fraction of Y in the binary Y-Z, both evaluated at the same activity of solute Y.  $\Delta N_Y^X$  was known to be relatively insensitive to temperature for many alloys. His calculations demonstrated that the ratio,  $\frac{\Delta N_Y^X}{N_Y^Y}$ , was independent of the activity of Y in most systems for which data was available. He defines a parameter,  $Q_Y^X$ , by the following procedure. Division of the expression for  $\Delta N_Y^X$  by  $N_Y^Y$  yields:

$$\frac{\Delta N_Y^X}{N_Y^Y} + 1 - \frac{N_Y^X}{N_Y^Y} = \frac{\gamma_Y^Y}{\gamma_Y^X} \quad \text{for constant activity of Y.} \quad (5)$$

$$Q_Y^X = \left( \frac{\gamma_Y^Y}{\gamma_Y^X} \right)_{T, a_Y} \quad \text{at a given temperature and activity of Y.} \quad (6)$$

A term  $P_Y^X$  is defined for a given temperature and fixed concentration of Y as follows:

$$P_Y^X = \left( \frac{\gamma_Y^Y}{\gamma_Y^X} \right)_{T, N_Y} \quad (7)$$

This term corresponds to the  $\gamma_Y^X$  used previously by Wagner in his expression  $\gamma_2 = \gamma_2^2 \gamma_2^3 \gamma_2^4 \dots$ . As  $N_Y$  approaches zero,  $Q_Y^X$  and  $P_Y^X$  become equal. A plot of  $\ln Q_Y^X$  vs  $N_X$  yields a curve which is independent of the concentration of Y.

Of the alloys for which data was available only the Fe-Mn-C system failed to yield values for the parameter which were independent of activity.

Interactions in multicomponent systems were handled in a similar manner to that proposed by Wagner. The procedure assumed the effects of various solutes on the activity coefficient of a particular solute were additive and that second order effects were negligible. Thus the following expression results:

$$\ln Q_Y^X = \ln Q_Y^{X_1} + \ln Q_Y^{X_2} + \ln Q_Y^{X_3} + \dots \quad (8)$$

This equation reproduced the data extremely well in solutions of C-Al-Si-P-MnS in iron for values of  $\log Q_S^X < 0.5$ . However, recent evidence (53) has shown that the individual effects of silicon and phosphorus on the solubility of graphite in iron are not additive. One would also expect that, although this relationship is valid at higher concentrations for ternaries, difficulty with second order effects might enter the picture when additional components are added at these higher concentration levels.

Ohtani and Gokcen (39) have also derived a relationship which they claim to be valid for any concentration range. For a three component system they derive the following expression which defines the parameter,  $\alpha_2^{(3)}$ :

$$\left( \frac{\partial \ln \gamma_2}{\partial N_3} \right)_{\frac{N_2}{N_1}} = \frac{N_1 + N_3}{N_1 + N_2} \left( \frac{\partial \ln \gamma_3}{\partial N_2} \right)_{\frac{N_3}{N_1}} = \alpha_2^{(3)} \quad (9)$$

where  $N_1$  stands for the atom fraction of component 1 etc. Hence

$$\alpha_2^{(3)} = \frac{N_1 + N_3}{N_1 + N_2} \alpha_3^{(2)} \quad \text{and for } N_2 \rightarrow 0 \quad (10)$$

and  $N_3 \rightarrow 0$  this relationship reduces to Wagner's derivation.

An attempt was made to correlate interaction parameters with atomic numbers. A plot of self-interaction parameter vs atomic number suggested a linear relationship for elements within the same period. Carbon, hydrogen and nitrogen as solutes in an iron matrix yielded virtually a straight line for such a plot. A different line segment was generated by aluminum, silicon and sulfur from the second period. In both cases the value of the parameter decreased with increasing atomic number. Although the results appear promising, additional information will be required to establish a definite correlation between the atomic number and self-interaction parameter.

An investigation of the effect of third elements on the carbon solubility in liquid iron produced rather suggestive results. The  $\Delta N_C^X$  suggested by Turkdogan and discussed earlier in this review was shown to produce a straight line when plotted vs the atomic fraction of X. Ohtani and Gokcen have demonstrated that the term  $\frac{\Delta N_C^X}{\% X}$  when plotted vs the atomic number of X also yields a series of straight lines. Data for aluminum, silicon, phosphorus and sulfur all fell on one straight line whereas points for vanadium, chromium, manganese iron, and cobalt and nickel fell on a second straight line. The available information for copper produced a point which fell slightly below the latter curve.

A definite periodicity is also displayed by two other parameters considered by these authors.  $\lambda_C^X$  which they defined as follows,

$$\lambda_C^X = \left( \frac{\partial \ln \gamma_c}{\partial N_X} \right)_{a_c} = - \left( \frac{\partial \ln N_c}{\partial N_X} \right)_{a_c} \quad (11)$$

and  $\lambda_C^X$  discussed earlier, both increase for increasing atomic number within a period. This corresponds to an increasing value of  $\lambda_C^X$  for decreasing carbon solubilities. Positive values are obtained for aluminum, silicon, phosphorus, sulfur, cobalt, nickel and copper and negative values for titanium, vanadium, chromium and manganese. The authors conclude that electron contributions of the solutes alone cannot account for this behavior. However they do attach significance to the fact that the negative values occur for elements with strong carbide-forming tendencies. They conclude that, if the X-C bond energy exceeds that for iron-carbon, the solubility will be increased and the activity coefficient decreased. If the iron-carbon bond energy is greater, then the reverse is expected to be true.

Kitchener, et al (32) utilized a crude structural model to explain the phenomena displayed in iron-base systems. They consider the interaction process as a competition between solutes to coordinate adjacent solvent atoms into a preferred orientation. Carbon and sulfur were used as an example of solutes which prefer to coordinate iron in different forms which display little compatibility. Consequently the different clusters tend to isolate themselves with a resulting increase in the activity coefficient of each solute.

Their structural interpretation of the process emphasizes the interaction of solutes with the solvent as well as with each other. Additional consideration is given to size effects and the state of ionization in rationalizing the observations. In the solid state carbon is known to fit with slight strain into the interstices of the iron lattice. Resonating covalent

bonds between iron and carbon atoms are postulated as contributing to the metallic-like structure. Transference measurements on carbon in austenite have revealed that the bonding must be partially ionic and that the carbon atom possesses a positive charge of from 1-4. The electrons transferred are shared among coordinated iron atoms. Such polarization in metallic bonding is quite common according to Kubaschewski and Reinartz (35) and reflects differences in the electronegativity between atoms. The effect is greatest between systems exhibiting intermetallic "electron" compounds such as  $Mg_3Bi_2$ . As additional carbon is added to the structure, the octohedral holes existing between iron atoms are gradually filled; and the carbon atoms begin to repel one another as suggested by their reluctance to occupy adjacent holes. This explanation proves consistent with the observations of the iron-carbon system. There is little reason to believe the behavior in the liquid state would differ significantly from that in the solid.

The iron-sulfur system is assumed to possess a different type of structure. Sulfur is virtually insoluble in the iron crystal lattice, whereas iron-sulfide is completely miscible in molten iron and in iron-oxygen and  $FeO-SiO_2$  melts. The latter are certainly ionic so that iron-sulfur must possess a transitional character that will blend with either. Analogy with iron-sulfur suggests that in liquid iron sulfur ions would tend to coordinate six iron atoms. Increasing sulfur concentration enhances the ionic character of the melt at the expense of the metallic, as the average charge per iron atom is increased. This change is postulated as effecting the reduction in  $\gamma_S$  as the  $N_S$  increases.

These two structural pictures provide a consistent picture when applied to the Fe-C-S ternary. Increasing sulfur tends to create an ionic type melt in contrast to the metallic environment preferred by carbon. Thus, carbon is no longer accommodated as in a purely metallic medium and an increasing activity coefficient is observed.

Other more metallic solutes such as nickel, vanadium, manganese and chromium are discussed in less detail by the Kitchener, et.al. Nickel, similar in size and electronic structure to iron, is assumed to substitute for it readily with little effect on solutes. Manganese although similar in size evidently differs appreciably in electron affinity. Smoluchowski and Koehler (49) have shown, by comparing optical and excitation levels of atomic iron and manganese that the 3d manganese electrons occupy higher energy levels than the 3d iron electrons. In solution manganese is assumed to lose them to the lower energy levels available in iron and to acquire a positive charge such that it interacts strongly with negatively charged sulfur. This accounts for the depression of  $\gamma_S$  by manganese. The authors admit to the speculative nature of their interpretations in reaching the foregoing conclusions, but feel in the absence of a sound quantitative theory these considerations provide a satisfactory grounds for comparison.

Alcock and Richardson (2) have discussed the electron: atom ratio theory proposed by Himmler and further developed by Wagner. They observed inconsistencies which substantiated Wagner's conclusion with respect to the importance of the chemical potential of the ions. Their experiments showed that sulfur in a gold-copper solution possessed an activity coefficient 80 times greater than in pure copper. Since the electron: atom ratios are

approximately the same for copper and gold, the change must be attributable to the different chemical potential of the sulfur ion in the two systems. Furthermore, in accordance with Himmler's theory, the activity coefficient of hydrogen in copper is decreased by both platinum and nickel, while gold displays no effect. However, platinum and gold have been shown to increase the activity coefficient of sulfur in copper, whereas nickel produces a decrease. These findings demonstrate the inadequacies of the electron: atom ratio theory for the copper-sulfur system and emphasize the importance of the ion potentials in rationalizing behavior in certain alloy systems. Since these individual potentials can neither be measured nor calculated accurately, these authors suggest attacking the problem from the chemical or thermodynamic standpoint.

Their considerations assign energy to the various types of bonds existing in the ternary solution. Assuming the atoms to be randomly distributed and to possess the same coordination number as the solvent, they proceed to derive an expression for the partial heat of solution of component P, in the binary solvent, X-Y. If component Y is present only at high dilution so that Y-Y bonds have a low probability of existing, then the following expression can be derived. The terms  $\Delta\bar{H}_S(X)$ ,  $\Delta\bar{H}_Y(X)$  etc. represent the partial heats of solution of S, P and Y in X etc. Furthermore they assume for low concentrations of Y that  $\Delta\bar{S}_{P(\bar{X}Y)} \approx \Delta\bar{S}_{P(X)}$  so that:

$$\left( \frac{\partial \Delta\bar{H}_{P}}{\partial N_Y} \right)_{N_Y \rightarrow 0} \approx RT \left( \frac{\partial \ln \gamma_S}{\partial N_Y} \right)_{N_Y \rightarrow 0}$$



For the following assumptions:

- 1)  $\Delta \bar{S}_P(Y) = \Delta \bar{S}_P(X)$  at low concentrations of P;
- 2)  $\gamma_P(Y)$  and  $\gamma_P(X)$  are taken relative to the same standard state; and
- 3)  $\Delta \bar{S}_Y(X)$  is Raoultian,

$$\frac{\partial \ln \gamma_P}{\partial N_Y} \Big|_{N_Y \rightarrow 0} = \epsilon_P^{(Y)} = \ln \gamma_P(Y) - \ln \gamma_P(X) - \ln \gamma_Y(X) \quad (12)$$

The preceding expressions permit an evaluation of solute effects if a knowledge of binary behavior is available. For systems in which P represents the metalloids, an appreciable difference between  $\Delta \bar{H}_P(Y)$  and  $\Delta \bar{H}_P(X)$  is not likely to be reversed by  $\Delta \bar{H}_Y(X)$  since this is generally small for true metal-metal mixtures. In other instances where the difference is small the Y-X interaction has been shown to be of significance. For purely metallic systems one might expect the  $\Delta \bar{H}_Y(X)$  contribution to have the same significance as  $\Delta \bar{H}_P(X)$ . Nevertheless, in view of the assumptions necessary the values of  $\epsilon$  generated by these equations cannot be expected to be of great accuracy.

The authors give detailed consideration to the validity as well as to the magnitude of the error introduced by these simplifying assumptions. For cases where the coordination number of P differs from that of the solvent X-Y it has been shown that the term  $\Delta \bar{H}_Y(X)$  must be corrected by the ratio  $C'/C$  where  $C'$  represents the coordination of P, and  $C$  that of the solvent. Certainly the assumption of complete randomness has been shown to be invalid

in many systems possessing high interaction energies. Preferential clustering of Y relative to X about  $n_{PY}$  atoms would produce X-Y bonds in excess of those predicted by the equation. This necessitates multiplying  $\frac{\partial \bar{H}_P}{\partial N_Y}$  by  $\frac{n_{PY} \text{ actual}}{n_{PY} \text{ random}}$  to correct for this phenomenon. The authors in subsequent work have given greater consideration to this correction. Despite these considerations this theory can only yield qualitative results. It needs to be subjected to further tests in which the three terms on the right are known more accurately.

Table III

Summary of Proposed Interaction Parameters

1) Wagner

A. Neglecting positive ion interactions and considering only electron effects:

$$\frac{\partial \ln \gamma_2}{\partial N_3} = \frac{\partial \ln \gamma_3}{\partial N_2} = \pm \left( \frac{\partial \ln \gamma_2}{\partial N_2} \quad \frac{\partial \ln \gamma_3}{\partial N_3} \right)^{1/2}$$

Qualitative considerations determine sign.

B. Taylor Series Expansion of solute activity coefficients:

$$\ln \gamma_2 = N_2 \left( \frac{\partial \ln \gamma_2}{\partial N_2} \right) + N_3 \left( \frac{\partial \ln \gamma_2}{\partial N_3} \right) + N_4 \left( \frac{\partial \ln \gamma_2}{\partial N_4} \right) + \dots$$

$$\epsilon_2^{(3)} = \left( \frac{\partial \ln \gamma_2}{\partial N_3} \right)_{T, N_2} \text{ evaluated as } N_3 \rightarrow 0$$

$$\epsilon_2^{(3)} = \epsilon_3^{(2)}$$

For expression:

$$\gamma_2 = \gamma_2^{(2)} \gamma_2^{(3)} \gamma_2^{(4)} \text{ etc.}; \ln \gamma_2 = \ln \gamma_2^{(2)} + \ln \gamma_2^{(3)} + \dots$$

where  $\gamma_2^{(2)}$  represents activity coefficient of 2 in binary

at  $N_2$  and

$$\gamma_2^{(3)} = \frac{\gamma_2}{\gamma_2^{(2)}} \text{ for } N_4 = 0 \text{ evaluated as } N_3 \rightarrow 0. \text{ Therefore,}$$

$$\ln \gamma_2^{(3)} = N_3 \epsilon_2^{(3)}$$

2) Turkdogan

$$Q_2^{(3)} = \left( \frac{\gamma_2}{\gamma_2^{(2)}} \right)_{T, a_2}$$

$$P_2^{(3)} = \left( \frac{\gamma_2}{\gamma_2^{(2)}} \right)_{T, N_2} = \gamma_2^{(3)} \text{ (of Wagners)}$$

As  $N_2$  approaches zero,  $Q_2^{(3)} = P_2^{(3)} = \gamma_2^{(3)}$

3) Ohtani and Gokcen

$$\eta_2^{(3)} = \left( \frac{\partial \ln \gamma_2}{\partial N_3} \right)_{\frac{N_2}{N_1}}$$

$$\lambda_2^{(3)} = \left( \frac{\partial \ln \gamma_2}{\partial N_3} \right)_{a_2, T} = - \left( \frac{\partial \ln N_2}{\partial N_3} \right)_{a_2, T}$$

4) Alcock and Richardson

$$\epsilon_2^{(3)} = \left( \frac{\partial \ln \gamma_2}{\partial N_3} \right)_{N_3 \rightarrow 0} = \ln \gamma_2(3) - \ln \gamma_2(1) - \ln \gamma_3(1)$$

where 1 represents solvent, and 2 and 3 solutes; hence  $\gamma_2(3)$  represents activity coefficient of component 2 in binary system 2-3.

## EXPERIMENTAL PROGRAM

### Theoretical Considerations.

The preceding theoretical considerations and correlations have been substantiated in part by experimental results in iron-base alloy systems. One of the purposes of this study was to assess their applicability for explaining interactions between metallic constituents in bismuth-rich systems.

The present investigation was also intended to provide additional data on solute interactions with uranium in a bismuth solvent. Solubility effects were measured and used in conjunction with earlier data in an attempt to generalize on the behavior of the ternary liquidus for Bi-U-X systems. In addition carbide decomposition studies were undertaken to provide a more direct measure of uranium activity coefficient variations resulting from interactions with other solute species.

Previous measurements of the solubility had produced numerous discrepancies in the literature. Therefore, the first phase of this study was concerned with the evaluation of the binary liquidus in the temperature region of interest (400°C to 800°C). This curve was then used as the basis for measuring deviations produced by the added solute elements. Although the curve is generally referred to as a solubility curve, the solid phase in equilibrium with the solution is  $UBi_2$  and not metallic uranium. A plot of the  $\ln N_U$  vs  $1/T$  ( $N_U$  = mole fraction of uranium at liquidus) yields the partial molal enthalpy change of uranium in passing from solution to the compound,  $UBi_2$ .

A number of factors were considered in selecting the third components to be studied. An observed periodicity of behavior for elements in bismuth aided in the selection. Solubility studies (59) in bismuth had shown that groups of elements tended to behave similarly. This was further confirmed by examination of binary alloy phase diagrams. Consequently, certain groups were omitted from consideration on the basis of the extremely low solubility demonstrated by certain members. Other groups presented extremely difficult analytical problems and thus were excluded from this study. These two considerations eliminated all but the titanium, cobalt, nickel and copper groups among the transition metals. Brookhaven studies had included zirconium from the titanium group and nickel. The latter had produced a tremendous depression of the solubility for relatively small additions, thus focusing attention on this region of the periodic chart. On the basis of the foregoing considerations, copper and palladium were studied, and the results compared with earlier data for neighboring elements. The effects of other elements including sodium, zirconium, magnesium, cerium, rhodium, lead and zinc were examined semi-quantitatively.

The bismuth-uranium system exhibits strong negative deviations from ideality as suggested by its compound-forming tendencies (App. 4C 1). The bismuth-copper system (App. 4C 5) displays complete solubility in both the liquid and solid states, whereas the copper-uranium (App. 4C 6) system demonstrates immiscible tendencies. The palladium-bismuth system (App. 4C 7) appears to deviate negatively from ideal solution behavior. The uranium-palladium phase diagram (App. 4C 8) contains several high melting compounds suggesting negative departures from Raoult's law in this system also.

A temperature of 600°C was selected for the study since it was near the range of practical interest for nuclear fuels and high enough to produce a reasonable uranium concentration. Dilute concentrations of the perturbing element were used in an attempt to minimize second order effects arising from self-interaction of the third components. Coefficients expressing the solubility change as a simple function of third component concentration were calculated.

The equilibrium constant for the reaction  $U + 2Bi \rightarrow UBi_2$  can be expressed as:

$$K_a = \frac{a_{UBi_2}}{a_U a_{Bi}^2}$$

If the addition of a third component does not alter the composition of the solid phase, then the value of the equilibrium constant and the  $a_{UBi_2}$  should remain unchanged for small additions of a third component. If one can assume that bismuth, as the major component, obeys Raoult's law in this region, then  $a_{Bi}$  should maintain a value close to unity. Negligible change in these three terms requires that the activity of uranium in solution also remain constant at the liquidus. The activity can be regarded as the product of the uranium mole fraction,  $N_U$ , and its activity coefficient,  $\gamma_U$ . Any change in the equilibrium value of  $N_U$  must therefore be compensated for by a corresponding change in  $\gamma_U$ . If the above assumptions are valid, the measurement of solubility changes would permit an estimate of the effect of solute interactions on the thermodynamic properties of the components. It should be mentioned that coefficients expressing such effects might be expected to be functions of temperature and uranium concentration as well as third component concentration.

A more direct way of evaluating interaction effects on the activity coefficients of uranium in bismuth utilizes the second reaction presented above. The uranium-carbon phase diagram (See figure 9) indicates a series of high melting uranium-carbon compounds formed across the diagram. The  $UC_2$ -C region is of particular interest in this investigation. In this two phase region the activity of both carbon and uranium must remain constant. The activity of uranium can be calculated by using the free energy of formation of  $UC_2$ . For the reaction:  $U + 2C \rightarrow UC_2$  the equilibrium constant can be expressed as follows:

$$K_a = \frac{a_{UC_2}}{a_U a_C^2}$$

The phase diagram reports negligible solubility of carbon in  $UC_2$  and hence both of these phases are present as pure solids in their standard state and will have unit activity. Determinations of  $K_a$  from  $\Delta G^\circ = -RT \ln K_a$  permits one to express  $a_U = 1/K_a = \text{constant}$  for a given temperature.

The equilibrium value for  $a_U$  is unaffected by the medium in which the reaction occurs providing the equilibrium is not disturbed. Consequently, the above relationship remains valid for a decomposition occurring in bismuth since the bismuth acts only as a solvent for the free uranium. Carbon and  $UC_2$  continue to exist as pure, solid phases. The equilibration of molten bismuth and  $UC_2$  at some temperature results in the decomposition of  $UC_2$  until the uranium concentration achieves its equilibrium value. Measurement of this concentration permits an evaluation of  $\gamma_U$  since the activity had been previously evaluated from the  $UC_2$  free energy. This calculation provides a check on other values of the activity coefficient reported in the literature.



For elements displaying weak carbide-forming tendencies this reaction can be used to evaluate interaction effects on  $\gamma_U$  with a minimum of assumptions. The elements previously considered as third components are very weak carbide formers compared to uranium and should not interfere with the solid phases in the equilibrium. The two solid phases remain at unit activity and the same equilibrium constant applies. The bismuth does not enter into the reaction at all; therefore, no assumption regarding its activity is necessary. Changes in the equilibrium uranium concentration can now be directly related to changes in  $\gamma_U$ . The third component concentration can be varied continuously in the dilute region for any given temperature.

The experimental portion of the investigation necessitated equilibrating solid and liquid phases. The "solubility" portion of the study involved the reaction of metallic uranium with molten bismuth to form a bismuth solution of uranium and the compound  $UBi_2$ . Interaction effects were studied by simply adding the desired amounts of copper and palladium to the charge. A filtration operation was used to separate phases following equilibration. The filtrate was analyzed for uranium and the third component using spectrophotometric techniques (See Appendix D). These results yielded the liquidus composition from which the solubility parameters were determined. Whereas the above reaction required a complete transformation of the solid phase from metallic uranium to  $UBi_2$  and uranium in solution, the carbide decomposition reaction maintained the same solid phase throughout. At equilibrium the uranium in the solution should have an activity equal to that of uranium in the  $UC_2$ -C region. Excess carbide was added to insure an adequate supply of uranium and to decrease the time required to reach equilibrium. Although earlier

studies (13) had suggested that decomposition would not occur, previous work (54) in our laboratory had shown a reasonable rate for this reaction. As in the solubility studies, third elements were introduced along with bismuth and  $UC_2$  in the charging operation. In this phase of the work none of the third components were pre-alloyed with the bismuth. A filtration operation again separated solid and liquid phases prior to chemical analysis.

### Equipment

The reactions described above had to be performed in an inert atmosphere to minimize the oxidation of uranium. At the same time one had to suppress the volatilization of bismuth from the melt at reaction temperatures. Likewise, precise temperature control was important since temperature differences would also produce changes in solution composition which might conceal interaction effects. To accomplish the above conditions, equipment designed for this study which was somewhat different than the apparatus utilized by other investigators for solubility determinations.

A horizontal reaction chamber was employed which permitted eleven separate equilibrations. Each reaction was conducted in a graphite filter crucible (See Figure 3) from which a single filtrate sample could be obtained. The apparatus permitted varying the third element concentration at a fixed temperature for each run. Previous apparatus described in the literature allowed little composition control, but could be sampled repeatedly at different temperatures. Since composition, rather than temperature variations was of primary interest, this design seemed more advantageous.

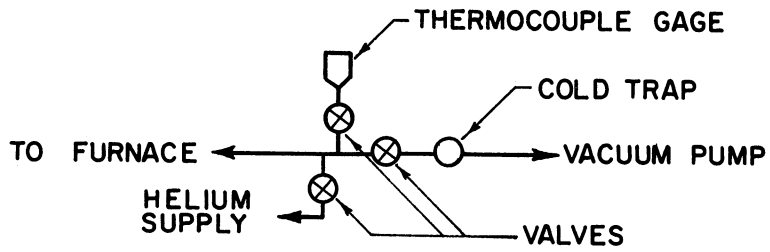


Figure 2. Valve Arrangement on Equipment.

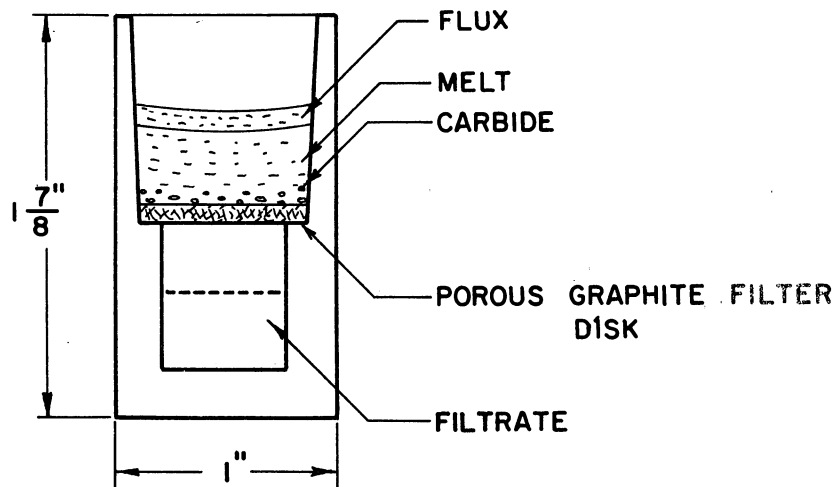


Figure 3. Filter Type Crucible.

The reaction chamber consisted of a 2 1/2" ID Mullite tube inserted in a split-wound resistance furnace (See Figure 42). The furnace was two feet long and contained compensating windings at each end to minimize end-effects. The furnace power supply was varied through a 0-220 volt variac. A Foxboro on-off temperature controller activated by a chromel-alumel thermocouple was used to maintain the reaction temperature. The control thermocouple was placed between the mullite tube and the furnace windings to improve sensitivity and minimize temperature fluctuations within the furnace. The response of the system was sufficient to maintain the reaction temperature within 1°C in the temperature range of interest.

The temperature profile was checked during the early stages of the program by means of five chromel-alumel thermocouples spaced along the reaction zone. The couples were enclosed in stainless steel hypodermic tubing to eliminate corrosion from bismuth vapors. They were introduced to the furnace through conax glands mounted on the face of the brass end plate. The ends of the couples were then inserted in holes in the walls of every other crucible. At 600°C the reaction zone was practically isothermal. A maximum variation of 5°C was observed at 800°C. This difference was attributable largely to the fact that, despite radiation shields used at the open end of the tube, the end crucible "saw" temperatures somewhat below the rest of the furnace. However, it acted as a radiation shield for the remaining crucibles so that the other ten were virtually isothermal. Most runs were made without utilizing the eleventh crucible. No problem was encountered at the closed end of the tube since it remained three inches inside the heated zone. An insulating plug was

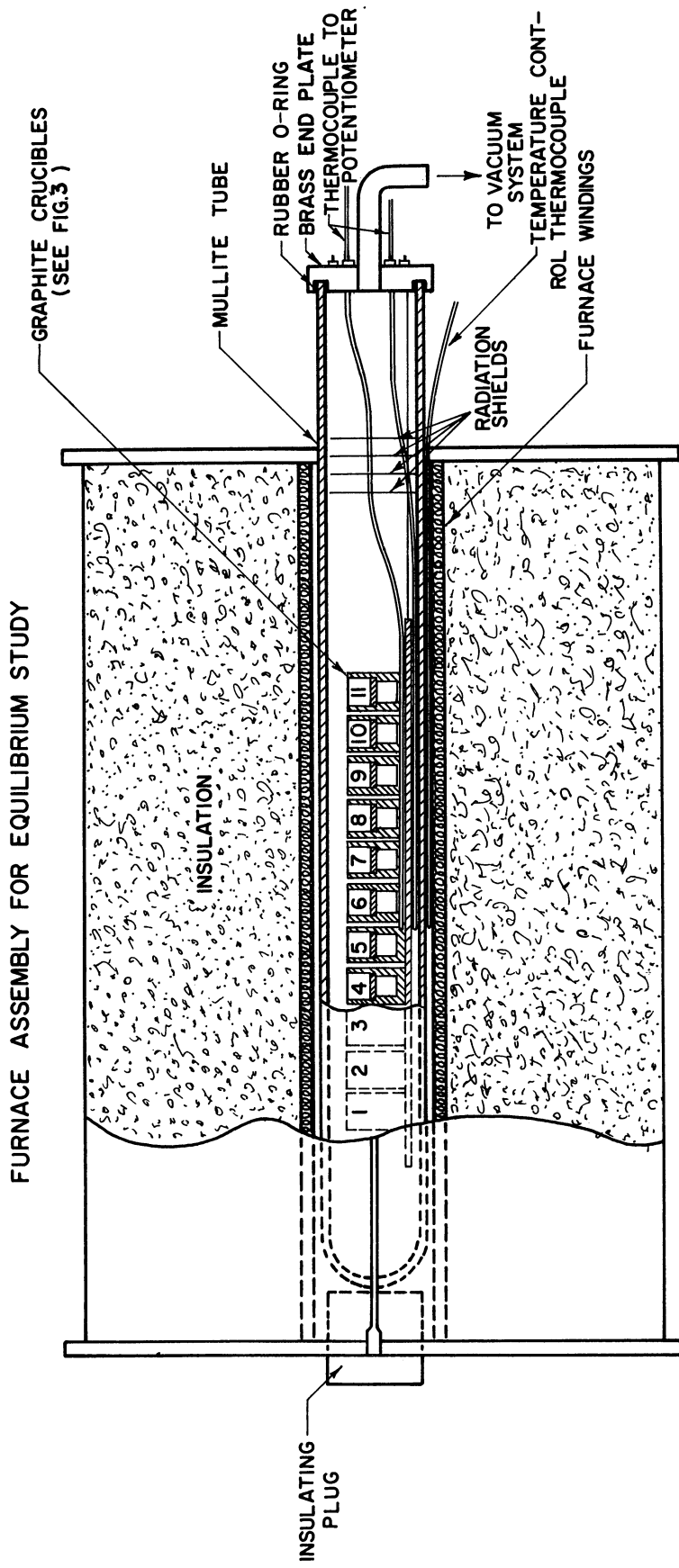


Figure 4.

inserted to minimize radiation and convection losses at that end. The latter stages of the investigation were conducted using only two thermocouples in the reaction zone. They rested beside the central crucibles in the charge.

The equipment (See Figure 2) permitted complete environmental control from pressures in the micron range up to one atmosphere. A vacuum pump connected to the system through a cold trap was used to evacuate the system. The combination was capable of producing vacuums of about one micron as measured by a thermocouple gage. A mercury manometer indicated pressures up to atmospheric pressure. Commercial helium passed through a charcoal trap at liquid nitrogen temperatures was used for environmental control and for providing the pressure differential necessary to induce filtration.

An O-ring seal between the ground end of the mullite tube and a brass end plate provided access to the reaction zone. The sample tray was attached to the end plate by stainless steel connecting rods. This connection facilitated charging and removing the crucibles and assured proper positioning for each run.

### Materials

#### 1) Crucibles

The graphite crucibles (Figure 31) were fabricated in our shops from Graph-i-tite "G", an impervious graphite obtained from Graphite Specialties Corporation. Filters were machined from blocks of porous graphite stock obtained from the National Carbon Company. Both grades 50 and 60 were used without detectable differences in the results. Both have effective porosities

of 48%, but the former retains particles 0.00079" compared to 0.00047" for the latter. The disks were 1/16" - 1/8" thick and had a diameter slightly greater than the ID of the crucible just above the shoulder. The filters were force-fitted into position thus reducing the probability of leakage around the disk. The finished crucible was then outgassed at least 200°C above the run temperature to eliminate volatile constituents present in the impregnating medium. Crucibles used in the decomposition study at 800°C were outgassed initially at 1400°C and then again at 1000°C just prior to use. This treatment was adopted when outgassing studies indicated that significant desorption was not detected below 1000°C. Wetting of the crucible was desired in these studies as it further assured a carbon activity of unity. In all these outgassing treatments helium was introduced and reabsorbed prior to discharge. These crucibles were then charged immediately and the run initiated. Any crucibles which were exposed to the atmosphere for greater than 12 hours were given a rapid outgassing at 1000°C before being used.

Both residue and filtrate were removed readily from the crucible. This permitted its reuse in subsequent runs with the same element. New filters were installed and the outgassing treatment repeated. Since the equilibrium uranium concentration along the liquidus in the uranium-bismuth system was above that required to form carbide in the presence of graphite, the use of graphite crucibles was initially discouraged. However, the results of earlier investigations (58) coupled with our experience in trying to form the carbide indicated that the kinetics of such a reaction were not rapid

enough to interfere. Graphite, alumina, and vycor samplers had all yielded comparable results in the Brookhaven investigation (58). Excess uranium was added to permit some reaction with the crucibles, as well as with any oxygen in the system, without disturbing the uranium-bismuth equilibrium.

## 2) Uranium

Mallinckrodt's reagent grade uranium of 99.97% purity was used for the solubility studies. The one quarter pound slugs provided by the manufacturer were turned on a lathe to produce fine spirals. These turnings were first dropped in trichloroethylene to remove the oil and then cleaned electrolytically in a solution of chromic oxide and  $H_2SO_4$  to remove the oxide layer. The above treatment assured a solid phase which reacted readily with the molten bismuth at reaction temperatures.

## 3) Bismuth

The bismuth used throughout this investigation was obtained from Belmont Smelting and Refining Company and was reported to be 99.998%. It was received in 1" lumps which were vacuum cast into  $7/8$ " cylinders. The slug was then cut into pieces of the desired weight and was charged directly to the crucible. All bismuth used in the solubility phase of the work was filtered through pyrex frit in the casting operation. This practice was eliminated in the later stages of the study. A hydrogen refining operation originally used by Brookhaven and Armour investigators was found unnecessary with the bismuth presently attainable (3).



4) Palladium

The palladium was obtained in powdered form from Chemical Commerce Company and was reported as 99.98% pure. During the early stages of the work palladium was added in the form of a master alloy. The alloy containing 5-6% palladium was filtered and cast under vacuum prior to its use. However, subsequent experiments demonstrated that it could be added quantitatively directly to the individual charges. This procedure was employed exclusively in the decomposition work.

5) Copper

Fine copper wire, 99.999% pure, was used for copper additions. As in the case of palladium, copper additions were originally made through a master alloy. This procedure was abandoned in the decomposition studies as copper readily dissolved in the bismuth solvent.

6) Uranium Dicarbide

Three different types of uranium carbide were procured for this study. A granular mixture of the mono and dicarbides supplied by NUMEC\* was used in most tests. The carbon analysis of 7.95%C would indicate 71%UC<sub>2</sub> and 29%UC. X-ray diffraction studies of the mixture confirmed quantitatively the above percentages. Negligible UO<sub>2</sub> was present and no free uranium was detected. Other impurities were maintained at a level consistent with reactor grade quality. This carbide appeared more metallic than either the UC<sub>2</sub> or the UC, both of which were provided by Davison as a partially sintered powder. In

\* Nuclear and Materials Equipment Corporation.

the absence of carbon the UC-UC<sub>2</sub> mixture would generate a higher uranium activity consistent with that region of the UC-UC<sub>2</sub> phase diagram. However, if carbon is involved in the equilibrium the UC portion of the mixture would be converted to either UC<sub>2</sub> or would decompose to uranium in solution and carbon. However, a uranium concentration in the melt above that required for the UC<sub>2</sub> equilibrium should result in a reaction with graphite producing the UC<sub>2</sub> and reducing uranium to its equilibrium value. Fluxing aided in assuring a more intimate contact between the graphite and the solution. The UC<sub>2</sub> was used in several runs to confirm the results obtained with the more readily handled NUMEC product. The fines in the UC<sub>2</sub> created numerous difficulties in both the handling and equilibrating operations. The larger particles were used but they did not afford the surface area that the granular carbide supplied.

#### 7) Flux

The flux used for promoting wetting in the decomposition studies was composed of 56%KCl and 44%NaCl by weight. This composition corresponds to the eutectic composition which melts at 611°C. Reagent grade chlorides were used for the mixture.

### Procedure

#### 1) Solubility Studies

After the pretreatments just described, the reactants were charged to the crucibles. Uranium, at least 10% in excess of that required to

saturate the solution, was charged first. The bismuth slugs were then inserted and ten crucibles placed in the furnace. The pressure was reduced to the micron region before heating was begun. Runs were made with the vacuum system in operation throughout the run and with its removal. The furnace proved to be sufficiently vacuum-tight to permit the latter. The charge was equilibrated at temperature for periods ranging from 2 to 43 hours with very little difference observed in the results. Cosgarea's observations (12) confirmed this very rapid approach to equilibrium for this particular reaction. Most runs were permitted to remain at temperatures for 12-24 hours before filtering.

Filtration was effected by suddenly introducing helium to the system. An increase in pressure of several hundred millimeters was sufficient to push the solution through the filter disk very rapidly. The possibility of seepage around or through the filter was checked repeatedly and was never observed to occur. Even pressures of 50 mm of mercury have failed to filter some solutions.

The filtrate and residue were removed from the crucible by inverting and tapping. The entire filtrate slug was sent for analysis because of the segregation produced on cooling. The residue was analyzed in several instances in an attempt to establish a second point on the tie line. Extrapolation of these lines permitted an estimate of the composition of the solid phase in the equilibrium.

The binary liquidus was studied from 400°C to 800°C with repeated runs. Each run contained approximately 10 independent determinations. Ternary

Studies were confined to runs at 600°C. Some were heated initially to 650° or 700°C and then reduced to 600°C for 24 hours in an attempt to approach the equilibrium from both directions. Concurring results were obtained for both procedures.

## 2) Decomposition Studies

After the pretreatments previously described the reactants were charged to the furnace. The optimum charge size appeared to consist of 3 gm of the carbide, 20 gm of bismuth and the desired amount of third component. The uranium content of 3 gm of carbide was far in excess of that required to saturate the solution. However, the increased contact area was essential in producing reasonable equilibration times. Charges of up to 8 gm of carbide yielded results in 50 and 75 hour runs similar to those for 3 gm charges. Bismuth charges of less than 20 gm did not distribute consistently over the entire filter and thus failed to yield samples. Larger charges required more decomposition and hence longer periods to reach equilibrium.

The carbide was always charged first. If third components were involved they were added along with the carbide. The bismuth slugs were placed above the carbide and finally the flux (when used) was added. Graphite caps with a 1/8" hole were added to reduce bismuth vaporization. The initial position of the carbide was important as the density differences between it and the melt were not significant enough to produce a change in its position. Consequently carbide placed above the bismuth floated and only a small percentage of the phase was contacted. Significantly lower concentrations were

observed in these samples when compared to those with the carbide beneath the melt.

Assuring intimate contact between carbide and solution afforded the major experimental difficulty. Many of the data inconsistencies apparently resulted from poor wetting of the solid. The equipment was not designed to permit agitation of any kind and thus it was necessary to rely on the bismuth wetting and flowing around the carbide. Much time was devoted to the development of techniques to improve the contact problem. The carbide phase was cathodically etched prior to charging in an attempt to clean the surface. Consistent improvement was not observed in these charges. Size reduction was attempted using a mortar and pestle, but the pyrophoric nature of the carbide resulted in almost immediate oxidation of the newly created surfaces. A pre-wetting treatment accomplished by heating carbide and bismuth to above  $800^{\circ}\text{C}$  in an evacuated, agitated, vycor tube succeeded in producing wetting of the NUMEC carbide, but not the Davison  $\text{UC}_2$ . However, the result failed to improve the consistency of the data.

## RESULTS

1) The solubility determinations over the temperature range 400° to 800°C yielded the following expression for the liquidus composition:

$$\log_{10} \text{ wt. \%U} = 3.272 - \frac{2690}{T^{\circ}\text{K}}$$

No suggestion of a break in the curve was detected between 400° and 500°C as was reported by Schweitzer and Weeks, and the Armour Research Foundation. Determinations at eight different temperatures yielded average values for solubility which deviated only slightly from the above relationship (See Figure 5).

2) The partial molar enthalpy change for uranium in the reaction:

$\text{UBi}_2 \rightarrow \text{U} + 2\text{Bi}$ , equalled  $+ 12,300 \frac{\text{cal}}{\text{gm mole}}$ . This value was obtained from the slope of the solubility curve using the following relationship (See Appendix B for derivation):

$$-\left(\frac{\partial \ln N_{\text{U}}}{\partial \left(\frac{1}{T}\right)}\right)_{\text{a}} = \frac{\Delta \bar{H}_{\text{U}}}{R} = \frac{\bar{H}_{\text{soln}} - \bar{H}_{\text{cpd}}}{R}$$

3) Copper additions to the uranium-bismuth system depressed liquidus uranium concentrations at 600°C, as is shown in Figure 6. Figure 7 shows that the reduction when plotted as the natural logarithm of atomic percent uranium vs atomic percent copper was linear for copper concentrations less than 3 atomic percent. A plot of the liquidus at 600°C (See Figure 8) suggests that the solid phase in equilibrium with the established portion

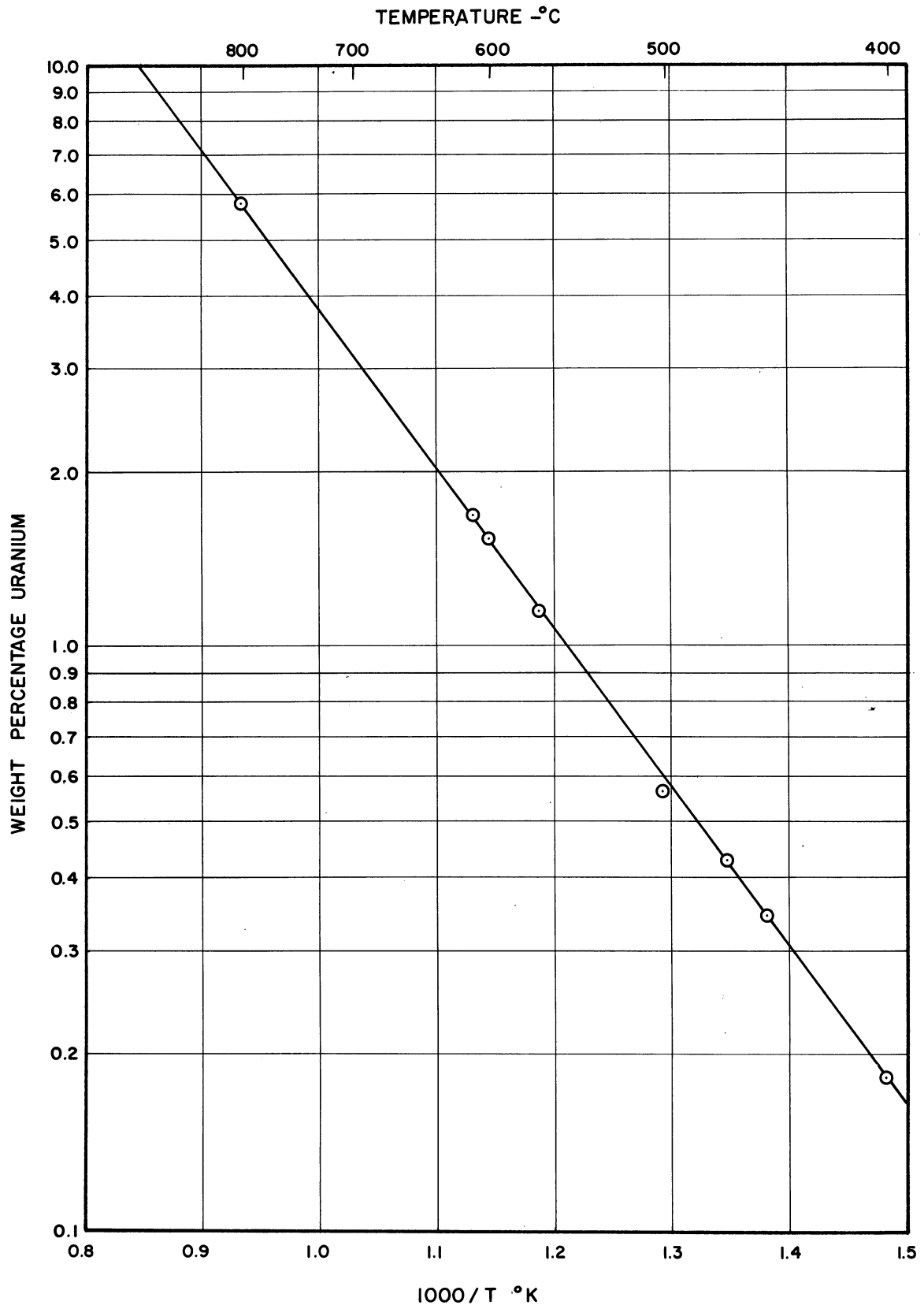


Figure 5. Solubility of Uranium in Bismuth.

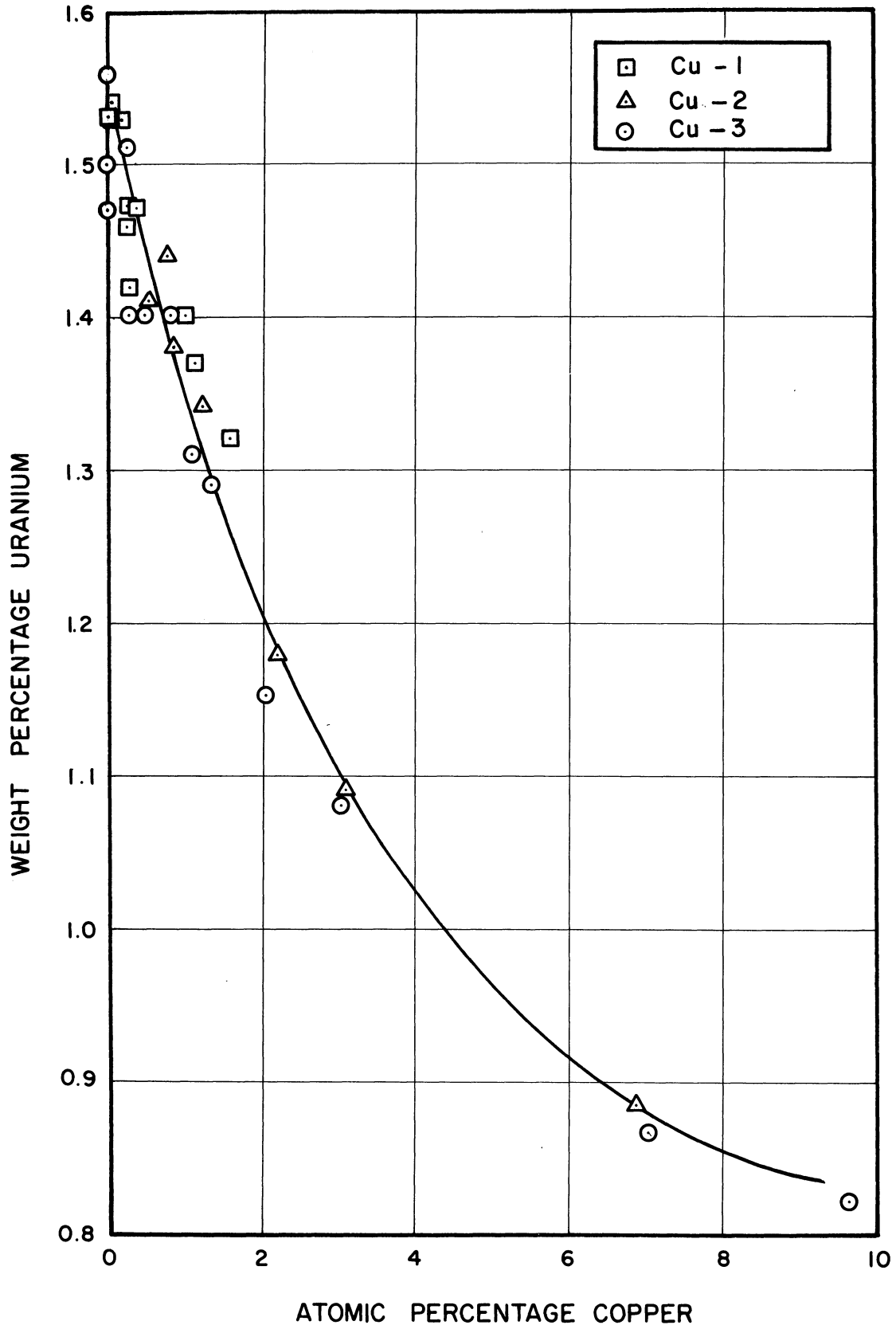
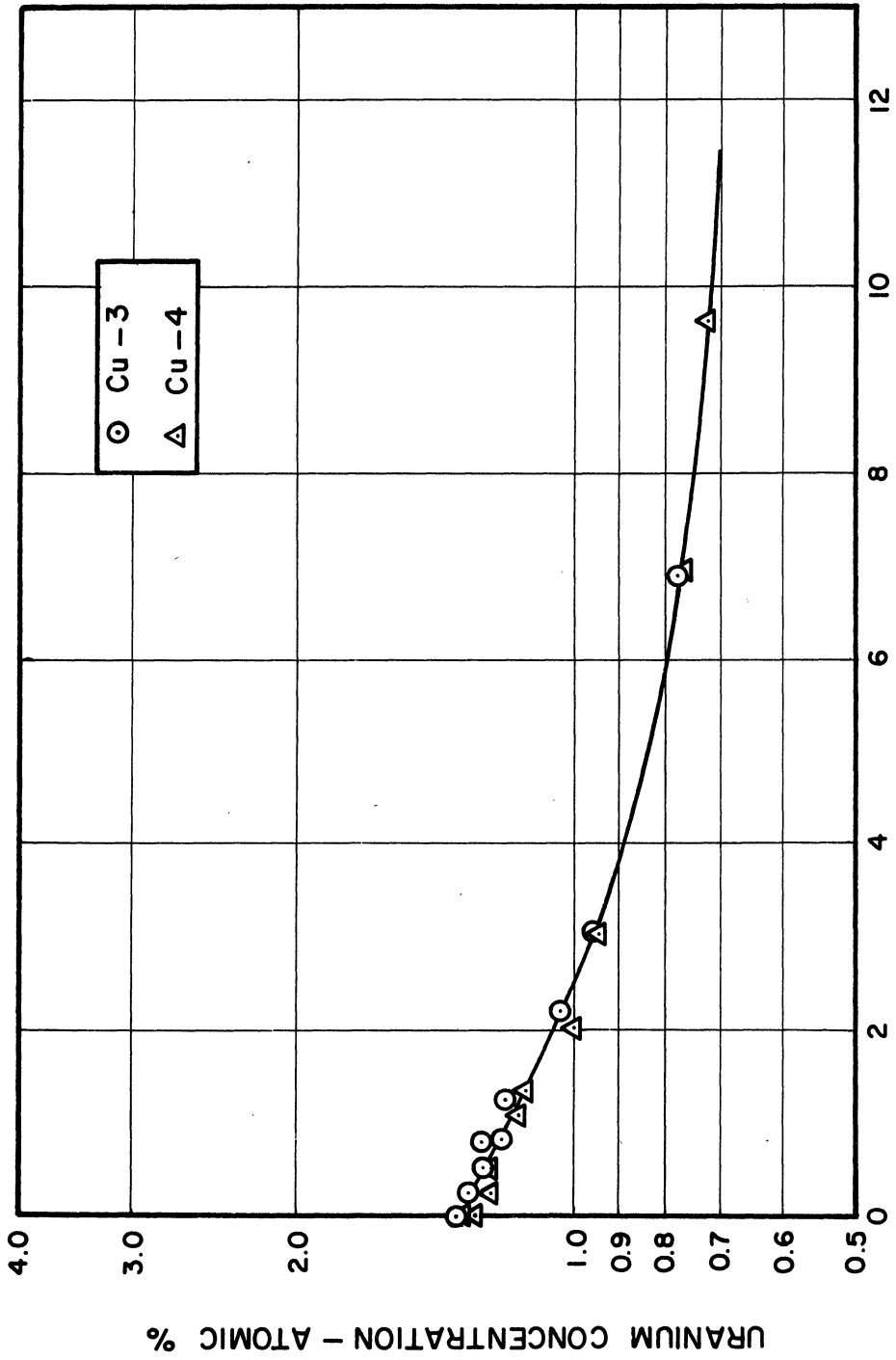


Figure 6. Effect of Copper on U-Bi Liquidus at 600°C.





COPPER CONCENTRATION - ATOMIC %

Figure 7. Evaluation of  $\epsilon_{U}^{(Cu)}$  at 600°C.

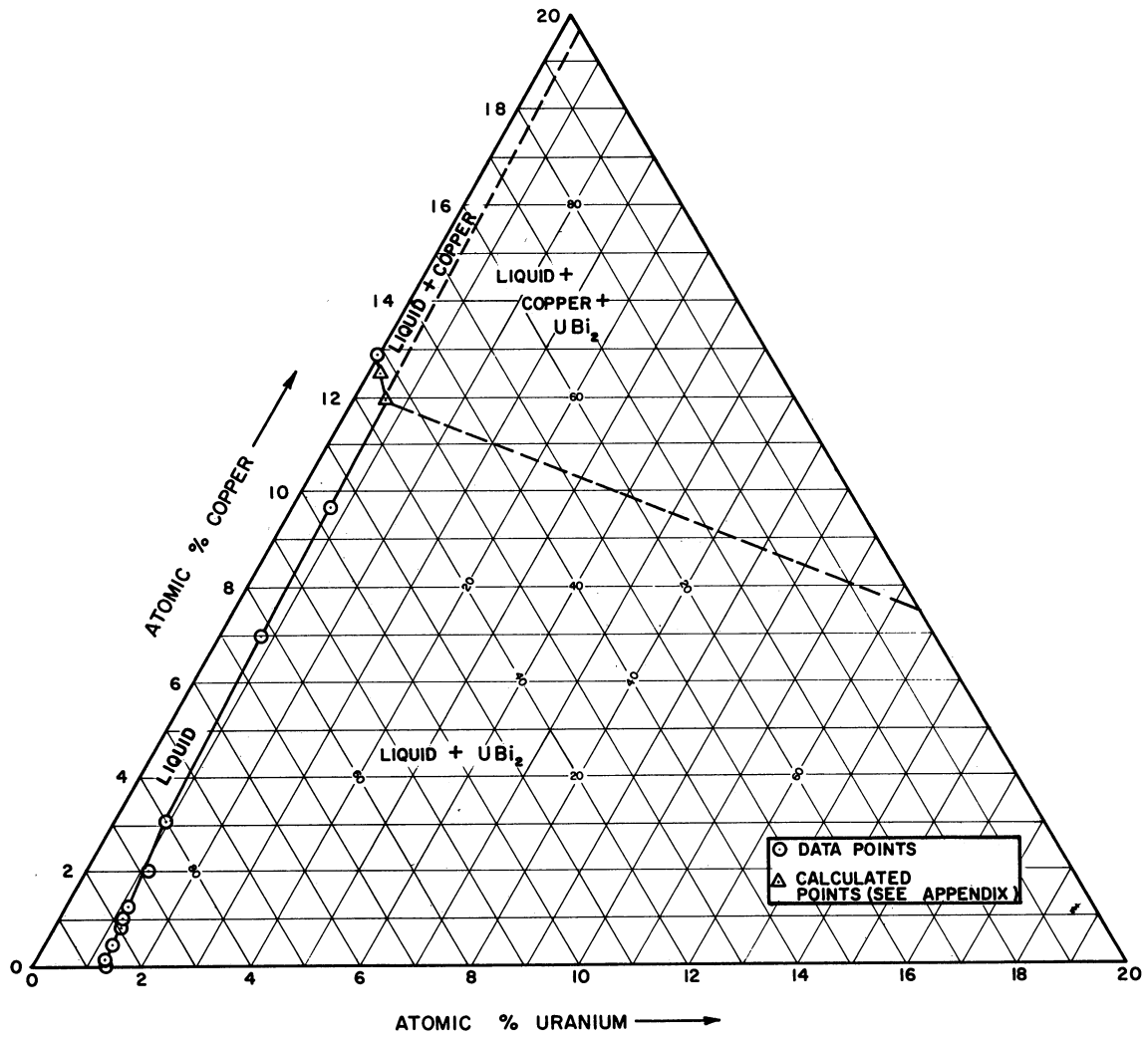


Figure 8. Suggested Bismuth Corner of Bi-Cu-U Ternary at 600°C.

of the liquidus is very likely  $\text{UBi}_2$ . Consequently, the data permitted the evaluation of Wagner's interaction parameter,  $\epsilon_{\text{U}}^{(\text{Cu})}$ , from Figure 7.

$$\epsilon_{\text{U}}^{(\text{Cu})} = \frac{\partial \ln \gamma_{\text{U}}}{\partial N_{\text{Cu}}} = - \frac{\partial \ln N_{\text{U}}}{\partial N_{\text{Cu}}} = 11.0$$

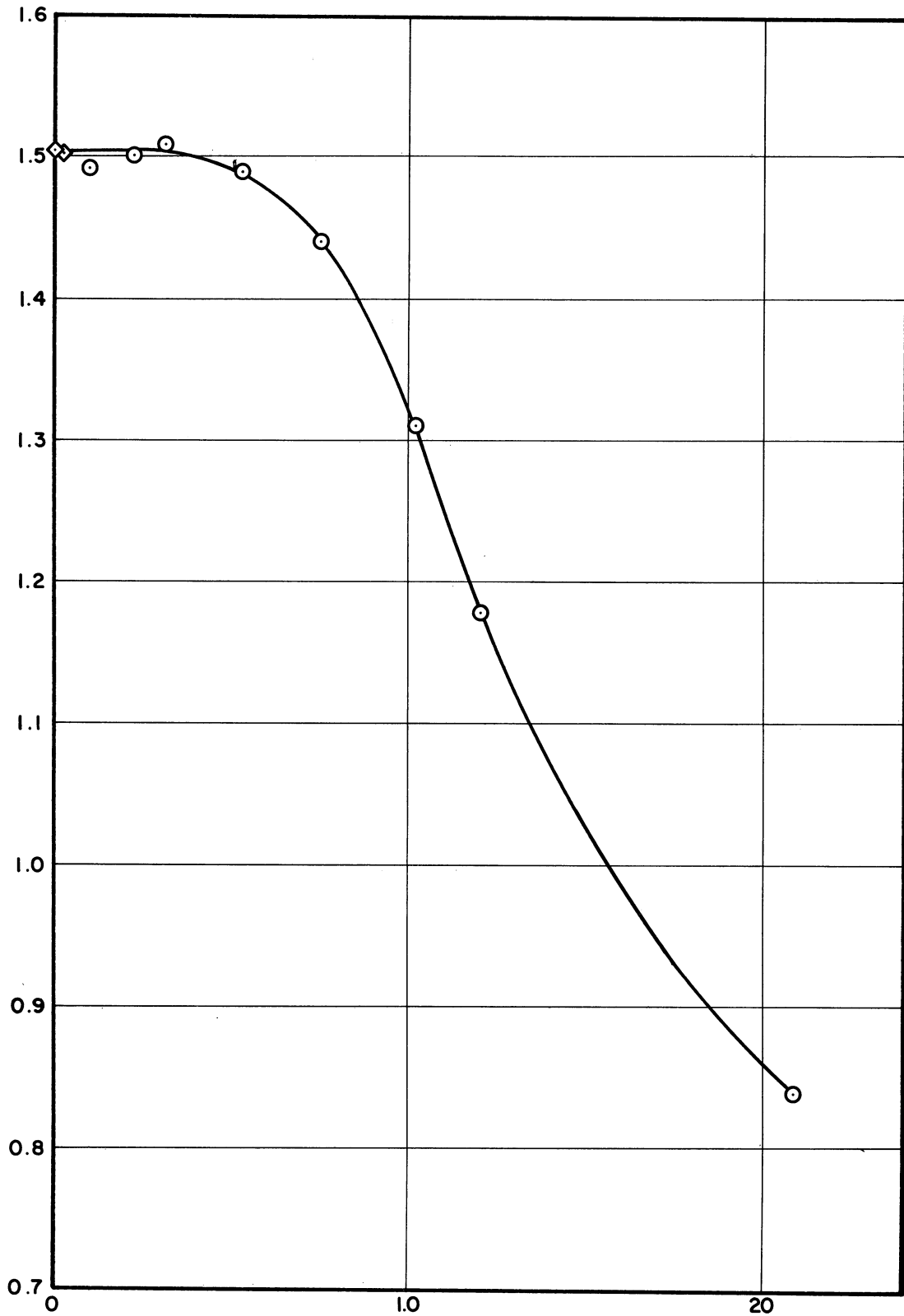
for constant uranium activity over that portion of the liquidus.

Since  $\epsilon_{\text{U}}^{(\text{Cu})} = \epsilon_{\text{Cu}}^{(\text{U})}$ , it was possible to estimate the other extreme of the liquidus where  $N_{\text{U}} \rightarrow 0$ . This portion has been included in Figure 8.

4) Palladium additions to uranium-bismuth melts at  $600^\circ\text{C}$  effected a sharp reduction in the uranium liquidus concentration for palladium concentrations greater than 0.6 atomic percent (see Figure 9). 2.09 atomic percent palladium produced a 43% decrease in the uranium concentration. At palladium concentrations below 0.6 atomic percent there was no evidence of any change in uranium concentration.

5) Qualitative studies showed that sodium increased the uranium concentration at  $600^\circ\text{C}$ . Rhodium, cerium, lead and nickel all produced decreases.

6) The reaction,  $\text{UC}_2 \rightarrow \underline{\text{U}} + 2\text{C}$ , produced an equilibrium uranium concentration of 1.86 weight percent in a bismuth medium. This concentration, when used in conjunction with Grieverson and Alcock's  $\Delta G^\circ$  for  $\text{UC}_2$ , yielded an activity coefficient of  $1.22 \times 10^{-4}$  at  $800^\circ\text{C}$  (see Appendix B-1).



**ATOMIC PERCENTAGE PALLADIUM**

Figure 9. Effect of Palladium on U-Bi Liquidus at 600°C.

7) Carbide decomposition studies in bismuth-copper solvents concurred with the findings in the liquidus study. Although the data exhibited considerably more scatter than the liquidus work, the interaction parameter,  $\epsilon_U^{(Cu)}$ , was also found to equal approximately +11.0. Figure 10 contains data from two different runs which produced slopes similar to that in Figure 6 for the liquidus at 600°C.

8) Palladium produced an increase in the equilibrium uranium concentration for the carbide decomposition at 800°C. The effect appeared to vary linearly with palladium concentration below 5 atomic percent palladium (See Figure 11). A plot of the natural logarithm of atomic percent uranium vs atomic percent palladium yielded a value for  $\epsilon_U^{(Pd)}$  of -4.8 (Figure 12).

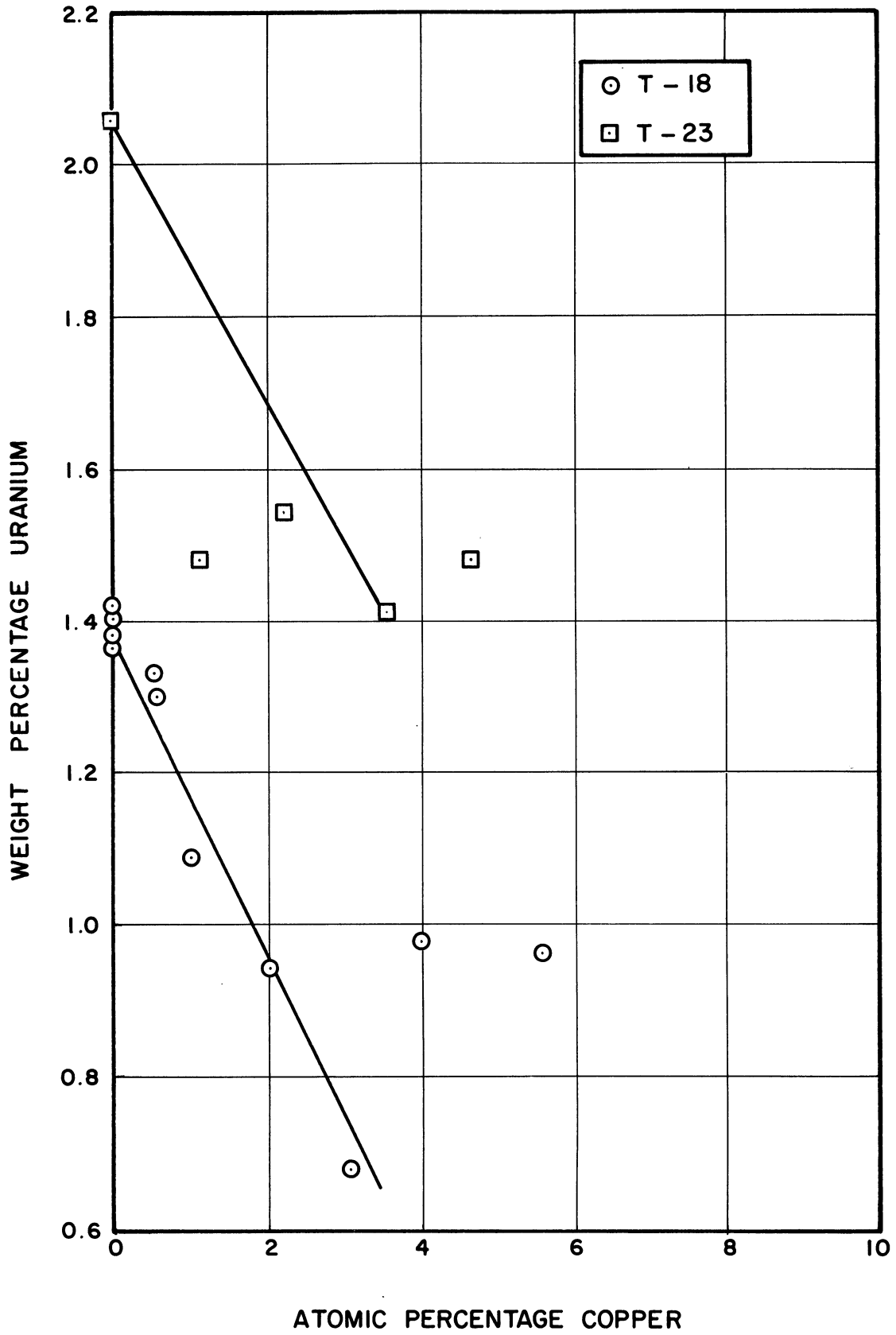


Figure 10. Effect of Copper on  $UC_2$  Decomposition at  $800^\circ C$ .

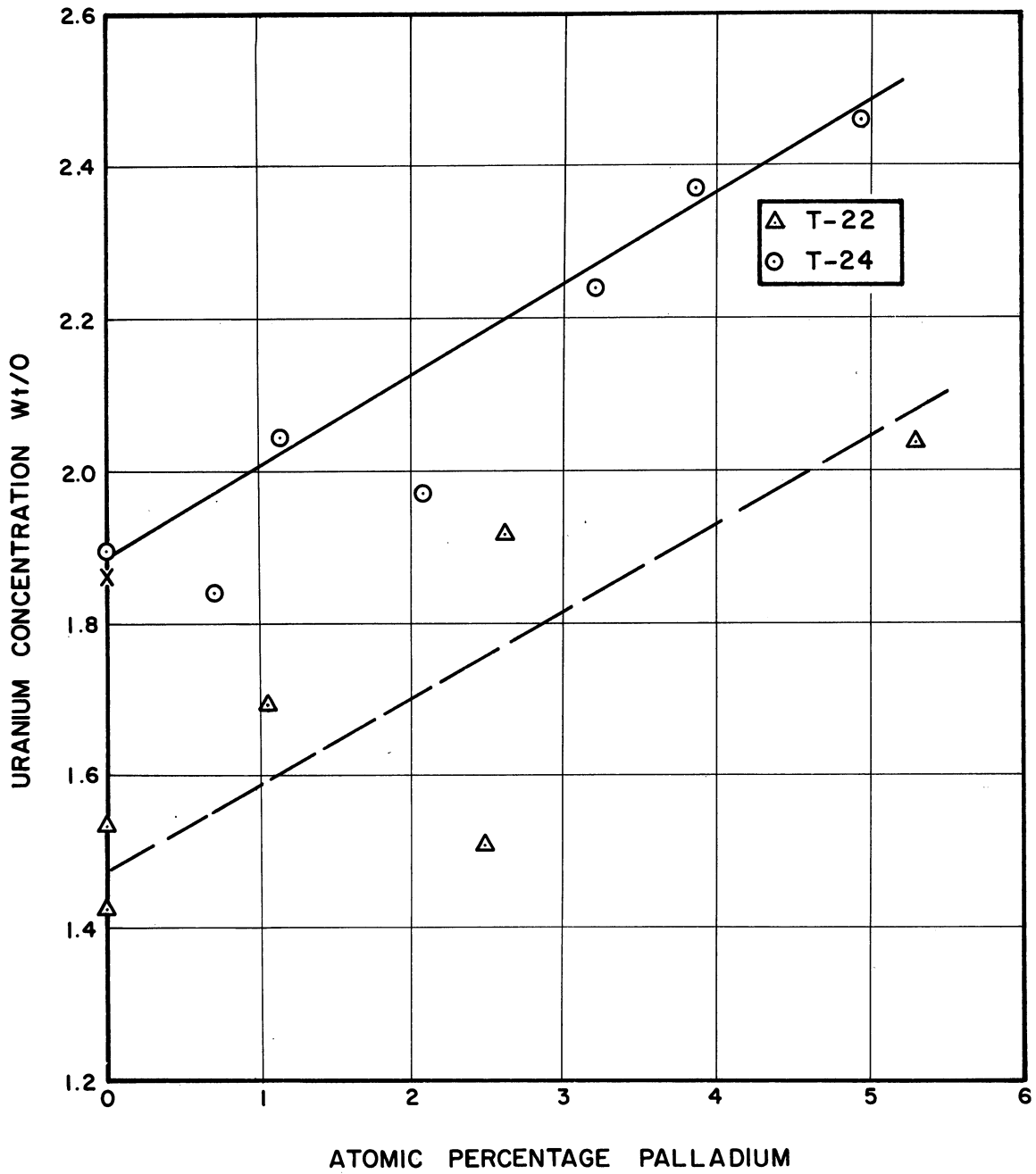


Figure 11. Effect of Palladium on  $UC_2$  Decomposition at  $800^\circ C$ .

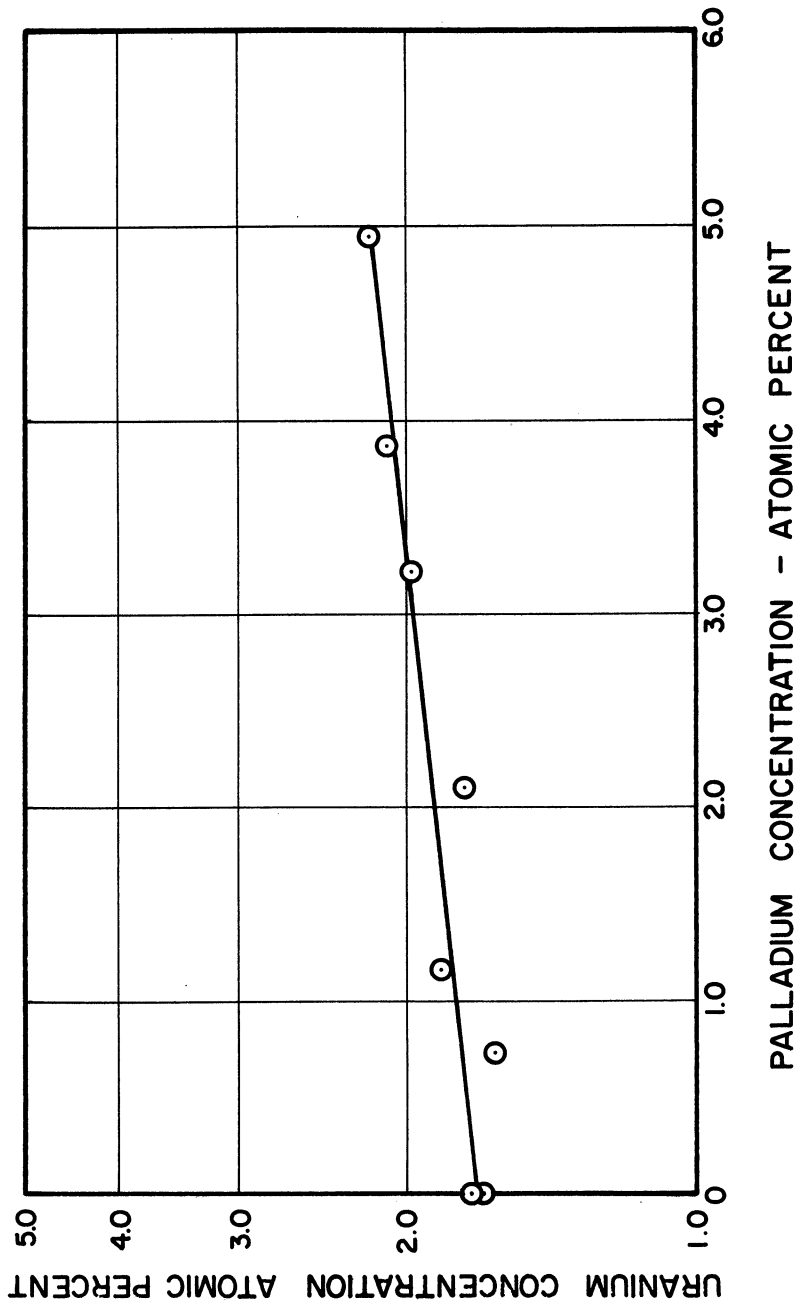


Figure 12. Evaluation of  $\epsilon_{\text{Pd/U}}$  at 800°C.



## DISCUSSION OF RESULTS

The data obtained in this study for the uranium-bismuth liquidus determination proved to be exceptionally consistent and reproducible. Individual samples varied less than 3 percent from the average value used to establish the curve in Figure 5. This variation is no greater than the uncertainty introduced by the chemical analysis. As Figure 5 demonstrates, the average values for the solubility at the eight temperatures studied fall on a straight line when plotted as  $\ln \text{ wt } \% \text{ vs } 1/T$ . This data, as Figure 1 indicates, also confirms the data of Bareis and Greenwood at temperatures below  $650^{\circ}\text{C}$ . Greenwood's data above  $650^{\circ}\text{C}$  deviates to the high side, but Barton's more recent determination at  $800^{\circ}\text{C}$  confirms precisely the values obtained in this study. Although Schweitzer and Weeks reported values 15% below those found by the author above  $480^{\circ}\text{C}$ , they did concur on the slope of the curve. However, their data suggested a break in the curve at  $480^{\circ}\text{C}$  which resulted in a second linear segment at lower temperatures. Armour investigators found a more exaggerated break around this temperature, but their data deviated so substantially from that of all previous investigators that the significance of the break appears questionable. No satisfactory explanation for such behavior has been offered by either of these groups.

Two logical explanations for the different results reported by various investigators involve the analytical procedures and the purity of the reactants. The former could very well account for the vertical displacement of the curve of Schweitzer and Weeks from that produced in this study. An error in the standard curve or difficulty with the stability

of the standard solution could produce the type of discrepancy observed. The extreme sensitivity of this curve to certain impurity atoms could likewise produce such deviations. Most elements likely to be present as impurity atoms in either bismuth or uranium have been shown to have depressing effects on the binary liquidus. This factor might account for the unusually low values reported by the Armour group.

An analysis of the thermodynamics of the liquidus permitted an evaluation of the change in the partial molar enthalpy of uranium for the reaction:  $UBi_2 \rightarrow U + 2Bi$ . (See Appendix B-2). The value for  $\Delta\bar{H}_U$  of +12,300 cal/gmmole was obtained by assuming the activity of uranium remained constant along the liquidus. If the activity is assumed to be a function of uranium concentration and temperature, the expression for the total differential of activity with respect to these two independent variables yields the relationship,  $-\frac{\partial \ln N_U}{\partial 1/T} = \frac{\Delta\bar{H}_U}{R}$ . It was necessary to assume that  $\left(\frac{\partial \gamma_U}{\partial N_U}\right)_T = 0$ . This condition is certainly satisfied in the Henry's law region, but is not necessarily valid at liquidus concentrations. Although Egan has suggested the system conforms to regular solution theory, this fact was disputed by Cosgarea, and hence was not used to estimate  $\left(\frac{\partial \gamma_U}{\partial N_U}\right)_T$  in the derivation. Regular solution theory would produce a 3% decrease in  $\Delta\bar{H}_U$ .

Both copper and palladium were found to depress liquidus uranium concentrations, but in slightly different manners. Copper, as shown in Figures 6 and 8, effects a smooth decrease originating at zero copper concentration. An attempt was made to estimate the composition of the solid phase by analyzing the residue in each crucible, and thus establish a second

point on the equilibrium tie line. In all cases the copper concentration in the residue slightly exceeded that in the filtrate. This would suggest that the ternary liquidus is in equilibrium with a ternary solid field as the tie lines are directed away from the  $UBi_2$  composition. It should be pointed out that the total uranium concentrations in these charges was approximately 3%. Since the filtrate concentration is between 1% and 1.5% uranium as compared to 36% for  $UBi_2$ , the two points on the tie line are fairly close together and could not be extrapolated with a great deal of accuracy. Incomplete solution of the copper could also account for the higher copper analyses in the residues. A metallographic examination of the residue would have permitted a more positive identification of the solid phase.

The presence of a ternary solid phase would likely produce a definite change in the uranium activity from that in  $UBi_2$ . Consequently, at the point along the liquidus where the transition occurs an abrupt change in slope should occur. Nickel, immediately adjacent to copper in the periodic chart, exhibits such behavior, as does zirconium. The liquidus established in this study for the Cu-U-Bi ternary did not possess such a break. The reluctance of copper to form compounds with either uranium or bismuth (See phase diagrams Appendix C) diminished the likelihood of a ternary compound in this system. These considerations led to the construction of the bismuth corner of the ternary shown in Figure 8.

For the equilibrium as postulated above, it was possible to evaluate the interaction parameters for copper and uranium solutes in bismuth.

Wagner's parameter,  $\epsilon_U^{(Cu)}$ , was evaluated from Figure 7 and yielded a value of +11.0. Using his reciprocity relationship  $\epsilon_U^{(Cu)} = \epsilon_{Cu}^{(U)}$  it was possible to determine the liquidus for low uranium concentrations. Two points were

calculated:  $N_U = 0.0025$  for  $N_{Cu} = 0.124$  and  $N_U = 0.006$  for  $N_{Cu} = 0.119$ .

These are shown in Figure 8. The parameter proposed by Ohtani and Gokcen,  $\lambda_U^{(Cu)}$ , is likewise equal to +11.0. It is defined similarly to Wagner's  $\epsilon_U^{(Cu)}$ , but it has the restriction of constant activity, as opposed to constant concentration for  $\epsilon_U^{(Cu)}$ . The former was true for these studies, but the difference between the two restrictions vanishes as  $N_U$  approaches zero. Similarly for a given copper concentration, the parameters  $Q_U^{(Cu)}$  and  $P_U^{(Cu)}$  can be evaluated from the relationship  $\ln P_U^{(Cu)} = N_{Cu} \epsilon_U^{(Cu)} = \ln Q_U^{(Cu)}$ .

Alcock and Richardson's analysis requires some speculation as to the thermodynamics of the respective binary systems. The uranium-bismuth system has been shown to deviate negatively from Raoult's law. The copper-bismuth system has been shown to be a slight positive deviator. The uranium-copper system exhibits some immiscibility which suggests a positive deviation. The expression proposed by Alcock and Richardson (See Table III) for  $\epsilon$  produces the following results. Terms 1 and 2 are positive and 3 is negative. Term 2,  $-\ln \gamma_{U(Bi)}$ , has been shown to equal approximately +10. Terms 1 and 3 are probably small in magnitude compared to  $\ln \gamma_{U(Bi)}$  and might be expected to cancel each other as a first approximation. Thus this approach suggests a value of approximately 10 which agrees remarkably well with the measured value of 11.0.

Mechanistically one can interpret the results in terms of copper atoms, which have little affinity for uranium, competing with the uranium atoms to coordinate bismuth. The effective number of bismuth atoms or clusters

available for the uranium is thus decreased, and hence, an increased uranium activity is achieved for a given uranium concentration.

The carbide decomposition studies in the binary bismuth-copper solvent seemed to confirm these results. Although the data appears to exhibit considerable scatter, a critical evaluation of the individual samples provides some justification for the curves in Figure 10. Run T-23 yielded two particularly good samples in which the wetting and filtering both appeared satisfactory. The curve has been drawn to pass through these two points. Run T-18 appears not to have reached equilibrium for lower copper concentrations.

The behavior of palladium provides a contrast to that of copper. The liquidus uranium concentration undergoes a sudden depression at  $600^{\circ}\text{C}$  when the palladium concentration reaches 0.6 atomic percent. The sharp reduction suggests the presence of a new solid phase in which the uranium probably assumes a new activity. Hence the solubility studies, while defining the liquidus, were not useable in evaluating the interaction parameters. The absence of any change in uranium concentration for palladium concentrations up to 0.6 atomic percent, the range in which the solution is likely to be in equilibrium with  $\text{UBi}_2$ , suggests that the activity coefficient may be unaffected by palladium in dilute solutions. However later results from the carbide decomposition studies indicated that palladium exerted a depressing effect on the uranium activity coefficient. The interaction parameter  $\epsilon_{\text{U}}^{(\text{Pd})}$  and  $\lambda_{\text{U}}^{(\text{Pd})}$  were found to equal -4.8. Although the data exhibited some scatter within runs and appreciable vertical displacement between runs, most runs concurred in the sign of the effect. The data from run T-24 plotted in Figure 11 appeared to be the most reliable. It converged at 1.89 percent

uranium for no palladium which agreed with the earlier values for the decomposition in bismuth. A similar slope was observed for T-22 which is also plotted.

Contact problems between the carbide and the solution provided difficulty in these studies. Poor wetting resulted in negligible decomposition and, hence, low results in some samples. It is possible that preheating at  $1000^{\circ}\text{C}$  caused the decomposition to proceed beyond that required for equilibrium at  $800^{\circ}\text{C}$ . This condition would necessitate the formation of  $\text{UC}_2$  from the excess uranium in solution and the graphite crucible. Consequently, poor wetting or insufficient time could also explain high results under these circumstances. Failure of the filter disk to function properly could also contribute to the scatter.

An analysis of these results using the expression of Alcock and Richardson is not particularly revealing. Both the palladium-bismuth and palladium-uranium systems appear to be negative deviators. The palladium-uranium interaction appears exceptionally strong based on the high melting compound in the binary system. To confirm the value predicted in this study the term  $\ln \gamma_{\text{U}(\text{Pd})}$  would have to overcome the large positive contributions of the other two terms. Sufficient thermodynamic data is not available to postulate on the likelihood of such a confirmation.

The process appears to involve a competition between uranium and bismuth for palladium. Apparently the strong interaction between uranium and palladium results in the uranium being held more strongly in solution. This effect is apparently not overcome by the palladium-bismuth interaction which would tend to reduce the bismuth available for combination with uranium.

Electron effects are difficult to evaluate for these systems. Mott and Jones (38) report bismuth to have 0.04 free electrons per atom. No value for uranium has been found in the literature. Both of these elements have complex electron structures such that their behavior at elevated temperatures and in alloy systems is difficult to predict. Electronegativities provide some measure of the ability of elements to attract electrons. In this connection it might be noted that positive electronegativity differences ( $E_{\text{solvent}} - E_{\text{solute}}$ ) are displayed by the copper group elements whereas the nickel group shows negative values. This seems to indicate that bismuth has a greater affinity for electrons than copper, but less of an affinity than nickel or palladium. The electronegativity of lead which has been shown to increase the activity coefficient of uranium in bismuth differs only slightly from that of bismuth. Uranium exhibits a negative value of -0.30. On the basis of this limited data it seems that solutes which possess electronegativities greater than bismuth and greater than uranium tend to depress the activity coefficient. Palladium with a difference of -0.49 ( $E_{\text{Bi}} - E_{\text{Pd}}$ ) and nickel with a difference of -0.65 ( $E_{\text{Bi}} - E_{\text{Ni}}$ ) both seem to conform to this postulate. Copper with an electronegativity difference of + 0.61 ( $E_{\text{Bi}} - E_{\text{Cu}}$ ) produces an increased activity coefficient. Further study will undoubtedly reveal the significance of this term in predicting interaction effects. Certainly no definite conclusions can be reached with this limited data.

Solubility studies to date seem to conform to no general pattern. Behavior in the copper group suggests that as the size of the solute increases

its effect becomes less depressing. Whereas copper was shown to decrease the solubility, both silver and gold increased it, with the latter having the more pronounced effect. Although no consistent behavior is observed from group to group, definite regularity seems to occur within the cobalt, nickel, copper and tin groups. Other groups were not studied in sufficient detail to evaluate their consistency.

The value obtained for the uranium activity coefficient in this investigation,  $1.22 \times 10^{-4}$ , confirms reasonably well the values obtained in earlier investigations. Egan's reported value of  $10^{-5}$  at  $500^{\circ}\text{C}$  increases to  $1.6 \times 10^{-4}$  when corrected to  $800^{\circ}\text{C}$  using the regular solution theory. Similarly the value reported by Gross, Levi and Lewin becomes  $2.25 \times 10^{-4}$  when their assumption of ideality in the liquid region is replaced with Cosgareas data over that portion of the diagram. However, Cosgarea's reported value still remains an order of magnitude higher. This discrepancy is presently under investigation and will likely be explained in the future.



APPENDIX A - DATA

Data: Solubility of Uranium in Bismuth

Summary:

<u>Run</u>	<u>Temperature °C</u>	<u>Length of Run-hrs.</u>	<u>Average Uranium Concentration-wt. %</u>
A-19	400	24	0.185
A-21	613	14.5	1.70
A-22	500	21	0.57
A-23	600	22	1.54
A-24	470	14	0.434
A-25	450	12	0.350
W-19	800	25	5.8

Data:

<u>Run</u>	<u>Uranium Concentrations-% by weight</u>	
A-19	0.182 0.184 0.188	0.188 0.192 0.188 0.184
A-21	1.63 1.82 1.75 1.74 1.70 1.70	1.57 1.73 1.62 1.75 1.71
A-22	0.54 0.58 0.56 0.58 0.59	0.57 0.57 0.54 0.56
A-23	1.45 1.57 1.55 1.53 1.53	1.50 1.57 1.58 1.56

<u>Run</u>	<u>Uranium Concentrations-% by weight</u>		
A-24	0.432		0.431
	0.447		0.440
	0.434		0.424
	0.437		0.422
A-25	0.354		0.307
	0.343		0.353
	0.356		0.343
W-10	5.9	5.9	5.6

Data: Effect of Copper on Uranium-Bismuth Liquidus

Run	Temperature <sup>o</sup> C	Time-hr.	Copper Conc. Atomic %	Uranium Conc. Atomic %	Uranium Weight %
Cu-1	600 <sup>o</sup>	28	None	1.34	1.53
			None	1.37	1.56
			0.05	1.35	1.54
			0.174	1.34	1.53
			0.262	1.30	1.48
			0.323	1.30	1.48
			0.525	1.28	1.46
			0.602	1.25	1.42
			1.05	1.23	1.40
			1.19	1.20	1.37
			1.60	1.16	1.32
			Cu-3	600 <sup>o</sup>	30
0.272	1.32	1.51			
0.550	1.24	1.41			
0.790	1.26	1.44			
0.868	1.21	1.38			
1.25	1.18	1.34			
2.20	1.03	1.18			
3.11	0.956	1.09			
6.88	0.776	0.885			
Cu-4	600 <sup>o</sup>	27	None	1.29	1.47
			None	1.32	1.50
			0.279	1.23	1.40
			0.521	1.23	1.40
			0.845	1.23	1.40
			1.10	1.15	1.31
			1.36	1.13	1.29
			2.07	1.01	1.15
			3.03	0.949	1.08
			7.01	0.761	0.867
			9.64	0.722	0.823

Data: Effect of Palladium on Uranium-Bismuth Liquidus

Run	Temperature <sup>o</sup> C	Time-hr.	Atomic % Palladium	Atomic % Uranium	Weight % Uranium
Pd-1	600 <sup>o</sup>	24	None	1.34	1.53
			None	1.37	1.56
			0.0622	1.26	1.44
			0.0951	1.33	1.52
			0.119	1.41	1.61
			0.168	1.35	1.54
			0.206	1.37	1.56
			0.252	1.31	1.49
			0.348	1.29	1.47
			0.411	1.32	1.50
Pd-2	600 <sup>o</sup>	20	None	1.25	1.43
			None	1.34	1.53
			0.0680	1.28	1.46
			0.099	1.33	1.52
			0.131	1.31	1.50
			0.180	1.29	1.47
			0.204	1.31	1.50
			0.242	1.34	1.53
			0.334	1.26	1.44
			0.423	1.33	1.52
Pd-4	600 <sup>o</sup>	23	None	1.32	1.51
			None	1.35	1.54
			0.163	1.36	1.55
			0.425	1.29	1.47
			0.553	1.36	1.55
			0.623	1.30	1.48
			0.746	1.29	1.47
Pd-6	600 <sup>o</sup>	27	None	1.32	1.50
			None	1.32	1.50
			* 0.0557	1.26	1.44
			0.1057	1.31	1.49
			0.219	1.32	1.50
			0.306	1.32	1.51
			0.528	1.31	1.49
			0.753	1.26	1.44
			1.01	1.15	1.31
			1.196	1.03	1.18
2.09	0.736	0.84			

\* In end position during run

Data: Effect of Sodium on Uranium-Bismuth Liquidus

<u>Run</u>	<u>Temperature°C</u>	<u>Time-hrs</u>	<u>Atomic % Sodium</u>	<u>Atomic % Uranium</u>	<u>Weight % Uranium</u>
Na-1	600	15	0.123	1.23	1.40
			0.183	1.31	1.49
			0.256	1.31	1.49
			0.404	1.29	1.47
			0.569	1.28	1.46
			0.731	1.32	1.51
			0.926	1.25	1.43
			1.24	1.32	1.51
			2.54	1.42	1.62
			* 3.24	1.40	1.60

\* End Position

Data: Effect of Various Third Components on Uranium-Bismuth Liquidus

Run	Temperature <sup>o</sup> C	Time-hr.	Element	Weight % Uranium
S-1	600 <sup>o</sup>	27	None	1.44
			Rhodium	1.21
			Rhodium	1.16
			Rhodium	1.38
			Nickel	1.02
			Nickel	1.45
			Tin	1.44
			Tin	1.44
			Tin	1.43
S-2	600 <sup>o</sup>	15	None	1.39
			None	1.41
			None	1.42
			Lead	1.39
			Lead	1.33
			Lead	1.13
			Zinc	1.43
			Zinc	1.41
			Zinc	1.45
			Nickel	0.800
			Nickel	0.208
Ce-1	600 <sup>o</sup>	68	None	1.47
			None	1.51
			Cerium	1.39
			Increasing	1.40
				1.38
				1.38
				1.40
				1.34
				1.30
				1.31
	1.21			

Data: Determination of Equilibrium Uranium Concentration for Carbide Decomposition in Bismuth at 800°C.

Run	Time-hr.	Flux	Preheat Time-1000°C	Carbide	Uranium Concentration weight %
T-8	75	Yes	None	NUMEC*	1.03
	75	Yes	None	NUMEC	3.50
	75	Yes	None	NUMEC	1.29
	75	No	None	NUMEC	1.14
	75	No	None	NUMEC	2.10
	75	No	None	NUMEC	1.23
	75	No	None	NUMEC	1.14
T-15	100	No	None	NUMEC	1.30
	100	No	None	NUMEC	1.28
	100	No	None	NUMEC	1.46
	100	No	None	NUMEC	1.31
	100	No	None	NUMEC	1.19
	100	No	None	NUMEC	1.38
	100	No	None	NUMEC	1.20
T-16	70	No	None	NUMEC	1.862
	70	No	None	NUMEC	1.813
	70	No	None	NUMEC	1.899
	70	No	None	NUMEC	1.857
	70	No	None	NUMEC	1.909
	70	No	None	NUMEC	1.844
	70	No	None	NUMEC	1.862
	70	No	None	NUMEC	1.878
70	No	None	NUMEC	1.648	
T-18	87	Yes	None	NUMEC	1.37
	87	Yes	None	NUMEC	1.38
	87	Yes	None	NUMEC	1.42
	87	Yes	None	NUMEC	1.23
T-20	96	Yes	1	NUMEC	1.87
	96	Yes	1	NUMEC	1.53
T-22	90	Yes	5	NUMEC	1.42
	90	Yes	5	NUMEC	1.53
	90	Yes	5	NUMEC	1.26

Run	Time-hr.	Flux	Preheat Time	Carbide	Uranium Concentration weight %
T-23	64	Yes	9	NUMEC	2.06
	64	Yes	9	NUMEC	1.40
T-24	50	Yes	7	NUMEC	1.89
	50	Yes	7	NUMEC	1.44
	50	Yes	7	Davison UC <sub>2</sub>	1.95
T-26	95	Yes	10	NUMEC	2.12
T-27	95+57	Yes	11	NUMEC	1.38
T-28	53	No	2	NUMEC	1.86
	53	No	2	NUMEC	1.89
T-29	120	No	2	NUMEC	0.846
	120	No	2	NUMEC	1.21
	120	No	2	NUMEC	1.57
T-30	100	Yes	12 (1100°C)	NUMEC	1.95
	100	Yes	12	NUMEC	2.10
	100	Yes	12	NUMEC	2.17
T-31	50	?	18	Davison UC <sub>2</sub>	0.550
	50	?	18	Davison UC <sub>2</sub>	1.90
	50	?	18	Davison UC <sub>2</sub>	1.59
	50	?	18	NUMEC	1.17
	50	?	18	NUMEC	2.68
T-32	105	Yes	2	NUMEC	0.957
	105	Yes	2	NUMEC	0.877

\* NUMEC - A UC-UC<sub>2</sub> mixture provided by Nuclear Materials and Equipment Corporation.



Data: Effect of Copper on Carbide Decomposition

Run	Temp. °C	Time-hr	Flux	Length of Preheat-hr	Atomic % Cu	Atomic % U	Weight % U
T-18	800°	80	Yes	None	None	1.20	1.37
					None	1.21	1.38
					None	1.24	1.42
					0.573	1.17	1.33
					0.998	0.956	1.09
					2.05	0.825	0.942
					3.07	0.596	0.680
					4.00	0.857	0.978
					5.63	0.843	0.962
T-23	800°	73	Yes	9 (1000°C)	None	1.81	2.06*
					None	1.23	1.40**
					0.585	1.14	1.30**
					1.16	1.30	1.48
					2.24	1.35	1.54
					3.58	1.24	1.41*
					4.67	1.30	1.48
					5.99	1.50	1.71**
					T-29**	800°	120
None		1.21					
None		0.846					
0.612		1.12					
1.32		1.12					
2.18		1.05					
3.52		1.34					
4.80		1.29					
5.47		1.52					
T-30***	800°	110	Yes	12(1100°C)	None		2.17
					None		2.10
					None		1.95
					1.10		1.82
					3.88		2.12
					6.21		2.28
					7.02		2.34

\* Excellent wetting

\*\* Poor wetting; Data not plotted in Figure 10

\*\*\* Run not at equilibrium at 800°C; Data not included in Figure

Data: Effect of Palladium on Carbide Decomposition

Run	Temp, °C	Time-hr	Flux	Length of Preheat	Atomic % Palladium	At % U	Weight % U
T-20	800°	96	Yes	1(1000°C)	None	1.34	1.53
					None	1.64	1.87
					2.59	2.30	2.62
					3.66	2.28	2.60
T-22	800°	93	Yes	5(1000°C)	None	1.24	1.42
					None	1.10	1.26
					None	1.34	1.53
					0.543	0.561	0.64
					1.045	1.47	1.68
					2.48	1.32	1.51
					2.61	1.68	1.92
					3.65	2.27	2.59
					5.30	1.79	2.04
T-24*	800°	57	Yes	7(1000°C)	None	1.71	1.95
					None	1.66	1.89
					None	1.26	1.44
					0.725	1.61	1.84
					1.15	1.79	2.04
					2.08	1.73	1.97
					3.21	1.96	2.24
					3.86	2.08	2.37
					4.94	2.16	2.46
T-28**	800°	55	No	2(1000°C)	None	1.63	1.86
					None	1.66	1.89
					0.459	1.54	1.76
					1.55	1.62	1.85
					2.61	1.61	1.84
					4.30	1.03	1.18
T-32**	800°	107	Yes	2(1000°C)	None	0.839	0.957
					None	0.768	0.877
					2.58	1.23	1.41
					3.34	1.10	1.25
					4.95	1.87	2.13
					5.05	1.20	1.37

\* Run T-24 yielded most consistent data; used to evaluate  $\epsilon_U^{(Pd)}$  in Figure 12.

\*\* Poor wetting

APPENDIX B - CALCULATIONS

1) Calculation of Activity Coefficient of Uranium in Bismuth.



$$\Delta G^\circ = -RT \ln K_a$$

$$K_a = \frac{a_{UC_2}}{a_U a_C^2}$$

Standard States:

C - pure solid at 800°C

UC<sub>2</sub> - pure solid at 800°C

U - pure solid at 800°C

$$K_a = \frac{1}{a_U} = \frac{1}{N_U \gamma_U} \quad \text{for decomposition in bismuth}$$

Using  $\Delta G^\circ = -29,610 + 1.5 T$  from Grieveson and Alcock

$$-\log K_a = \frac{-29,610 + 1.5 (1073)}{(1.987)(1073)(2.303)} = -5.7$$

$$K_a = 5.01 \times 10^5 = \frac{1}{N_U \gamma_U} ; N_U = 0.0186 \left(\frac{209}{238}\right) = 0.0163$$

$$\gamma_U = \frac{1}{(5.01 \times 10^5) 1.63 \times 10^{-2}} = 1.22 \times 10^{-4}$$

2) Partial Molar Enthalpy Change of Uranium for Dissolution of UBi<sub>2</sub>



Along liquidus the activity of uranium is assumed constant. Assume activity to be a function of T and  $N_U$ . The total differential for activity can be expressed as:

$$da = \left( \frac{da}{dN} \right)_T dN + \left( \frac{da}{dT} \right)_N dT = 0$$

$$\left( \frac{da}{dN} \right)_T \left( \frac{dN}{dT} \right)_a + \left( \frac{da}{dT} \right)_N = 0 \quad a = N\gamma$$

$$N \left( \frac{d\gamma}{dN} \right)_T + \gamma \left( \frac{dN}{dT} \right)_a + N \left( \frac{d\gamma}{dT} \right)_N = 0$$

If  $\left( \frac{d\gamma}{dN} \right)_T = 0$  (e.g. Henry's law region),

$$\text{then } \frac{1}{N} \left( \frac{dN}{dT} \right)_a = \frac{1}{\gamma} \left( \frac{d\gamma}{dT} \right)_N$$

$$\text{or } \left( \frac{d \ln N}{d(1/T)} \right)_a = - \left( \frac{d \ln \gamma}{d(1/T)} \right)_N$$

$$\text{Since } \left( \frac{\partial \ln \gamma_U}{\partial (1/T)} \right)_{N_U} = \frac{\Delta \bar{H}_U}{R}$$

$$- \left( \frac{\partial \ln N_U}{\partial (1/T)} \right)_a = \frac{\bar{H}_U(\text{soln.}) - \bar{H}_U(\text{UBi}_2)}{R}$$

### 3) Determination of Uninvestigated Portion of Cu-U-Bi Liquidus

$$\epsilon_U^{(\text{Cu})} = \frac{\partial \ln \gamma_U}{\partial N_{\text{Cu}}} = - \frac{\partial \ln N_U}{\partial N_{\text{Cu}}} = + 11.0$$

$$\text{but } \epsilon_U^{(\text{Cu})} = \epsilon_{\text{Cu}}^{(U)} = \frac{\partial \ln \gamma_{\text{Cu}}}{\partial N_U} = - \frac{\partial \ln N_{\text{Cu}}}{\partial N_U}$$

$$\frac{\partial \ln N_{\text{Cu}}}{\partial N_U} = - 11.0$$

For  $N_U = .0025$

$$\ln \text{Atomic } \% \text{ Cu}_{N_U = 0} = \ln 12.8 = 2.54$$

$$\Delta \ln \text{Atomic } \% \text{ Cu} = (11.0)(0.0025) = -0.0275$$

$$\ln \text{Atomic } \% \text{ Cu} - 2.54 = -0.0275$$

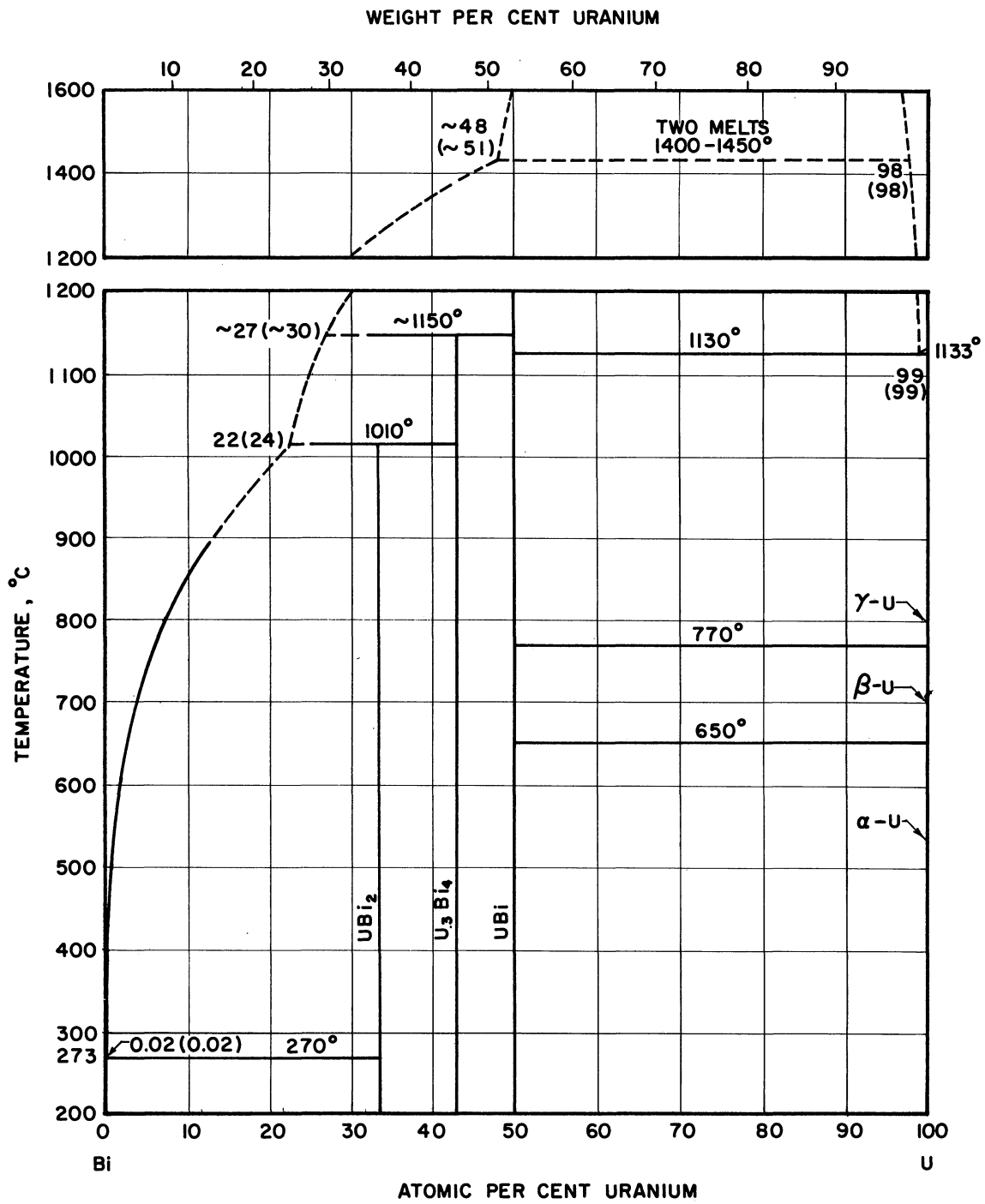
$$\ln \text{Atomic } \% \text{ Cu}_{N_U = 0.0025} = 2.51 \quad \text{Atomic } \% \text{ Cu} = 12.4$$

For  $N_U = .006$

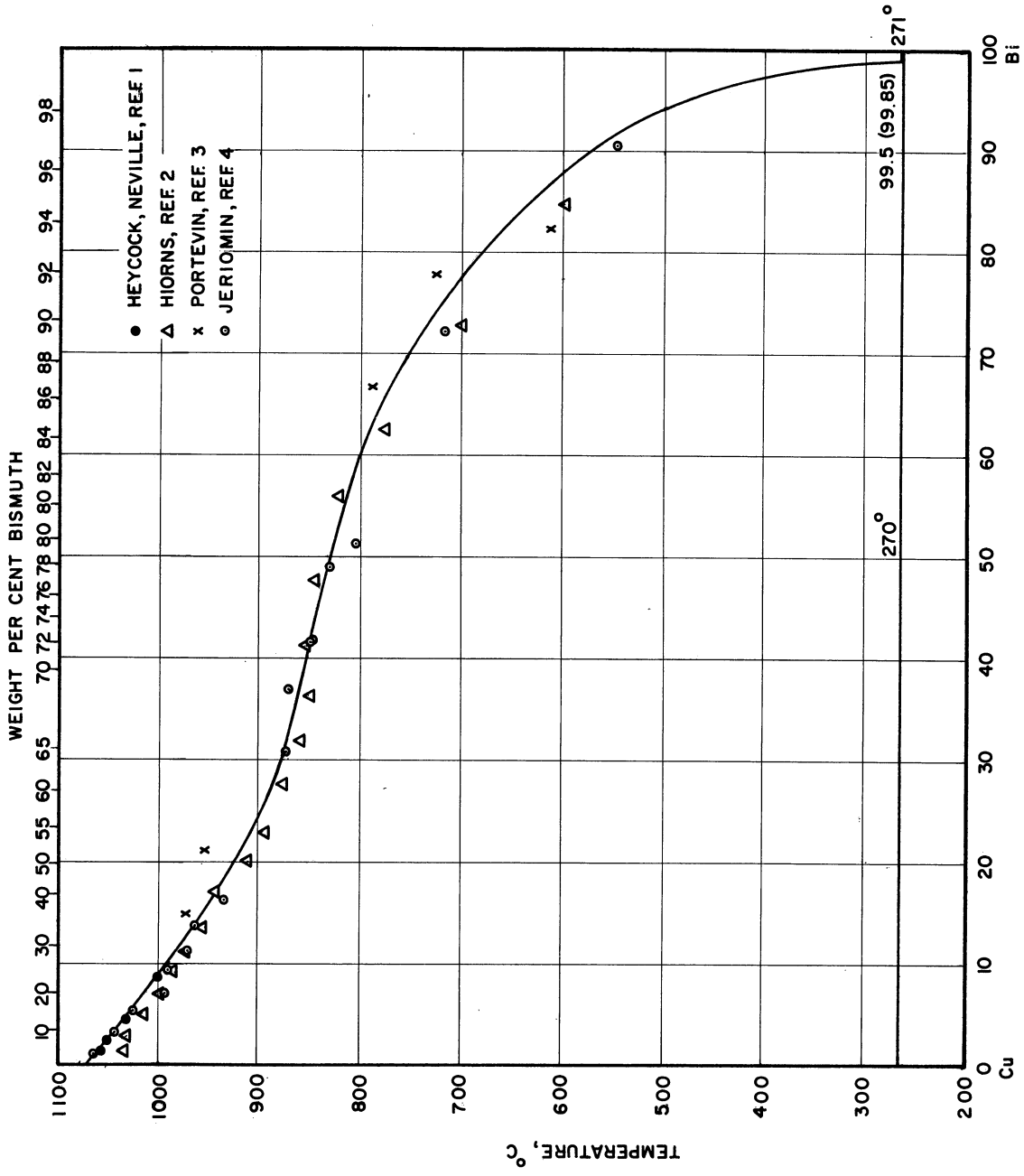
$$\ln \text{Atomic } \% \text{ Cu} = + 2.54 - 0.066 = 2.47$$

$$\text{Atomic } \% \text{ Cu} = 11.9$$

APPENDIX C

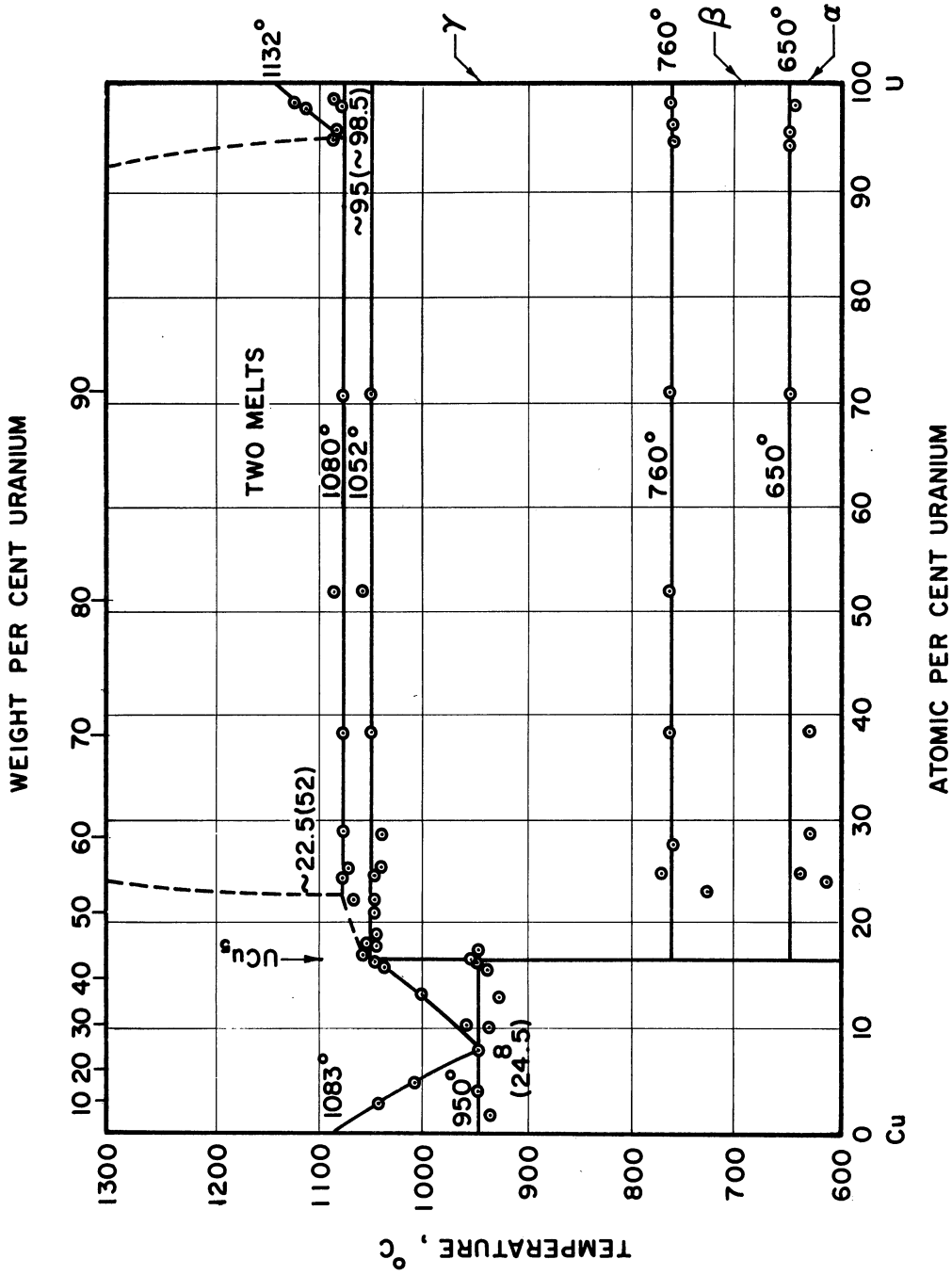


Uranium-Bismuth Phase Diagram

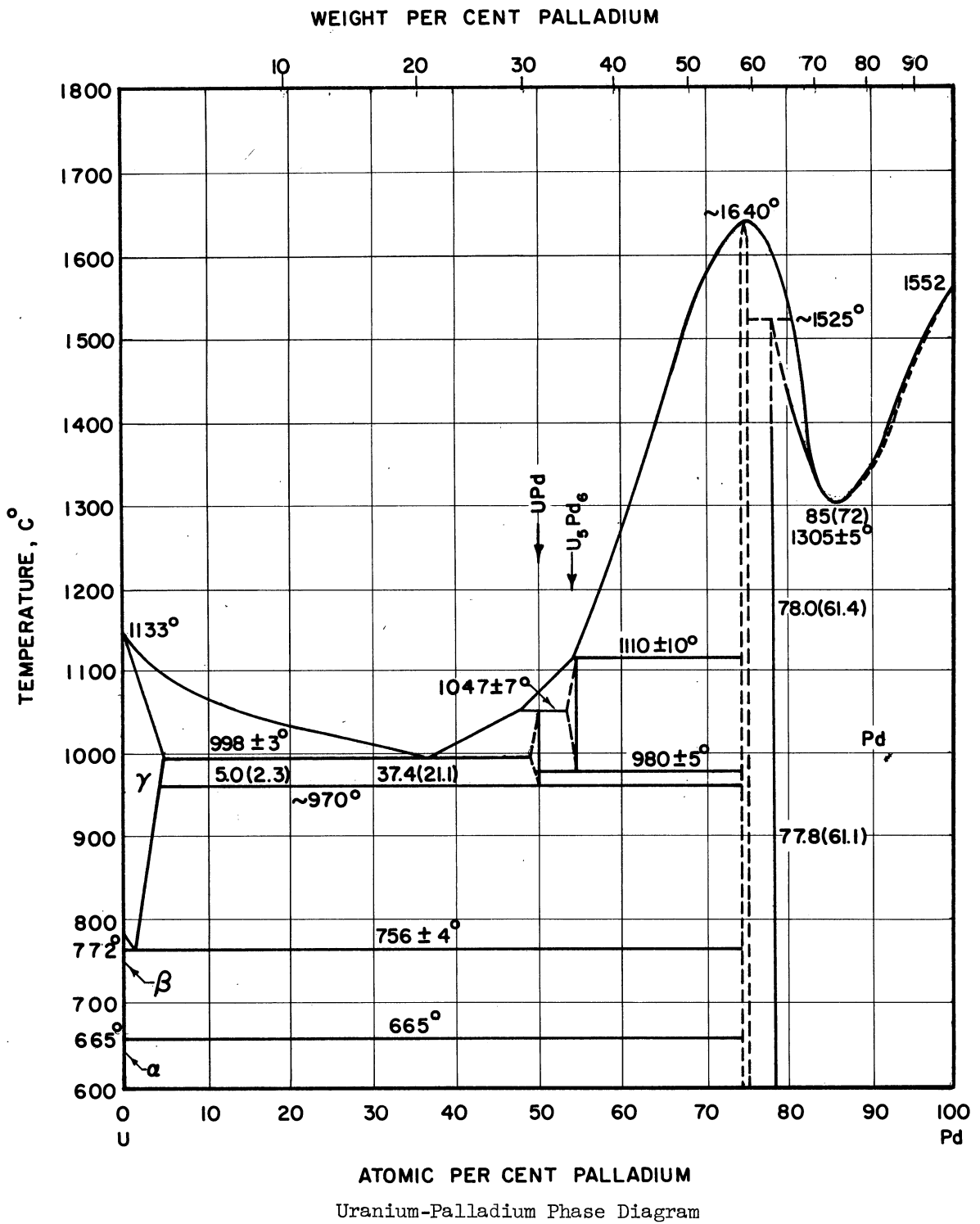


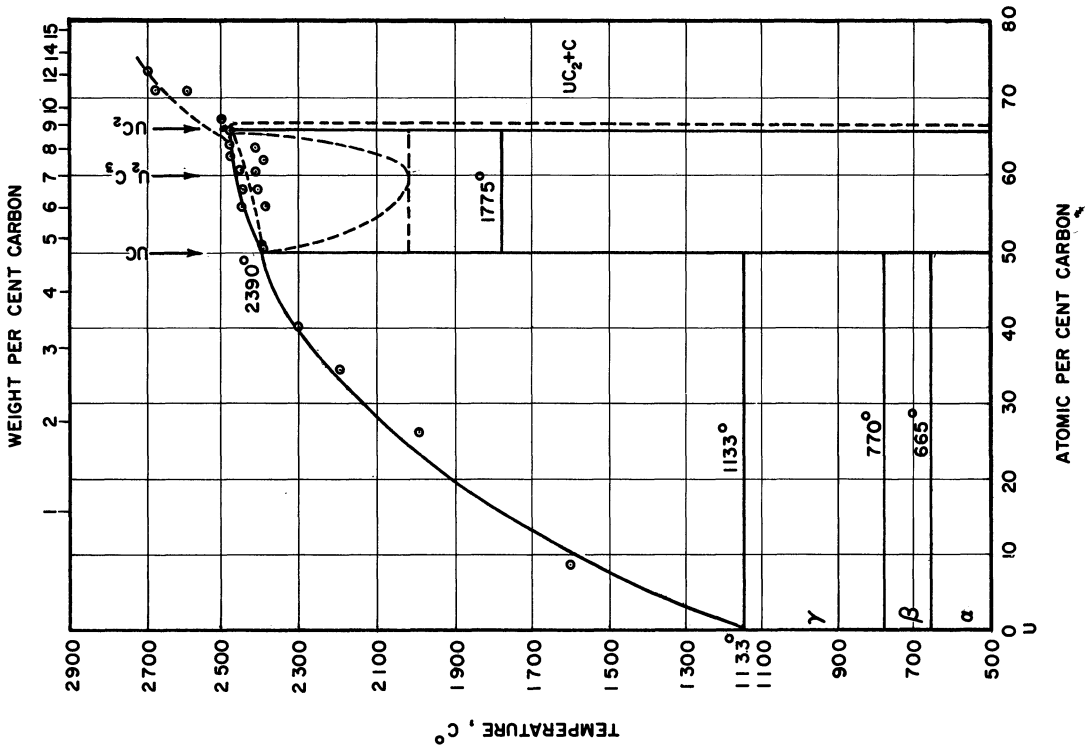
ATOMIC PER CENT BISMUTH  
Copper-Bismuth Phase Diagram



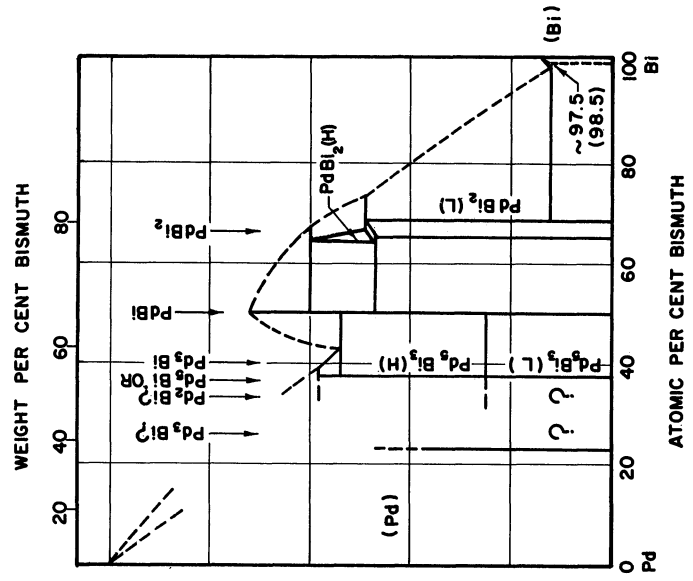


Copper-Uranium Phase Diagram

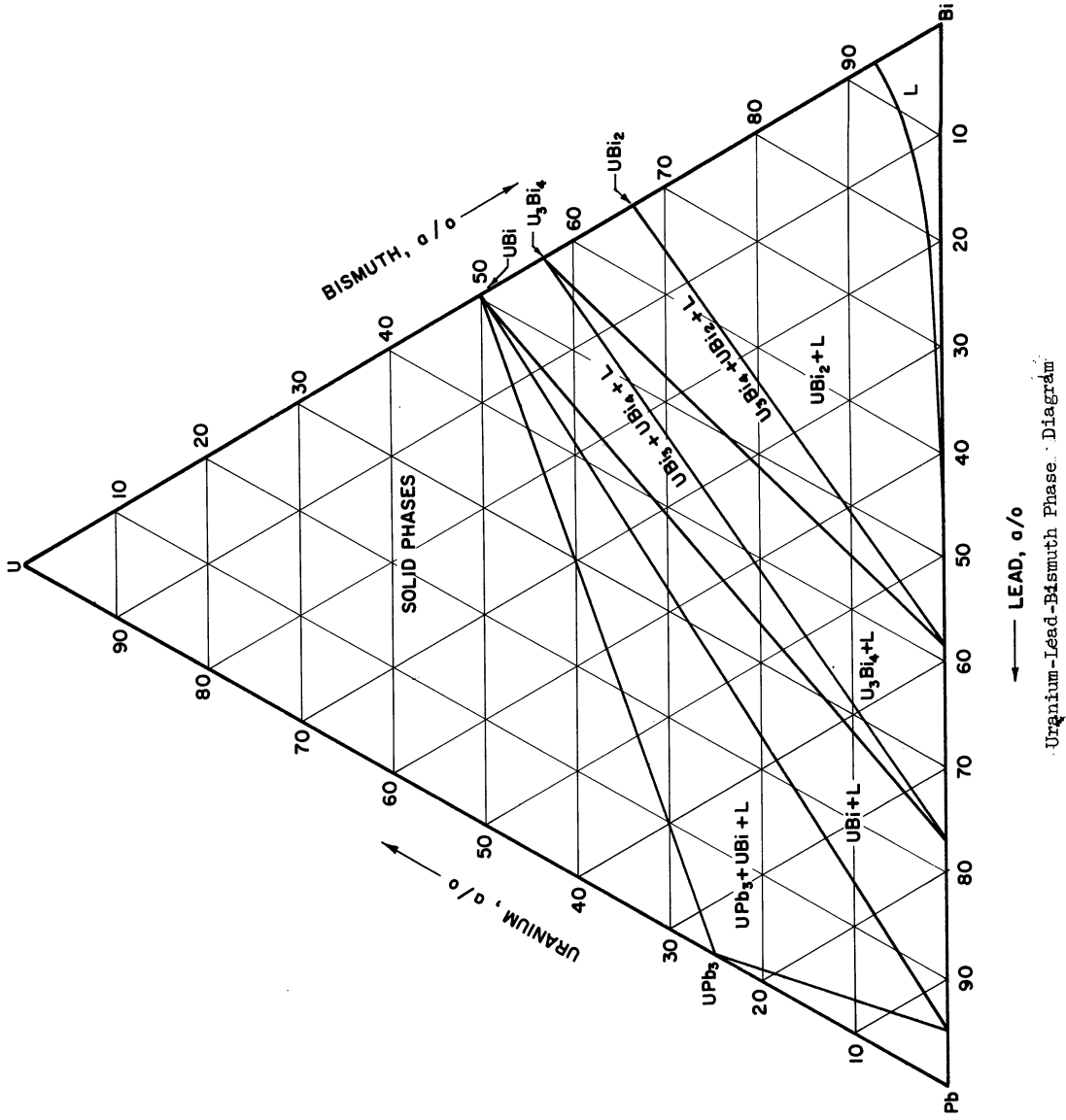


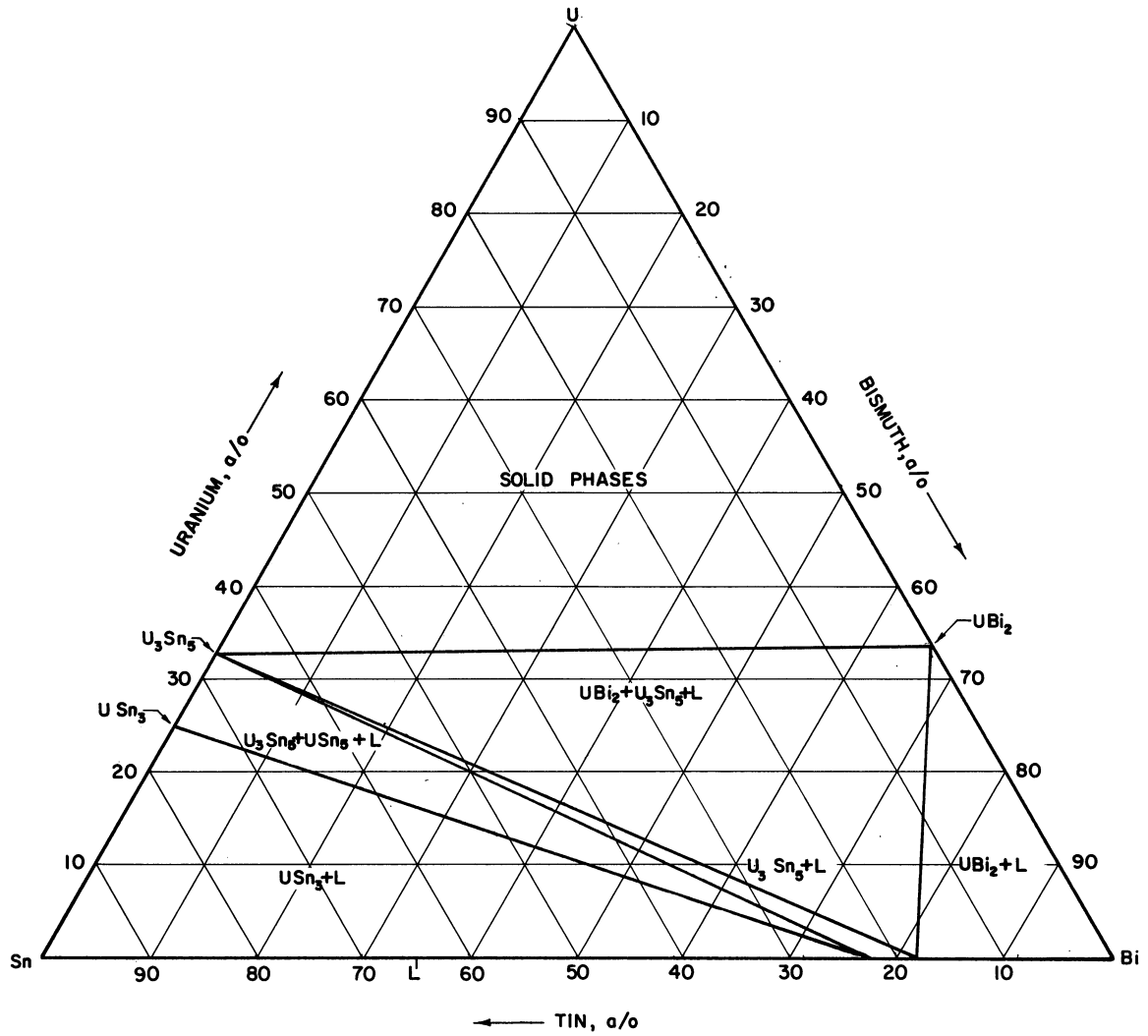


Uranium - Carbon Phase Diagram



Palladium-Bismuth Phase Diagram





Uranium-Tin-Bismuth Phase Diagram

## Appendix D

### A. SPECTROPHOTOMETRIC DETERMINATION OF URANIUM IN BISMUTH

#### I. INTRODUCTION

Uranium is determined spectrophotometrically at 412 m $\mu$  and 390 m $\mu$  the dibenzoylmethane-uranium complex. The applicable range is 50 to 120  $\mu$ g of uranium; up to 300 mg of bismuth can be tolerated. This method has been used for samples containing 99+% bismuth and 1000 ppm uranium with respect to bismuth.

The bismuth is complexed with diaminocyclohexane tetraacetic acid (DCTA), and the uranium is complexed with dibenzoylmethane. The dibenzoylmethane-uranium complex is extracted into amyl acetate, and the absorbance of the resulting organic layer is measured at two wavelengths.

#### II. APPARATUS

Spectrophotometer, Beckman Model DU with tungsten lamp and blue-sensitive cell; Absorption cells, 1 cm. path length, Corex or quartz (Pyrex cells also seem to be satisfactory).

#### III. REAGENTS

Nitric acid, concentrated, reagent grade

Ammonium hydroxide, 5 M

Hydrochloric acid, 3 M

Saturated ammonium chloride solution

Bromcresol green indicator solution, 0.04%

Dibenzoylmethane solution, 1% in ethanol (absolute or 95%). Amyl acetate, reagent grade. The isoamyl acetate was the only amyl acetate available in a reagent grade; consequently, it was used since the original reference did not specify which ester was used.

Diaminocyclohexane tetraacetic acid (DCTA) solution: 100 g. is dissolved in 300 ml of 5 M NaOH; after dissolution, the pH is adjusted to 5.2 with HCl and NaOH; finally the solution is diluted to 500 ml.

#### IV. PREPARATION OF SAMPLES

1. Weigh the bismuth sample and dissolve in concentrated nitric acid.
2. Transfer to a volumetric flask and dilute to the mark with water.  
This dilution should be such that an aliquot no larger than 10 ml will be required for an analysis.

#### V. PROCEDURE

1. Withdraw an aliquot (no more than 10 ml) containing 50 to 100  $\mu$ gms. of uranium and no more than 300 mg of bismuth. Transfer to a 60-ml separatory funnel. (See Note 1)
2. Add water to bring volume up to 10 ml.
3. Add 5 ml of the DCTA solution. (See Note 2)
4. Add 3 drops of the bromcresol green indicator solution.
5. Add dropwise ammonium hydroxide, 5 M, and/or hydrochloric acid, 3 M, until the solution just turns from blue to yellow.
6. Add 5 ml of saturated ammonium chloride solution.
7. Add water to make the volume about 20 ml. (See Note 3)

8. Add 1.00 ml (pipet) of dibenzoylmethane solution while rotating the funnel. (See Note 4)
9. Immediately add from an eye dropper 12 drops of 5 M ammonium hydroxide.
10. Add 10.00 ml (pipet) of amyl acetate.
11. Shake the contents of the funnel thoroughly and allow the two layers to separate. (See Note 5) Centrifuge for 1 minute.
12. Pipet enough of the organic layer (top layer) into the absorption cell to fit it.
13. Measure the absorbance at 412  $m\mu$  and at 390  $m\mu$  against a blank which has been prepared in the same manner as the sample using water instead of uranium containing sample. (See Notes 6 and 7)

#### VI. NOTES AND PRECAUTIONS

1. A 10-ml aliquot is maximum because the final volume of the aqueous layer is 20 ml, and 10 ml of reagents must be added.
2. 5 ml of DCTA will keep in solution about 300 mg of bismuth. If a precipitate does occur, add more DCTA.
3. The diluted solution should be clear at this point; if not, probably insufficient DCTA was added.
4. After the addition of dibenzoylmethane, the solution will be turbid and a small amount of precipitate will be present. Keep the dibenzoylmethane in ethanol solution tightly stoppered to prevent volatilization.



5. The two layers should be clear now with the aqueous layer colored blue and the organic layer yellow. The intensity of the yellow color will be determined by the amount of uranium present.
6. Unless one has tightly stoppered absorption cells, it will be necessary to work rapidly during the photometry because of the volatility of amyl acetate.
7. It has been found that good soapy water followed by thorough rinsing with water and a final rinse with acetone will clean the absorption cells very nicely.

## VII. CALCULATIONS

The concentration of uranium is read from a calibration curve of absorbance versus uranium concentration which is best prepared from a series of standard uranium solutions. These solutions should be treated in the same manner as the sample and their absorbances read at the two wavelengths.

$$\% \text{ U} = \frac{\mu\text{g of U read from calibration curve}}{1000 \times \text{sample wt. in mg}} \times \frac{\text{dilution volume}}{\text{aliquot volume}} \times 100$$

$$\text{ppm U} = \frac{\mu\text{g of U} \times 10^6}{1000 \times \text{sample wt. in mg}} \times \frac{\text{dilution volume}}{\text{aliquot volume}}$$

The concentration of the uranium as read from the 412 m $\mu$  curve should agree with that as read from the 390 m $\mu$  curve. The two readings taken together should show if any interference is present. The ratio of absorbances A(412 m $\mu$ ): A(390 m $\mu$ ), is constant at 1.9 to 2.0 over the range studied, (50 to 120  $\mu\text{g U}$ ).

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## B. SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN BISMUTH ALLOYS

### I. INTRODUCTION

The spectrophotometric method for the determination of copper reported by G. Frederick Smith and W. H. McCurdy, Jr. Anal. Chem., 24, (2) 371 (1952) and Y. Yshihara and Y. Taguchi Japan Analyst, 6, (9), 588-89 (1957) has been successfully applied to the determination of copper in the presence of uranium and large quantities of bismuth.

Copper is extracted from an aqueous solution of pH 5-6 as a neocuproine complex<sup>1</sup> with isoamyl alcohol and measured at 454 m $\mu$ . Berr's law is obeyed over the range of 0.15 to 10.6 ppm copper in isoamyl alcohol. The method is quite selective for copper and may be used for copper in the presence of many cations and anions. A minor modification of the original procedure was made in order to more rapidly determine the pH of the aqueous phase prior to extraction<sup>2</sup>.

### II. INTERFERENCES

Smith et al. report that no other cation other than the cuprous ion was found to form a colored complex which was extractable under the conditions employed. The common anions chloride, sulfate, nitrate, perchlorate, tartarate, citrate and acetate do not interfere. Many other anions which either react with hydroxylamine or give a yellow colored solution may be eliminated employing suitable conditions. The following cations were found to produce no detectable interference:

<u>Cation</u>	<u>Weight Ratio</u>
Bi <sup>+3</sup>	$\frac{\text{Cation: Cu}^{+1}}{28,000: 1}$
UO <sub>2</sub> <sup>+2</sup>	234: 1

### III. APPARATUS

Beckman DU Quartz Spectrophotometer with Tungsten lamp.

### IV. REAGENTS

- (1) Concentrated nitric acid.
- (2) p - Bromocresol Green, 0.04% (W/V) aqueous solution.
- (3) Ammonium Hydroxide - 5 M.
- (4) Hydrochloric acid - 1 M.
- (5) Hydroxylamine hydrochloride, 30%, (W/V) aqueous solution.
- (6) Sodium Citrate, 30% (W/V) aqueous solution.
- (7) Neo - cuproine, 0.1% (W/V) ethanol - water solution (1:9 by volume).
- (8) Isoamyl alcohol<sup>3</sup> (Reagent Grade).

### V. PROCEDURE

1. Dissolve the bismuth alloy in concentrated nitric acid, heat to expel nitrogen oxides, cool and dilute to volume.
2. Transfer an aliquot of sample containing 5 to 75 µg copper to a 60 ml separatory funnel.
3. Add 10 ml hydroxylamine hydrochloride (30%).
4. Add 2 ml of sodium citrate (30%)<sup>4</sup>.
5. Add 2 drops of p-Bromocresol Green<sup>5</sup> .m
6. Add ammonium hydroxide (5M) and/or hydrochloric acid (1M) till the solution changes from a blue to a green-yellow color.
7. Add 8 ml of sodium citrate.
8. Add 2 ml of neo-cuproine solution (0.1%) with mixing<sup>6</sup>.

9. Make up to a volume of 30 ml with distilled water.
10. Add 10 ml of isoamyl alcohol and shake for 20 seconds. Allow phases to separate<sup>7</sup>.
11. Remove a portion of the organic phase and measure the absorbancy at 454 m $\mu$  against a reagent blank.

#### VI. CALIBRATION CURVE

A calibration curve was prepared from a stock solution of copper (99.9%) in 1N nitric acid. Amounts of bismuth up to 47,860  $\mu$ g and uranium up to 400  $\mu$ g were added to as small amount of copper as 1.71  $\mu$ g without any noticeable interference.

#### VII. NOTES

1. The complex contains a molar ratio of copper to neo-cuproine of 1:2 with copper present as the cuprous ( $\text{Cu}^{+1}$ ) ion.
2. p-Bromocresol green indicator (pH 3-5) was introduced for determining the pH of the aqueous phase prior to extraction. The indicator exhibited an absorbancy of 0.010/1 drop at 454 m $\mu$ , a sufficiently low value to permit its use in the determination by inclusion in the blank.
3. This solvent exhibits a nauseating odor and should be used in a hood.
4. Addition of sodium citrate prevents hydrolysis and precipitation of heavy metals during the subsequent neutralization operation.
5. Exactly 2 drops of indicator is used in both blank and sample (See note 1).

6. Complex formation, for all practical purposes, occurs instantaneously.
7. Smith et al. performed two extractions, however, it was found in this laboratory that one 10 ml extraction was sufficient to remove the copper complex and proved through reproducibility of the reported molar extinction coefficient for the copper complex in isoamyl alcohol. The use of a single extraction significantly decreased the time required to perform the analysis.

## C. SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM IN BISMUTH ALLOYS

### I. INTRODUCTION

The spectrophotometric method for the determination of Palladium reported by Oscar Menis and T. C. Rains, Anal. Chem., 27, (12), 1932 (1955) has been applied to the analysis of bismuth alloys containing Palladium concentrations as low as 20 ppm. The presence of Uranium and high concentrations of bismuth in the alloys necessitated a more rigid control of the acidity and time for color formation than is implied in the original reference.

The absorbancy of the palladium-alpha-furildioxime complex<sup>1</sup> is measured at 380 m $\mu$  in chloroform, following extraction from a 1.3 N acid aqueous mixture. Time for color formation is exactly 5 minutes, if the time exceeds 30 minutes, bismuth causes interference. An acidity of 1.3 N in the aqueous phase prevents the precipitation of bismuth in any of the alloys analyzed, including alloys containing the minimum amount of palladium c.a. 20 ppm and allows complete color development to occur in 5 minutes.

### II. INTERFERENCES

The following cations were reported to have no effect in quantities given:

<u>Elements</u>	<u>Amt. present Mg</u>	<u>Pd ( )</u>
Ir <sup>+4</sup>	0.06	59.0
Pt <sup>+4</sup>	0.7	59.0
Fe <sup>+3</sup>	2.0	59.0
Cd <sup>++</sup>	2.1	59.0
Os <sup>+4</sup>	3.3	59.0
Cu <sup>+2</sup>	3.7	59.0
Na <sup>+1</sup>	3.8	59.0
U <sup>+6</sup>	8.4 <sup>2</sup>	59.0
Th <sup>+4</sup>	25.0	59.0
Rh <sup>+3</sup>	0.8	59.0
Zr <sup>+4</sup>	1.9	59.0
Pb <sup>+2</sup>	2.3	59.0
Mo <sup>+6</sup>	4.0	59.0
Cr <sup>+3</sup>	4.3	59.0
Mn <sup>+2</sup>	1.0	59.0
Ni <sup>+2</sup>	1.1	59.0
Au <sup>+3</sup>	2.5	59.0
Co <sup>+2</sup>	2.5 <sup>2</sup>	59.0
Bi	321.0	57.5

<u>Anions</u>	<u>mg present</u>	<u>Pd ( )</u>
F	7.15	59.0
SO <sub>4</sub> <sup>=</sup>	6.90	59.0
NO <sub>3</sub> <sup>-</sup>	7.29	59.0
ClO <sub>4</sub> <sup>-</sup>	7.15	59.0
CN <sup>-</sup>	4.0	0



### III. APPARATUS

Beckman DU Quartz Spectrophotometer with tungsten lamp; absorption cells 1 cm.; 50 ml burette.

### IV. REAGENTS

1. Alpha - Furildioxime<sup>3</sup> 1% solution. Prepare by dissolving 1 gm. of the reagent in 30 ml of ethanol and diluting to 100 ml with water.
2. 0.500 N Sodium Hydroxide.
3. Concentrated nitric acid.
4. Phenolphthalein Indicator.
5. Chloroform. Reagent Grade.

### V. PROCEDURE

1. Dissolve the sample in concentrated nitric acid and dilute to volume. Final normality of the sample solution should not exceed 3 N.
2. Remove an aliquot of sample solution and determine the free acid content using standard base and phenolphthalein indicator, e.g. total equivalents of base required minus the number of equivalents of bismuth present<sup>4</sup>.
3. Transfer an aliquot of sample solution containing 5.75 $\mu$ g to 57.5  $\mu$ g Pd to a 60 ml separatory funnel.
4. Add 2 N hydrochloric acid and water, sufficient to yield 35 ml total volume of a 1.3 N solution. The reagent blank should be

the same acidity as the sample solution and should contain 321 mg bismuth<sup>4</sup>.

5. Add 1 ml of - furildioxime (1% alcohol-water solution) while rotating the funnel. Allow the mixture to stand exactly 5 minutes.
6. Add 10 ml of chloroform, shake for 20 sec., allow the phases to separate and transfer the lower organic layer to a 25 ml volumetric flask. Time elapsed between the addition of alpha-furildioxime and the final extraction should not exceed 10 minutes.
7. Dilute the organic extracts to 25 ml with chloroform and mix thoroughly.
8. Add 0.3 gms. sodium sulfate, anhydrous, to chloroform extracts to remove traces of water.
9. Measure the absorbancy of the sample at 380 m $\mu$  against the reagent blank containing bismuth.

#### VI. CALIBRATION CURVE

A stock solution of palladium was prepared by dissolving the pure metal (99.9%) in concentrated nitric acid containing a small amount of hydrochloric acid, heating the mixture till the evolution of Cl<sub>2</sub> ceased and diluting to volume. Aliquot portions of the palladium stock solution were then treated according to the above procedure. Bismuth and uranium were added to the palladium aliquots and produced no effect upon the observed absorbancy of the palladium-alpha-furildioxime complex under the conditions of acidity and time for color development cited in the procedure.

VII. CALCULATIONS

1. Normality of sample solution:

$$N(\text{as free acid}) = \frac{(\text{Volume Base ml})(N \text{ Base}) \frac{\text{wt. sample gms.}}{69.6} \frac{\text{aliquot sample ml}}{\text{Dilution ml}}}{(\text{aliquot sample ml})}$$

2. Volume of 2.00 N hydrochloric acid required to prepare 1.3 N sample solution for extraction:

$$\text{ml of 2.00 N HCl required} = \frac{(35 \text{ ml})(1.3 \text{ N}) - (\text{aliquot sample ml})(N_S)}{(2.00 \text{ N})}$$

$N_S$  = Normality of sample as determined from (1).

3. Percent composition:

$$\% \text{ Pd} = \frac{(\mu\text{g Pd}) (\text{Dilution ml}) (100)}{(\text{ml aliquot})(\text{gms. sample}) (10^6)}$$

VIII. NOTES

1. The palladium-alpha-furildioxime complex is stable in chloroform for at least 24 hours.
2. Bismuth, cobalt and uranium were found to have no effect on the determination under the conditions outlined in the above procedure.

3. The reagent must be purified before use through recrystallization from water. If further purification is desired see, Reed, S. A., and Bank, C. U., Proc. Iowa Acad. Sci., 55, 267 (1948).
4. 321 mg bismuth represent the largest amount of bismuth encountered with the alloys studied in the aliquot used for the analysis.

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