

# Elemental Solubility Tendency for the Phases of Uranium by Classical Models Used to Predict Alloy Behavior

## TMS Spring Meeting

Van S. Blackwood  
Travis W. Koenig  
Jason M. Porter  
David L. Olson  
Bradjendra Mishra  
Robert D. Mariani  
Douglas L. Porter

The INL is a  
U.S. Department of Energy  
National Laboratory  
operated by  
Battelle Energy Alliance



March 2012

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint should not be cited or reproduced without permission of the author. This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights. The views expressed in this paper are not necessarily those of the United States Government or the sponsoring agency.

# Elemental Solubility Tendency for the Phases of Uranium by Classical Models Used to Predict Alloy Behavior

Van S. Blackwood<sup>1</sup>, Travis W. Koenig<sup>1</sup>, Jason M. Porter<sup>1</sup>, David L. Olson<sup>1</sup>, Brajendra Mishra<sup>1</sup>, Robert D. Mariani<sup>2</sup>, Douglas L. Porter<sup>2</sup>

<sup>1</sup>Colorado School of Mines, 1601 Illinois St.; Golden, CO, USA

<sup>2</sup>Idaho National Laboratory, Basic Fuel Properties and Modeling Department, Nuclear Fuels and Materials Division, P.O. Box 1625; Idaho Falls, Idaho, 83415, USA

Keywords: Uranium, Compatibility, Substitution, Darken-Gurry, Miedema

## Abstract

Traditional alloy theory models have been applied relative to the three solid phases of uranium: alpha (orthorhombic), beta (tetragonal), and mainly gamma (body centered cubic)[1]. The Darken-Gurry and Miedema models, with modifications based on concepts of Waber, Gschneidner, and Brewer have been used to predict the behavior of four types of solutes: 1) Transition associated with alloying in and containment of the uranium fuel 2) Transuranic elements in the uranium 3) Rare earth fragmentation elements (lanthanides) 4) Transition metals and other fragmentation elements. Using these solute map criteria, elemental behavior have been predicted as highly soluble, marginally soluble, or immiscible (intermetallic phase formers) and have been used to compare solute effects during uranium phase transformations. The overlapping of these solute maps are convenient first approximation tools for predicting alloy behavior.

## Introduction

An investigation is in progress to determine the role of various solute elements on size and shape of the  $\gamma$  phase field range for uranium to optimize the burning and material processing of nuclear fuel is in progress. Traditional alloy theory models based on correlations to elemental electronic and crystal properties are used to predict solubility and microstructural formation. The effectiveness of this model is based on microstructure property correlations. Darken and Gurry, and Miedema models, with modifications based on concepts of Waber, Gschneidner, and Brewer, models have been used to describe solute solubility with respect to uranium based the on correlation between elemental electronic structure and uranium phases. The alpha (orthorhombic), beta (tetragonal), and gamma (body centered cubic) phases have different solubilities for specific alloy additions as a function of temperature. Using the method of Waber, ellipse diagrams classified those solutes that should have broad solubility in the allotropes of uranium[2]. The predictive diagrams are made from four different correlations:

1. Transition metals associated as contaminant with alloying in and containment of the uranium fuel
2. Transuranic elements in the uranium

3. Rare earth heavy fission fragment elements (lanthanides)
4. Light fission fragment elements such as, alkaline earth, and some light transition metals and other (Figure 1)

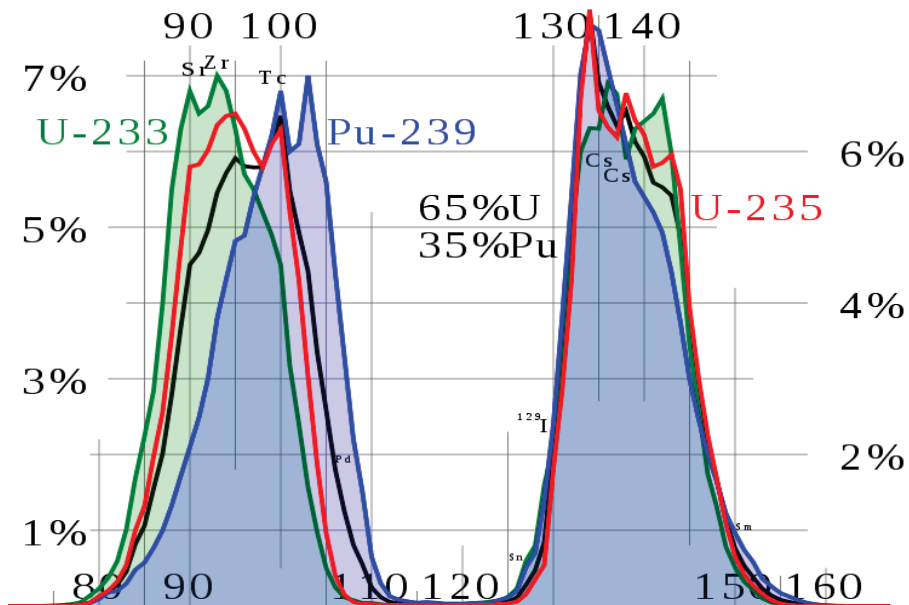


Figure 1: Thermal fission yield diagram of  $U^{235}$  indicates the ranges for atomic weights of fission fragment elements on the left light fission elements and on the right heavy fission fragment elements (<http://www.world-nuclear.org/education/phys.htm>)

### Analytical Practice

Using graphical alloy modeling schemes advanced by Hume-Rothery and Darken-Gurry and qualified by Gsniedener and Waber it is possible classify a specific solute element addition as highly soluble, marginally soluble, or immiscible elements. The diagrams will indicate whether a specific elemental solute addition will go in solution into the various solid phases of uranium or have been rejected. The Miedema plots exhibit the heat of mixing of solute elements into solvent with the heat of mixing much greater than zero promoting eutectic or eutectoidal microstructure and potential segregation and liquiation or a heat of mixing much less than zero forms an intermetallic phase[3-7]. Thus the Darken-Gurry model distinguish solubility effects during uranium phase transformations. The Miedema model will predict the potential microstructural evolution associated with the immiscible elements. Waber refined the ellipsoid by tightening the boundaries by about fifty percent to emphasize the elements that are predicted to have extensive solubility from micro soluble situations. This modeling is most effective in the Henrian solubility range and for the lower temperature phases since the models are primarily enthalpy (bonding) based and do not address the entropy term ( $-T\Delta S$ ). Overlapping of these solute maps are convenient as a first approximation tools for predicting alloy behavior.[2]

## Gschneidner Rules as Applied to Darken-Gurry Diagrams

Gschneidner used elemental electron configurations of solutes and solvents to establish a criteria for the selection of solute-solvent combinations which have been acceptable for this modeling scheme due to issues of elements that have “d” and “f” bands. The elements were classified as “d-shell” which included the transition metals, rare earth’s, and actinide metals and an “sp-shell” element which include alkali, alkaline earth, aluminum and silicon groups.

1. If both solute and solvent are “d-shell” elements, the Darken-Gurry method may be applied. Here uranium would be classified as “d-shell.” No major distortion of electronic bands occur. No large change in energy of the system occurs and small differences in electronic nature of two elements. The factors of size and electronegativity become dominant.
2. If both solute and solvent elements are “sp” elements, the Darken-Gurry method is valid only if the solvent and solute have the same crystal structure. Darken-Gurry method does not apply if “sp” solute and solvent have different crystal structures. Limited or not solid solution is expected. If different crystal structures or if the electronic configuration are sufficiently different causes impurity atoms in the matrix to raise the total energy high enough that solid immiscibility or compound formation occurs. Atomic size and electronegativity have no bearing on the solid solution. These factors play a role in determining stoichiometry and crystal structure of the second or mixed phase.
3. If the solvent is “d-shell” and the solute is an “sp” element, the Darken-Gurry method is valid only if one of the common metallic crystal structures. Here the uranium would be classified as “d-shell.” The electronic structures can be different. “d-shell” solvents have available “d” orbitals which are electronically tolerant of “sp” solute impurities. If crystal structures of the “sp” element is not one of the common metallic structures then solid solution is unlikely to occur or if it does, solid solution will occur at less than 5 wt. pct. In this case, Gschneidner rules do not need to be invoked.
4. If the solvent is “sp” and the solute is a “d-shell” element, only limited solid solution have been observed regardless of their crystal structures. The Darken-Gurry criteria are not needed. “sp-shell” solvent has no tolerance for a “d-shell” element impurity and the lack of empty “d-shell” levels in the matrix. This situation is true even if, both have common metallic crystal structures.[8]

## Miedema Heat of Mixing Correlations

The Miedema Method of analysis will predict heat of mixing of solutes in uranium to assist in understanding whether solutes that are immiscible will form a eutectic or eutectoidal microstructures and potential segregation and liquiation, or inter-metallic phase. The Miedema-Chelikowsky use different electronic properties that Darken-Gurry and achieve similar results. Thus correlation enhances the credibility of these models.

Miedema-Chelikowsky analyses produce a similar ellipsoid to compare solubilities of elements in metallic solvents which have been used in this paper [5]. Miedema also applied graphically his heat of mixing assessment on to a solvent-solute property data plot of elemental work function and electron concentration of the Weitzner-Seitz cell[7]. This overlay distinguishes those solute atoms have a heat of mixing greater than zero from those that having a negative heat of mixing values. This distinction tells whether the solute element is going to report as segregation such as seen in eutectic and eutectoidal segregation behavior from the solute elements or it is going to promote intermetallic phases.

## Uranium Phase Descriptions and Modeling Data

Alloy theories account for structural effects and valency of the three allotropes of uranium,  $\alpha$ ,  $\beta$ , and  $\gamma$ .  $\alpha$  uranium forms partially and covalent bonds and electrons and do not usually represented with whole number valence electrons. The valence of  $\alpha$  uranium is 3.8 to 4 and is plotted on the (Darken-Gurry) diagram as UIV (Figure 2). Covalent bonding restricts the formation of solid solutions in  $\alpha$  uranium even though atomic sizes and valence may be favorable. [11]

Beta uranium ( $\beta$ ) has a valence of 5 and have been plotted on the Hume-Rothery diagram as UV. Beta uranium has a unique structure and only limited solid solubility is possible. If  $\beta$  uranium has a valence of 5, elements that are pentavalent such as vanadium, niobium, and tantalum should stabilize  $\beta$  uranium. If present in the right solute contents, vanadium, niobium, chromium, and molybdenum are capable of retaining the  $\beta$  phase during quenching. Gamma uranium,  $\gamma$ , is the most metallic of the three allotropes and has a valence of six (5.8-6)[11]. The size of metal atoms depends on the number of electrons given up or that have changed energy levels; the diameter is not easily determined[9-10]. The size of a solute atom depends on the number of electrons the atom has given up or the number that have changed energy levels and is used in the Gordy's formula for electronegativity is expressed as[2]:

$$en = 0.31 \frac{V + 1}{r} + 0.50 \quad (1)$$

where  $en$  is electronegativity and  $V$  is the valence of the atom. The electronegativity is a modeling parameter for the Darken-Gurry diagram.

Miedema analysis use the endothermicity or exothermicity of mixing to determine whether or not an intermetallic or eutectic is formed[3-7]. If an intermetallic is formed, the element will have a negative sign; if eutectic may form the sign have been positive. The equation describing the positive and negative sign convention is as follows[4]:

$$\Delta H = -Pe(\Delta\phi)^2 + Q_o(\Delta n_{ws}^{\frac{1}{3}})^2 - R \quad (2)$$

where  $P$  and  $Q_o$  are constants,  $e$  is the elementary charge,  $\Delta\phi$  is the change in chemical potential with respect to uranium,  $\Delta n_{ws}$  is the change in change in density of electrons with respect to uranium, and  $R$  is a constant added for liquid and solid alloys[4]. Chelikowsky further extended Miedema's models by incorporating an ellipsoid that encompassed substitutional elements within a specific range about a solvent element. The equation determining the position of the ellipsoid is as follows[5]:

$$\Delta H_f(o, t) = \Delta H_f(s) + N(o, t) \quad (3)$$

$$N(o, t) = \sum_{i=1}^2 a_{i,j}(o, t)X_iX_j + \sum_{i=1}^2 b_i(o, t)X_i + c(o, t) \quad (4)$$

where  $a_{ij}$ ,  $b_i$ , and  $c$  are coefficients described in [5].

$$X_1 = \phi(A) - \phi(U) \quad (5)$$

$$X_1 = n_{ws}^{\frac{1}{3}}(A) - n_{ws}^{\frac{1}{3}}(U) \quad (6)$$

The ellipsoid calculations were corroborated with phase diagram information.

### Modeling Diagrams for Uranium

Figure 2 shows the electronegativities and ionic radii of the phases  $\alpha$ ,  $\beta$ , and  $\gamma$ . The  $\gamma$  phase being the most electronegative and the  $\alpha$  phase being the least electronegative. This shift is in agreement with Gschneidner rule 2 which states that the Darken-Gurry method is useful for “sp” elements in uranium if they have the same crystal structure. So the shift between  $\alpha$ ,  $\beta$ , and  $\gamma$  phase uranium may reflect increased solubility of certain elements based on crystal structure. Figure 2 illustrates that the electronegativity changes with valence but the ionic radius is assumed to be constant for this study.

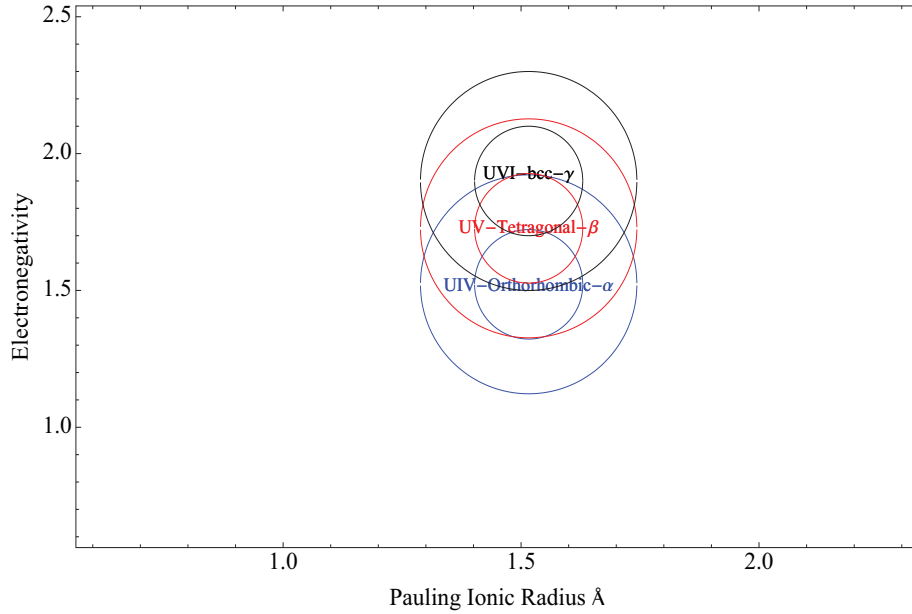


Figure 2: Darken-Gurry diagram illustrating changes in electronegativity with phase change for uranium. Note: In future diagrams the phase changes of uranium have been displayed as  $\alpha$ ,  $\beta$ , and  $\gamma$  for the orthorhombic, tetragonal, and body centered cubic crystal structures. The models have been updated with more refined ionic radius data in future publications.

Figure 3 shows the  $\gamma$  solubility ellipse to distinguish the potential alloying elemental solutes and additions that may be immiscible or compound forming and not suitable for alloy addition.

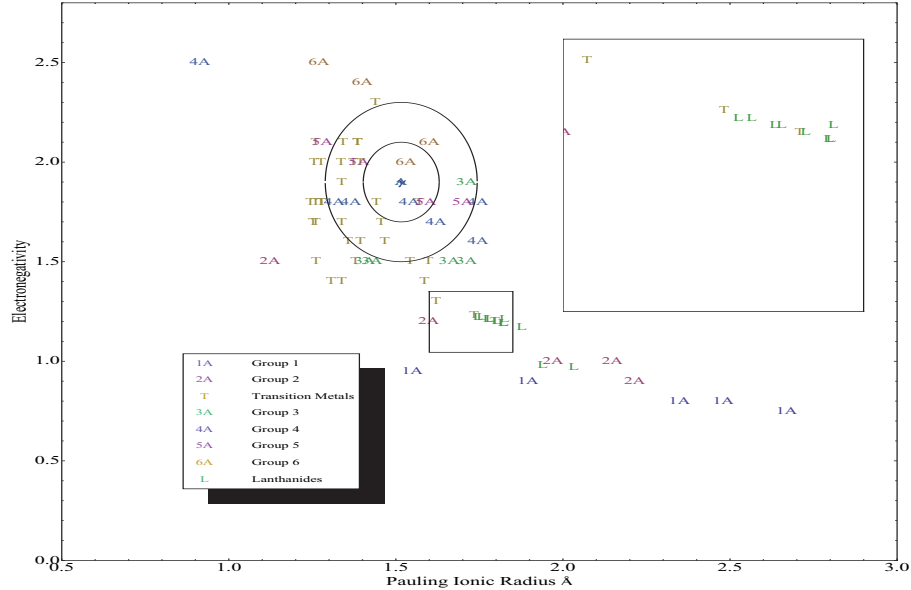


Figure 3: Darken-Gurry diagram representing potential elements for solubility in uranium fuel

Figure 4 is a Darken-Gurry diagram illustrating the light fission fragment elements of uranium. Many of the fission fragment elements fall outside of the  $\gamma$  ellipsoid and suggest a potential solubility issue within the fuel after a significant amount of fuel has decayed or burned. Elements of potential concern are yttrium, strontium, and rubidium.

Figure 5 represents heavy fission fragment products of uranium. Again, many if not all of the fission fragment elements fall outside the ellipsoids. These elements do not go into solution with uranium. They are predicted to be compound formers or immiscible in uranium as a solvent and become inter metallic phases. Two elements that will go into solution with uranium are tellurium and antimony.

Figure 6 represents the lanthanide elements. Again, these elements fall outside the ellipsoids and suggest potential issues within the fuel and should not be considered as a solute element using uranium as a solvent.

Figure 7 represents the Miedema diagrams using a Chelikowsky ellipsoid to indicate substitutional elements in solution or are highly soluble with uranium as the solvent element. Elements falling outside the ellipse either are partially soluble, immiscible, or potential inter metallic compounds (PI), or undergo potential eutectic segregation (PES). A slower look shows that there are few differences between what is predicted with Darken-Gurry diagrams and applying Gschneidner rules versus the Miedema diagram using Chelikowsky solubility ellipsoid.

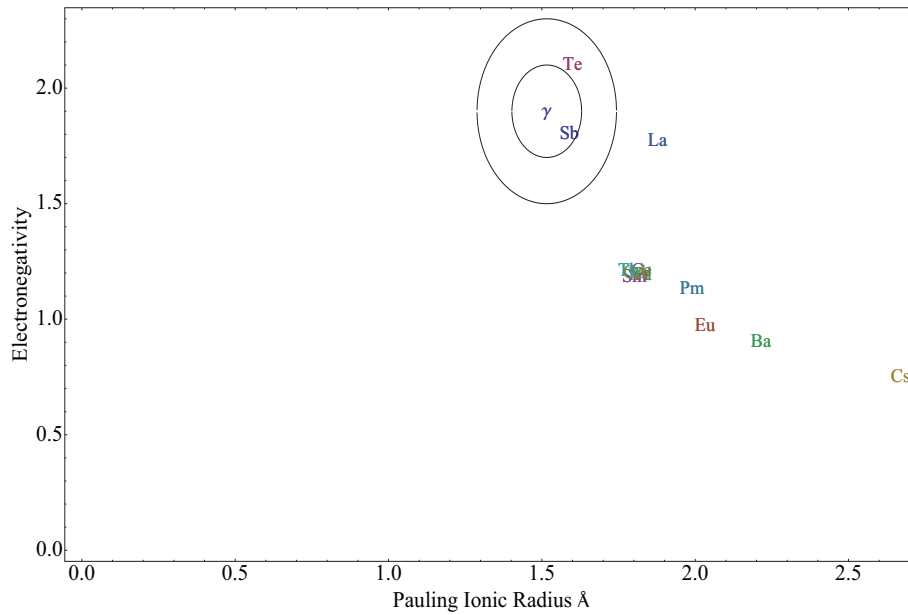


Figure 4: Darken-Gurry diagram illustrating the heavy fragment elements of  $U^{235}$  from atomic mass 139 to 175 amu

Figure 8 illustrates positive and negative heats of mixing as predicted by Miedema. The plot has a surface enthalpy of mixing overlaying a plot of change in charge density,  $\Delta n_{ws}$  as a function of the change in chemical potential,  $\Delta\phi$  with respect to uranium as the solvent.

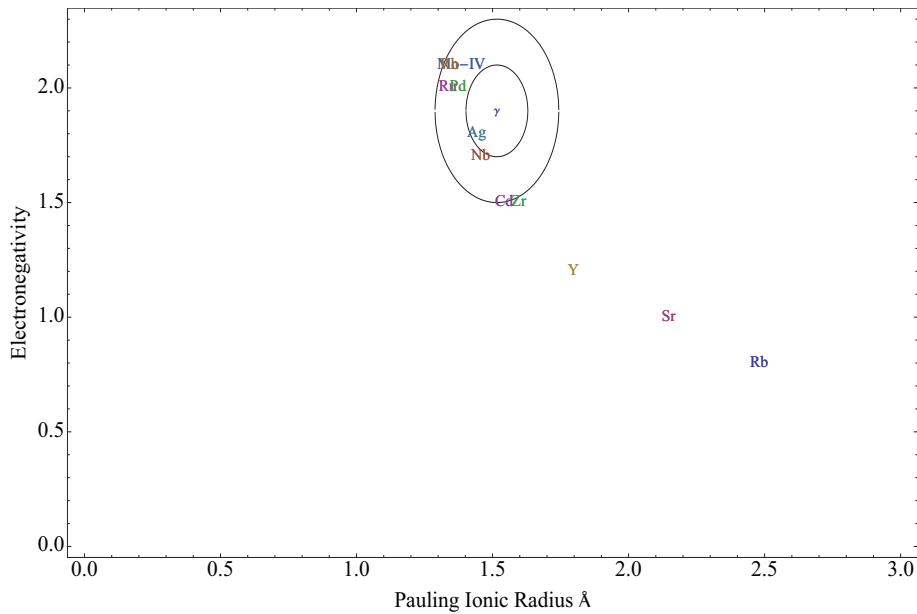


Figure 5: Darken-Gurry diagram illustrating the light fragment elements of  $U^{235}$  from atomic mass 80 to 110 amu.



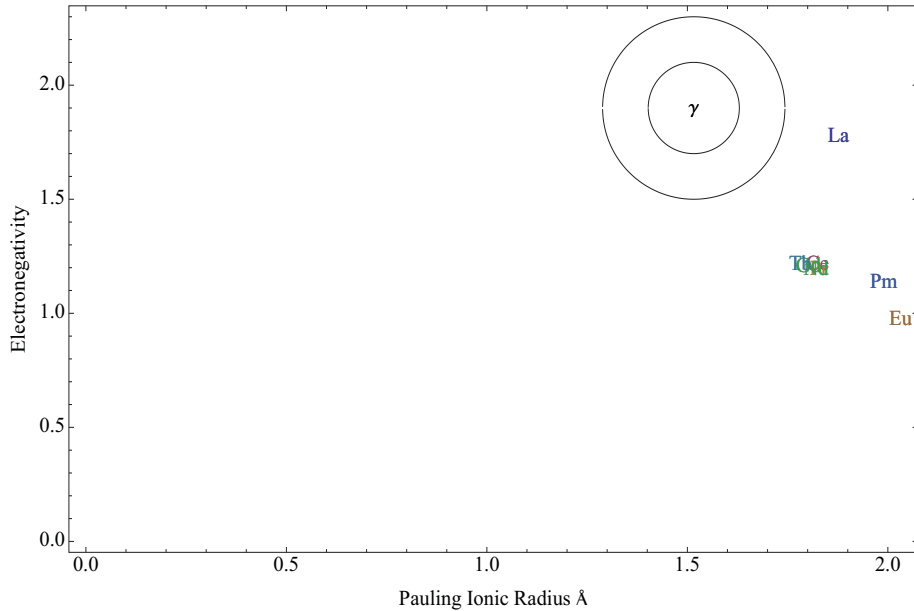


Figure 6: Darken-Gurry diagram illustrating lanthanide solubility. The diagram suggests immiscibility in uranium as a solvent because the elements sit outside the ellipsoids.

The surface representing enthalpy has been shifted to accommodate uranium as the solvent element. A solubility box has been constructed about the surface at the lines representing  $\pm 20 \frac{\text{kcal}}{\text{g-at}}$ . Any element located inside the box about uranium is highly soluble with respect to uranium as a solvent element. This relationship follows the prediction made by both Darken-Gurry diagrams and the extension to the Miedema model by adding Chelikowsky's ellipsoid. Elements with positive sign with respect to enthalpy of mixing forms potential eutectic and potential segregation liquiation. Elements with negative signs form potential inter metallic compounds.

Table 1 represents a list of elements and their potential solubility. The data is from phase diagrams and indicates percent solubility, compound formation and type, and if a potential eutectic or inter metallic have been formed upon mixing solute and solvent. The phase diagram information agrees with both Darken-Gurry diagrams and Miedema diagrams for most elements with in the solubility region in Figure 8. Some discrepancies exist between Darken-Gurry, Miedema, and phase diagram information. Table 1 also describes how well the models of Darken-Gurry and Miedema fit the data relative to phase diagram information. The phase diagram information predicts solubility where the Darken-Gurry plot and Miedema diagram may suggest a poor fit as a solute for uranium. For example, zirconium is 100 percent soluble in the gamma phase but is a misfit in the Darken-Gurry plot. Zirconium have been soluble in  $\beta$  phase uranium which is a lower temperature phase. This correlation suggests that the data used for elements may be low temperature. Zirconium is an excellent candidate for alloy addition using Miedema analysis. Using Darken-Gurry Rule 1 listed above, both uranium and zirconium have unfilled d-shell orbitals and in addition uranium has an unfilled f-shell orbital. Using Rule 1, zirconium should fit within Waber ellipse on the Darken-Gurry diagram. Other highly soluble elements such as copper and molybdenum are also misfits using Darken-Gurry plots but are excellent candidates for Miedema and correlate well

with phase diagram analysis.

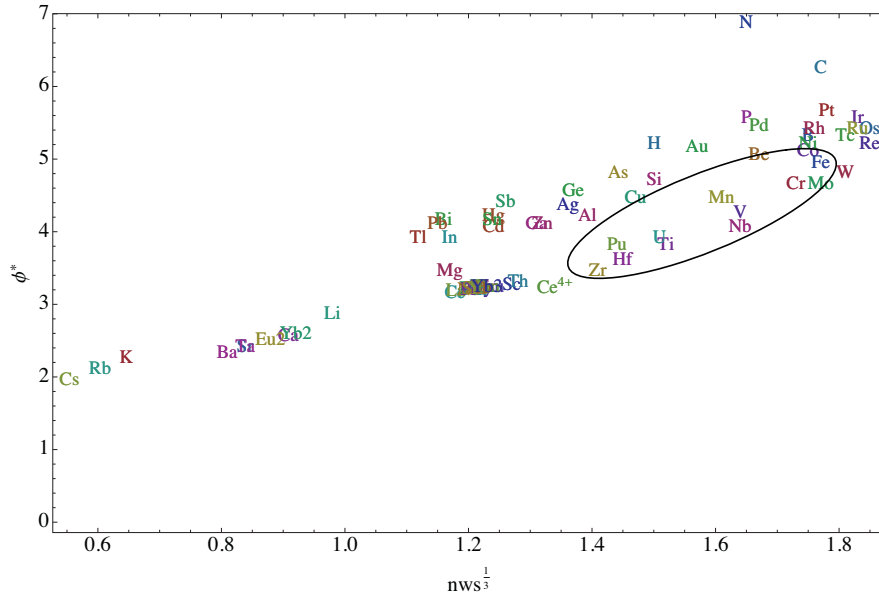


Figure 7: Miedema diagram using Chelikowsky interpretation of ellipsoid for solubility criterion for uranium.

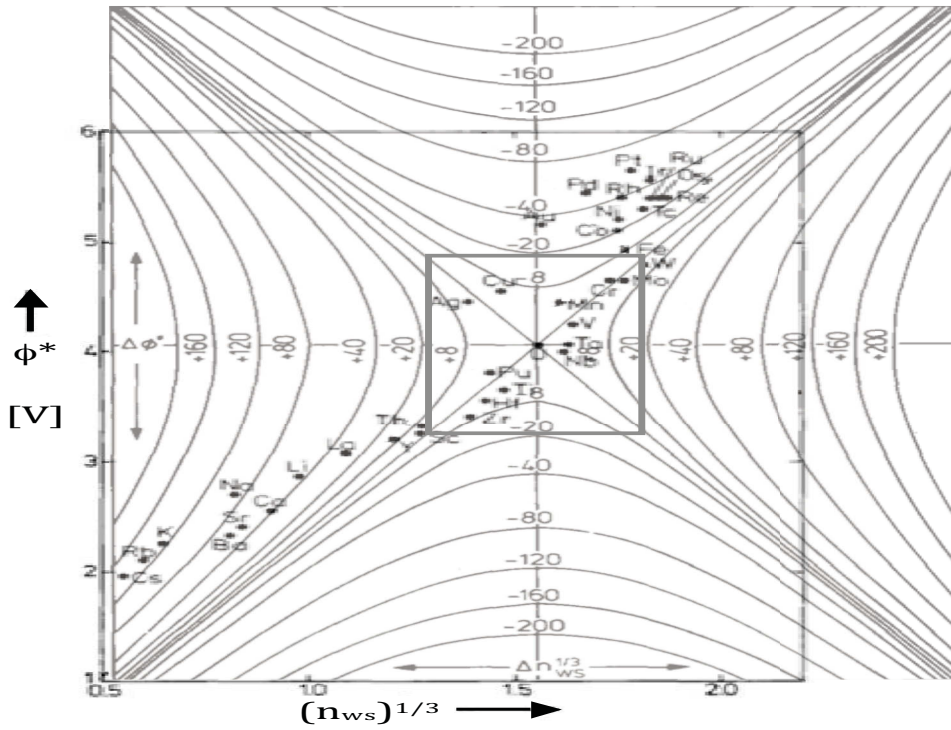


Figure 8: Miedema diagram using enthalpy of mixing overlay to determine substitutional solutes, potential intermetallic solutes, and eutectic solutes for uranium as the solvent.

Table 1: Table of Alloying Factors

	Max. Solubility in $\gamma$ U, a/o	Compound <sup>1</sup>	Model Fit Grade <sup>2</sup>
Zr	100	UZr <sub>2</sub>	MC-E, DG-MF
Ti	100	U <sub>2</sub> Ti	MC-E, DG-E
Hf	100	HS	MC-E, DG-MF
Nb	100	HS	MC-E, DG-MF
Pu	100	HS	MC-E, DG-M
Cu	83	HS	MC-M, DG-MF
Mo	42	HS	MC-E, DG-E
V	12	HS	MC-E, DG-E
Al	4	UAl <sub>2</sub> , UAl <sub>3</sub> , UAl <sub>4</sub>	MC-MF, DG-MF
Cr	4	HS	MC-E, DG-M
Ta	3	HS	MC-MF, DG-MF
Be	2	No	MC-M, DG-E
Fe	< 1	U <sub>6</sub> Fe, UFe <sub>2</sub>	MC-MF, DG-MF
W	< 1	PI	MC-MF, DG-E
Co	< 1	PI	MC-E, DG-MF
Mn	3	U <sub>6</sub> Mn, UMn <sub>2</sub>	MC-E, DG-MF
Ni	2	PI	MC-M, DG-MF
Os	< 1	PI	MC-MF, DG-MF
Ir	< 1	PI	MC-MF, DG-MF
Pt	5	UPt, UPt <sub>2</sub> , UPt <sub>3</sub> , UPt <sub>5</sub>	MC-MF, DG-MF
La	< 1	PES	MC-MF, DG-MF
Ce	< 1	No	MC-MF, DG-MF
Pr	< 1	No	MC-MF, DG-MF
Nd	< 1	No	MC-MF, DG-MF
Sm	< 1	No	MC-MF, DG-MF
Eu	< 1	No	MC-MF, DG-MF
Gd	< 1	No	MC-MF, DG-MF
Tb	< 1	No	MC-MF, DG-MF
Dy	< 1	No	MC-MF, DG-MF
Ho	< 1	No	MC-MF, DG-MF
Er	< 1	No	MC-MF, DG-MF
Tm	< 1	No	MC-MF, DG-MF
Yb	< 1	No	MC-MF, DG-MF
Lu	< 1	No	MC-MF, DG-MF

<sup>1</sup> HS-Highly Soluble, PI-Potential Intermetallic, PES-Potential Eutectic Segregation;

<sup>2</sup> MC-Miedema-Chelikowsky, DG-Darken-Gurry, E-Excellent, M-Marginal, MF-Misfit;

Another point of interest is that the solubility box in Figure 8 also contains zirconium. The solubility box was expanded to  $20 \frac{kcal}{g-at}$  from  $1.2 \frac{kcal}{g-at}$ . The expansion was performed to account for potential entropy contributions at temperatures where the gamma phase exists for uranium and potential alloys. The phase diagrams also provide

information as to compound formation. The various compounds formed are listed in Table 1. Table 1 was updated with data from ASM Alloy Phase Diagrams Center website (<http://www1.asminternational.org/asmenterprise/apd/>).

### Conclusion

The results of graphical analyses provided by Darken-Gurry, Gschneidner, Miedema, and Chelikowsky models correlate well. Zirconium is an outlier on the Darken-Gurry diagram. It appears to be immiscible with uranium as the solvent element. Phase diagram data and Chelikowsky-Miedema diagrams suggest that zirconium should be 100 percent soluble in  $\gamma$ -uranium. Figure 8 supports the fact that zirconium should be soluble in uranium also based on information obtained from phase diagrams. The discrepancy may lie in the lack of accounting for entropy ( $-T\Delta S$ ) during heat of mixing calculations for Miedema calculations. An adaptation to the equations describing these models should enhance the temperature dependence.

**Acknowledgment** We would like to thank the authors for their contribution to this work and Idaho National Laboratory for their support of research on uranium alloys.

### Works Cited

1. A.N. Holden, *Physical Metallurgy of Uranium*, (Addison Wesley Publishing Company, 1958).
2. J.T. Waber, "Some Principles of Alloying Behavior of Plutonium," Los Alamos Scientific Laboratory of true University of California, Los Alamos, New Mexico, 1959.
3. A.R. Miedema, R. Boom, and F.R. Boer, *Simple Rules for Alloying, Crystal Structure, and Chemical Bonding in Inorganic Chemistry*, (North Holland Publishing Company, The Netherlands, 1975), pp. 163-196.
4. A.R. Miedema, R. Boom, and F.R. Boer, "Cohesion in Alloys-Fundamentals of a Semi-Empirical Model," *Physica*, North Holland Publishing, 1980.
5. J.R. Chelikowsky, "Solid Solubilities in Divalent Alloys," *Physical Review B*, The American Physical Society, 1979.
6. A.R. Miedema and P.F. de Chitel, "A Semi Empirical Approach to the Heat of Formation Problem," pp. 344, *Met. Soc. AIME*, 1979.
7. H. Bakker. *Enthalpies and Alloys. Miedema's Semi-Empirical Model*, (Trans Tech Publications, Switzerland, 1998).
8. K.A. Gschneider Jr, "Theory of Alloy Phase Formation, L.S. Darkens Contribution to The Theory of Alloy Formation and Where We are Today," K.A. Gschneider, in *Solid State Physics*, vol 16, p.275, Academic Press, NY ,1964.
9. H.E. Faiman and A. Kelly, "Metallography and Microstructure of Uranium and Its Alloys," *Metallography and Microstructures*, ASM Intern., pp. 918-932 (2004).
- 10 L. Brewer, *In Phase Stability in Metals and Alloys*, (McGraw-Hill, New York, 1967), pp. 39-61, 241-249, 344-346.

11 W. Wilkinson and W. Murphy, *Nuclear Reactor Metallurgy*, Van Nostrand, New Jersey, 1958, pp. 70-81.