

# **Test of Darken's Mobility Assumption in Au-Ni & Cu-Ni-Zn Systems**

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***Multicomponent Multiphase Diffusion Symposium  
in Honor of John E. Morral: Session II***

**2005 TMS Annual Meeting  
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# Overview

1. Introduction: Diffusion Formalisms & Simplifications
2. Intrinsic Diffusion Simulation
  - Model System
3. Tests of Darken Relations
  - A: Binary : *Au-Ni*
  - B: Ternary: *Cu-Ni-Zn*
4. Conclusions
5. Comments on development of multicomponent diffusion databases

The Edward DeMille Campbell  
Memorial Lecture for 1961

LAWRENCE S. DARKEN, The 1961 Campbell Lecturer, was born in Brooklyn, New York, in 1909. He graduated from Hamilton College in 1930, and in 1933 received his doctorate from Yale University, where he held the Loomis Fellowship and also a post-doctoral University Fellowship. He is a member of the National Academy of Sciences, the American Institute of Mining, Metallurgical and Petroleum Engineers, the American Chemical Society, Phi Beta Kappa and Sigma Xi, and is a Fellow of the New York Academy of Sciences and of the American Association for the Advancement of Science.

Dr. Darken, Associate Director of the Edgar C. Bain Laboratory for Fundamental Research in Monroeville, Pennsylvania, has been associated with the United States Steel Corporation since 1935, when the predecessor of the present laboratory was in Kearny, New Jersey. He has been engaged in research in many areas of both physical and chemical metallurgy—the common threads being most frequently thermodynamics and diffusion.

For some years he was also Adjunct Professor at the Polytechnic Institute of Brooklyn where he taught graduate courses on the physical chemistry of metals, metallurgical thermodynamics and phase rule. He is author with Dr. R. W. Gurry of the book "Physical Chemistry of Metals".

After his doctoral research on ionization constants in aqueous solutions, his attention focused on high-temperature chemistry related to iron and steel-making, initially on the equilibria of the iron-oxygen system and equilibria pertaining to the open-hearth process. This was followed by investigations on equilibria and reaction rates in numerous binary and ternary ferrous systems. His work on the theory of the basic phenomenology of diffusion and a theorem he developed on the thermodynamics of ternary and multicomponent systems have served as a basis for experimental work in these areas. He helped lay the foundation of our understanding of chemical rate phenomena in the open-hearth process. His work on the interaction of atoms with imperfections, on pearlite growth and on filamentary growth are also well known. He was the Howe Lecturer (AIME) in 1961.



# 1. Introduction

- **Why is diffusion modeling needed?**
  - Ability to use thermodynamic, diffusion, property databases to predict microstructural evolutionary processes
    - Experimental studies: expensive, time-consuming, limited variability
  - Assess existing diffusion formalisms (many indeed!)
    - Examine inherent assumptions & simplifications
  - Examine newer formalisms and understand mechanisms
- **How is diffusion modeling done?**
  - Atomistic approaches
    - Monte Carlo, molecular dynamics, phase field, etc.
  - Finite difference methods
    - Solve Fick's second law for appropriate boundary conditions and geometry
    - *Use intrinsic flux expression for different time intervals (here)*

# Diffusion Formalisms: A. Interdiffusion

- Isothermal, isobaric system

$$J_k^o = - \sum_{i=1}^{n-1} L_{ki}^{o,n} \text{grad } \mu_i \quad (k = 1, 2, \dots, n-1)$$

$$\sum_{k=1}^n J_k^o = 0$$

- Multicomponent version of Fick's law

$$J_k^o = - \sum_{j=1}^{n-1} D_{kj}^{o,n} \text{grad } c_j \quad (k = 1, 2, \dots, n-1)$$

- There are  $(n - 1)(n - 1) = (n - 1)^2$  coefficients

## B. Intrinsic Diffusion Formalism

- Fluxes defined in the lattice frame

$$J_k = - \sum_{i=1}^{n-1} L_{ki}^n \text{grad } \mu_i \quad (k = 1, 2, \dots, n)$$

$$\sum_{k=1}^n J_k = - J_v$$

- Multicomponent version of Darken's equation

$$J_k = - \sum_{j=1}^{n-1} D_{kj}^n \text{grad } c_j$$

- There are  $n(n - 1)$  coefficients

# Simplified Version of Formalism

- Intrinsic flux expression that **ignores** cross-terms

$$J_k = - \sum_{i=1}^n L_{ki} \frac{\partial \mu_i}{\partial x} = -L_{kk} \frac{\partial \mu_k}{\partial x} = -c_k M_k \frac{\partial \mu_k}{\partial x} \quad (L_{ki} = 0, k \neq i) \quad (k = 1, 2, \dots, n)$$

- $M_k$  is known as the “mobility” [Darken 1948]
  - *One unique mobility for each component in a multicomponent system*
- **Multicomponent Darken theory connects mobilities with tracer diffusion coefficients**
  - Diffusion coefficients in other frames can be obtained from mobilities (or  $L_{kk}$ 's) by suitable transformations

$$L_{kk} = c_k M_k = \frac{c_k D_k^*}{R T}$$

# Simplified Formalism Questions (used by DICTRA)

- Not proven that  $L_{kk}$ 's or  $M_k$ 's are unique functions of composition
  - Need intrinsic measurements in diffusion couples with crossing composition paths
- Darken relations in binary systems not systematically tested with experimental data
  - *Tests in ternary systems where tracer diffusion information is available are rare*

$$D_k = D_k^* \left( 1 + \left( \frac{\partial \ln \gamma_k}{\partial \ln X_k} \right) \right) \quad (k = 1, 2)$$

$$D^o = (X_2 D_1^* + X_1 D_2^*) \left( 1 + \left( \frac{\partial \ln \gamma_k}{\partial \ln X_k} \right) \right)$$

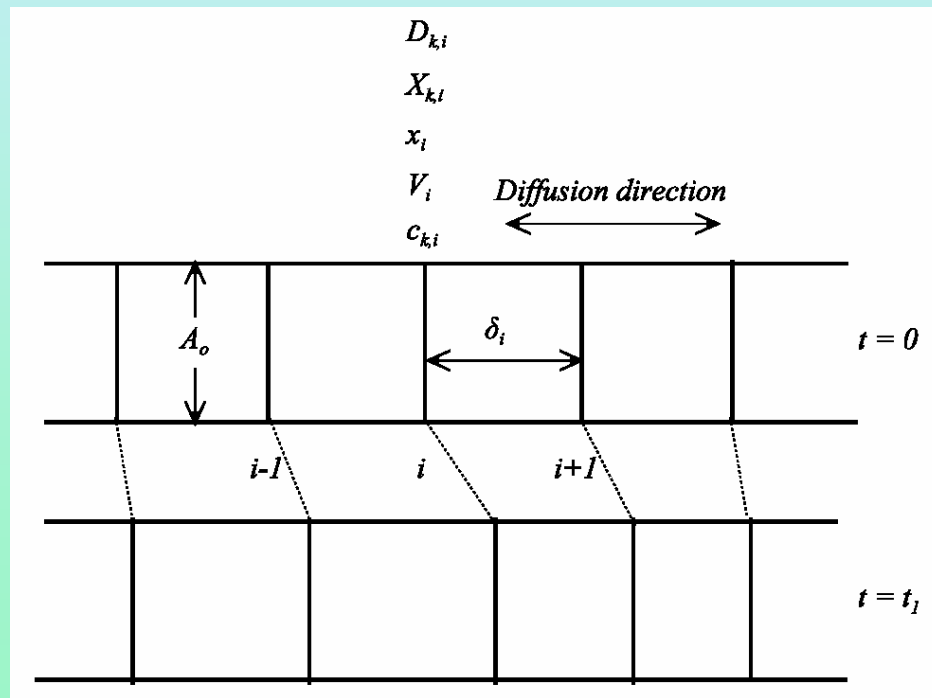
# Objectives

- Develop a *versatile* simulation capable of treating diffusion for different formalisms
- Test internal consistency of simulation with model systems
- Develop systematic procedure for the assessment of Darken theories
  - Binary: Ag-Cd, **Au-Ni**, Cu-Zn, Cu-Ni
  - Ternary: **Cu-Ni-Zn**



## 2. Single-Phase, Intrinsic Diffusion Simulation for Multicomponent Systems

1. Initial concentration distribution for each component
  2. Depending upon the formalism, kinetic descriptors as a function of composition, temperature or other variables
  3. Thermodynamics of phase, if needed
  4. Molar volume as a function of composition
- **Simple** yet effective algorithm



Finite difference method for semi-infinite couples

- Handles **variable molar volumes**
- Developed in MathCad – **user-friendly**
- **Efficient** – practical output for a single diffusion couple in less than a minute
- **Versatile** – adaptable to various formalisms

# Model System with Variable Molar Volume

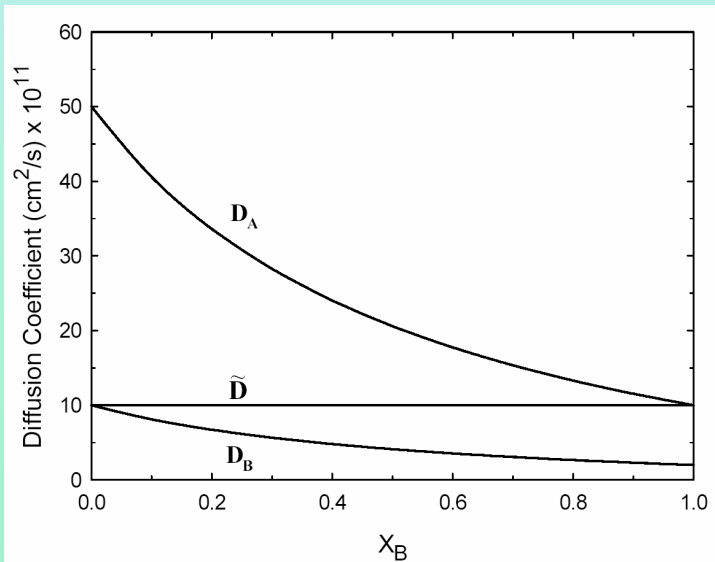
- $D^o = D^V = \text{constant}$ : Error function solution for  $c_k(x,t)$

$$c_A(x) = c_A^- + (c_A^+ - c_A^-) \operatorname{cerf}\left(\frac{x}{2\sqrt{\tilde{D}t}}\right)$$

$$\operatorname{cerf}(z) = \frac{1}{2}(1 + \operatorname{erf}(z))$$

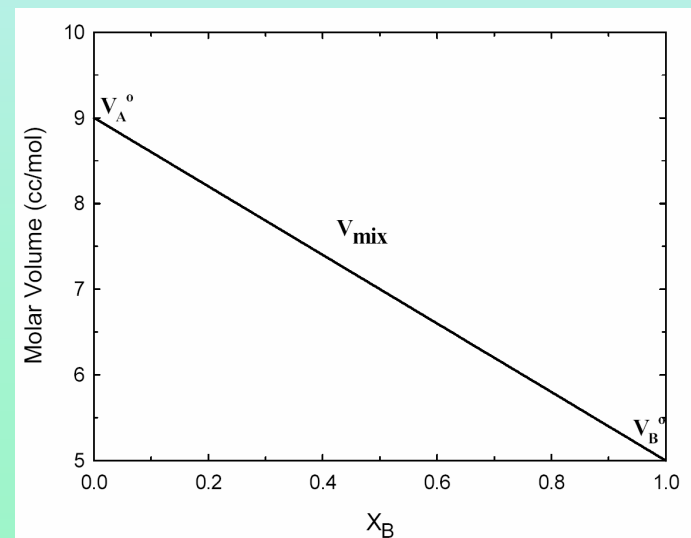
$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-u^2) du$$

- Ratio of intrinsic diffusion coefficients constant:  $R = \frac{D_A^K}{D_B^K}$



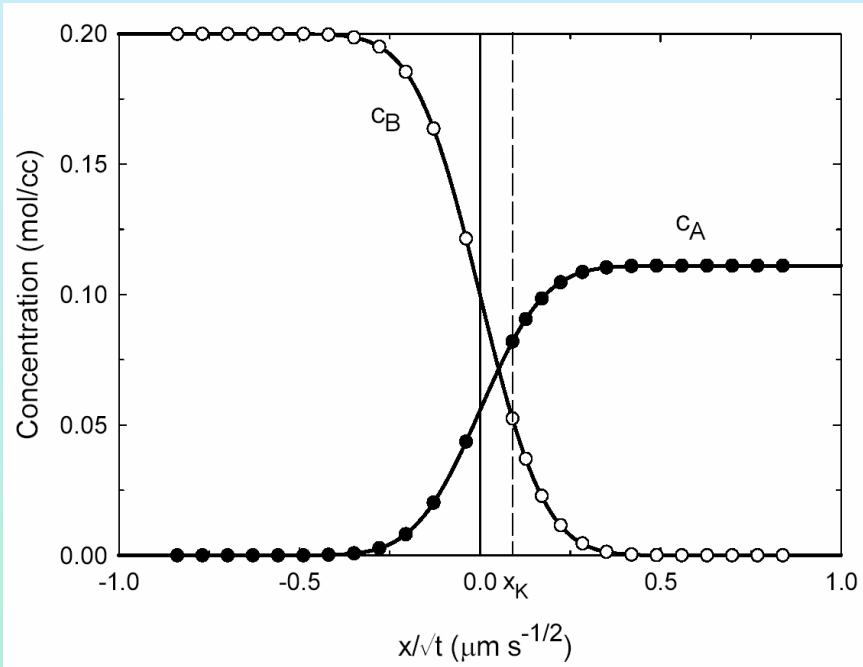
$$R = 5$$

$$D^o = 10^{-10} \text{ cm}^2/\text{s}$$



$$\bar{V}_A = V_A^o ; \quad \bar{V}_B = V_B^o$$

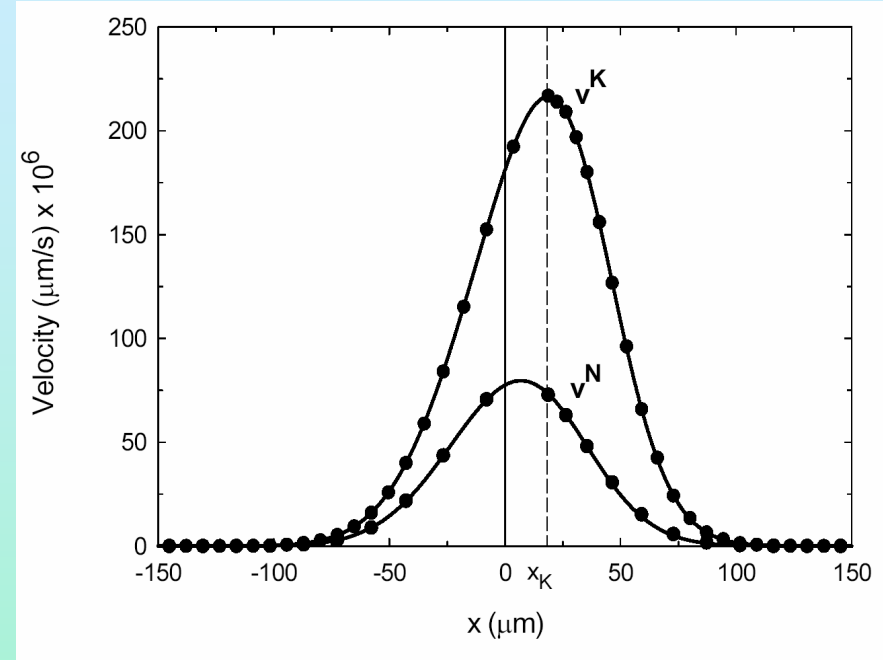
# Simulation Output for Model System



**Concentration profiles  $c_k$  (mol/cc)**

**Atom fraction  $X_k = c_k V$**

**$t = 12 \times 3600$  s**



**Lattice velocity ( $v^K$ )**

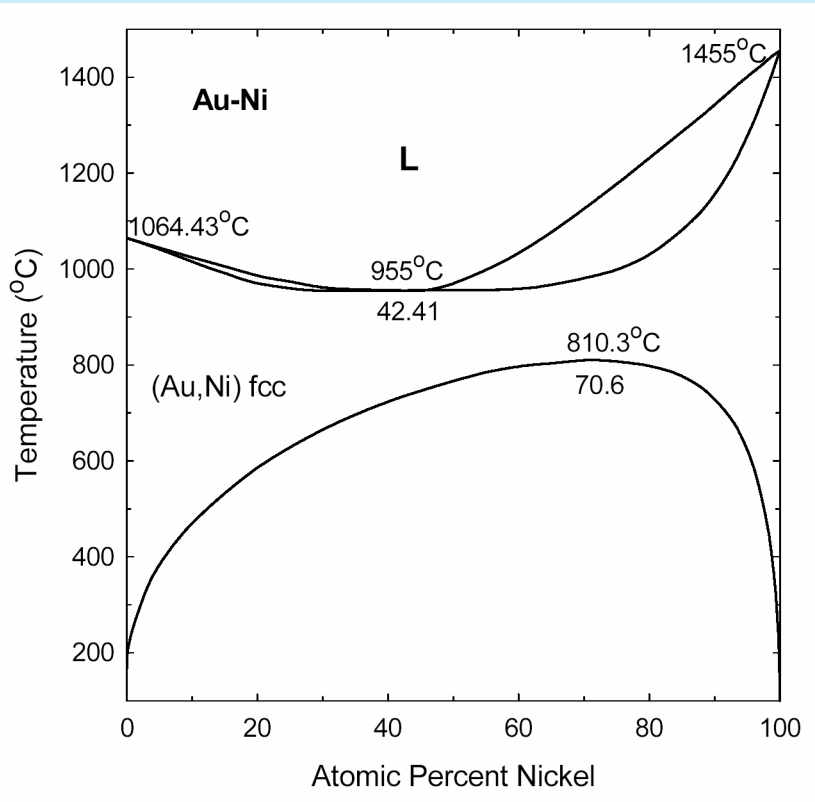
$$v^{KV}(x) = \left[ D_B^K(x) - D_A^K(x) \right] V_B^o \frac{dc_B(x)}{dx}$$

$$v^{KV}(x) = v^K(x) - v^V(x) = v^K(x)$$

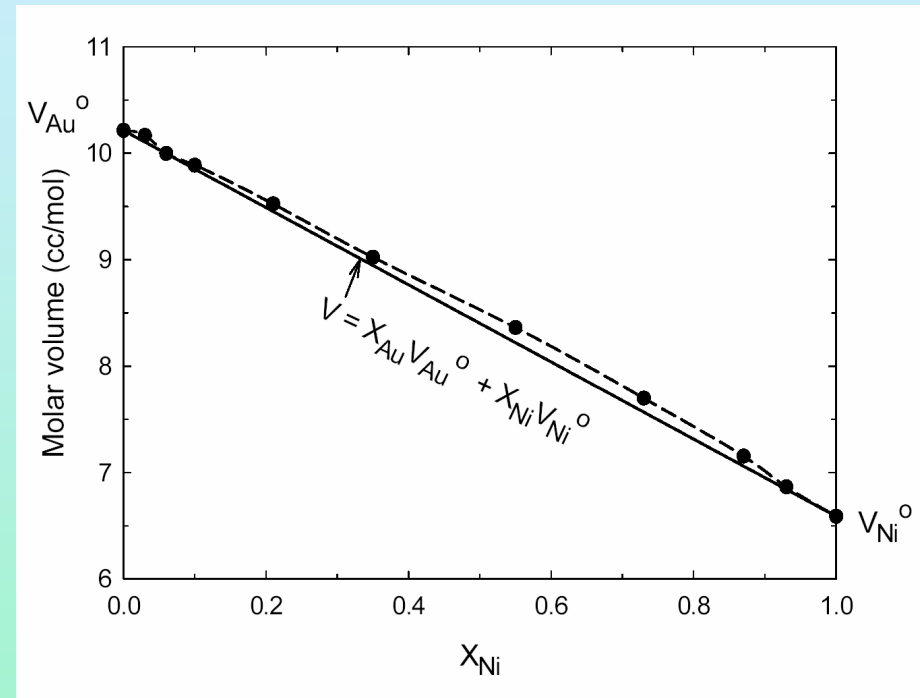
**Velocity in number frame ( $v^N$ )**

$$v^N(x) = V_{mix}(x) [J_A^o(x) + J_B^o(x)]$$

# 3. A: Tests of Darken Relations in Au-Ni at 900°C



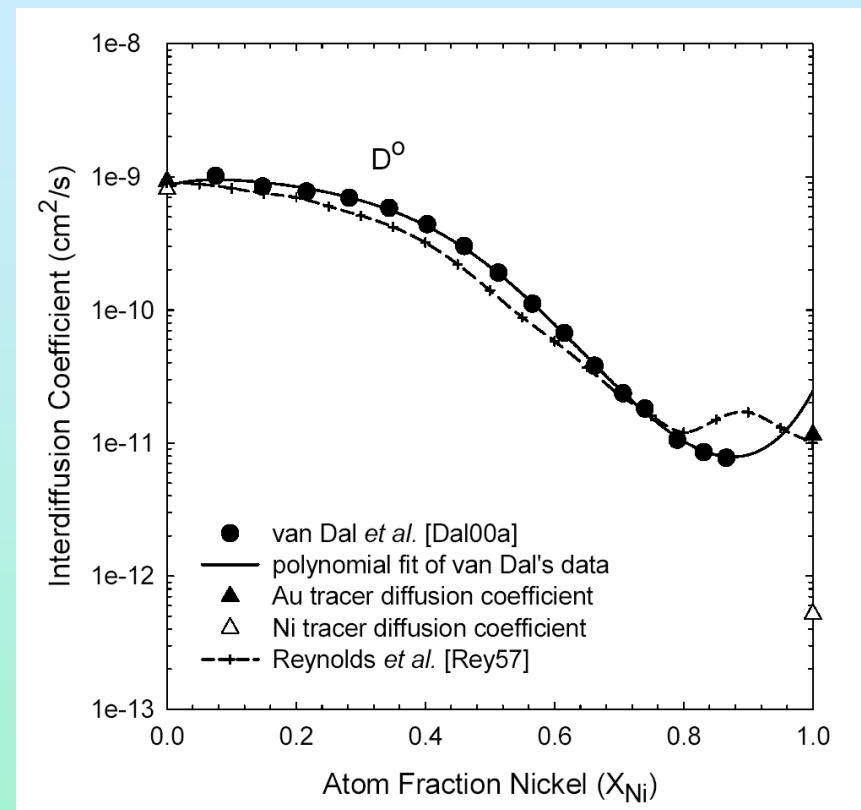
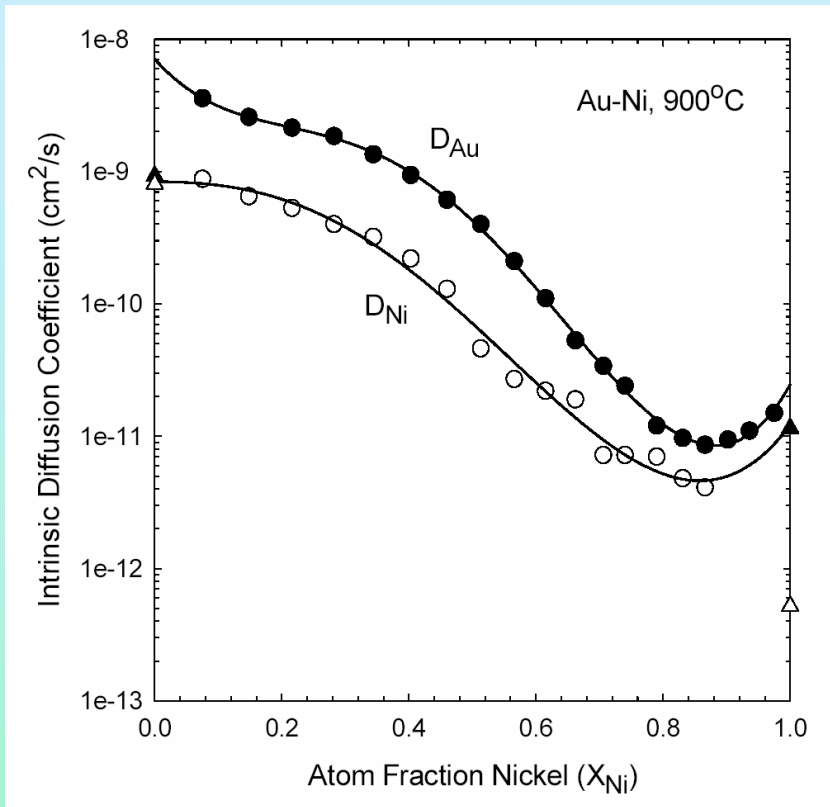
Phase diagram



Molar volume dependence on composition (almost ideal mixing)

- Classical system often quoted for the success of the Darken relation between the *tracer and interdiffusion coefficient*

# Darken Au-Ni (contd.)

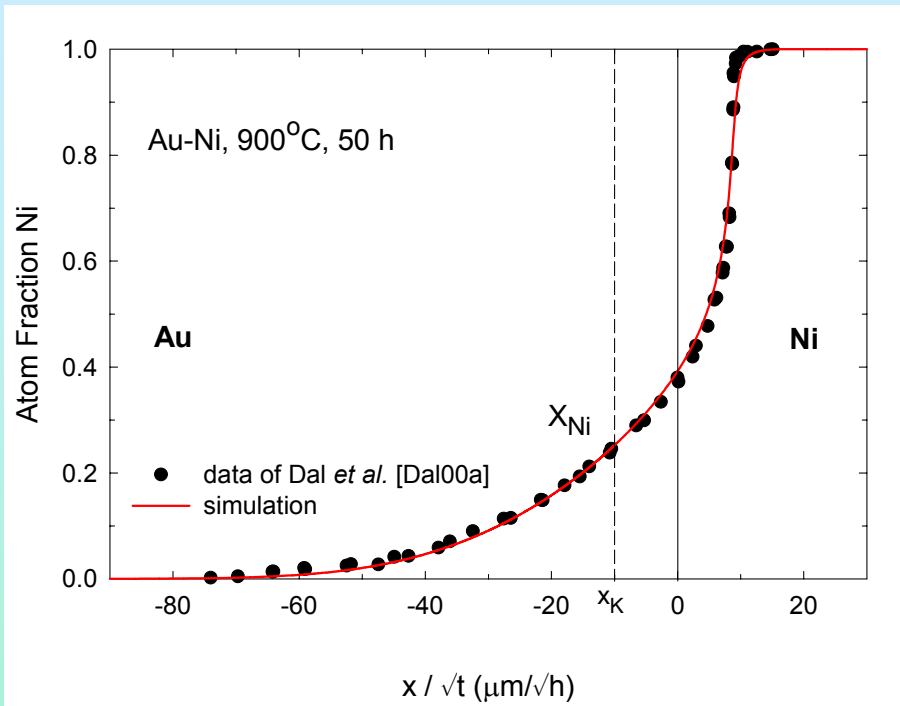


**Experimental intrinsic diffusion coefficients**  
[Van Dal *et al.* [J. Alloys & Comp., 2000]

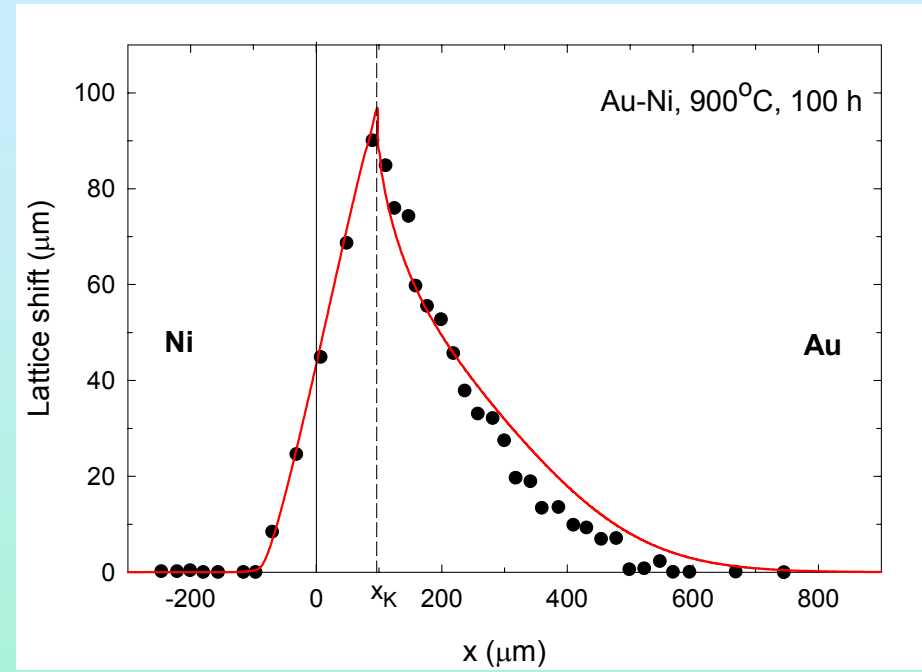
**Interdiffusion coefficient**

- Polynomial functions were used to fit the intrinsic diffusion data

# Darken Au-Ni: Assessing Experimental Data



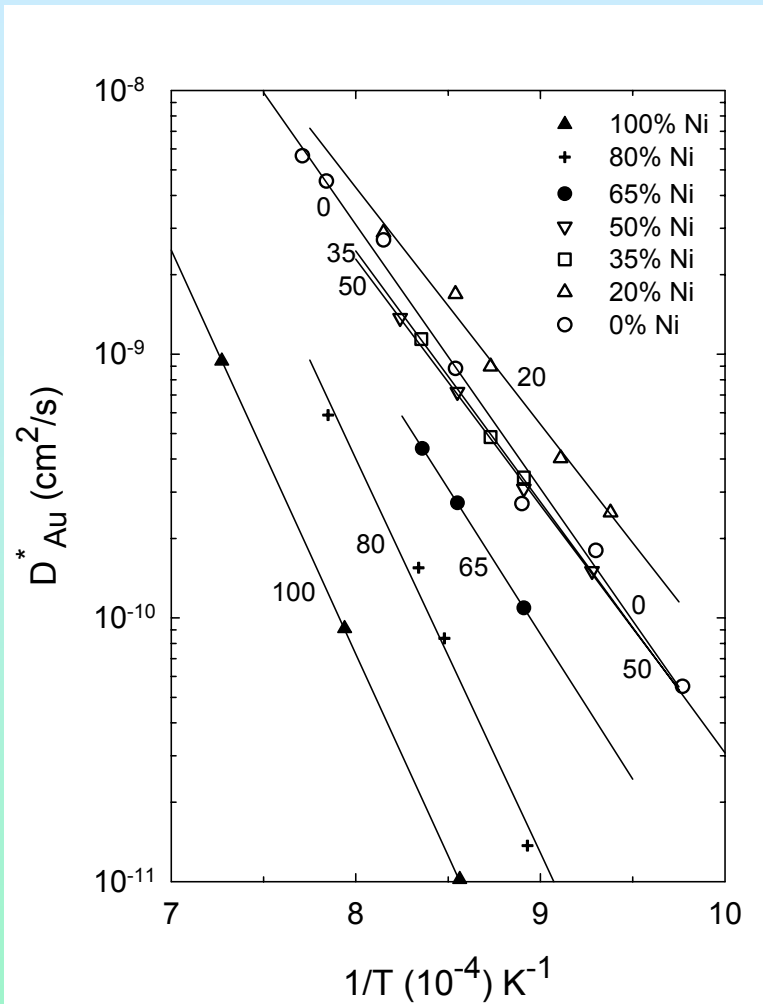
Concentration profile (6000 iterations)



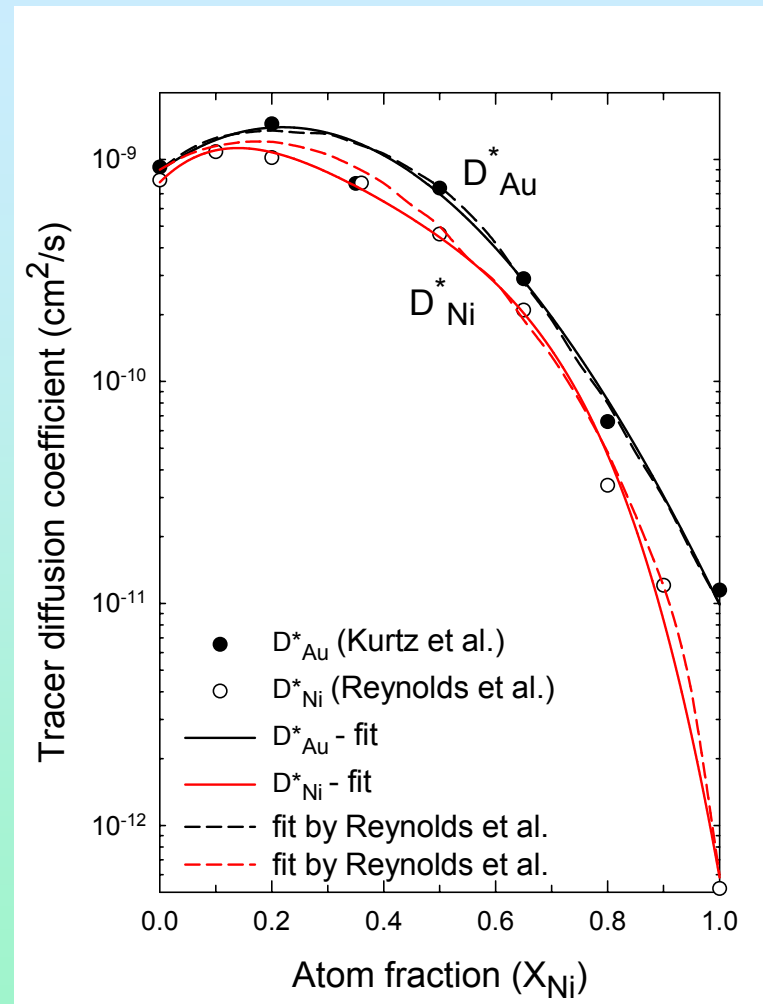
Lattice shift profile

➤ Quality of experimental intrinsic data appears excellent

# Darken Au-Ni: Tracer Diffusion

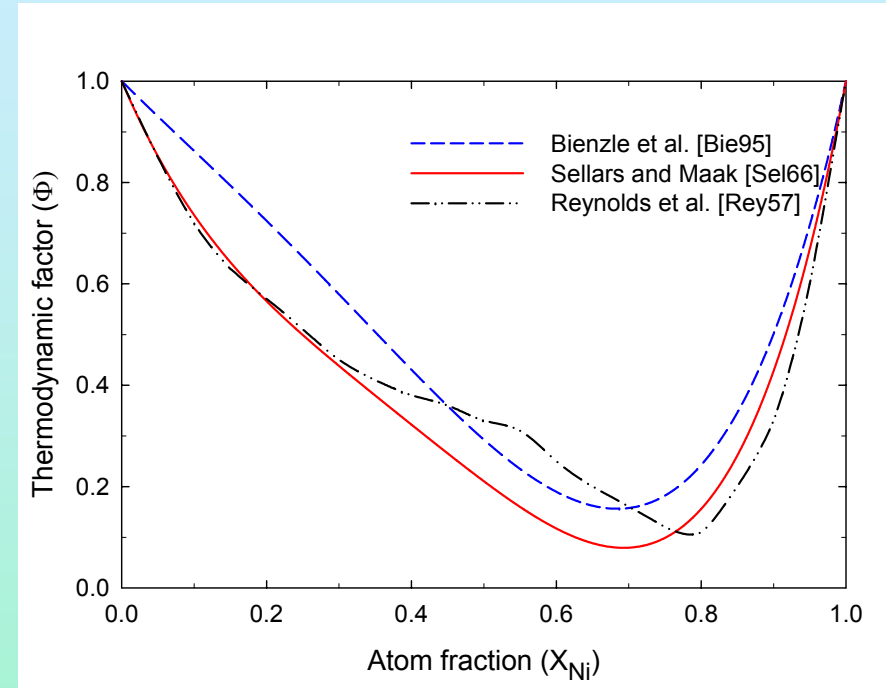
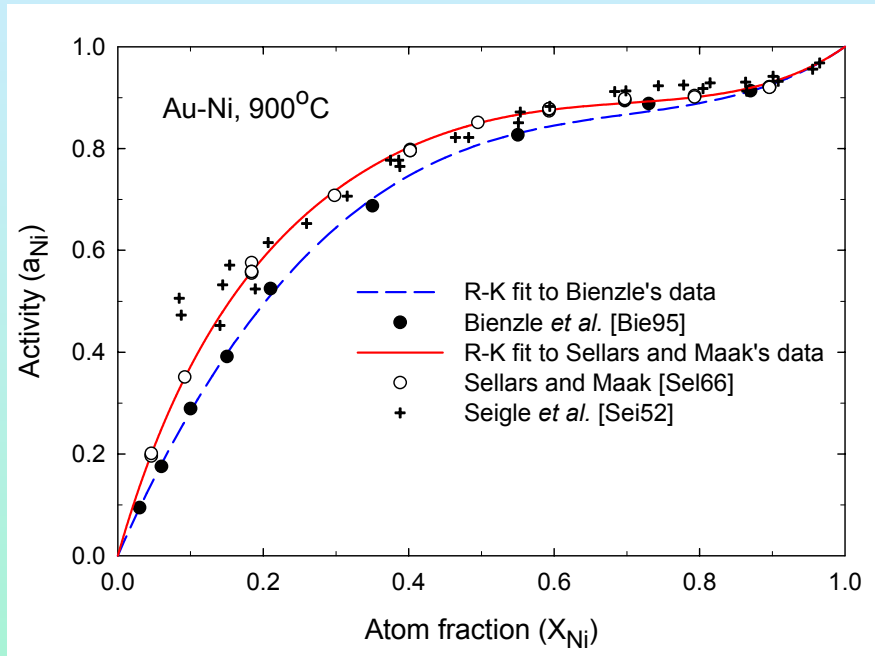


Tracer data for Au [Kurtz et al. , Acta Met., 1955]



Tracer diffusion coefficients of Au and Ni

# Darken Au-Ni: Thermodynamics



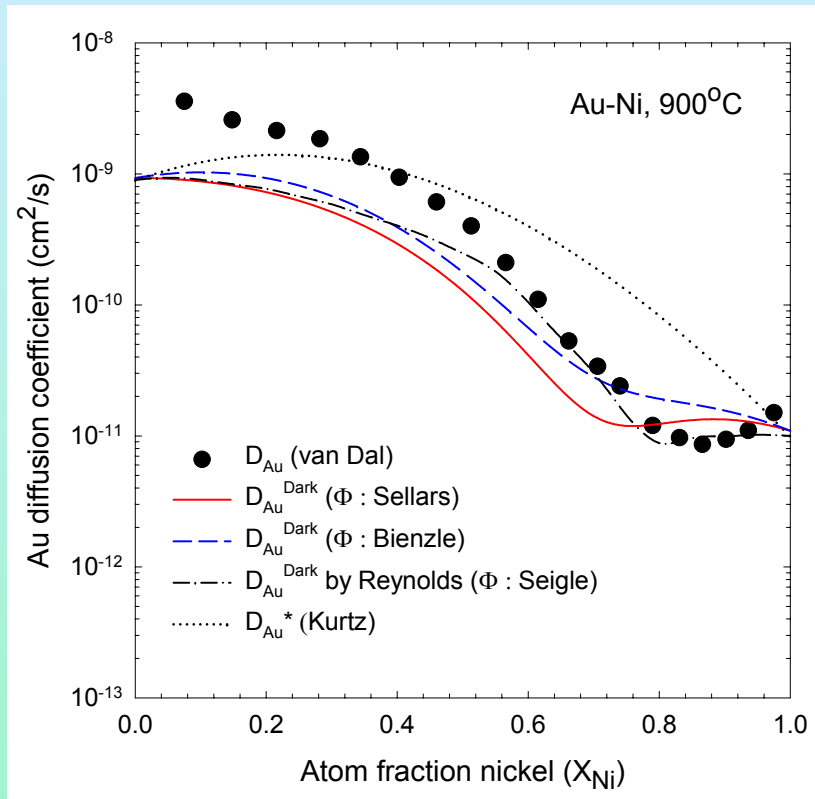
Redlich-Kister polynomial fits for activity data

Thermodynamic factor ( $\Phi$ )

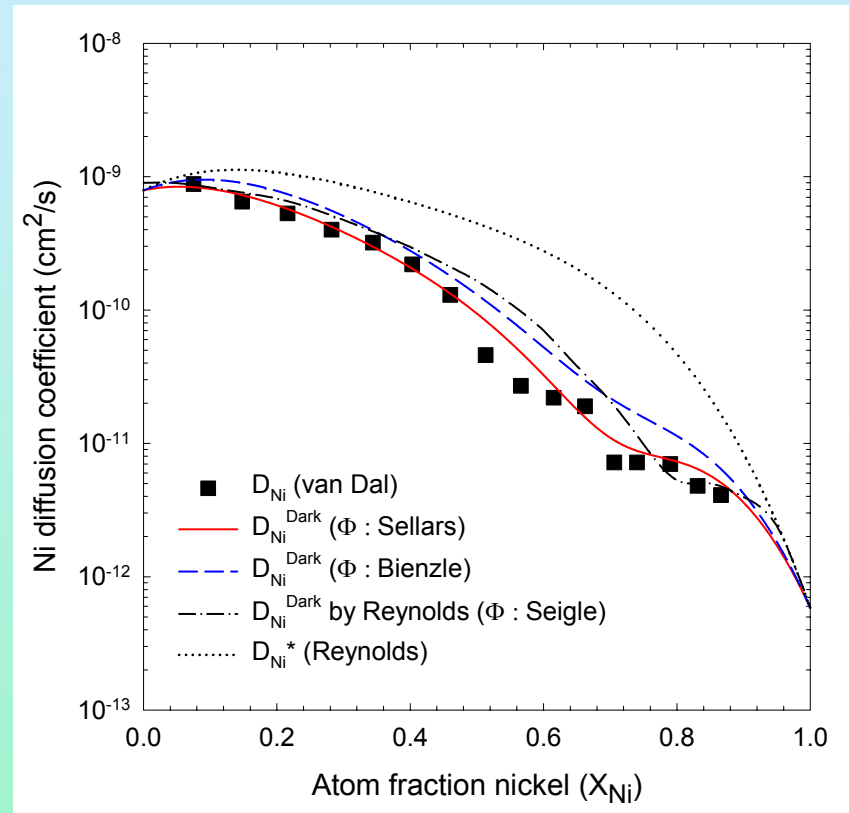
➤ Thermodynamic factor is less than unity



# Darken Relations for Au-Ni: Predicted Intrinsic Diffusion Coefficients



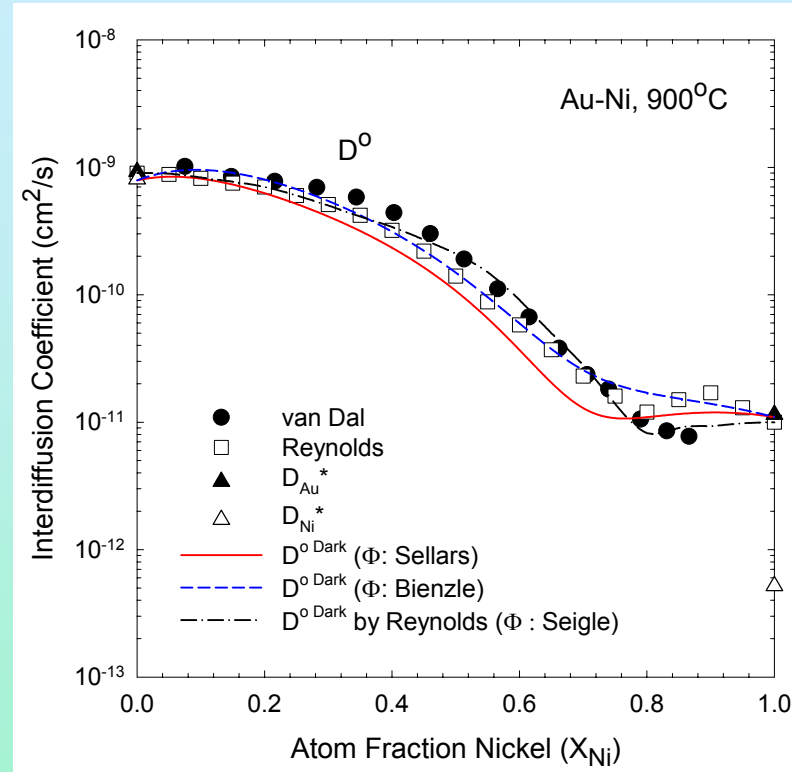
**Darken:  $D_{\text{Au}}$**



**Darken:  $D_{\text{Ni}}$**

➤ **Problem with predicted Au intrinsic diffusion coefficient**

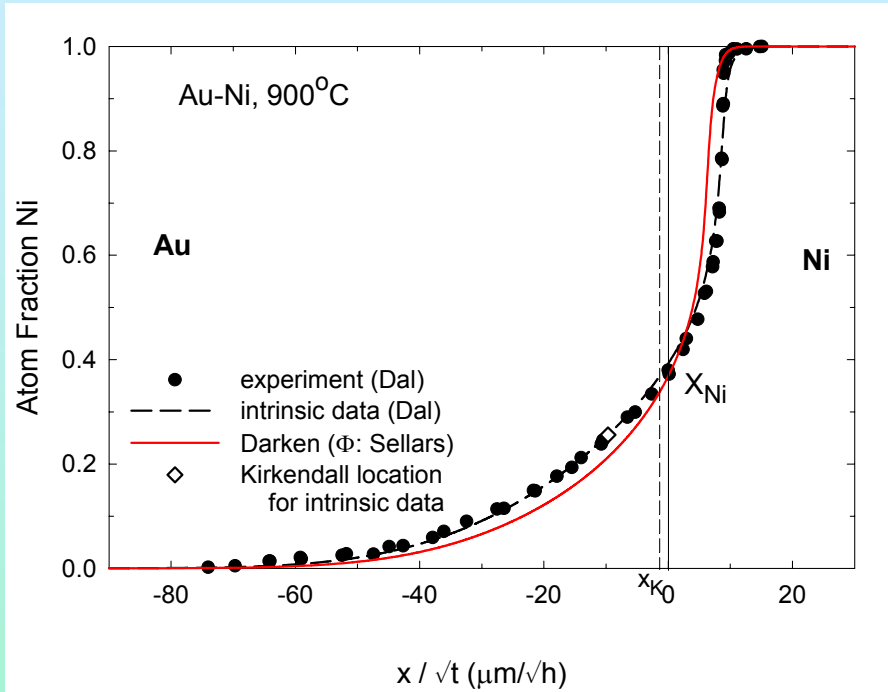
# Darken Relations for Au-Ni: Predicted Interdiffusion Coefficient



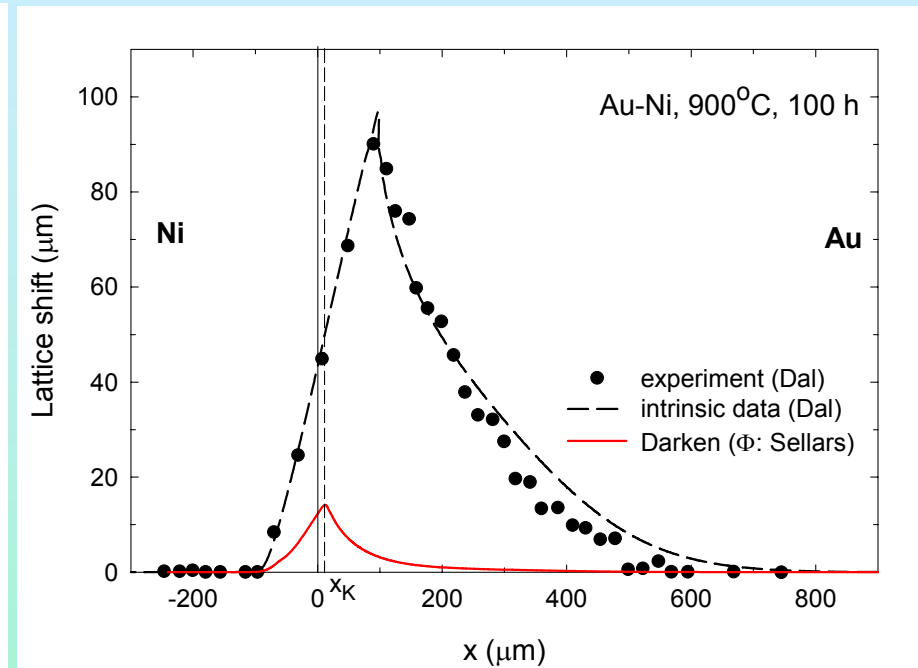
Darken:  $D^{\circ}$

➤ Predicted interdiffusion coefficient reasonably close to data

# Assessing Darken Relations for Au-Ni with Simulation



Concentration profile



Lattice shift profile

➤ Differences between predicted and experimental  $D_{Au}$  results in large differences in lattice shift profiles

### 3. B: Darken Relations in Cu-Ni-Zn at 900°C

Intrinsic fluxes in a multicomponent system ( $i = 1, 2, \dots, c$ ):

$$J_i = -L_{ii} \cdot \frac{d}{dx} \mu_i = -c_i \cdot M_i \cdot \frac{d}{dx} \mu_i = -\frac{Dt_i}{R \cdot T} \cdot c_i \cdot \frac{d}{dx} \mu_i = -Dt_i \cdot \frac{X_i}{V} \cdot \frac{d}{dx} \ln(a_i)$$

$Dt_i$  = tracer diffusion coefficient of component i

$\mu_i$  = chemical potential of i;

$a_i$  = activity of i

$V$  = molar volume;

$X_i$  = mole fraction of i

$$J_i = \frac{-Dt_i}{V} \cdot X_i \cdot \left( \frac{\Phi_{ii}}{X_i} \cdot \frac{d}{dx} X_i + \sum_{j=1 \neq i}^{c-1} \frac{\Phi_{ij}}{X_j} \cdot \frac{d}{dx} X_j \right)$$

$$\Phi_{ij} = \frac{d}{d \ln(X_j)} \ln(a_i)$$

$\Phi_{ij}$  = thermodynamic factors obtained from Gibbs free energy of phase

# Darken Relations in Cu-Ni-Zn: contd.

## Intrinsic fluxes in a ternary:

$$J_1 = \frac{-Dt_1}{V} \cdot X_1 \cdot \left( \frac{\Phi_{11}}{X_1} \cdot \frac{d}{dx} X_1 + \frac{\Phi_{12}}{X_2} \cdot \frac{d}{dx} X_2 \right)$$

$$J_2 = \frac{-Dt_2}{V} \cdot X_2 \cdot \left( \frac{\Phi_{22}}{X_2} \cdot \frac{d}{dx} X_2 + \frac{\Phi_{21}}{X_1} \cdot \frac{d}{dx} X_1 \right)$$

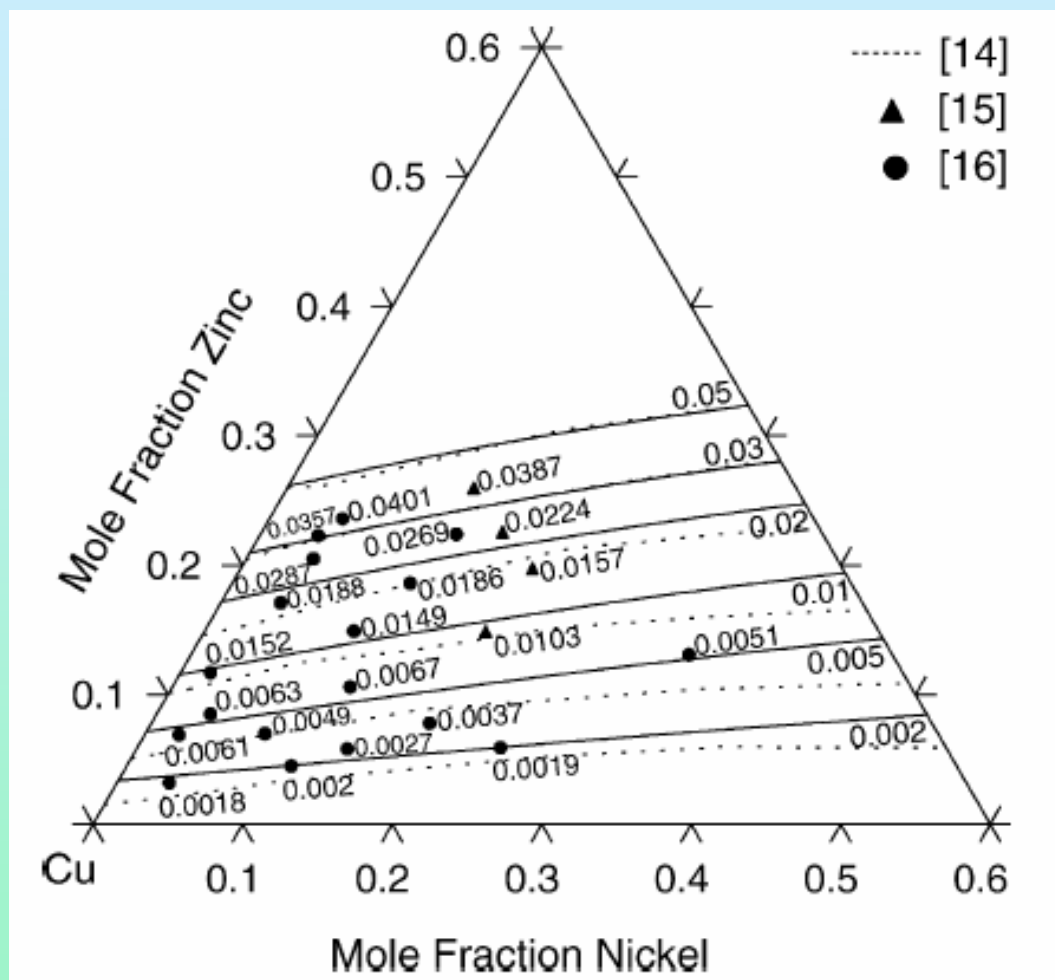
$$J_3 = \frac{Dt_3}{V} \cdot \left[ X_1 \cdot \left( \frac{\Phi_{11}}{X_1} \cdot \frac{d}{dx} X_1 + \frac{\Phi_{12}}{X_2} \cdot \frac{d}{dx} X_2 \right) + X_2 \cdot \left( \frac{\Phi_{22}}{X_2} \cdot \frac{d}{dx} X_2 + \frac{\Phi_{21}}{X_1} \cdot \frac{d}{dx} X_1 \right) \right]$$

## Relation between thermodynamic factors

$$\Phi_{21} = \frac{X_1}{(1 - X_1)} \cdot \left( \frac{1 - X_2}{X_2} \cdot \Phi_{12} + \Phi_{22} - \Phi_{11} \right)$$

# Cu-Ni-Zn: Thermo

Jiang, Ishida *et al.*, *J. Phys. Chem. Sol.*, 2004, in print



Isoactivity curves of Zn in fcc-CuNiZn at 727°C  
(liq. Zn ref.)

$${}^0 L_{\text{Cu,Ni}}^{\text{Fcc\_Al}} = +8047.72 + 3.42217T$$

$${}^1 L_{\text{Cu,Ni}}^{\text{Fcc\_Al}} = -2041.3 + 0.99714T$$

$${}^0 T_{\text{cCu,Ni}}^{\text{Fcc\_Al}} = -935.5$$

$${}^1 T_{\text{cCu,Ni}}^{\text{Fcc\_Al}} = -594.9$$

$${}^0 \beta_{\text{Cu,Ni}}^{\text{Fcc\_Al}} = -0.7316$$

$${}^1 \beta_{\text{Cu,Ni}}^{\text{Fcc\_Al}} = -0.3174$$

$${}^0 L_{\text{Cu,Zn}}^{\text{Fcc\_Al}} = -42803.75 + 10.02258T$$

$${}^1 L_{\text{Cu,Zn}}^{\text{Fcc\_Al}} = +2936.39 - 3.05323T$$

$${}^2 L_{\text{Cu,Zn}}^{\text{Fcc\_Al}} = +9034.2 - 5.39314T$$

$${}^0 L_{\text{Ni,Zn}}^{\text{Fcc\_Al}} = -58399.17 + 10.13337T$$

$${}^1 L_{\text{Ni,Zn}}^{\text{Fcc\_Al}} = -21974.79 + 16.38475T$$

$${}^2 L_{\text{Ni,Zn}}^{\text{Fcc\_Al}} = +30855.63 - 19.71684T$$

$${}^0 T_{\text{cNi,Zn}}^{\text{Fcc\_Al}} = -815$$

$${}^0 \beta_{\text{Ni,Zn}}^{\text{Fcc\_Al}} = -1.46$$

$${}^0 L_{\text{Cu,Ni,Zn}}^{\text{Fcc\_Al}} = -8614 + 15T$$

$${}^1 L_{\text{Cu,Ni,Zn}}^{\text{Fcc\_Al}} = +55000 - 20T$$

$${}^2 L_{\text{Cu,Ni,Zn}}^{\text{Fcc\_Al}} = -55000 + 10T$$

# Cu-Ni-Zn: Thermodynamics contd.

**Redlich-Kister model for Gibbs excess free energy:**

$$\Delta G_{\alpha \text{ mix}_{\text{xs}}} = X_1 \cdot X_2 \cdot L_{\alpha 12}(X_1, X_2, T) + X_1 \cdot X_3 \cdot L_{\alpha 13}(X_1, X_3, T) + X_2 \cdot X_3 \cdot L_{\alpha 23}(X_2, X_3, T) \dots \\ + X_1 \cdot X_2 \cdot X_3 \cdot L_{\alpha 123}(X_1, X_2, X_3, T)$$

$$L_{\alpha 12}(X_1, X_2, T) = L_{\alpha 0 12}(T) + L_{\alpha 1 12}(T) \cdot (X_1 - X_2)^1 + L_{\alpha 2 12}(T) \cdot (X_1 - X_2)^2$$

$$L_{\alpha 123}(X_1, X_2, X_3, T) = X_1 \cdot L_{\alpha 0 123}(T) + X_2 \cdot L_{\alpha 1 123}(T) + X_3 \cdot L_{\alpha 2 123}(T)$$

**Partial molal Gibbs free energy:**

$$\Delta G_{\text{xs}_k} = \Delta G_{\text{mix}_{\text{xs}}} + \frac{d}{dX_k} \Delta G_{\text{mix}_{\text{xs}}} - \sum_{j=1}^c X_j \cdot \frac{d}{dX_j} \Delta G_{\text{mix}_{\text{xs}}}$$

# Cu-Ni-Zn: Tracer diffusion

$$\log(Dt_{\text{Cu}}) = -3.53 \cdot X_{\text{Ni}}^{1.16} + 3.6 \cdot X_{\text{Zn}}^{1.02} - 9.46$$

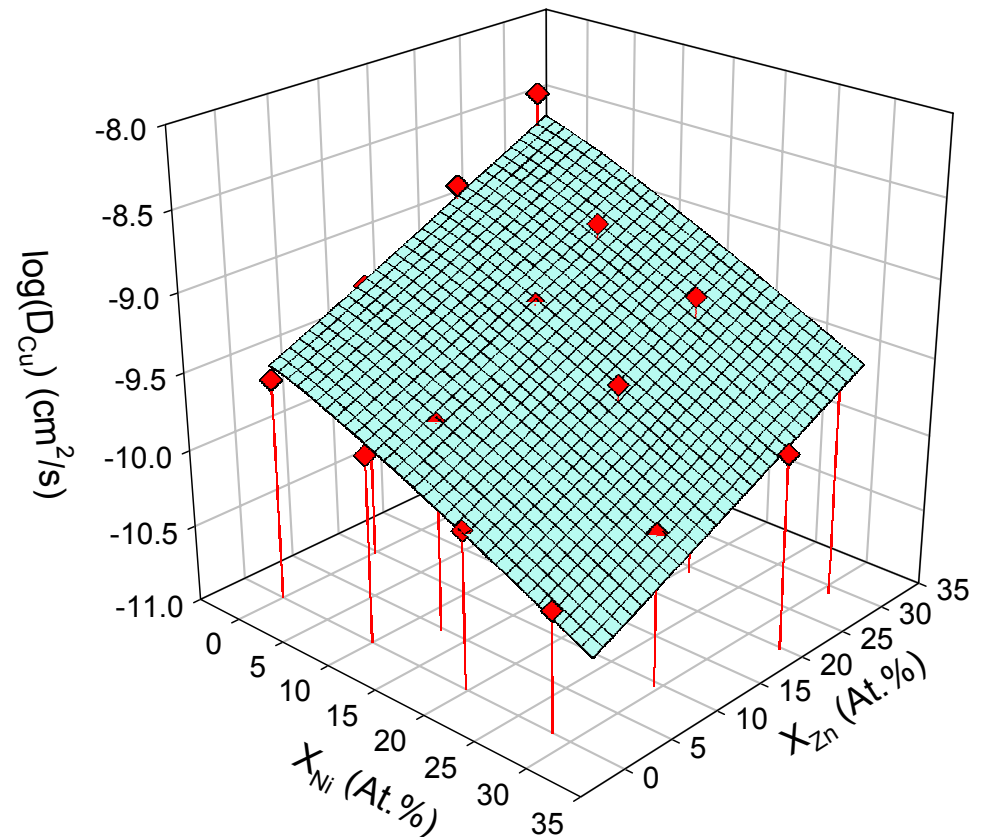
$$\log(Dt_{\text{Ni}}) = -4.05 \cdot X_{\text{Ni}}^{1.3} + 3.28 \cdot X_{\text{Zn}}^{1.07} - 9.96$$

$$\log(Dt_{\text{Zn}}) = -3.2 \cdot X_{\text{Ni}} + 5.21 \cdot X_{\text{Zn}}^{1.25} - 9$$

$$D_{\text{Zn}}^* > D_{\text{Cu}}^* > D_{\text{Ni}}^*$$

Similar composition dependence

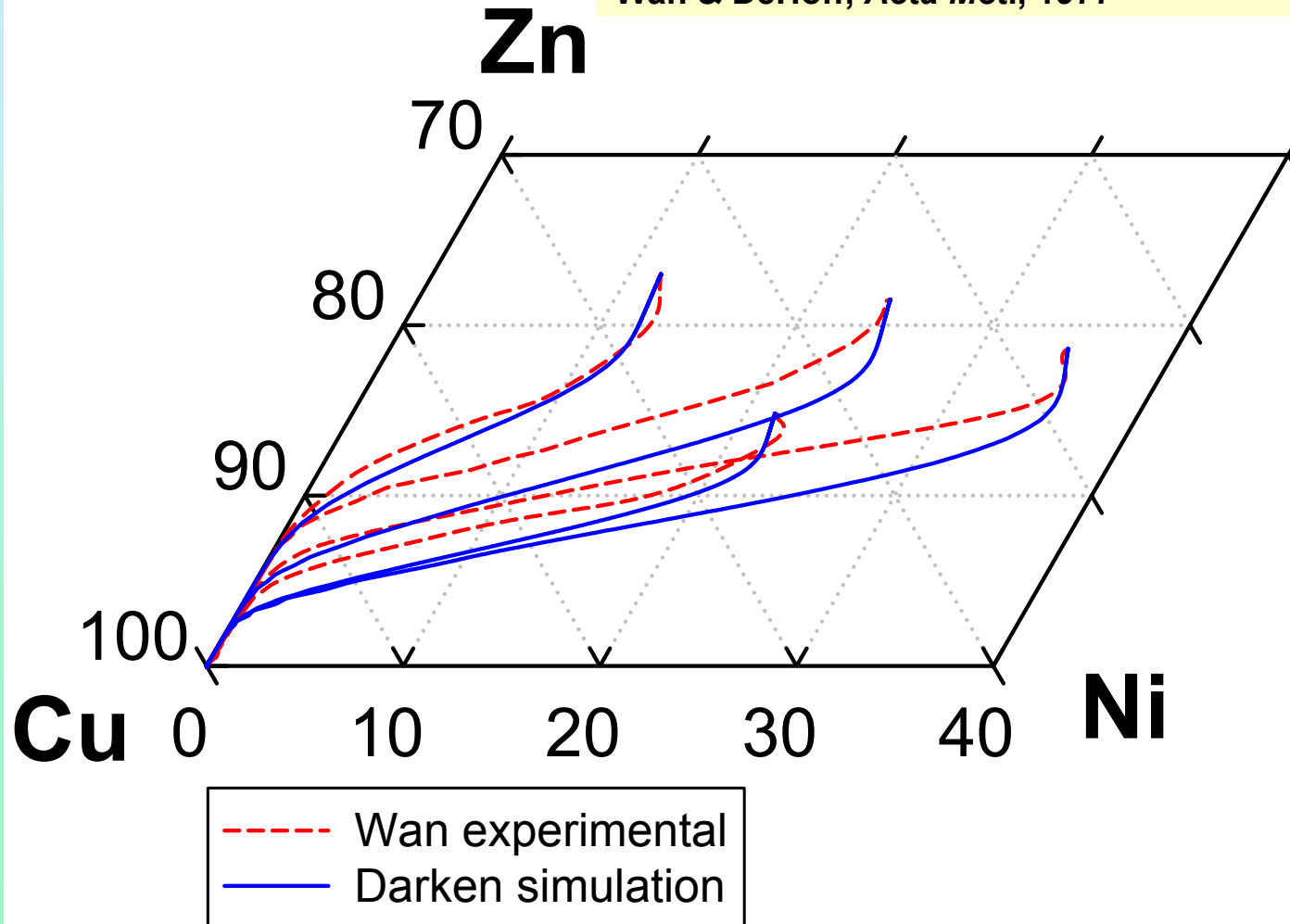
Anusavice & DeHoff, *Met. Trans. A.*, 1972





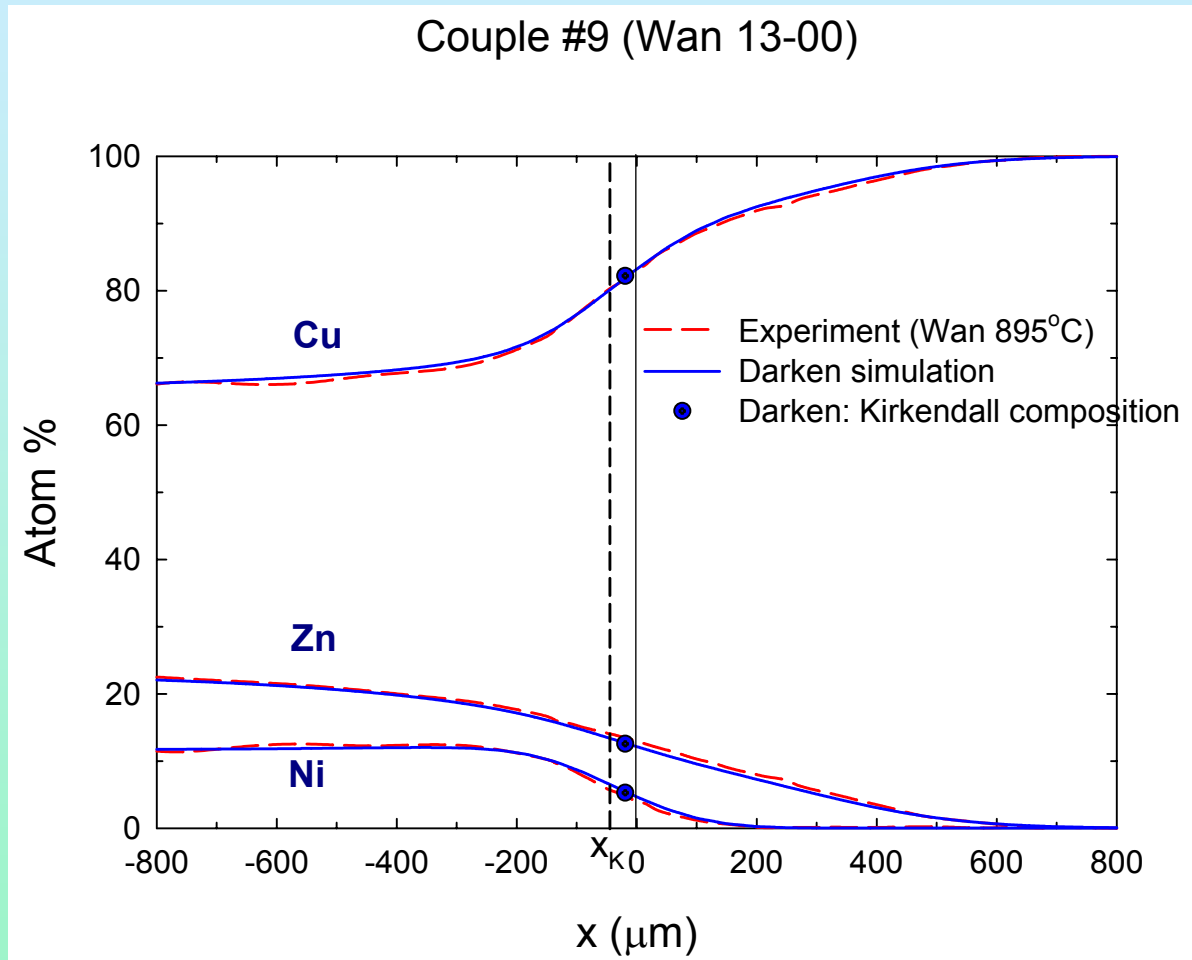
# Darken relations in Cu-Ni-Zn: Composition paths at 900°C

Wan, *Ph.D. Thesis*, Univ. of Florida, 1972  
Wan & DeHoff, *Acta Met.*, 1977

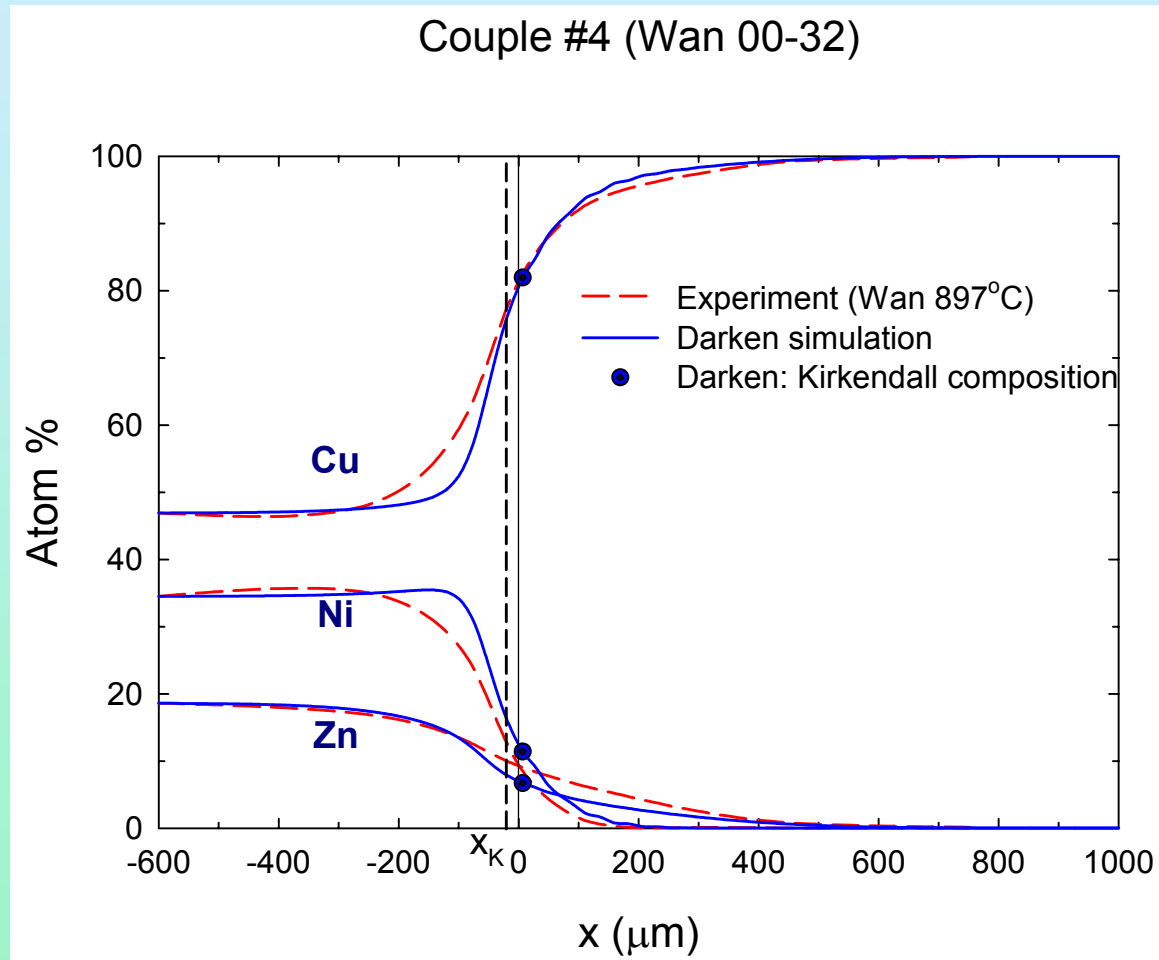


#4,5,7,9

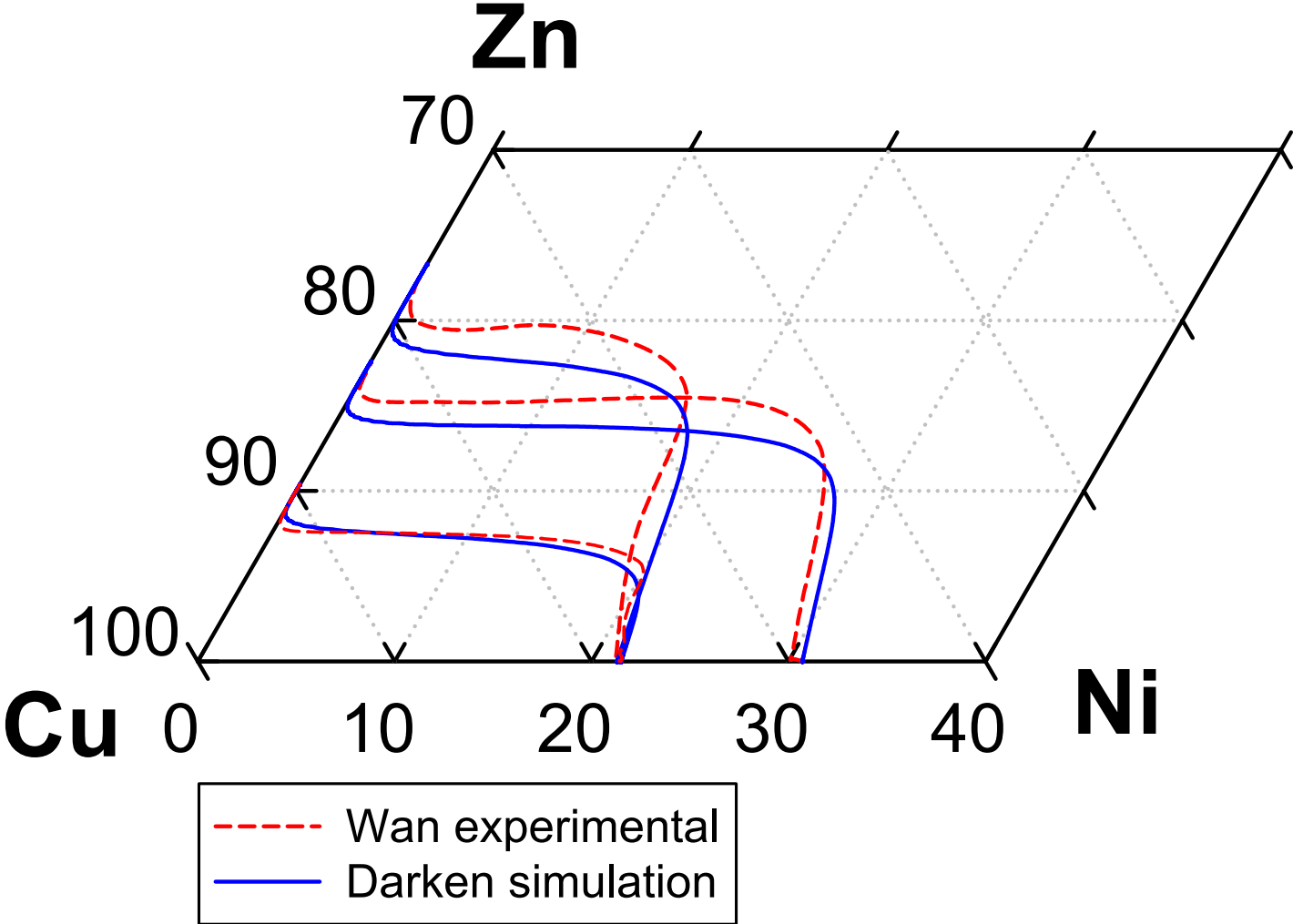
# Cu-Ni-Zn: Concentration profiles



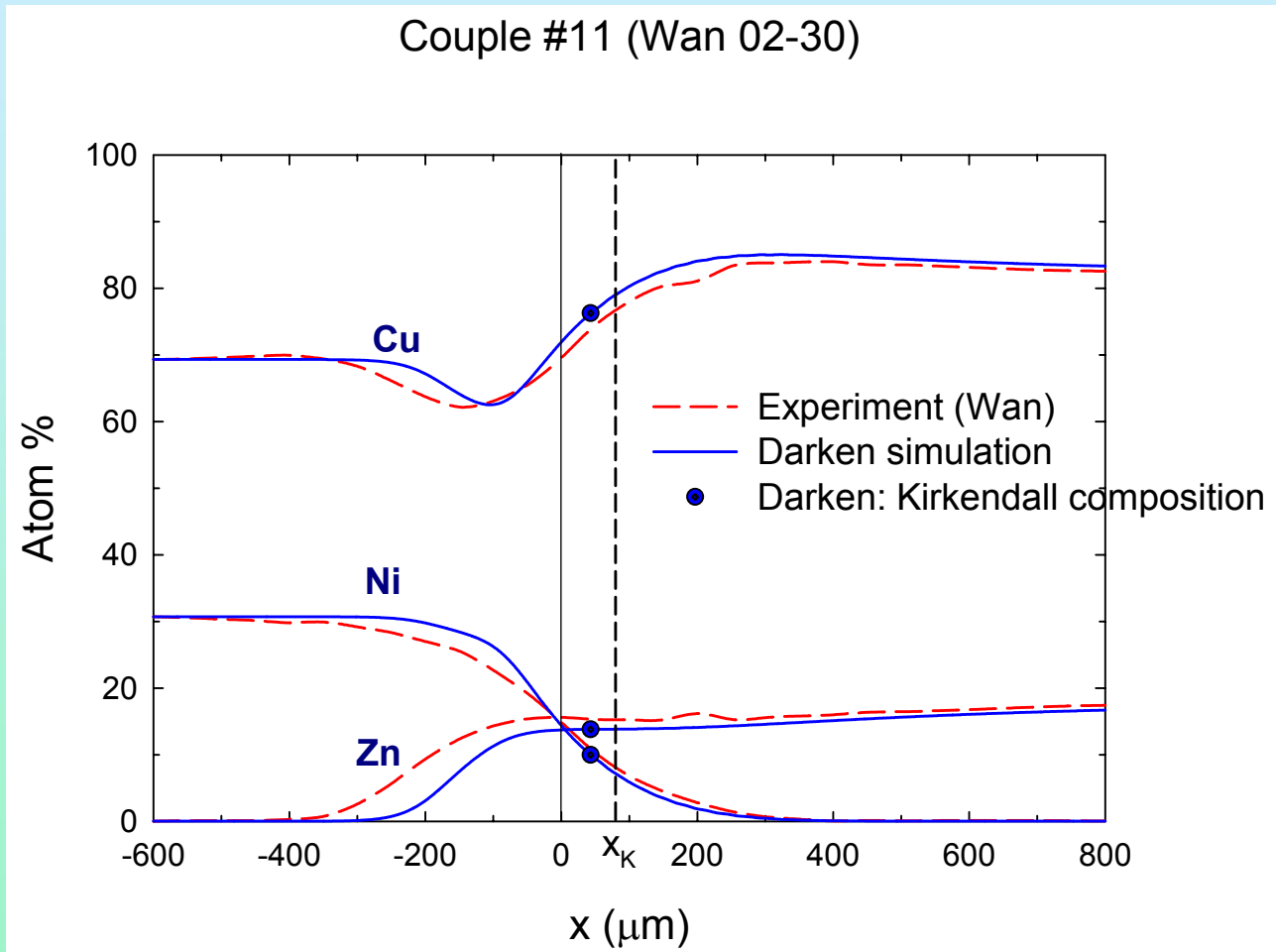
# Cu-Ni-Zn: Concentration profiles



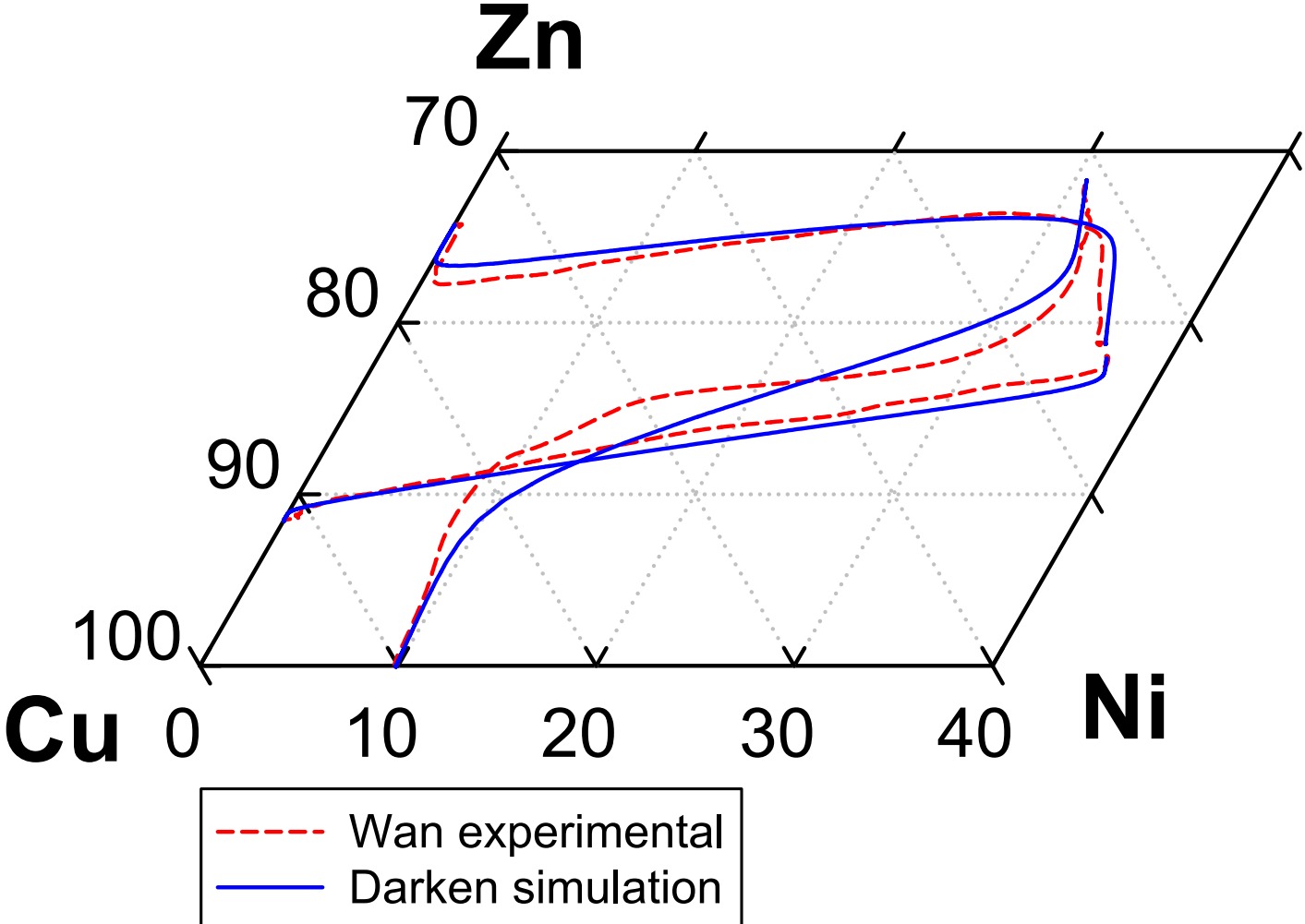
# Composition paths Cu-Ni-Zn contd.



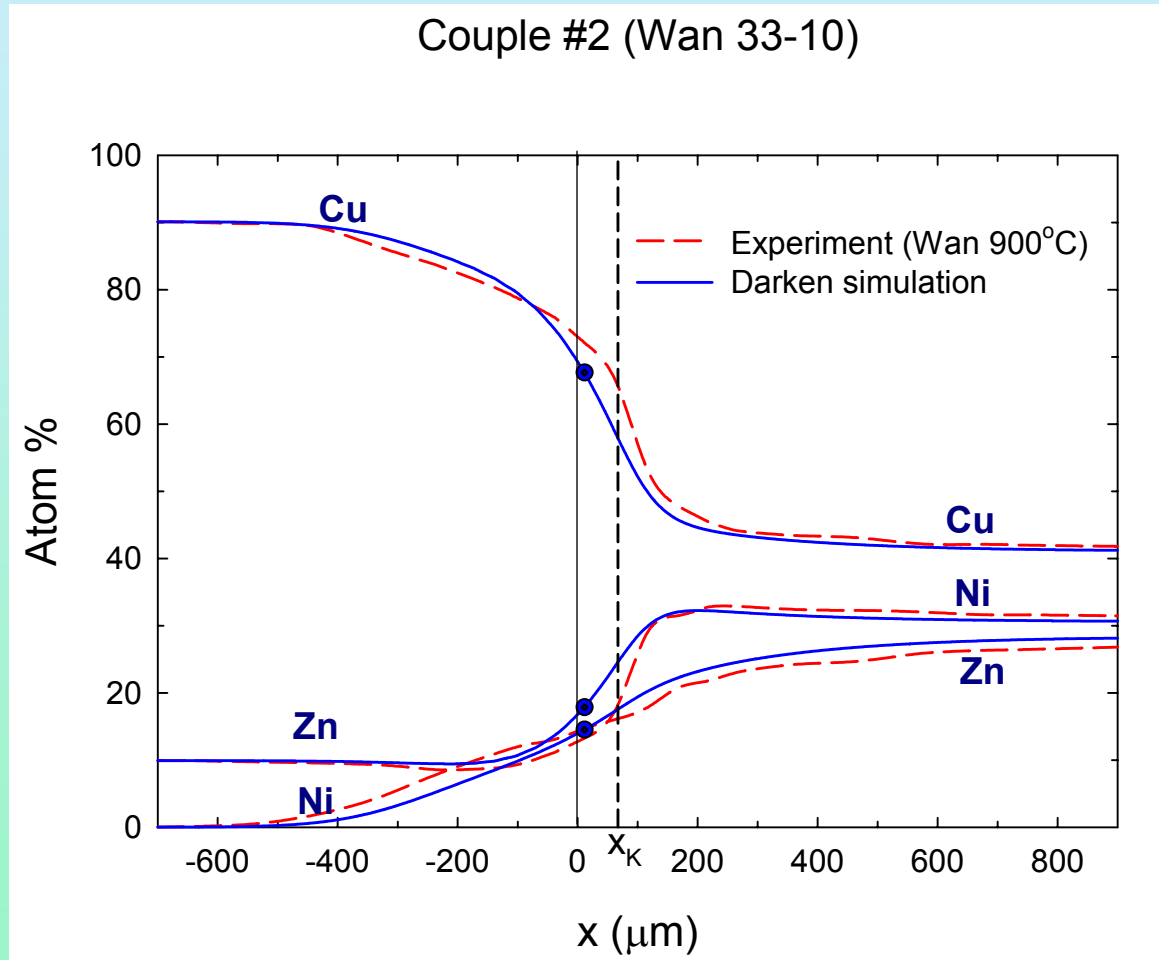
# Cu-Ni-Zn: Concentration profiles



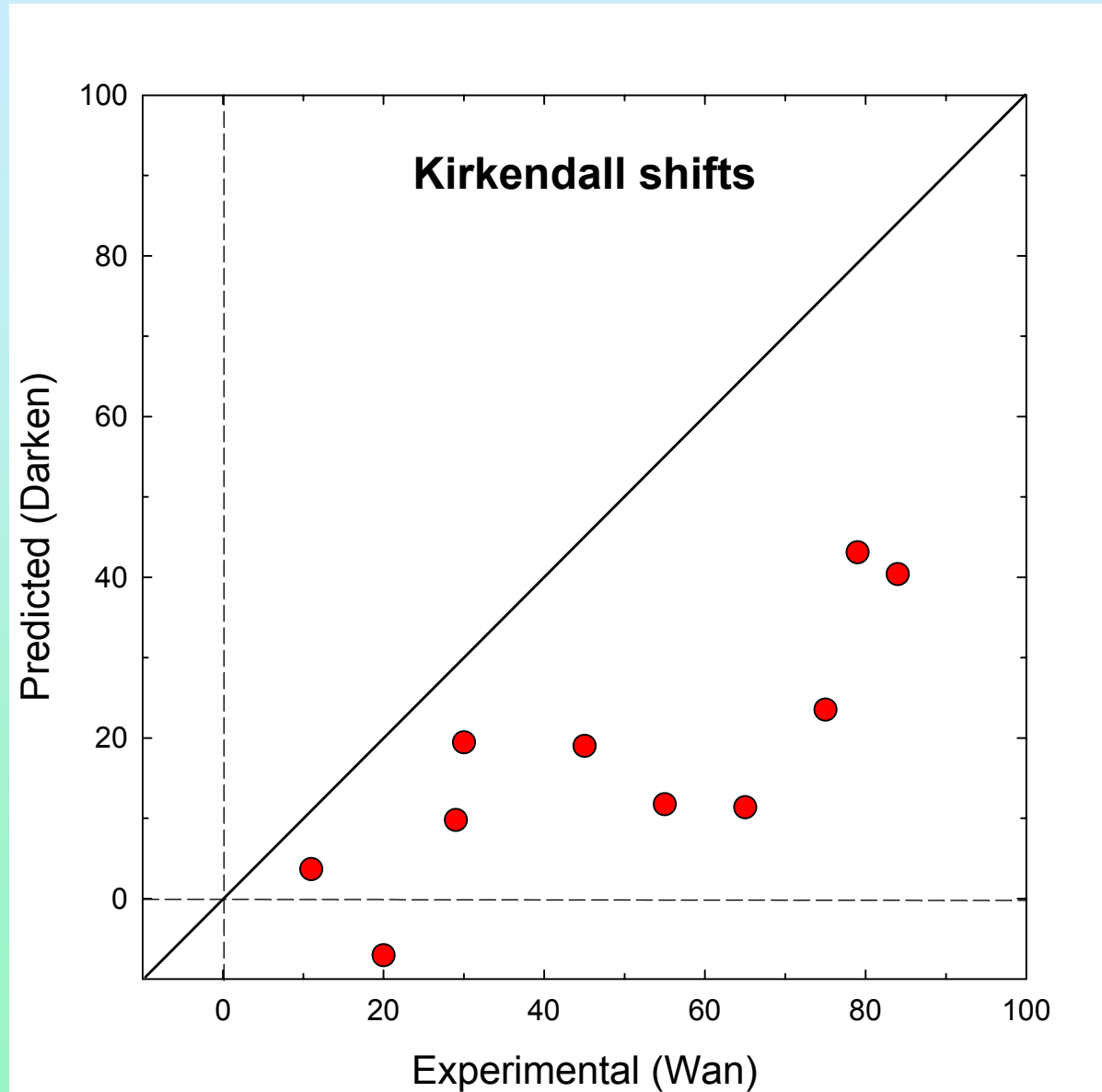
# Composition paths Cu-Ni-Zn contd.



# Cu-Ni-Zn: Concentration profiles



# Kirkendall Shift Comparison





# 4. Conclusions

- In the binary Au-Ni and the ternary Cu-Ni-Zn system, Darken relations result in
  - Reasonable concentration profiles; however
  - Kirkendall shifts are noticeably underestimated
  - Manning relations in Cu-Ni-Zn to be explored
- Intrinsic simulation powerful tool for testing quality of experimental data & various diffusion formalisms with their associated assumptions
  - Need to explore intermetallic phases with broad solubility ranges where vacancy concentrations & fluxes are likely to be important

## Alternate approach

- A *kinetic approach* based on tracer jump frequencies has also been found to have the same level of success in predicting diffusion paths in Cu-Ni-Zn using the same simulation
  - However the Kirkendall shifts are overestimated
  - But no thermodynamics necessary; tracer diffusion coefficients sufficient

## 5. On development of multicomponent diffusion databases

- Tracer diffusion data vital for high-quality databases
- More experimental efforts in this direction needed
  - But need not use radioactive isotopes
  - **Stable isotopes** (except Al) combined with mass spectrometry may be used instead (errors?)\*
- Explore use of combinatorial techniques for sample preparation and automated analysis of tracer (stable) isotope profiles

\* Schmidt, Schmalzried *et al.*, “Self-diffusion of B in TiB<sub>2</sub>,” *J. App. Phys.*, 2003

# **John Morral's other contributions...** **(thermodynamics, oxidation, solidification, phase diagrams, coarsening, etc.)**

- Morral & Davies, "Thermodynamics of Isolated Miscibility Gaps," *J. Chimie Phys. Physico-Chimie Bio*, 1997.
- Morral & Purdy, "Thermodynamics of Particle Coarsening," *J. Alloys & Comp.*, 1995.
- Hennessey & Morral, "Oxidation & Nitridation of Niobium in Air above 1150°C," *Oxid. Met.*, 1992.
- Morral & Gupta, "Phase-boundary, ZPF, and Topological Lines on Phase Diagrams," *Scripta Met.*, 1991.
- Gupta, Morral & Nowotny, "Constructing Multicomponent Phase Diagrams by Overlapping ZPF Lines," *Scripta Met.*, 1986.
- Pati & Morral, "The Effect of Quenching on Mushy Zone Microstructures," *Met. Trans. A*, 1986.
- Cameron & Morral, "The Solubility of Boron in Iron," *Met. Trans. A*, 1986.
- Ohriner & Morral, "Precipitate Distribution in Sub-Scales," *Scripta Met.*, 1979.
- Morral & Asby, "Dislocated Cellular Structures," *Acta Met.*, 1974.
- Morral & Cahn, "Spinodal Decomposition in Ternary Systems," *Acta Met.*, 1971.
- Morral, "Characterizing Stability Limits in Ternary Systems," *Acta Met.*, 1972.

**... and many more**