Intrinsic Diffusion Simulation for Tests of Darken-Manning Relations

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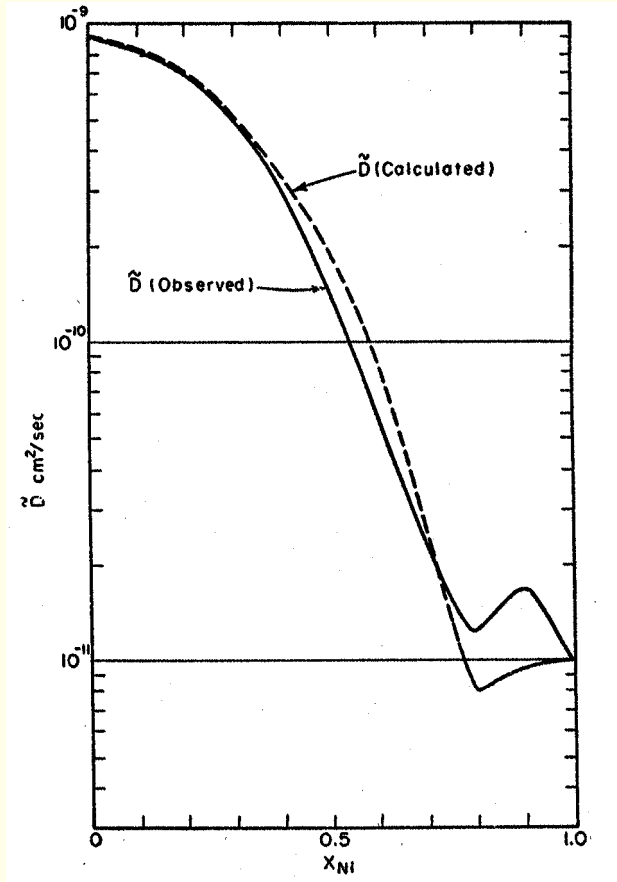
NIST Diffusion Workshop
April 19, 2005



Overview

1. **Diffusion Formalisms & Simplifications**
2. **Intrinsic Diffusion Simulation**
   - **Model System**
3. **Tests of Darken Relations**
   - **A: Binary : *i. Cu-Zn, ii. Au-Ni, iii. Cu-Ni***
   - **B: Ternary: *Cu-Ni-Zn***
4. **Conclusions**
5. **Future Work**

1. Diffusion Formalisms: A. Interdiffusion

- **Isothermal, isobaric system**

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

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

- **Multicomponent version of Fick's law**

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

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

B. Intrinsic Diffusion Formalism

- **Fluxes defined in the lattice frame**

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

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

- **Multicomponent version of Darken's equation**

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

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

Simplified Version of Formalism

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

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

  - ***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**

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

Simplified Formalism: Questions

- **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***

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

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

Manning Relations

- **Corrections to Darken relations based on detailed consideration of phenomenological equations**

Intrinsic diffusion

$$D_A = D_A^* \Phi (1 + V_A)$$

$$D_B = D_B^* \Phi (1 - V_B)$$

Interdiffusion

$$D^o = (X_B D_A^* + X_A D_B^*) \Phi S$$

$$S = 1 + \frac{2 X_A X_B (D_A^* - D_B^*)^2}{M_o (X_A D_B^* + X_B D_A^*)(X_A D_A^* + X_B D_B^*)}$$

Vacancy wind terms

$$V_A = \frac{2 X_A}{M_o} \left(\frac{D_A^* - D_B^*}{X_A D_A^* + X_B D_B^*} \right)$$

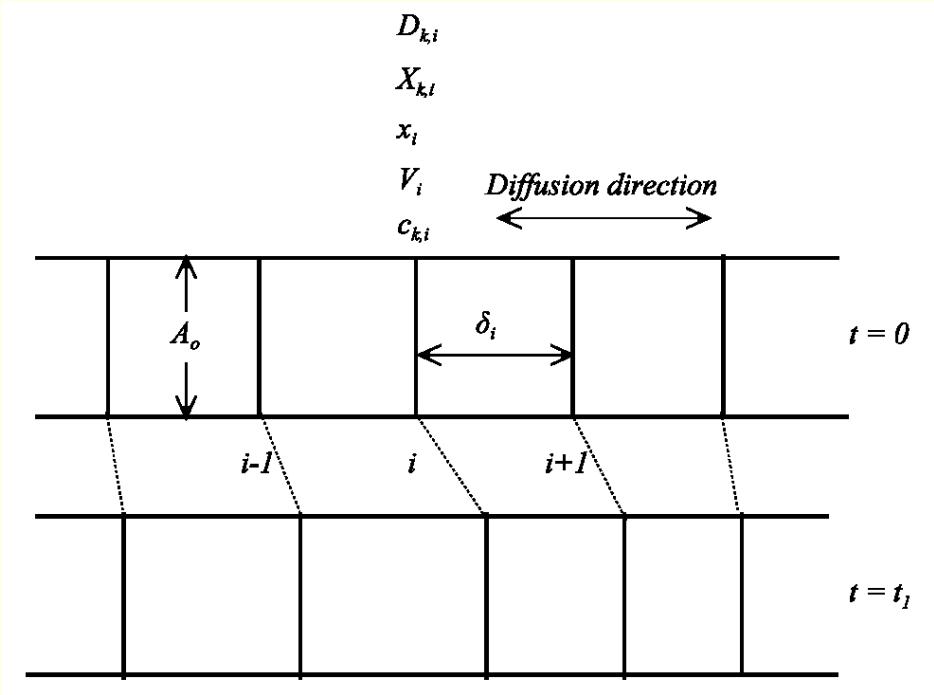
$$V_B = \frac{2 X_B}{M_o} \left(\frac{D_A^* - D_B^*}{X_A D_A^* + X_B D_B^*} \right)$$

M_o = 7.15 for fcc

➢ ***In most cases (fcc), Manning corrections are minor and within the realm of experimental error***

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

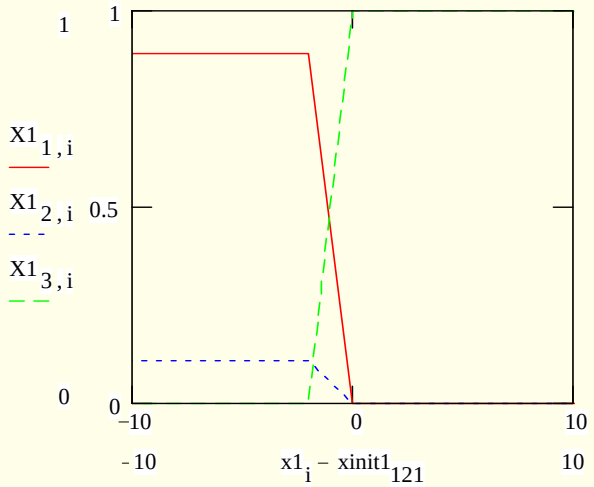
1. **Initial concentration distribution for each component**
2. **Depending upon the formalism, kinetic descriptors as a function of composition, temperature or other variables**
3. **Thermodynamics of phase, if needed**
4. **Molar volume as a function of composition**



Finite difference method for semi-infinite couples

- ***Simple*** **yet effective algorithm**
- **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**

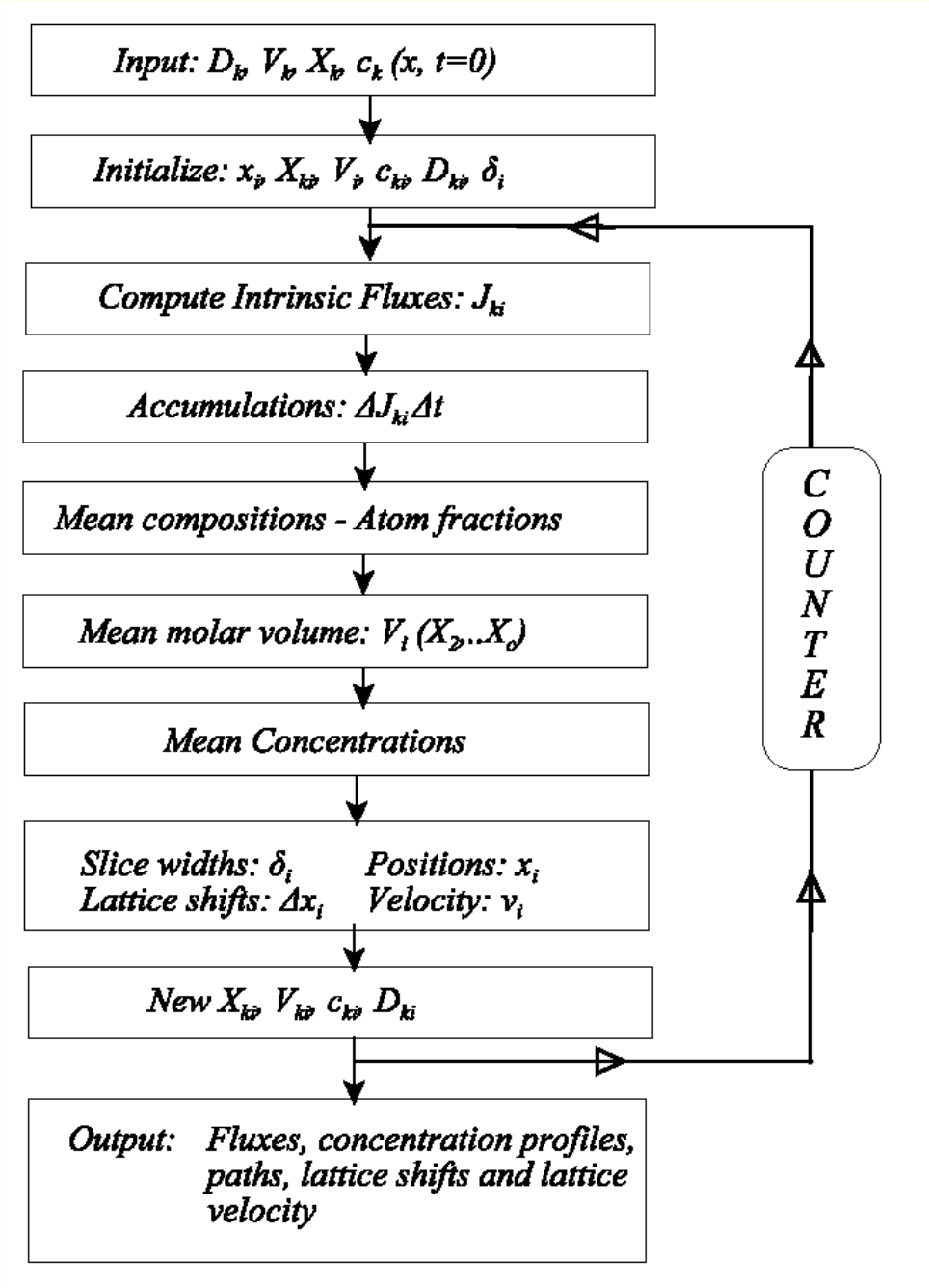
Simulation Algorithm



Initial concentrations ($c_{k,i} = X_{k,i} / V$)

$$J_{k,i}^{K} = -D_{k,i}^{K} \frac{c_{k,i+1} - c_{k,i-1}}{x_{k,i+1} - x_{k,i-1}}$$

Fluxes computed using finite difference form



Model System with Variable Molar Volume

- **$D^o = D^V$ = constant: Error function solution for c_k (x,t)**

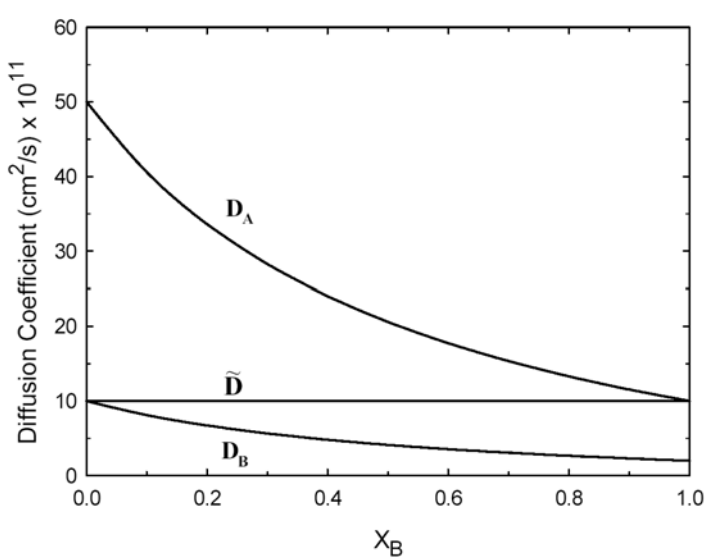
$$c_A(x) = c_A^- + (c_A^+ - c_A^-)\,cerf\left(\frac{x}{2\sqrt{\tilde{D}t}}\right)$$

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

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

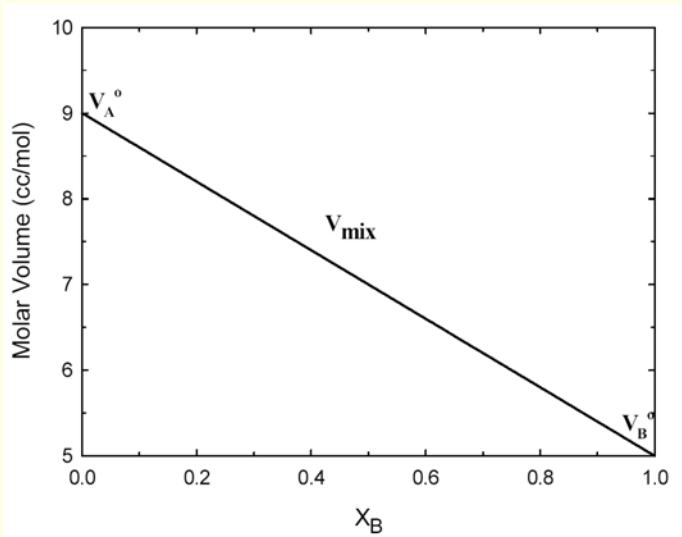
- **Ratio of intrinsic diffusion coefficients constant:**

$$R = \frac{D_A^K}{D_B^K}$$



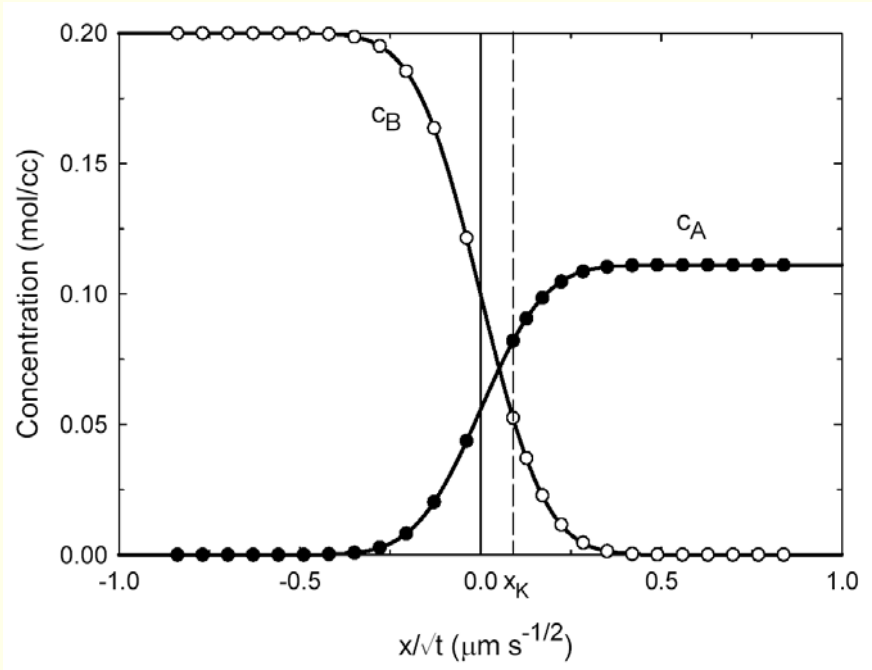
R = 5

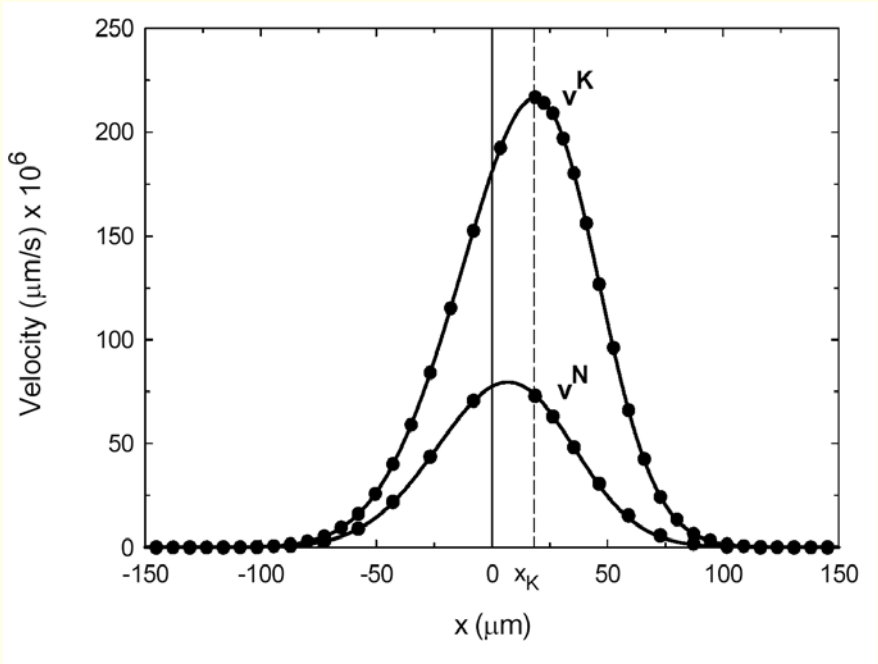
$D^o = 10^{-10}$ cm²/s



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

Simulation Output for Model System





Concentration profiles c_k (mol/cc)

Atom fraction $X_k = c_k V$

t = 12 x 3600 s

Lattice velocity (v^K)

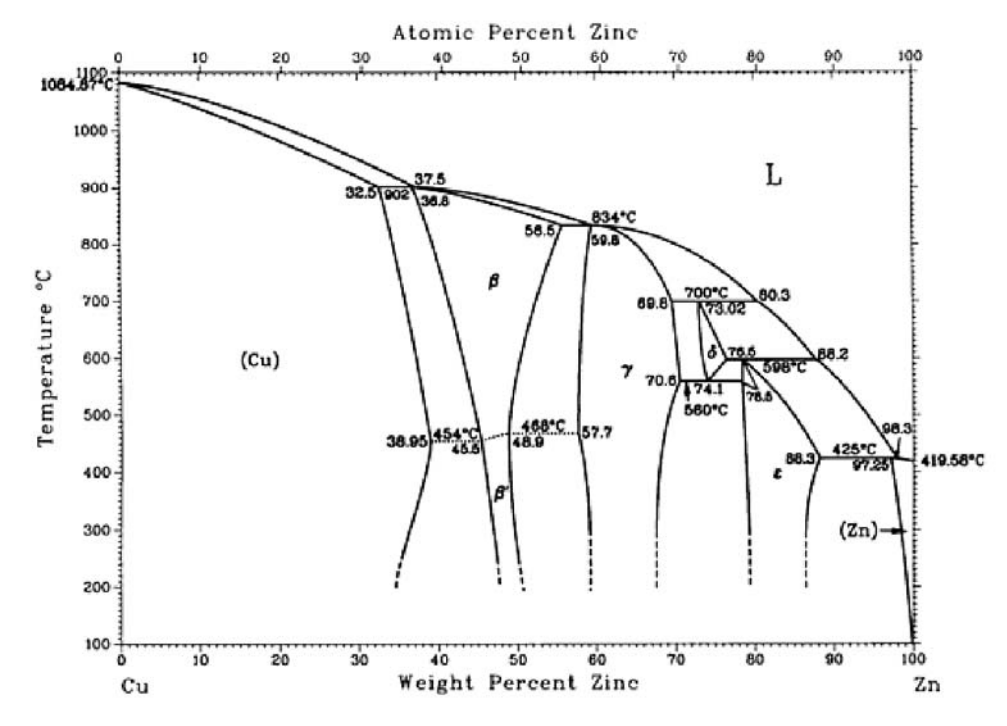
$$\boldsymbol{v}^{KV}(x) = \left[D_B^K(x) - D_A^K(x) \right] V_B^o \frac{dc_B(x)}{dx}$$

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

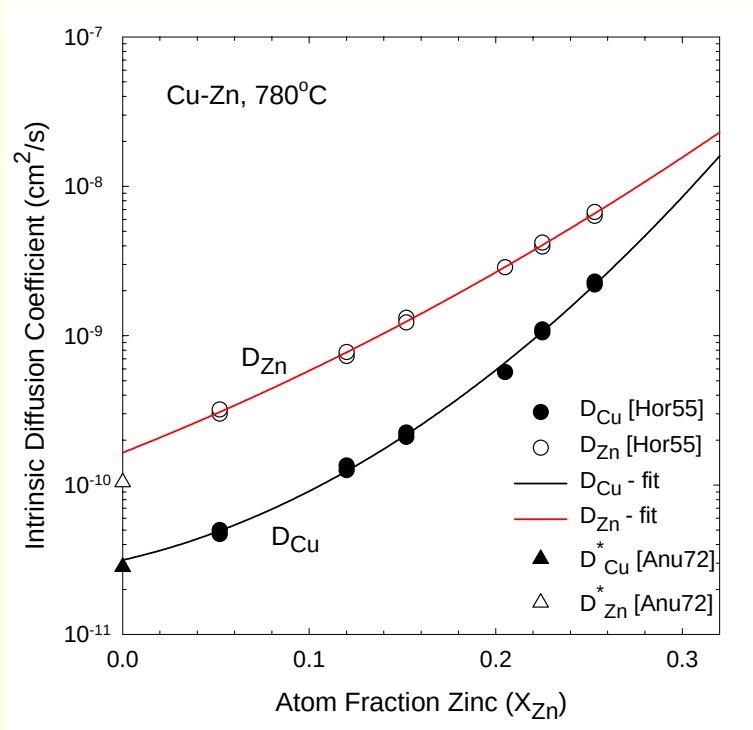
Velocity in number frame (v^N)

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

3A i. D-M Relations for Cu-Zn at 780°C



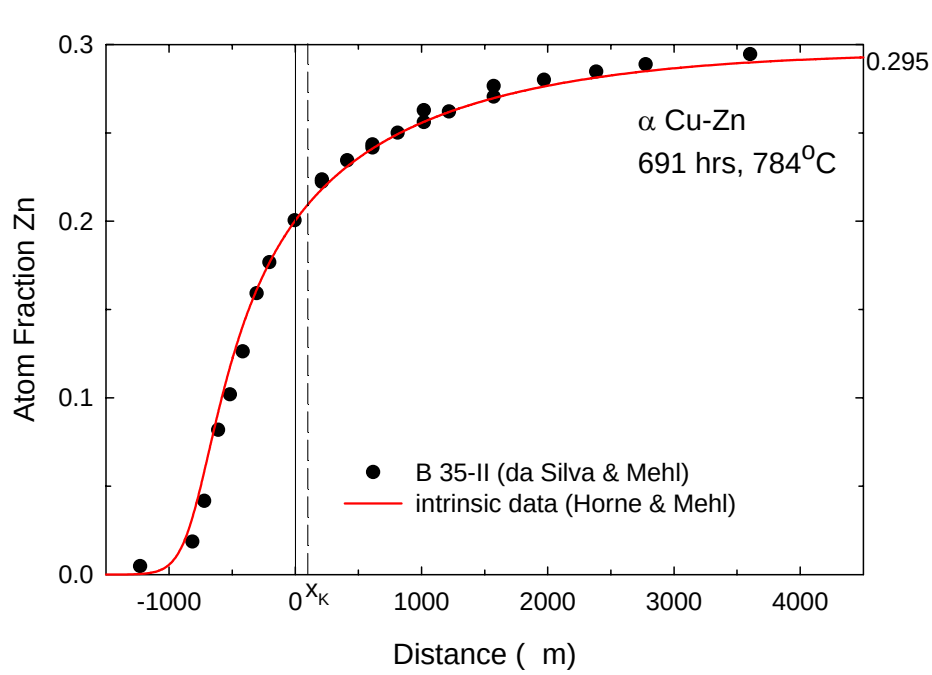
Phase diagram



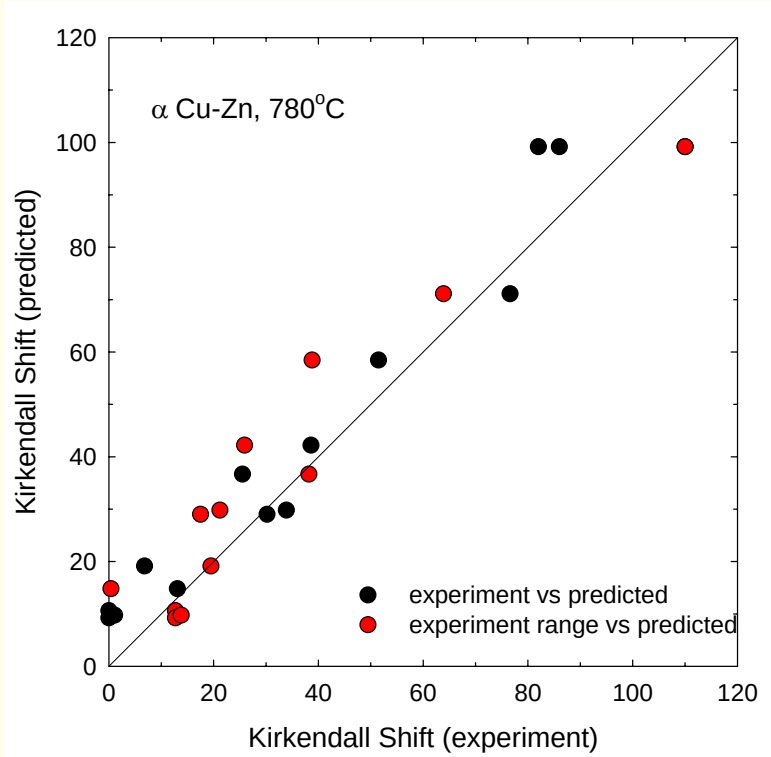
Experimental intrinsic diffusion coefficients [Horne & Mehl, Trans. AIME, 1955]

- **First system in which Kirkendall effect was demonstrated in solid state system [Smigelskas & Kirkendall, Trans. AIME, 1947]**

D-M for Cu-Zn: Assessing Experimental Data



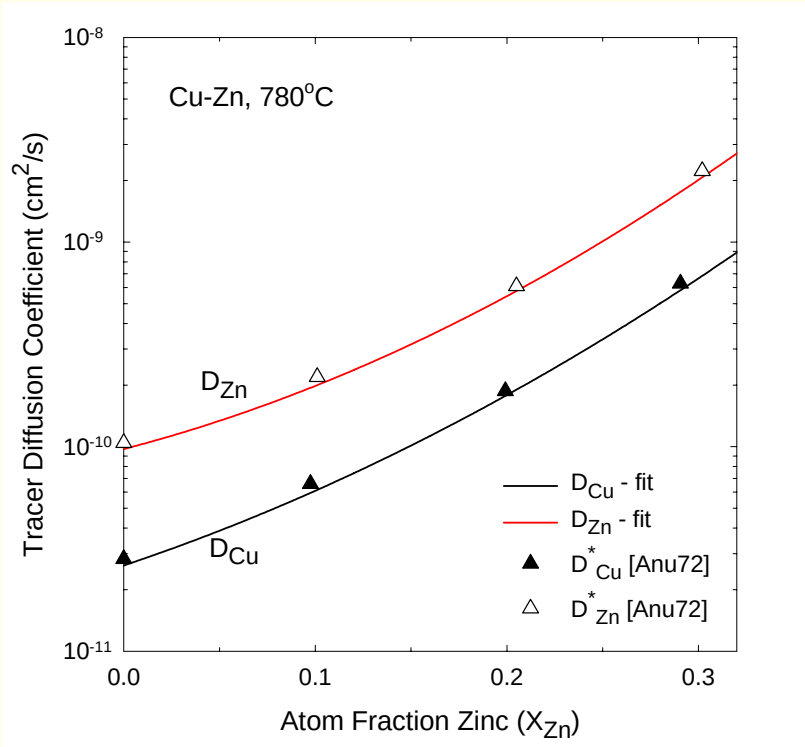
Concentration profile



Kirkendall shifts for incremental diffusion couples

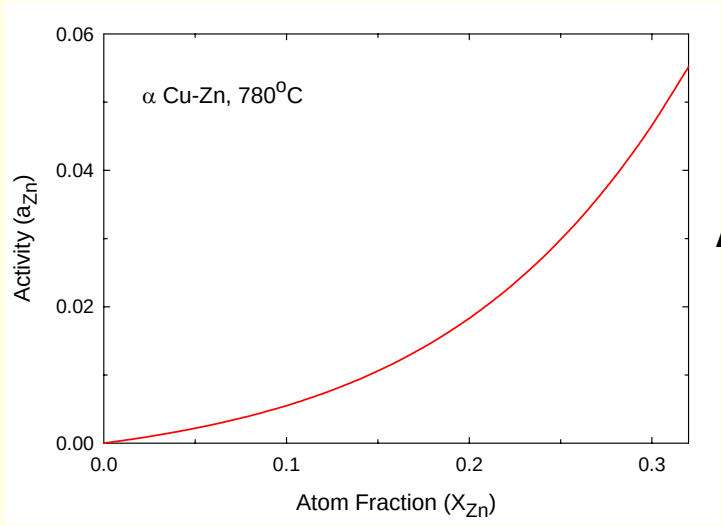
- **Quality of experimental intrinsic data appears reasonable**

D-M for Cu-Zn: Tracer & Thermodynamic Data

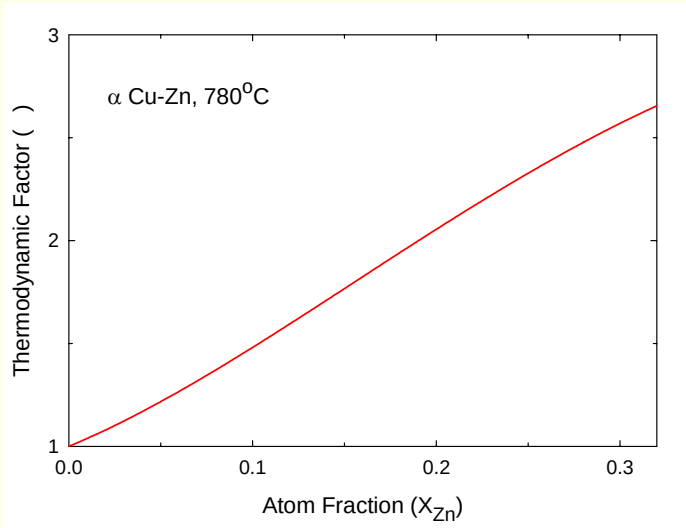


Tracer diffusion data

[Anusavice et al., Met. Trans., 1972]



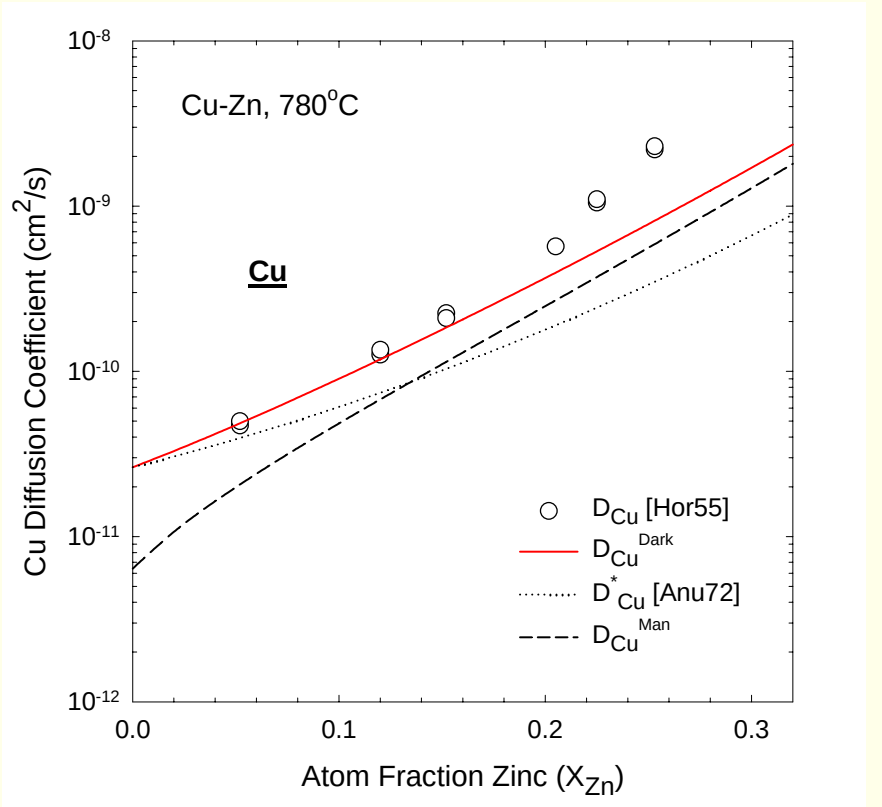
Activity Ni



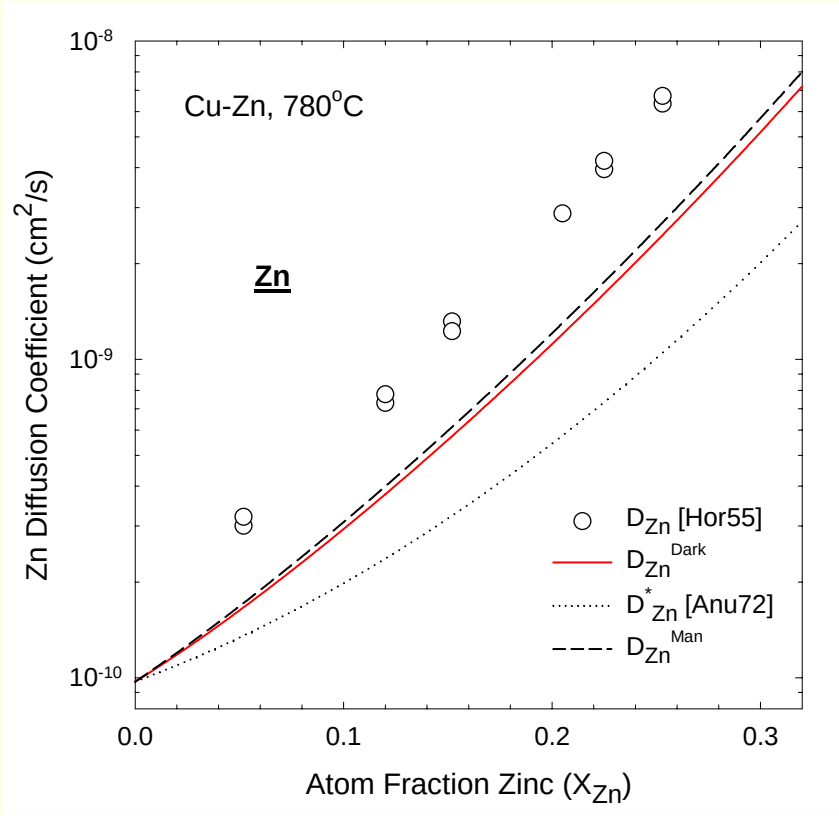
Thermodynamic assessment

[Kowalski & Spencer, J. Phase Equilib., 1993]

D-M Relations for Cu-Zn: Intrinsic Diffusion Coefficients



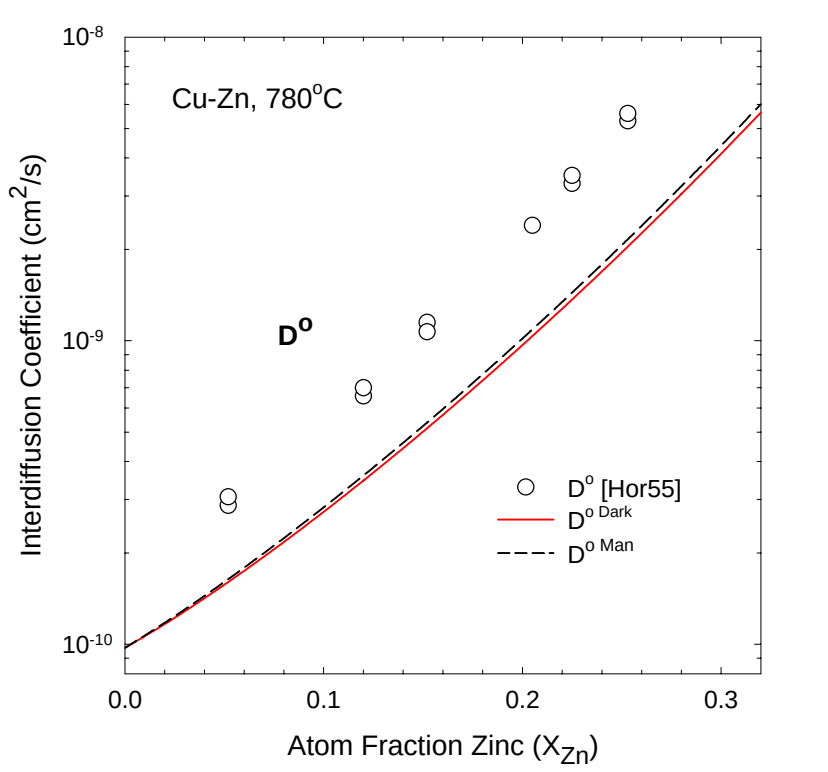
D_{Cu}



D_{Zn}

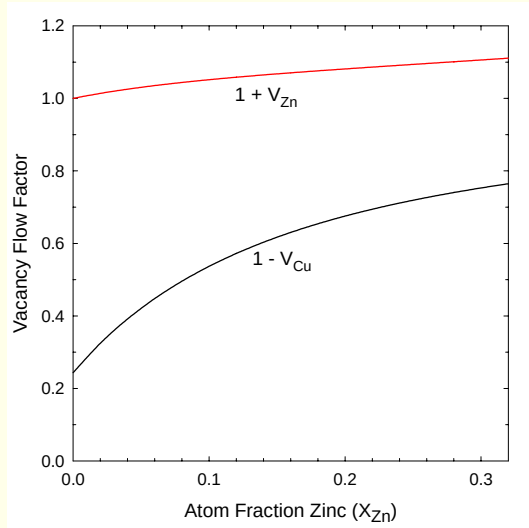
- **Problem with predicted intrinsic coefficients at high Zn compositions**

D-M Relations for Cu-Zn: Interdiffusion Coefficient & Vacancy Flow Terms

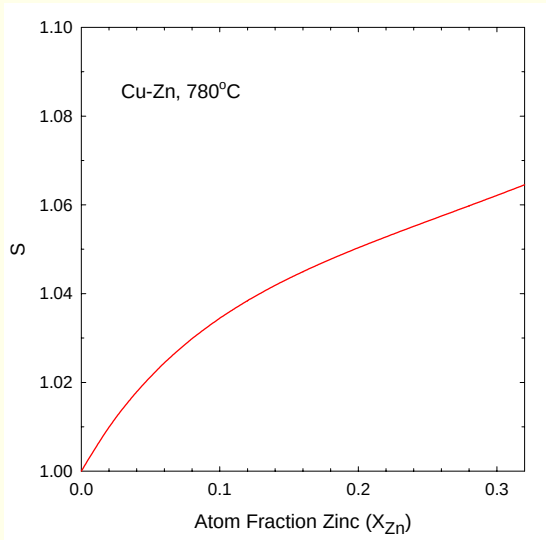


D^o

- **Predicted interdiffusion coefficient is smaller**

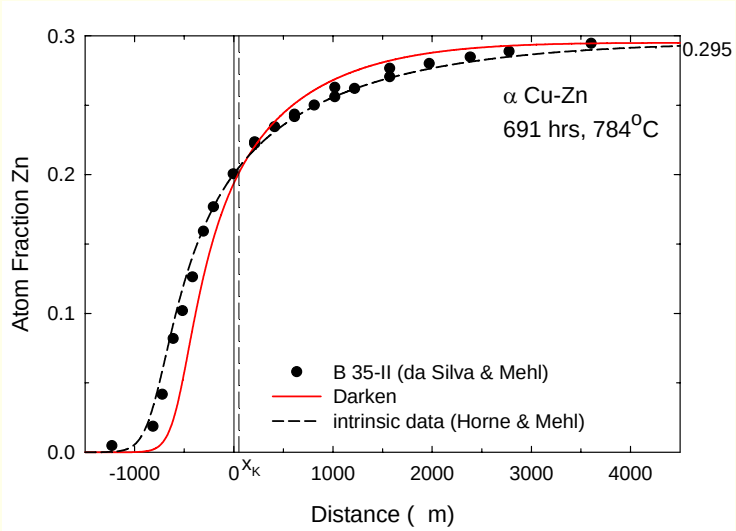


Vacancy flow terms: $1 \gtrless V_k$

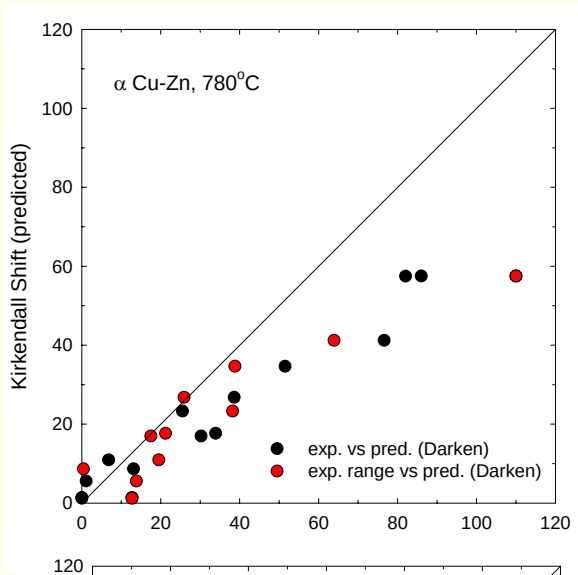


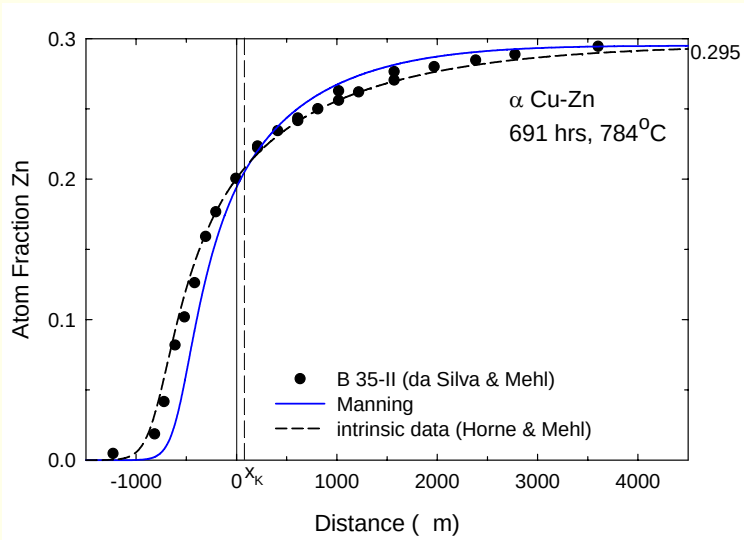
"S" correction factor for D^o

Assessing D-M Relations for Cu-Zn

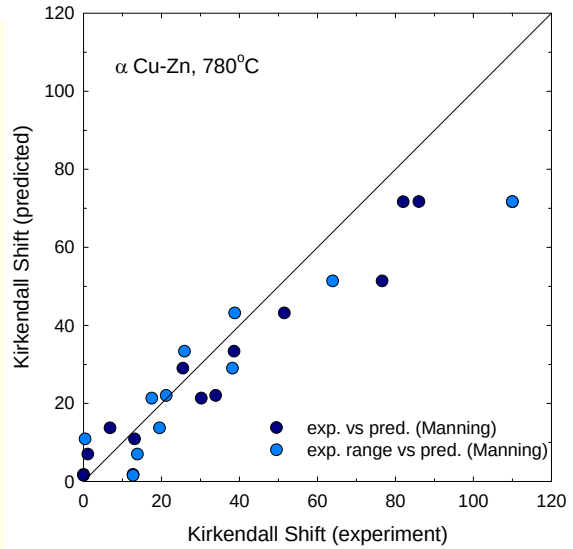


Darken





Manning

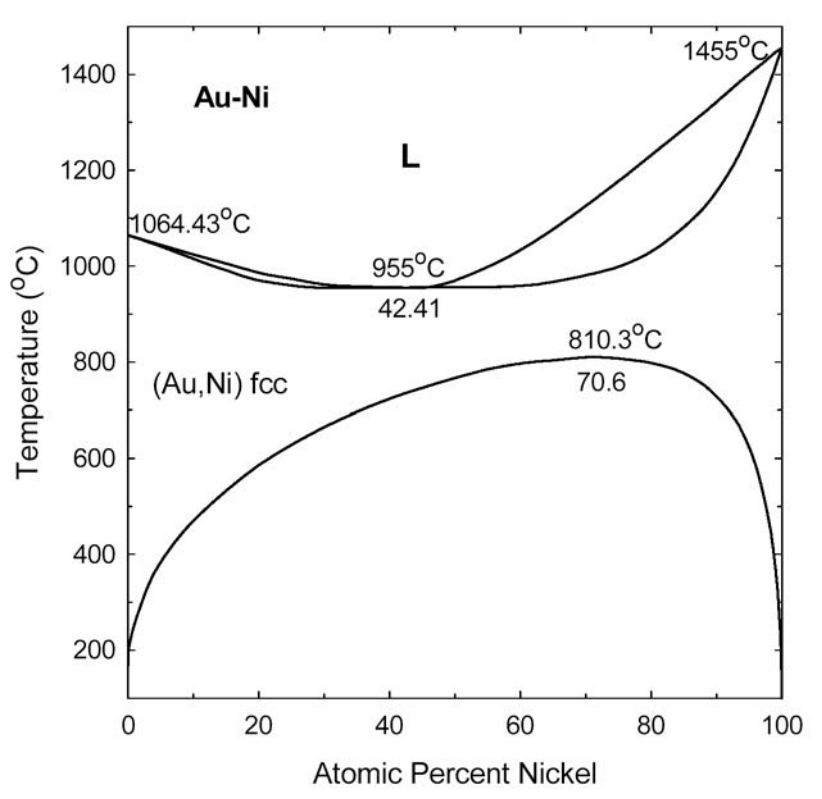


Concentration profiles

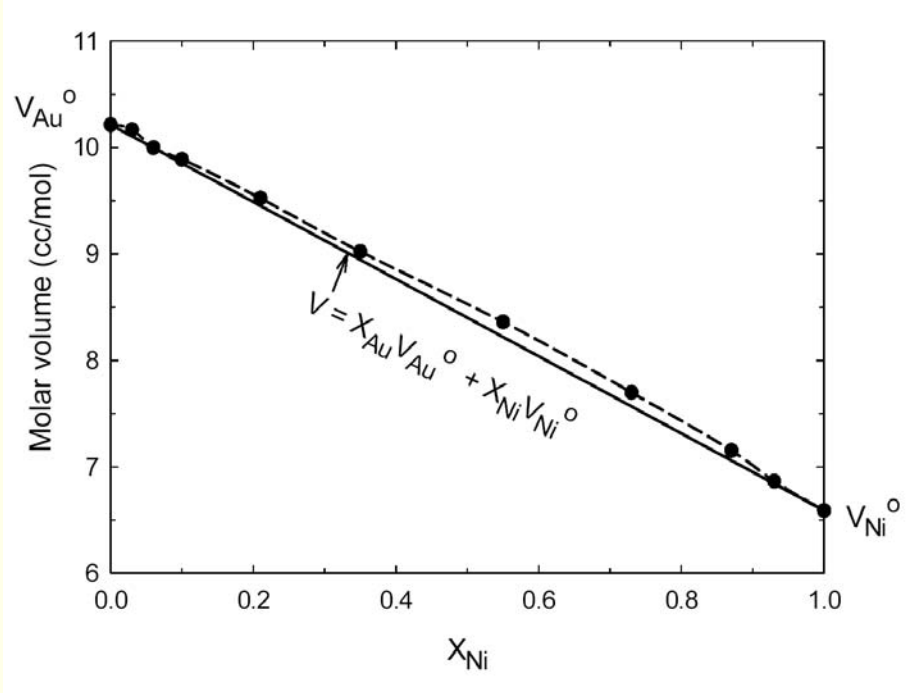
Kirkendall shifts

➢ **Differences in both concentration profiles and Kirkendall shifts**

ii. Tests of Darken Relations in Au-Ni at 900°C



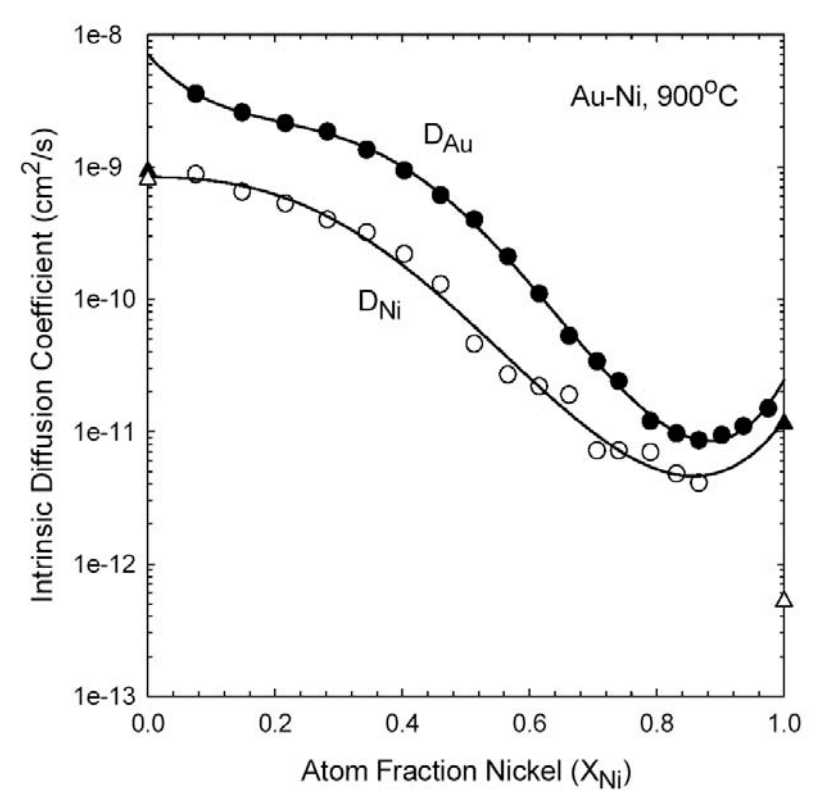
Phase diagram



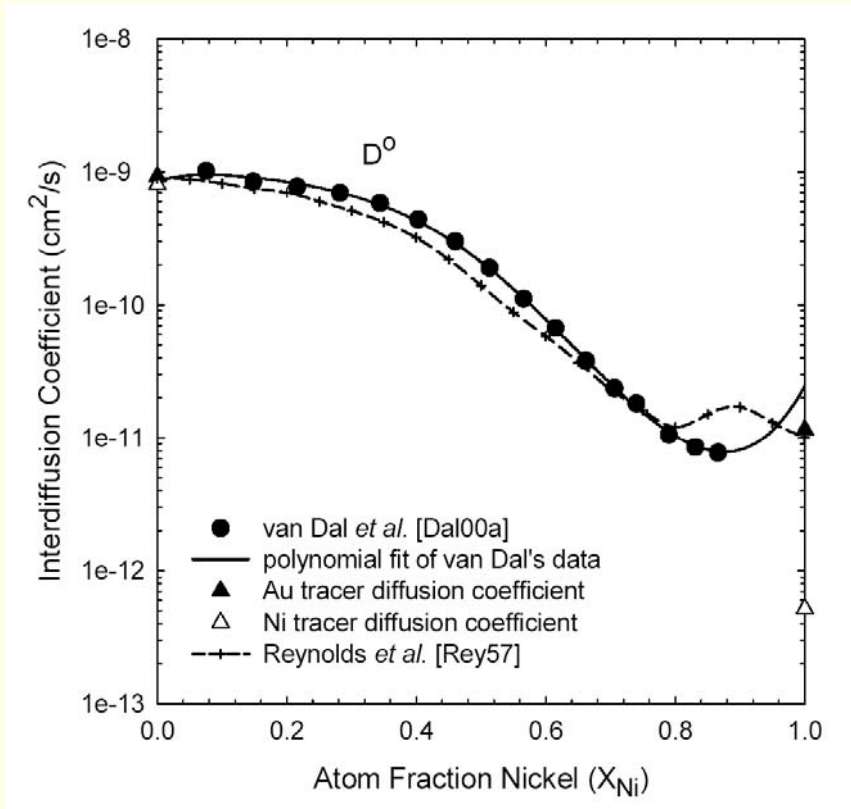
Molar volume dependence on composition (almost ideal mixing)

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

Darken Au-Ni (contd.)



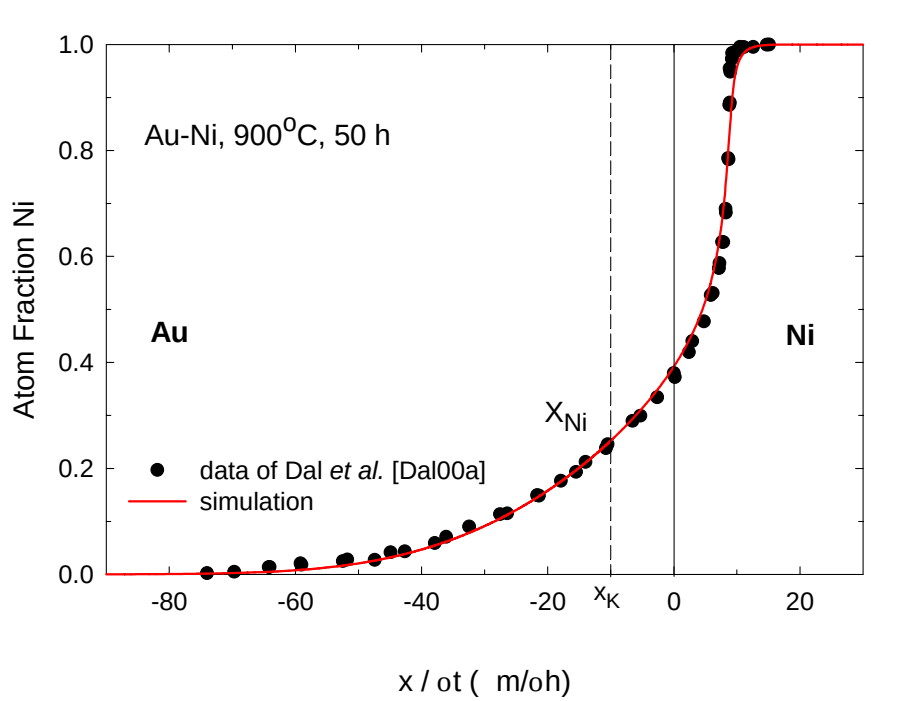
Experimental intrinsic diffusion coefficients
[Van Dal *et al.* [J. Alloys & Comp., 2000]



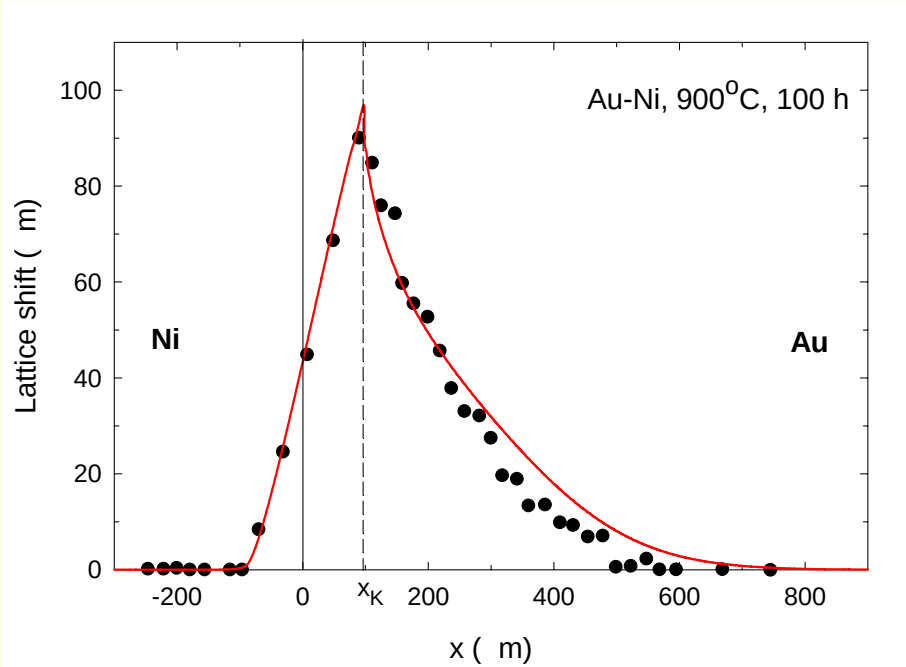
Interdiffusion coefficient

- **Polynomial functions were used to fit the intrinsic diffusion data**

Darken Au-Ni: Assessing Experimental Data



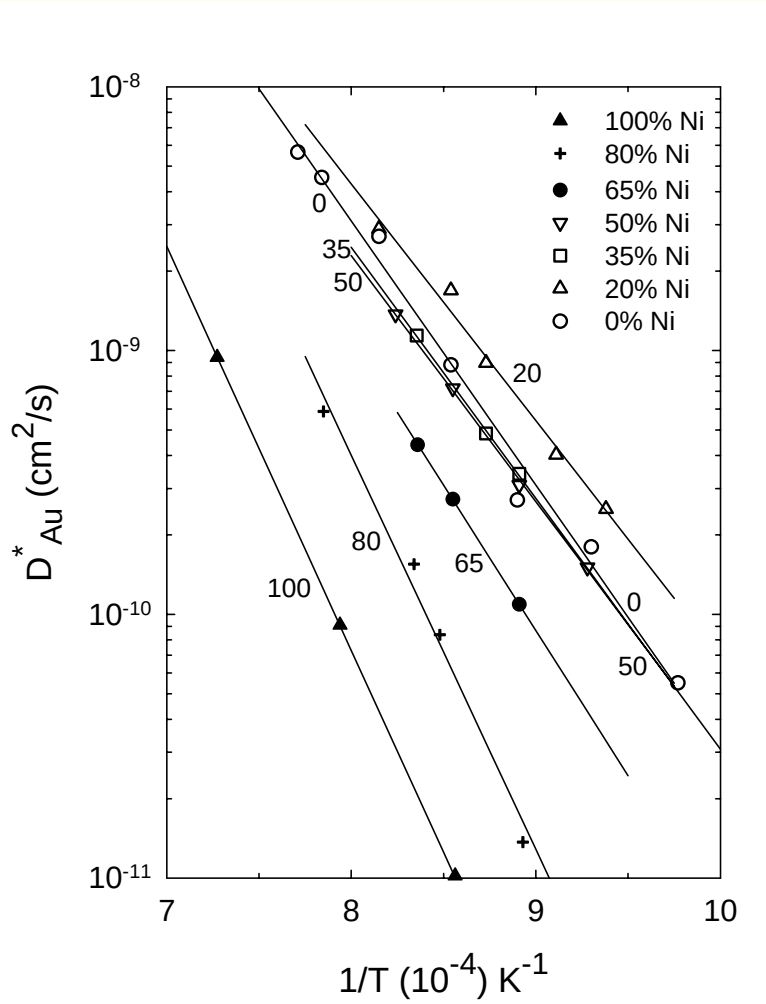
Concentration profile (6000 iterations)



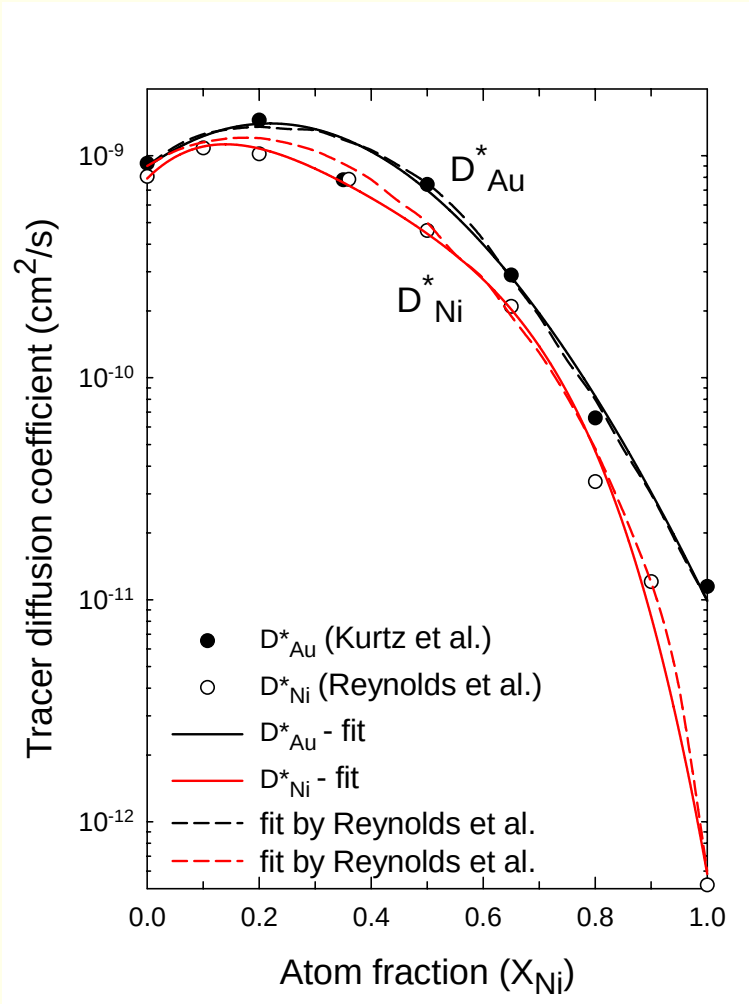
Lattice shift profile

➢ **Quality of experimental intrinsic data appears excellent**

Darken Au-Ni: Tracer Diffusion

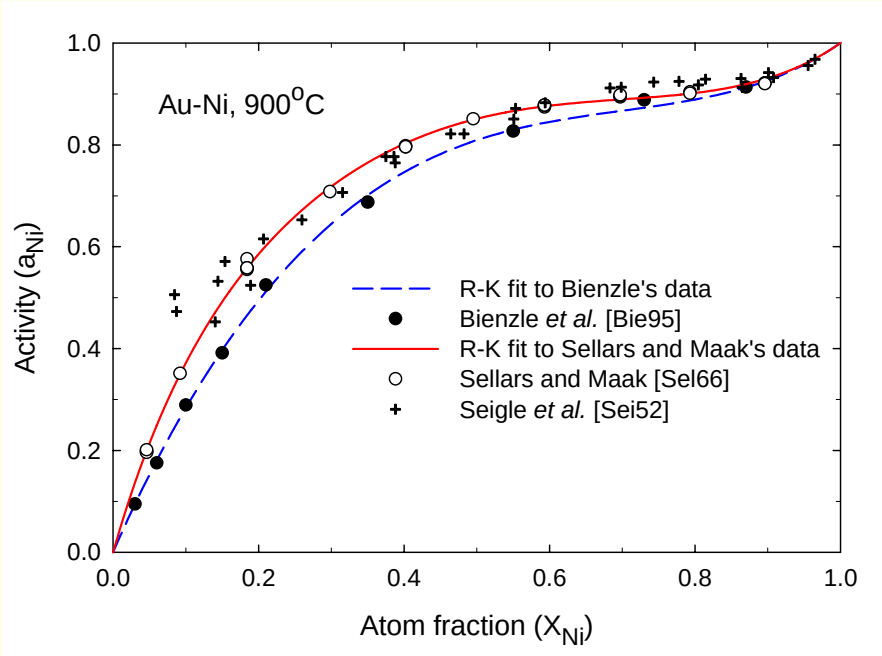


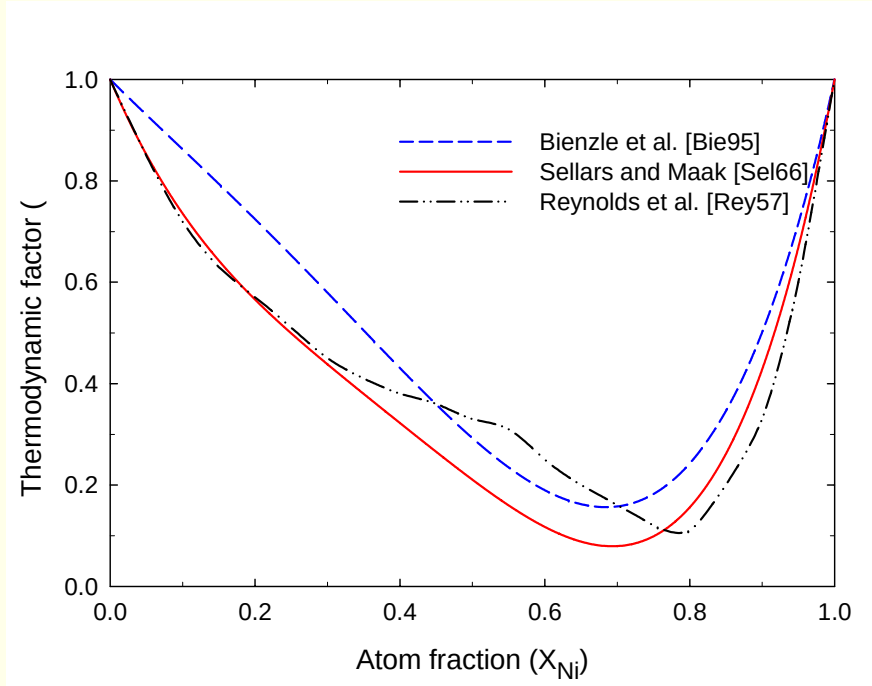
Tracer data for Au [Kurtz et al. , Acta Met., 1955]



Tracer diffusion coefficients of Au and Ni

Darken Au-Ni: Thermodynamics



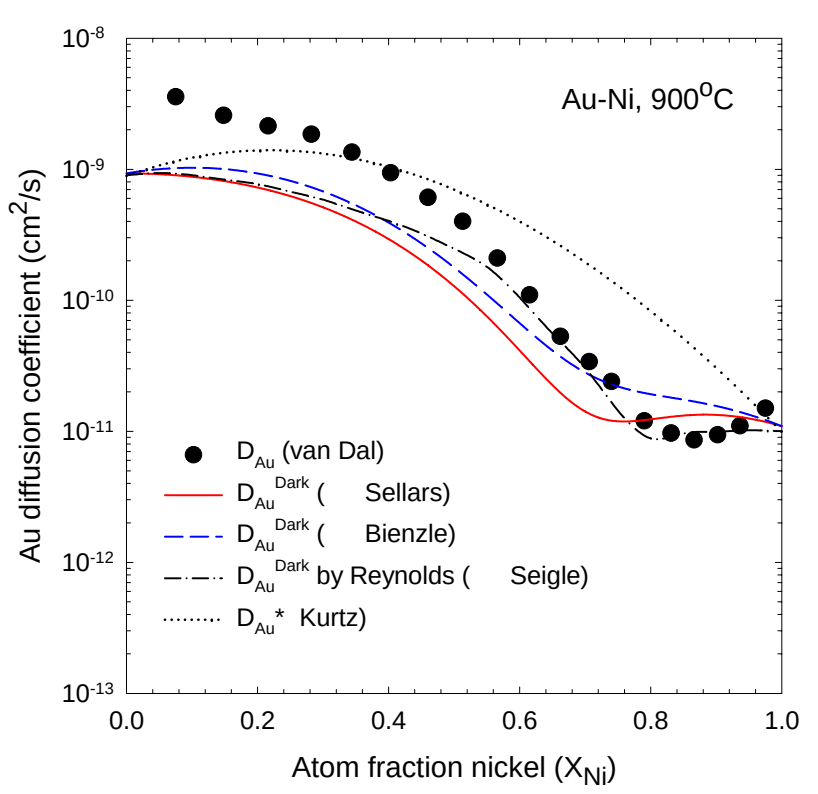


Redlich-Kister polynomial fits for activity data

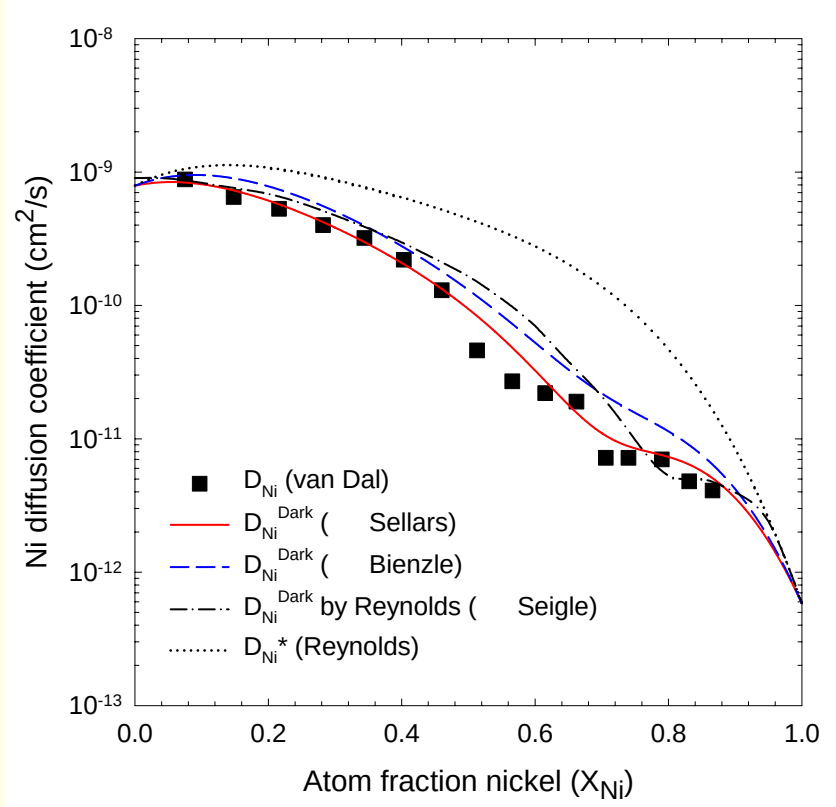
Thermodynamic factor (💣)

➢ **Thermodynamic factor is less than unity**

Darken Relations for Au-Ni: Predicted Intrinsic Diffusion Coefficients



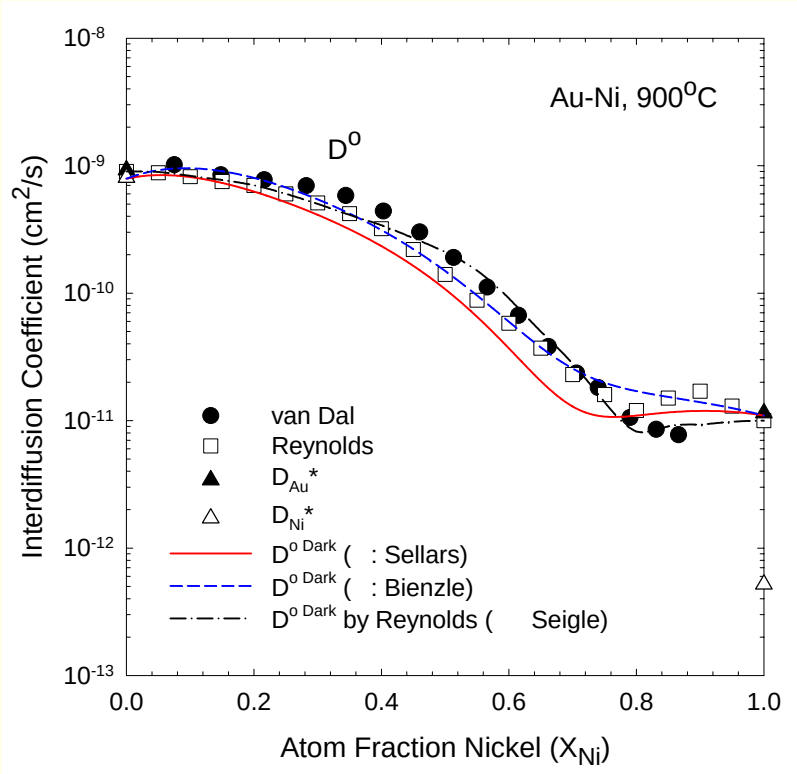
Darken: D_{Au}



Darken: D_{Ni}

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

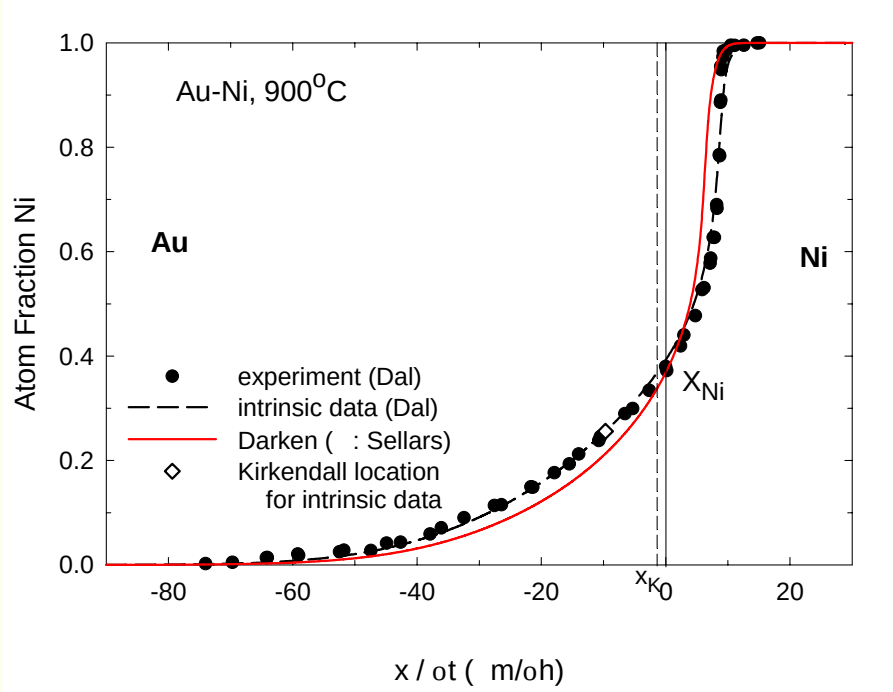
Darken Relations for Au-Ni: Predicted Interdiffusion Coefficient



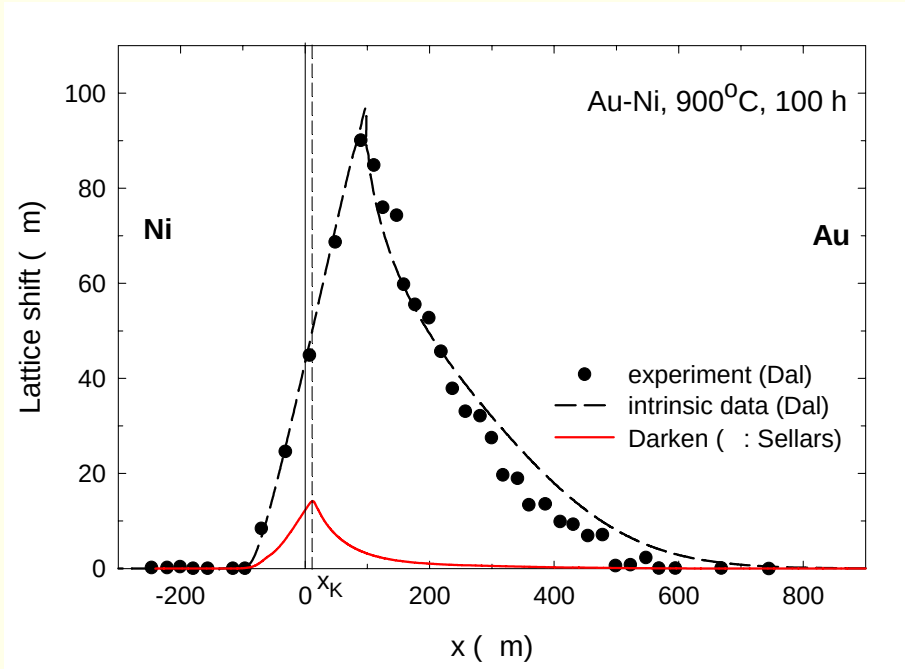
Darken: D°

- **Predicted interdiffusion coefficient reasonably close to data**

Assessing Darken Relations for Au-Ni with Simulation



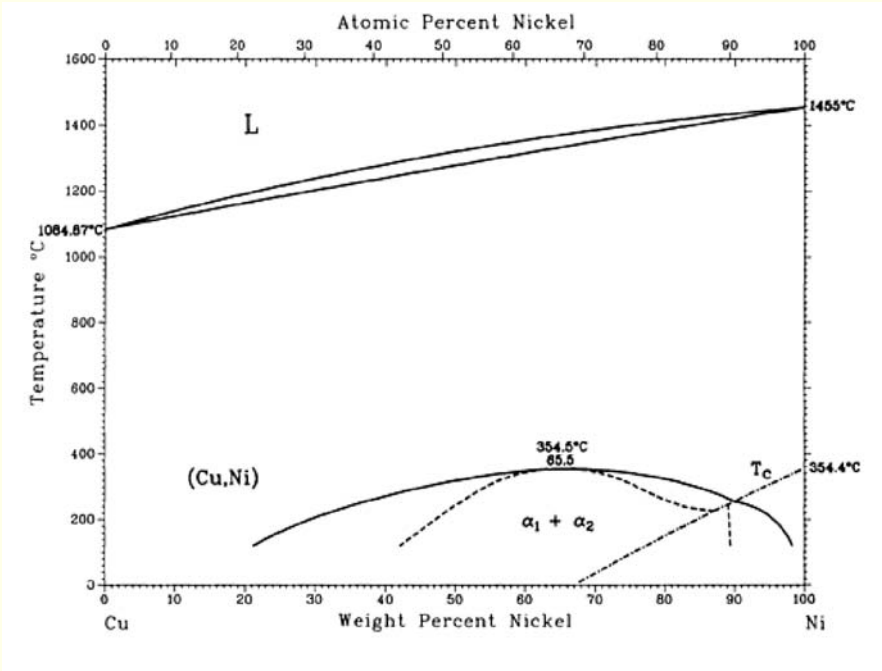
Concentration profile



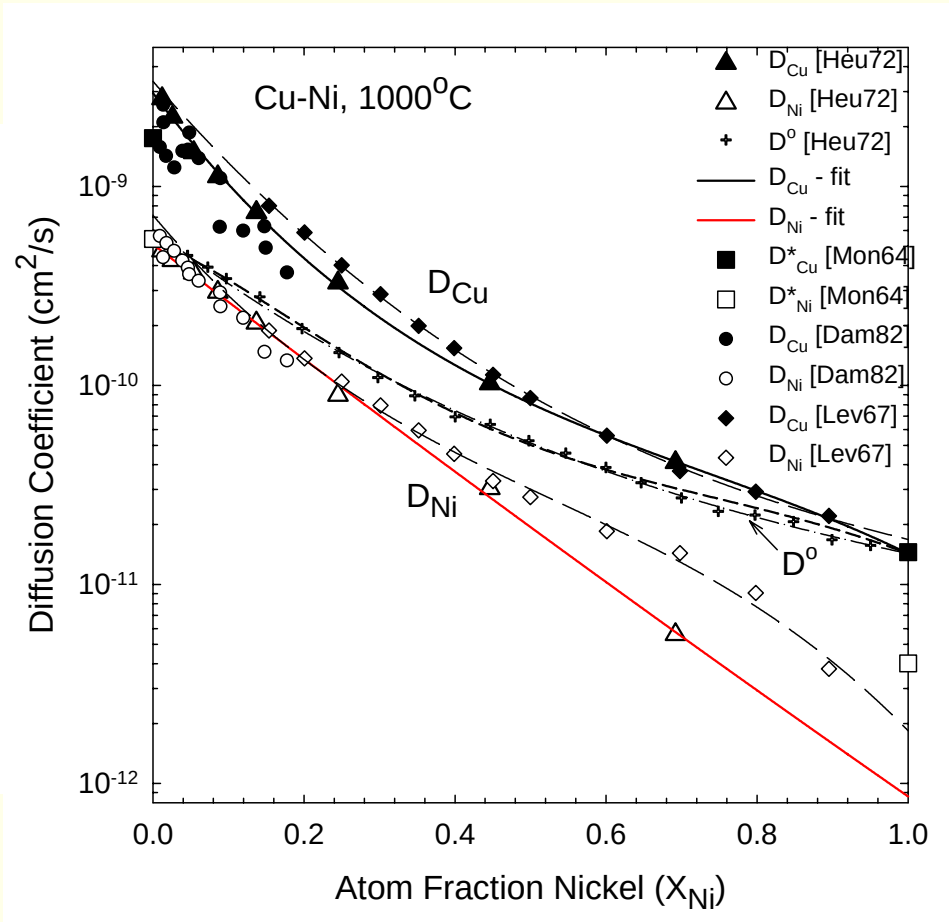
Lattice shift profile

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

iii. D-M Relations for Cu-Ni at 1000°C



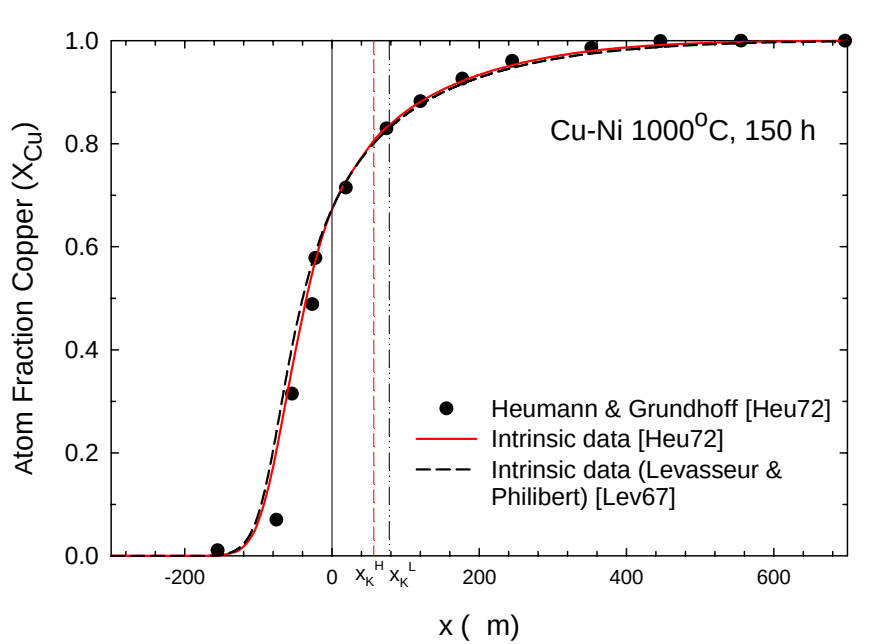
Phase diagram



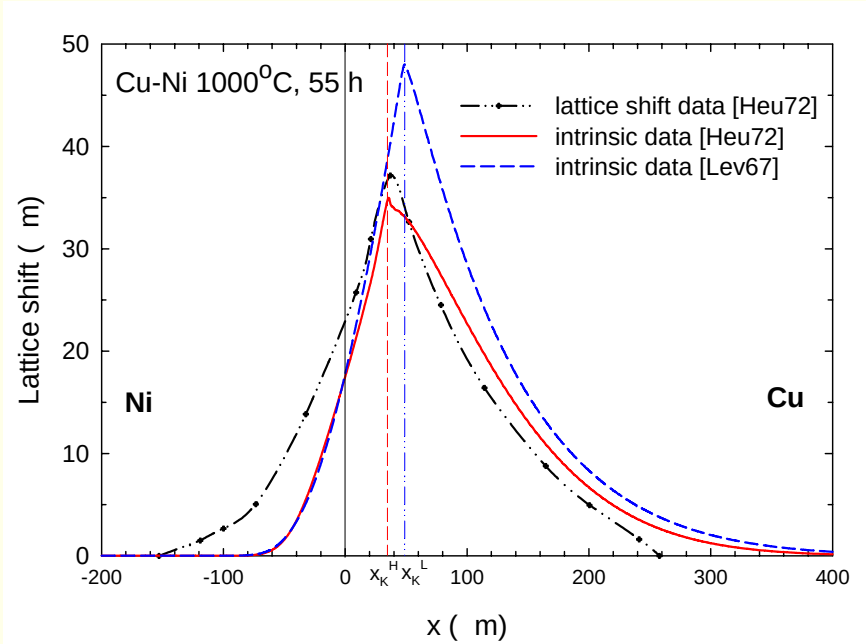
Experimental intrinsic diffusion coefficients
[Heuman & Grundhoff, Z. Metallk., 1972]

➢ **Heuman's data was used for fits, however no data near pure Ni composition**

D-M for Cu-Ni: Assessing Experimental Data



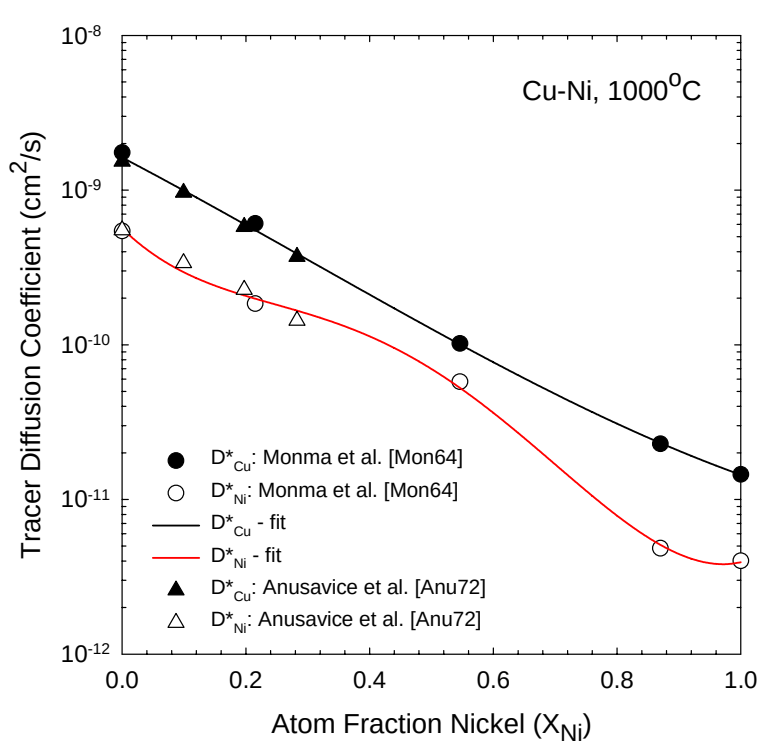
Concentration profiles



Lattice shift profiles

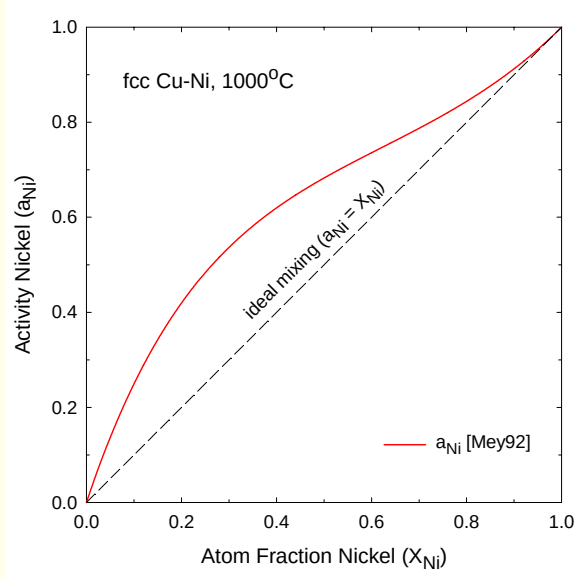
- **Both concentration and lattice shift profiles not accurate near pure Ni compositions**

D-M for Cu-Ni: Tracer & Thermodynamic Data

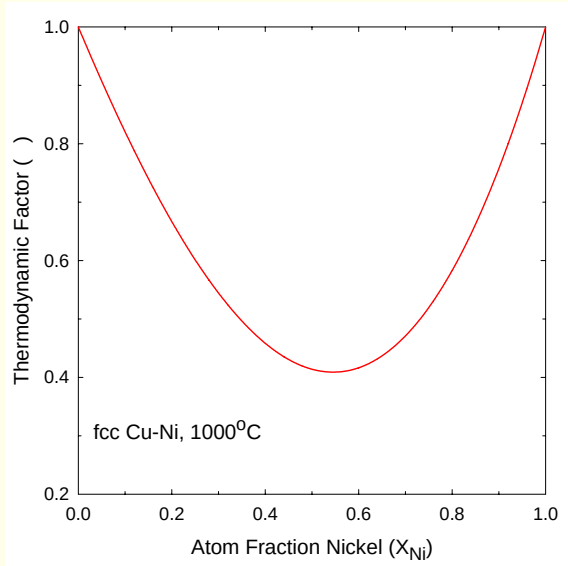


Tracer diffusion data

[Monma et al., J. Jap. Inst. Met., 1964]



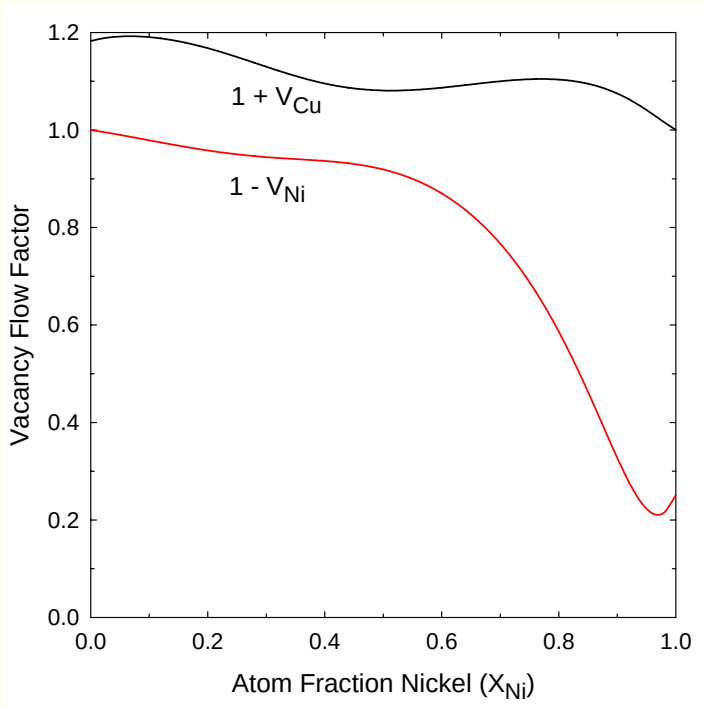
Activity Ni



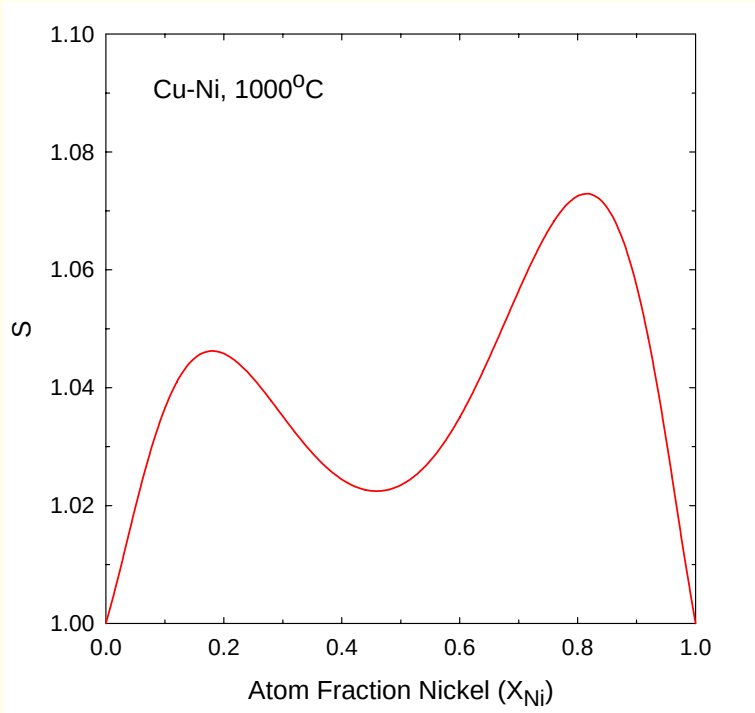
Thermodynamic assessment

[Mey, Calphad, 1992]

D-M Relations for Cu-Ni: Vacancy Flow Terms



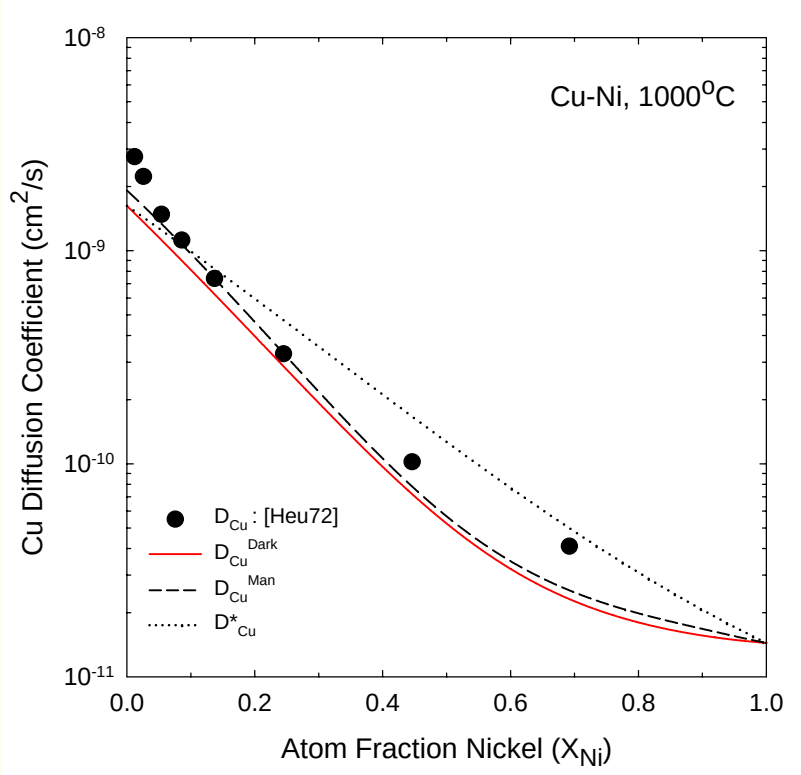
Vacancy flow terms: $1 \pm V_k$ for D_k's

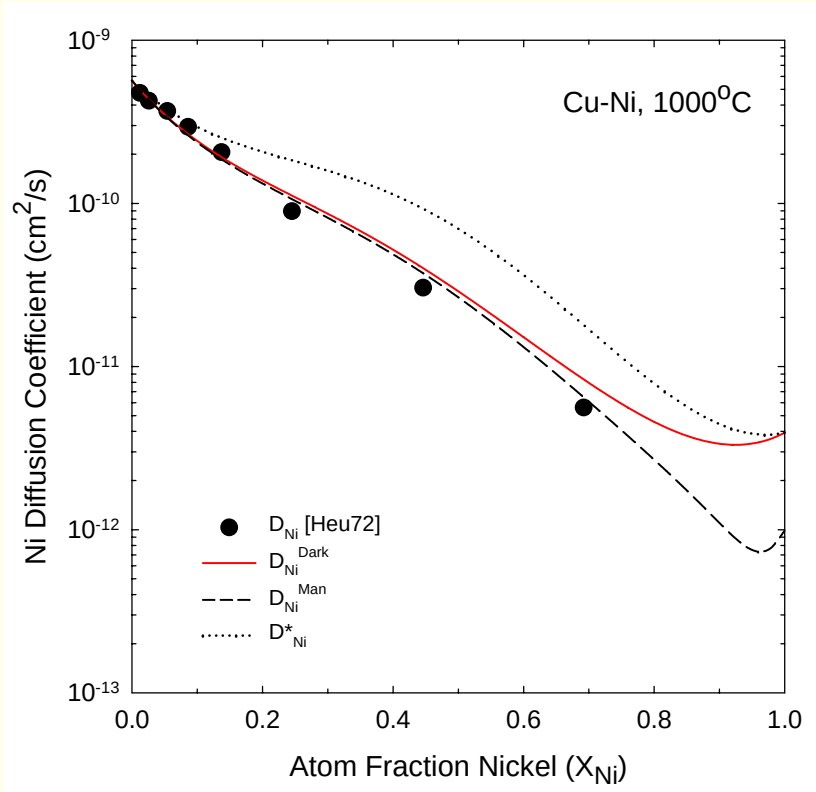


"S" correction factor for D^o

- **Manning's vacancy flow factor for Ni decreases near high Ni compositions**

D-M Relations for Cu-Ni: Intrinsic Diffusion Coefficients

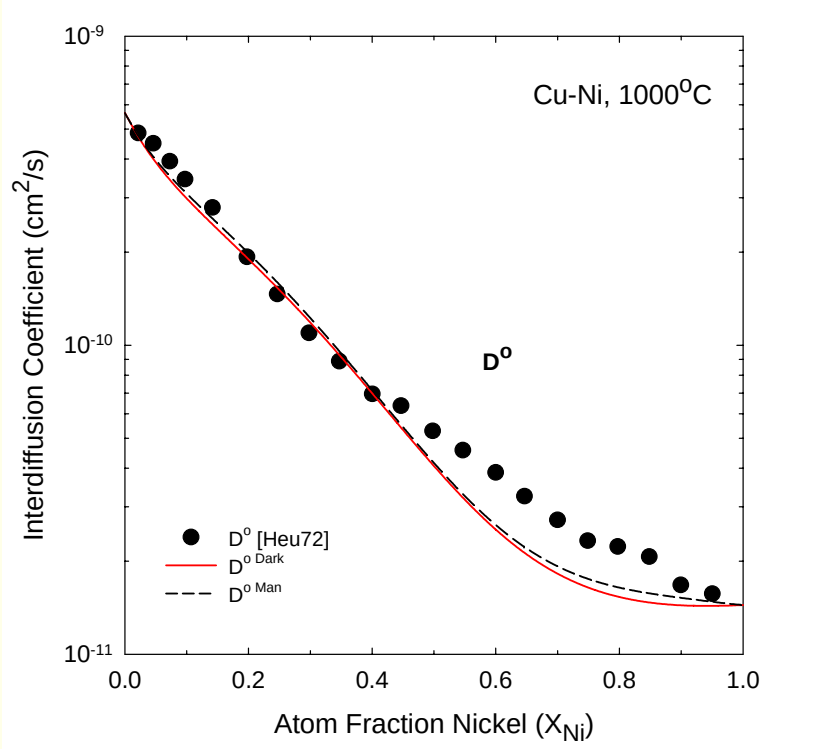




D_{Cu} **D_{Ni}**

➢ **Intrinsic coefficient of Ni better predicted by Manning relation**

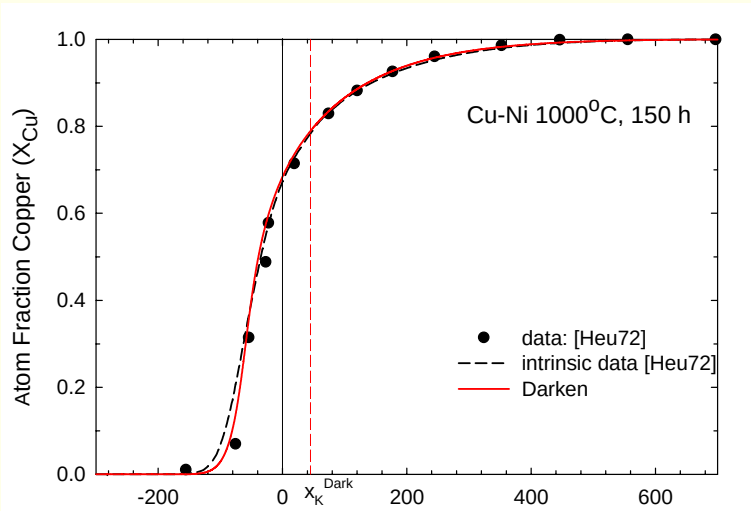
D-M Relations for Cu-Ni: Interdiffusion Coefficient



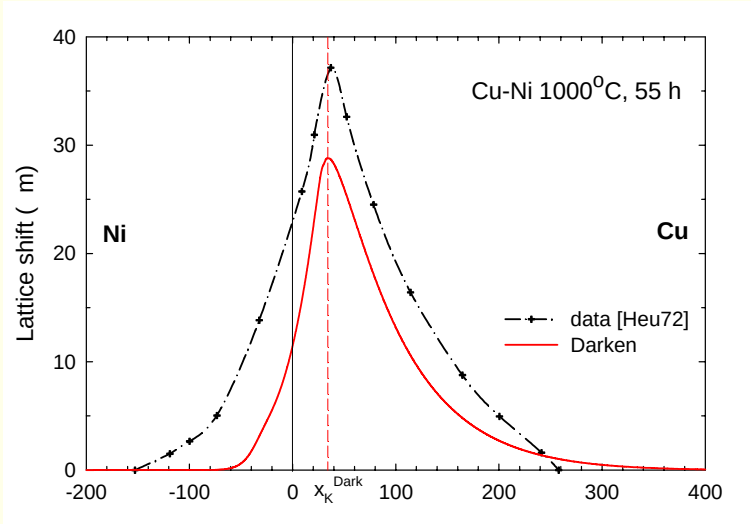
D°

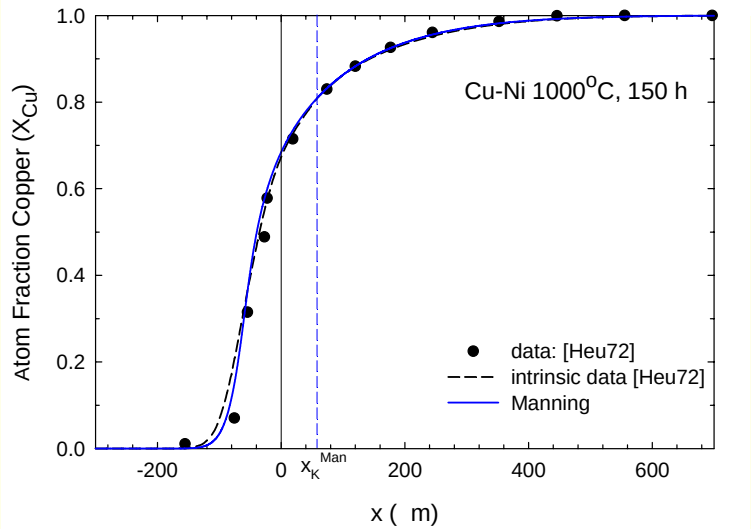
- **Problems in predicted interdiffusion coefficients for $X_{Ni} > 0.4$**

Assessing D-M Relations for Cu-Ni

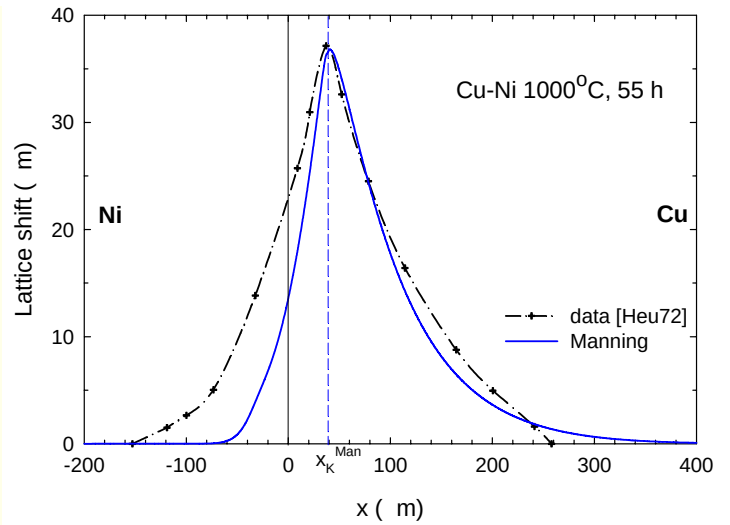


Darken





Manning

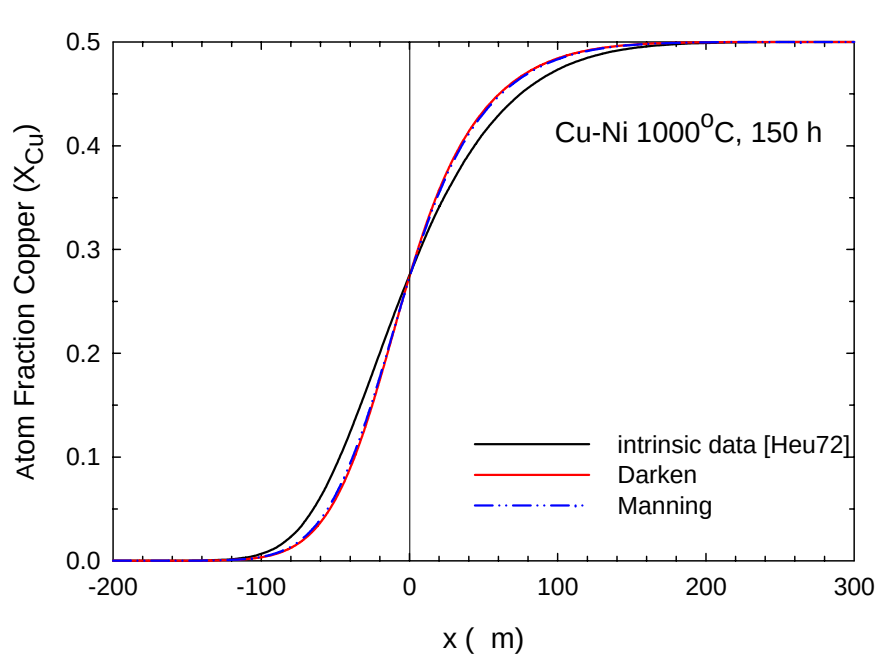


Concentration profiles

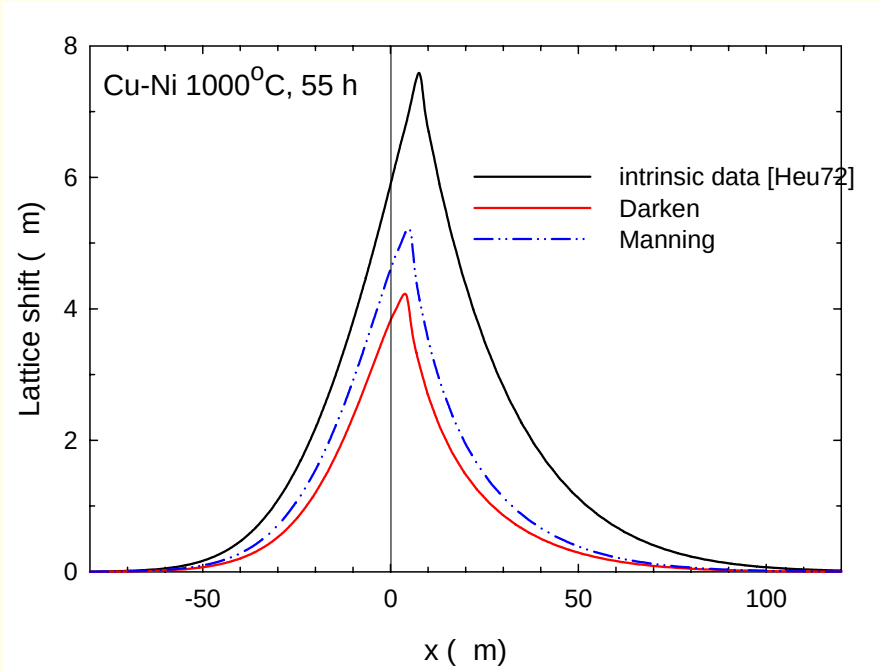
Lattice shift profiles

➢ **Lattice shift profile by Manning's relation better than Darken**

Assessing D-M Relations for Cu-Ni: Hypothetical Ni-rich Diffusion Couple



Concentration profiles



Lattice shift profiles

➢ **Hypothetical Ni-rich incremental diffusion couple reveals differences that a full-range couple did not**

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

Intrinsic fluxes in a multicomponent system (i = 1, 2, … , c):

$$J_i = L_{ii}\frac{d}{dx}\,_i = c_i M_i \frac{d}{dx}\,_i = \frac{Dt_i}{R\ T} c_i \frac{d}{dx}\,_i = Dt_i \frac{X_i}{V}\frac{d}{dx}\ln a_i$$

Dt_i = tracer diffusion coefficient of component i

μ_i = chemical potential of i; **a_i = activity of i**

V = molar volume; **X_i = mole fraction of i**

$$J_i = \frac{Dt_i}{V} X_i \sum_{j\ 1}^{c\ 1} \frac{{}_{ii}}{X_i}\frac{d}{dx}X_i - \frac{{}_{ij}}{X_j}\frac{d}{dx}X_j$$

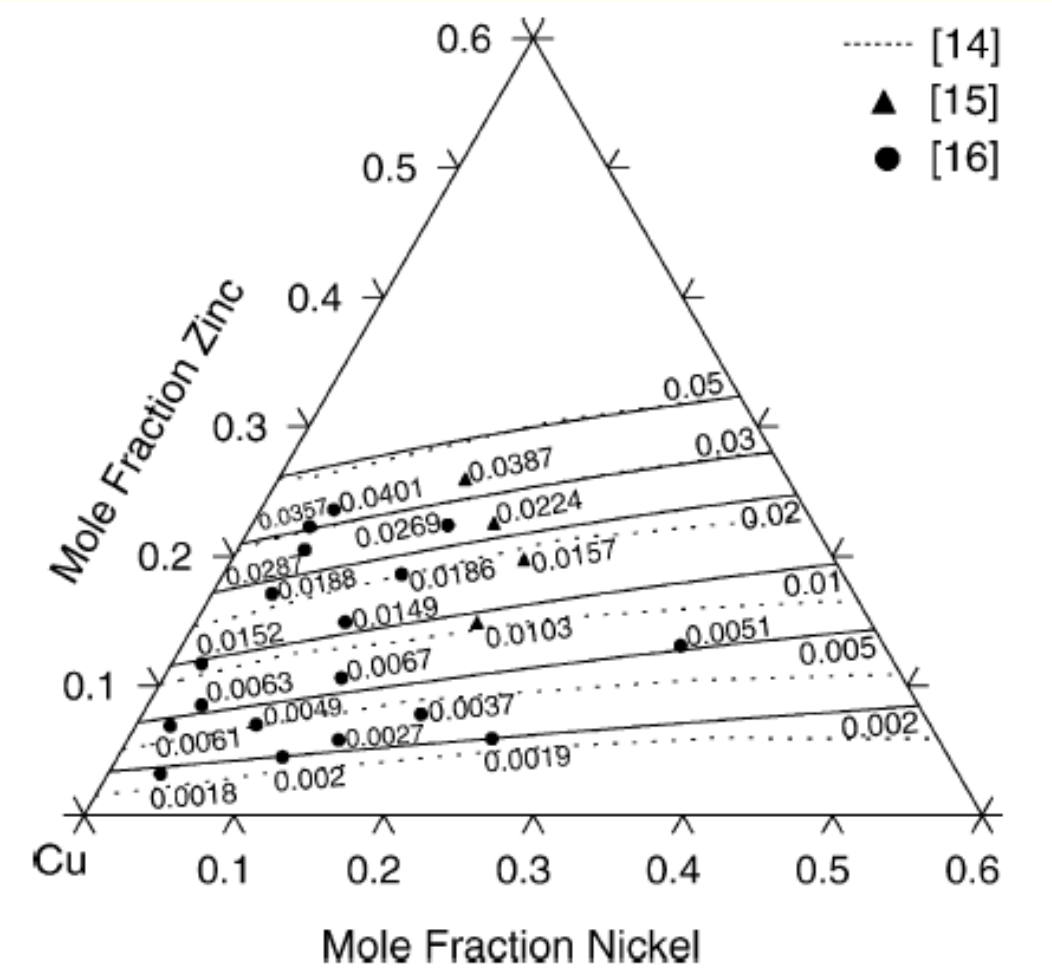
$$_{ij} = \frac{d}{d\ln\ X_j}\ln\ a_i$$

Φ_{ij} = thermodynamic factors obtained from Gibbs free energy of phase

Cserhati, Ugaste, van Loo *et al*., *Def. & Diff. For*., 2001

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.)

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

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

$${}^{0}T^{Fcc\_Al}_{cCu,Ni} = -935.5$$

$${}^{1}T^{Fcc\_Al}_{cCu,Ni} = -594.9$$

$${}^{0}\beta^{Fcc\_Al}_{Cu,Ni} = -0.7316$$

$${}^{1}\beta^{Fcc\_Al}_{Cu,Ni} = -0.3174$$

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

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

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

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

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

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

$${}^{0}T^{Fcc\_Al}_{cNi,Zn} = -815$$

$${}^{0}\beta^{Fcc\_Al}_{Ni,Zn} = -1.46$$

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

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

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

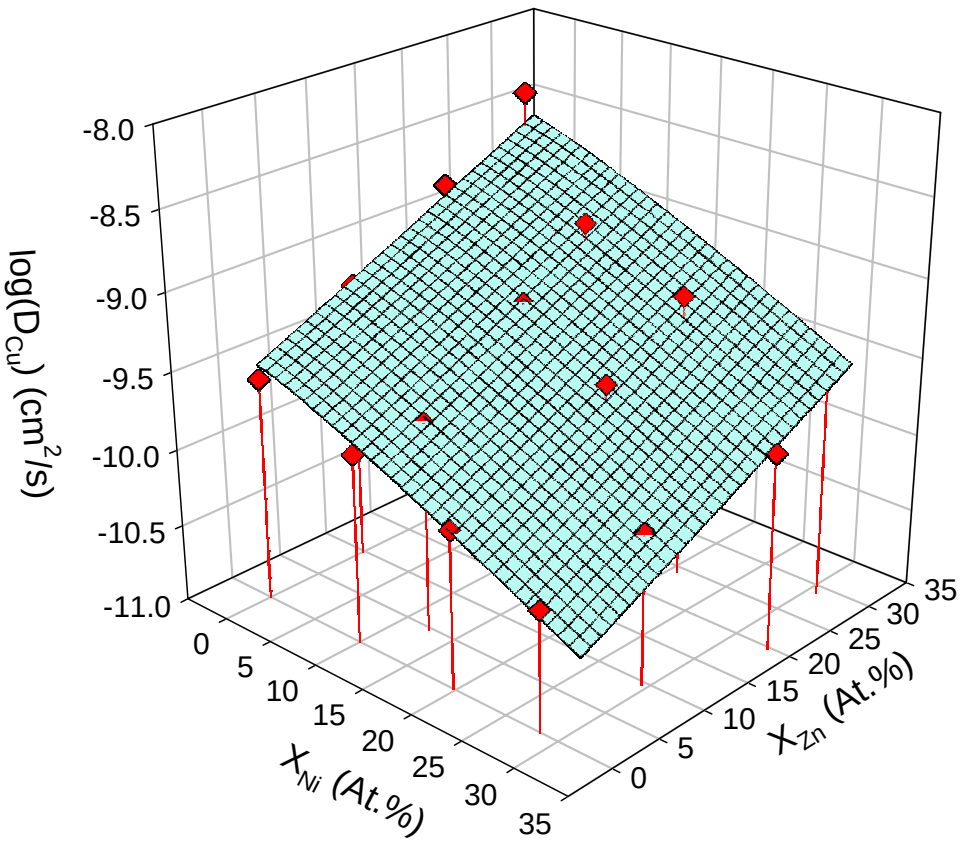
Cu-Ni-Zn: Tracer diffusion

$$\log Dt_{Cu} = 3.53\, X_{Ni}^{1.16} \quad 3.6\, X_{Zn}^{1.02} \quad 9.46$$

$$\log Dt_{Ni} = 4.05\, X_{Ni}^{1.3} \quad 3.28\, X_{Zn}^{1.07} \quad 9.96$$

$$\log Dt_{Zn} = 3.2\, X_{Ni} \quad 5.21\, X_{Zn}^{1.25} \quad 9$$

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

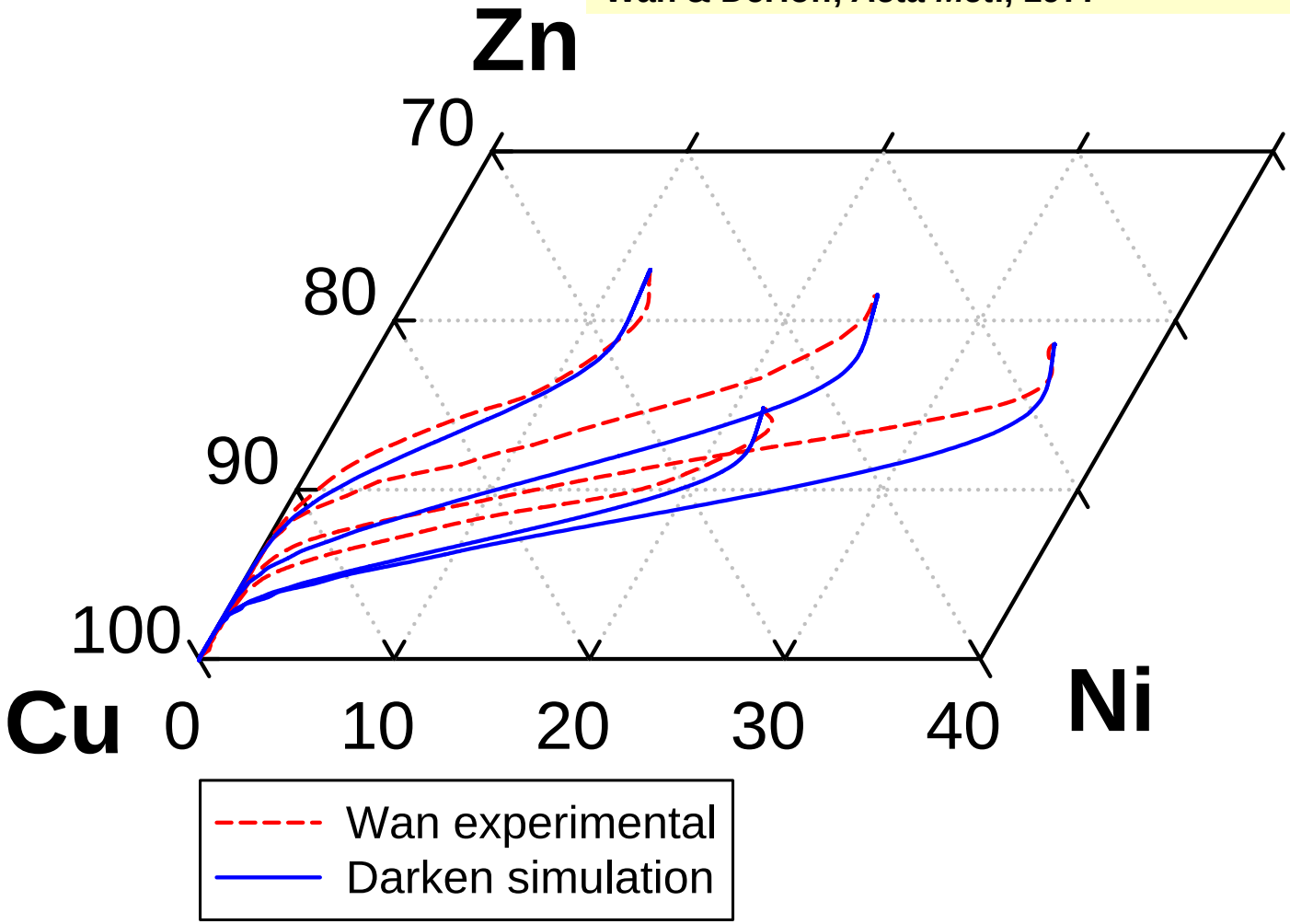


$D^*_{Zn} > D^*_{Cu} > D^*_{Ni}$

Similar composition dependence

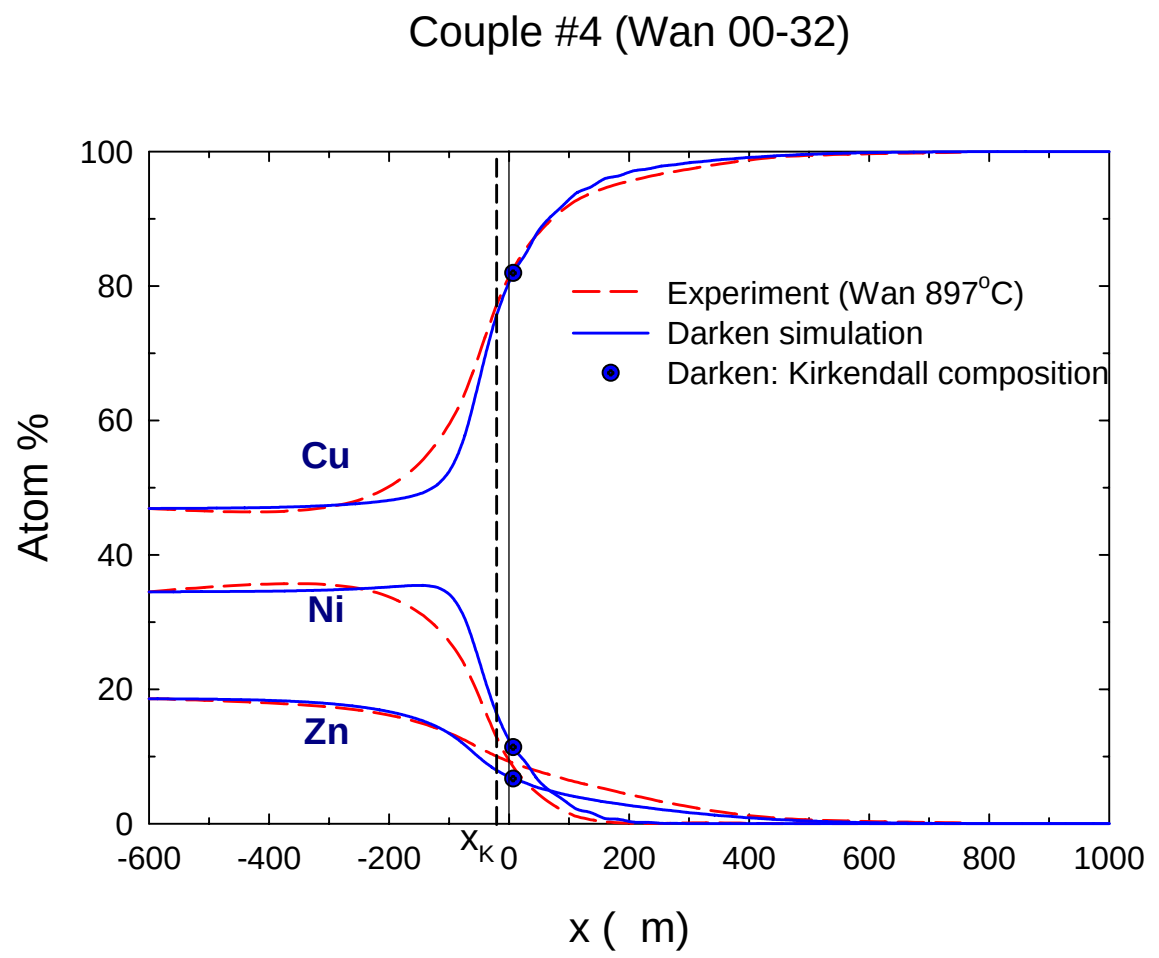
Darken relations in Cu-Ni-Zn: Composition paths at 900°C

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

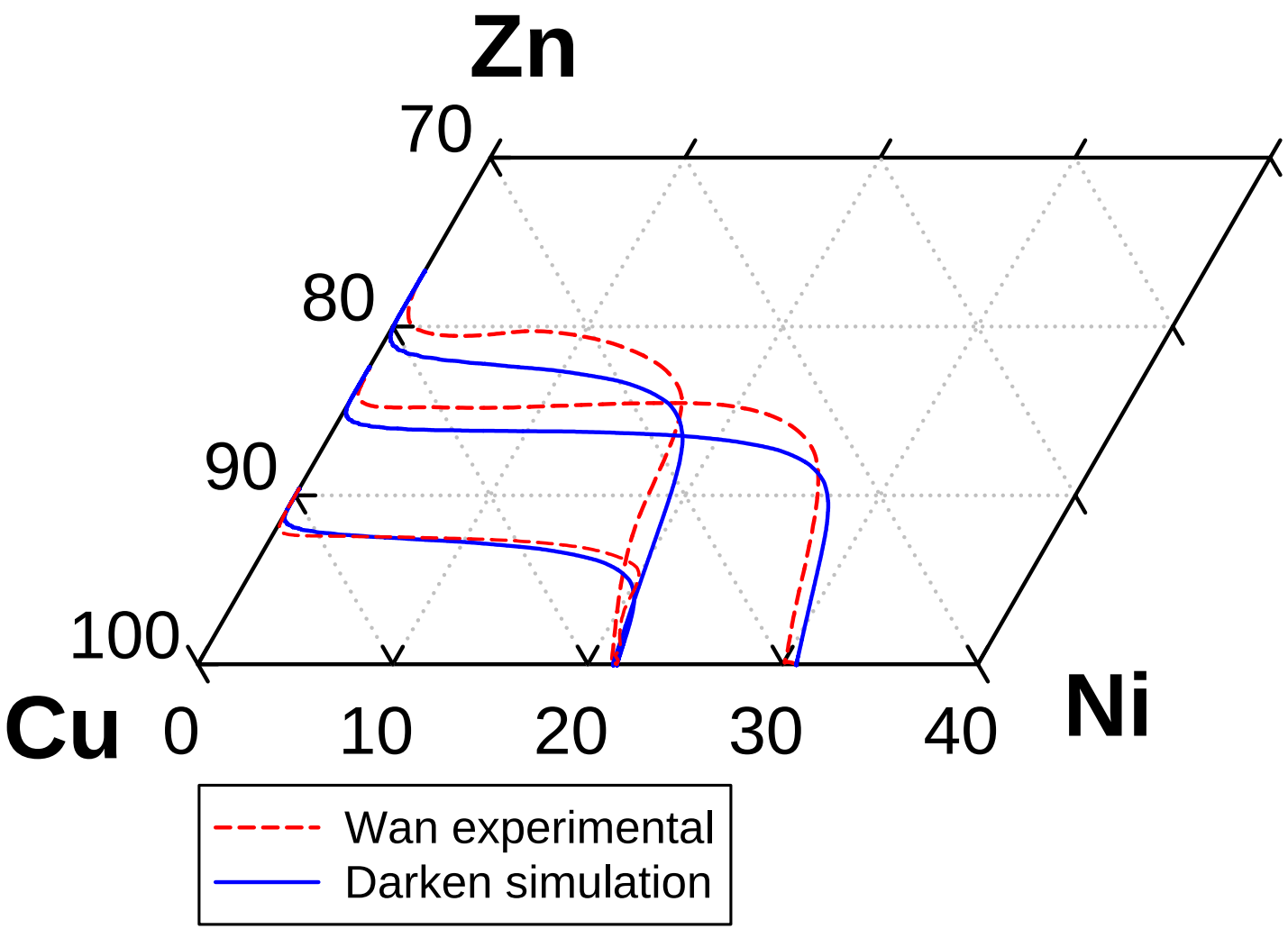


#4,5,7,9

Cu-Ni-Zn: Concentration profiles

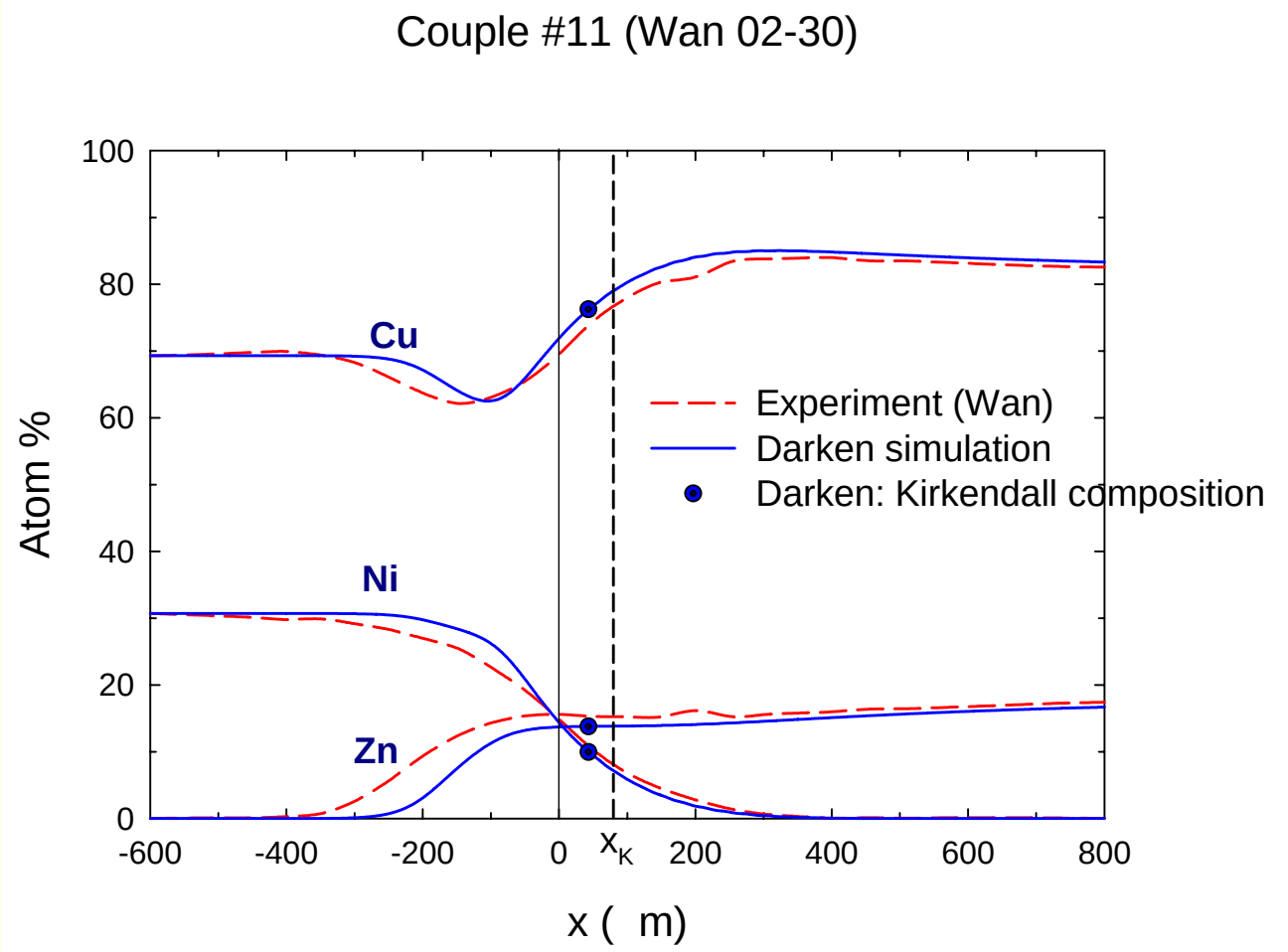


Composition paths Cu-Ni-Zn contd.

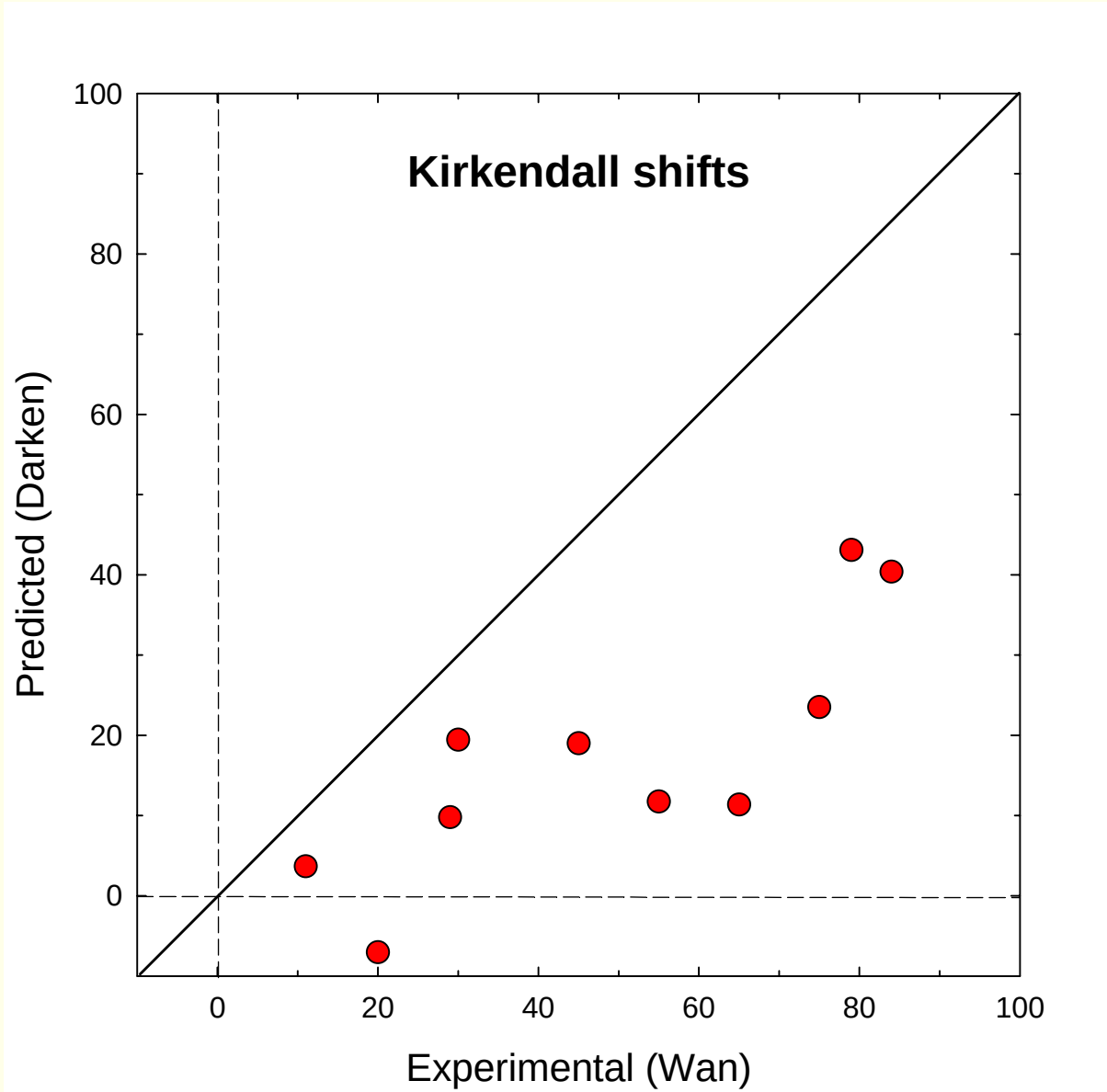


#6,8,11

Cu-Ni-Zn: Concentration profiles



Kirkendall Shift Comparison



4. Conclusions

- **In binary Au-Ni, Cu-Zn and ternary Cu-Ni-Zn system, Darken relations result in**
  - **Reasonable concentration profiles; however**
  - **Kirkendall shifts are usually 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. Future Work: Tracer diffusion measurements using stable isotopes

- **Tracer diffusion measurements**
  - 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**
  - Averaged* tracer diffusivity as a function of volume fraction in multiphase?
- **Extend intrinsic simulation to binary multi-phase**
  - Use ChemApp interface with FactSage, ThermoCalc, etc. thermodynamic databases
  - Explore nucleation, stress, finite boundary conditions, etc.