View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by NASA Technical Reports Server

199420647

N94-25131

A Thermodynamic Approach to Obtain Materials Properties for Engineering Applications

Y. Austin Chang

Department of Materials Science and Engineering
University of Wisconsin
1509 University Avenue
Madison, WI 53706

With the ever increases in the capabilities of computers for numerical computations, we are on the verge of using these tools to model manufacturing processes for improving the efficiency of these processes as well as the quality of the products. One such process is casting for the production of metals. However, in order to model metal casting processes in a meaningful way it is essential to have the basic properties of these materials in their molten state, solid state as well as in the mixed state of solid and liquid. Some of the properties needed may be considered as intrinsic such as the density, heat capacity or enthalpy of freezing of a pure metal, while others are not. For instance, the enthalpy of solidification of an alloy is not a defined thermodynamic quantity. It's value depends on the micro-segregation of the phases during the course of solidification. The objective of the present study is to present a thermodynamic approach to obtain some of the intrinsic properties and combining thermodynamics with kinetic models to estimate such quantities as the enthalpy of solidification of an alloy.

A schematic diagram illustrating our general approach in obtaining the thermodynamic description of an alloy is shown in Figure 1. The starting point is to have suitable and appropriate thermodynamic models for all the phases involved. All of these models have unknown parameters. The parameter values must be obtained from experimental thermodynamic data. Although most thermodynamic models are empirical or semi-empirical, we attempt to use models with some physical basis and certainly with the least number of parameters to describe such a phase. Once we have the thermodynamic properties of all the phases in a binary described, we can then calculate stable binary phase equilibria and compare them with the measured diagrams. If the thermodynamic data and phase diagram data are correct and the models used are suitable, the calculated diagram should agree with the measured equilibria. Since all experimental measurements have uncertainties, it is often necessary to use thermodynamic and phase equilibrium data simultaneously to optimize the parameter values of the thermodynamic models. Of

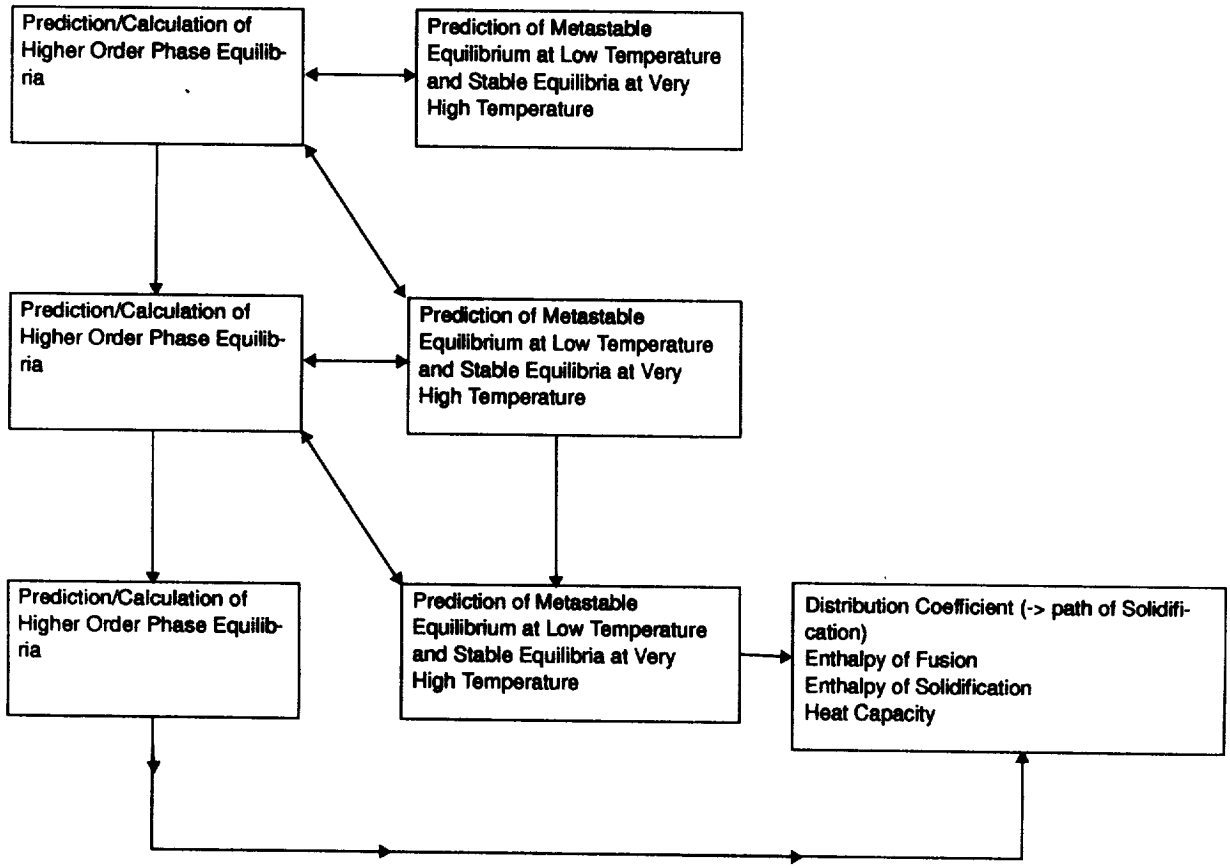


Figure 1

course, we always use the thermodynamic values as the starting point for our optimization. We can also calculate phase equilibria at either very high temperatures where measurements are difficult to carry out experimentally or at very low temperatures where the kinetics of reaction are so slow that achievement of equilibrium is difficult if not impossible. We can also calculate metastable equilibria from the thermodynamic models particularly those involving a supercooled liquid phase. A knowledge of the metastable equilibria is important in controlling the resulting microstructure of alloys during solidification. In several systems, our calculated metastable equilibria are in accord with experimental measurements. In addition, on the basis of the binaries, we may extend the calculations/ predictions to ternary and higher order systems. This is particularly important since most commercial alloys are of multi-components.

This type of approach allows us to have the thermodynamic descriptions of the phases involved as well as to obtain the values for the distribution coefficients as a function of composition and temperature. The distribution coefficient is a basic parameter in model-

ing the microsegregation of an alloy. Yet it is usually not available from experimental measurement for a multi-component alloy as a function of temperature. Coupling the thermodynamic descriptions of the phases with a kinetic model, we can compute such important quantities such as the enthalpy of solidification which is needed for macro-modeling of solidification. Moreover, coupling of the thermodynamic descriptions of the phases with semi-theoretical models, we can estimate/calculate the surface tensions of molten alloys provided the values of the component elements are known.

Nothing is better
than
good experimental data

But We Have To Be
Realistic

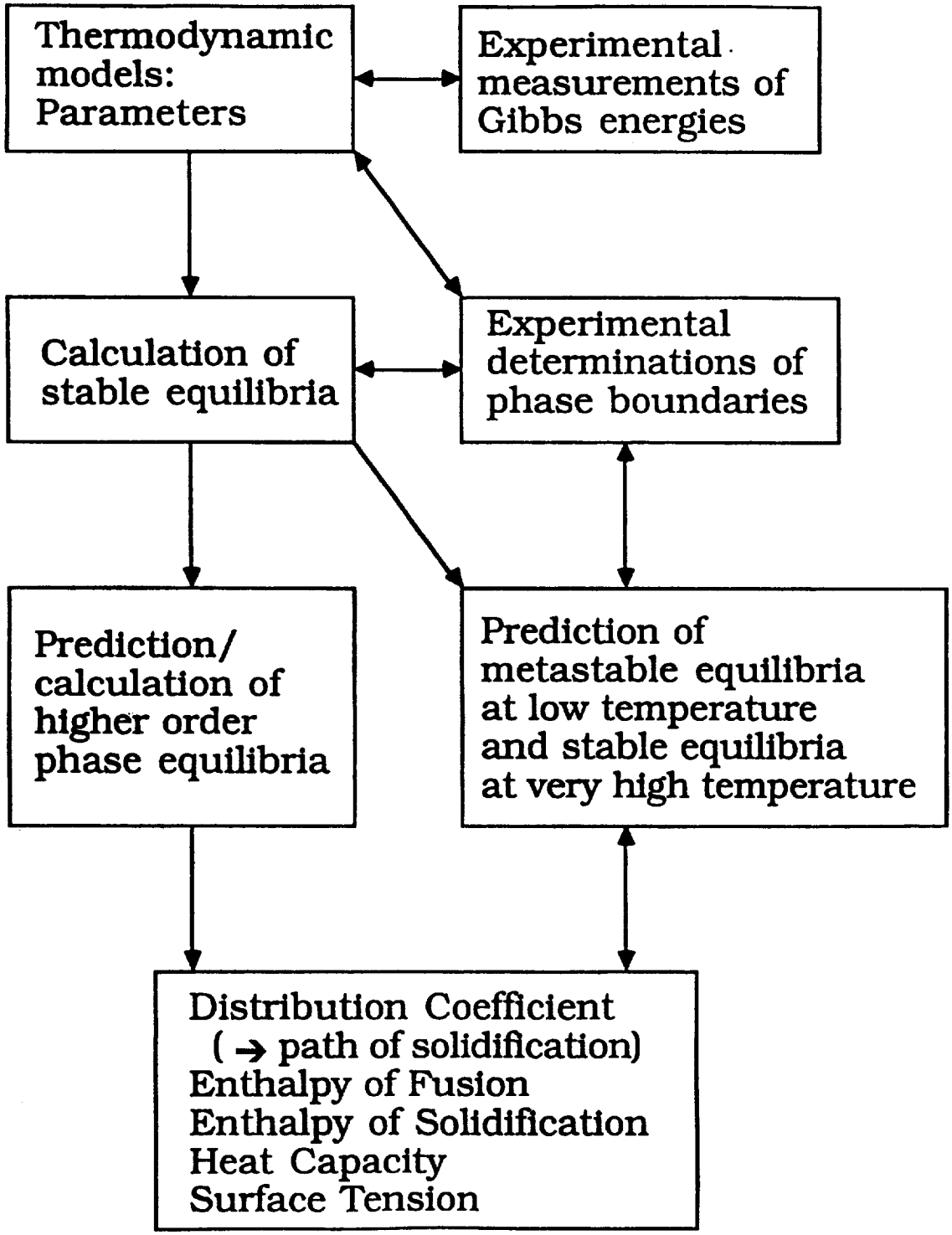
We don't have either the time or the resource to measure all the needed materials properties.

We must develop
methodologies
to estimate these
materials properties

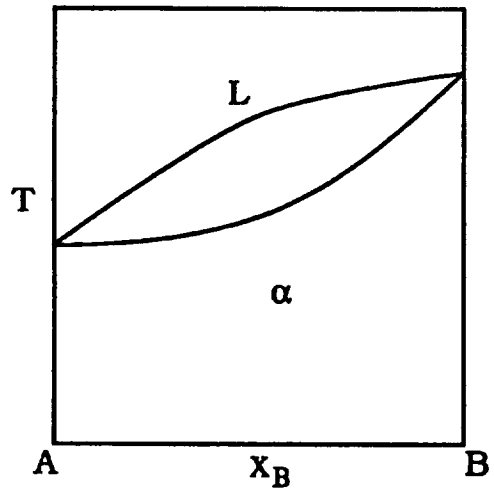
In fact, a combined thermodynamic modeling/experimental approach is the only sensible way to build up a material data base for engineering applications!

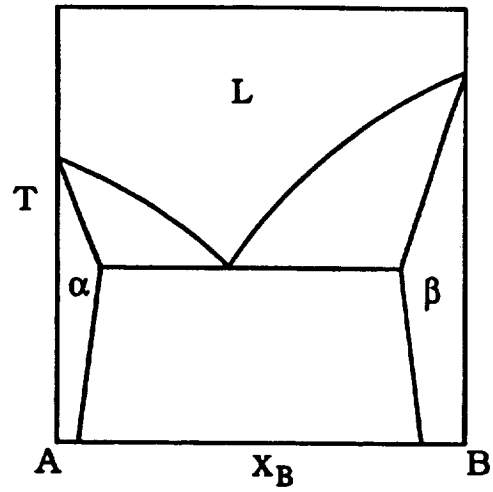
Solid-liquid equilibria
(distribution coefficient)
Enthalpy of fusion
Enthalpy of Solidification
Heat capacity
Surface tension

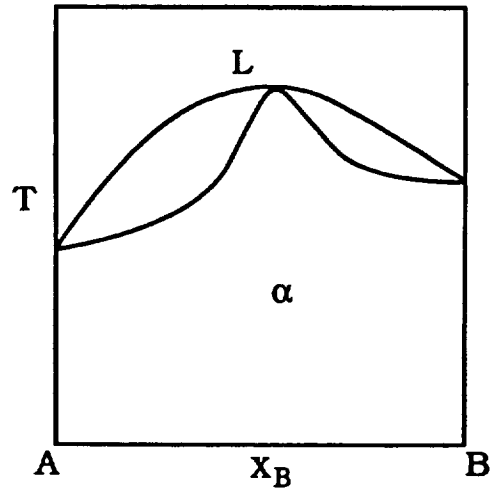
Thermodynamic Approach to Obtain Phase Equilibrium Data

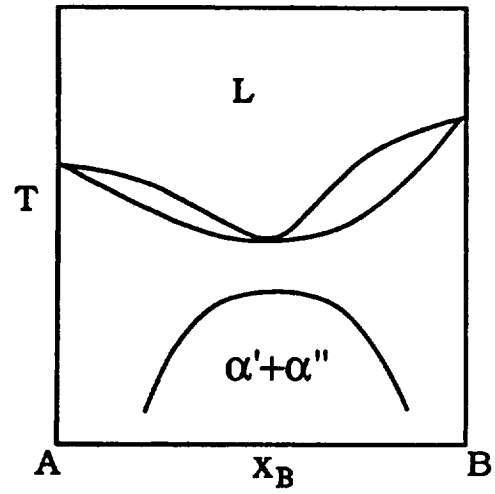

Thermodynamic models: Parameters
Experimental measurements of Gibbs energies
Calculation of stable equilibria
Experimental determinations of phase boundaries
Prediction/ calculation of higher order phase equilibria
Prediction of metastable equilibria at low temperature and stable equilibria at very high temperature
Distribution Coefficient
(→ path of solidification)
Enthalpy of Fusion
Enthalpy of Solidification
Heat Capacity
Surface Tension

Thermodynamic Models





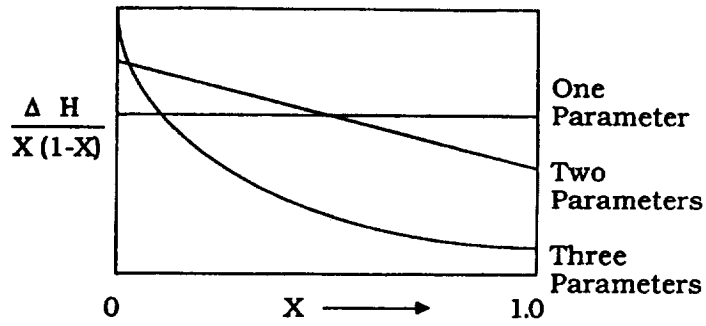


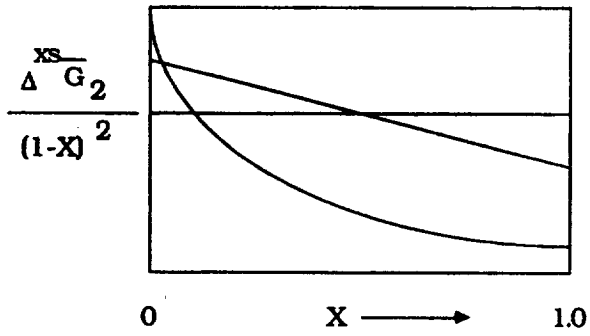


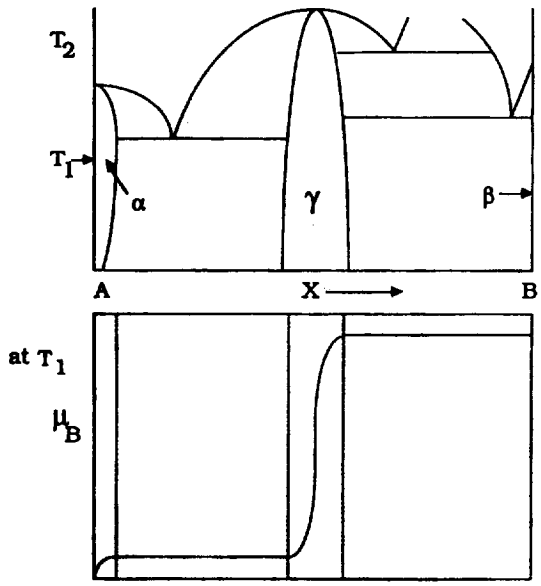
Thermodynamic Model (Equation) for Solutions (both Solid and Liquid) with Small Deviations from Regular Solution Behavior.

$$\Delta^{xs}G^{\alpha} = x(1-x)\,[u + vx + wx^2]$$

with u, v, w = A + BT + CT lnT, where A, B, C are constants.







Intermidiate Phases: Variation of the Wagner- Schottky (Bragg-Williams) Model.

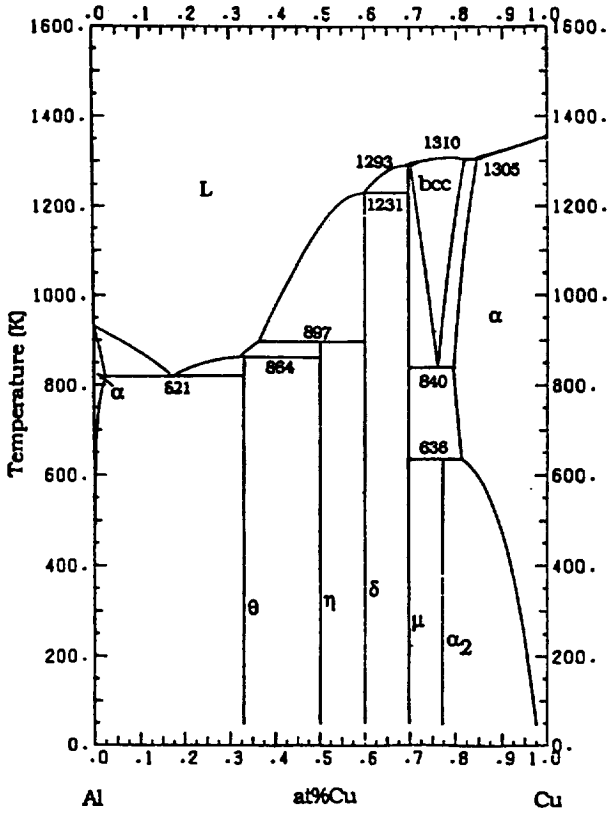
The Liquid Phase : Associated Solution Model,
Sublattice Model.

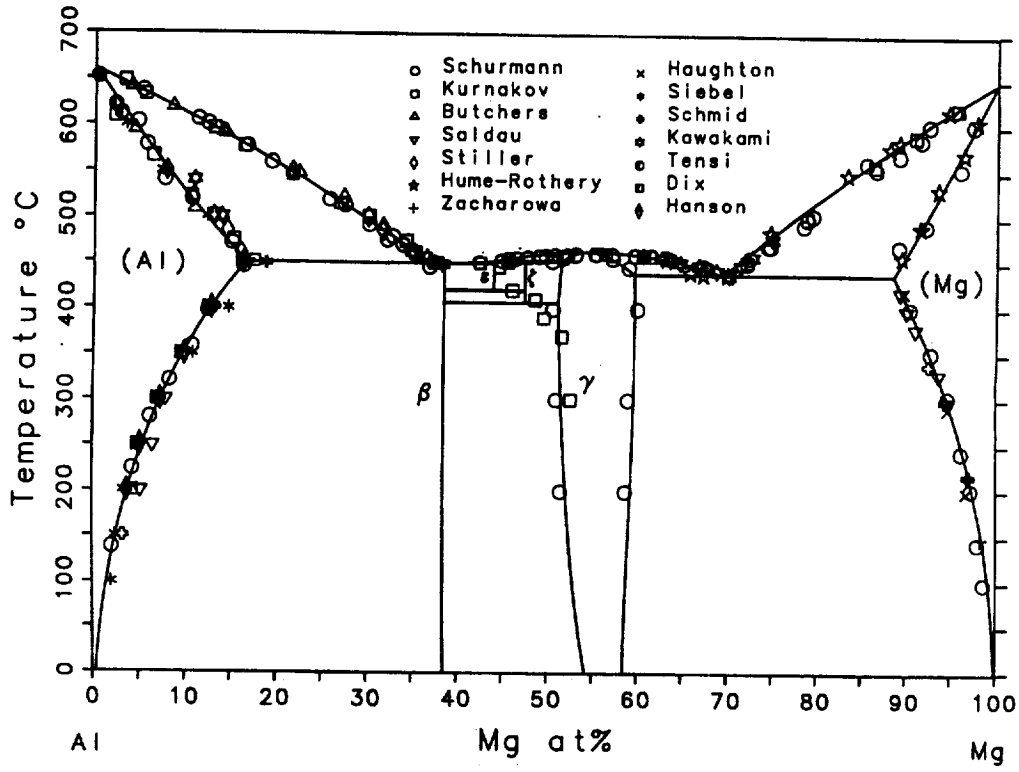
An Example

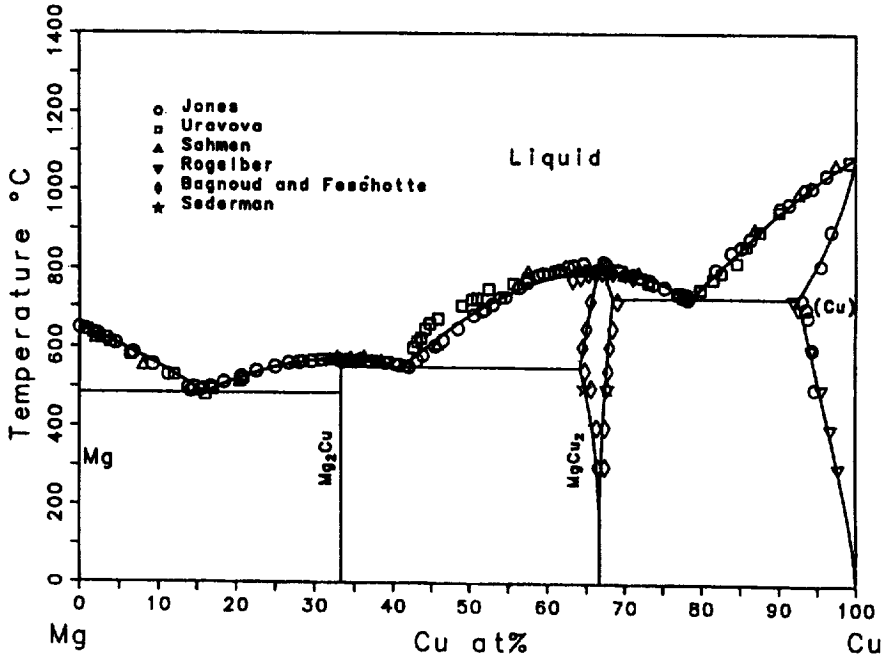
Al-Cu
Al-Mg
Mg-Cu
Al-Mg-Cu

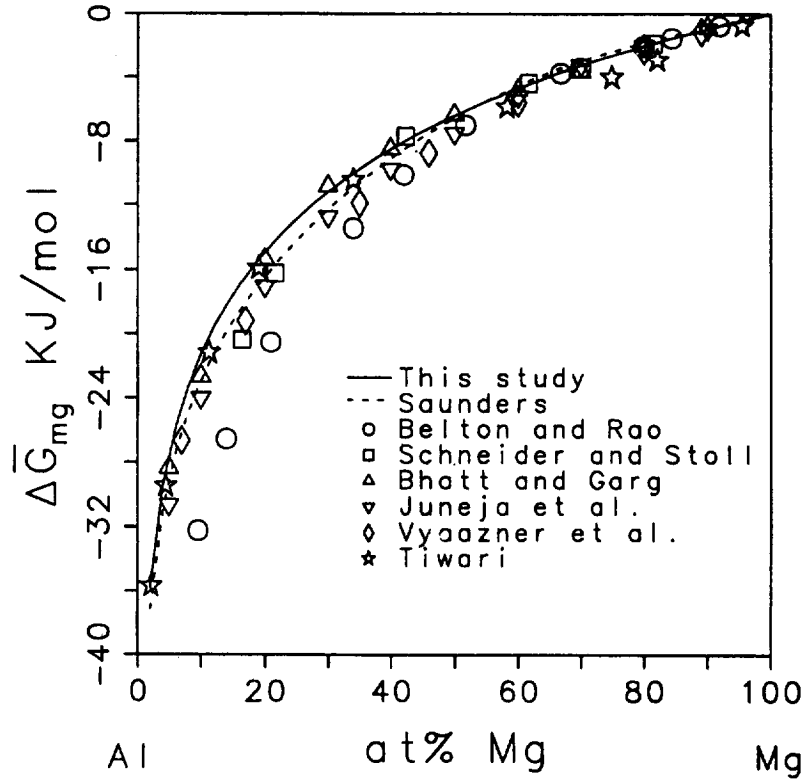
Al-Cu

Kaufman and Nesor, 1978
Murray, 1985
Chuang, 1984
Chen, Chuang, Chang and Chu, 1991




Schurmann
Kurnakov
Butchers
Saldau
Stiller
Hume-Rothery
Zacharowa
Haughton
Siebel
Schmid
Kawakami
Tensi
Dix
Hanson
(Al)
(Mg)
β
γ
Temperature °C
Al
Mg at%
Mg

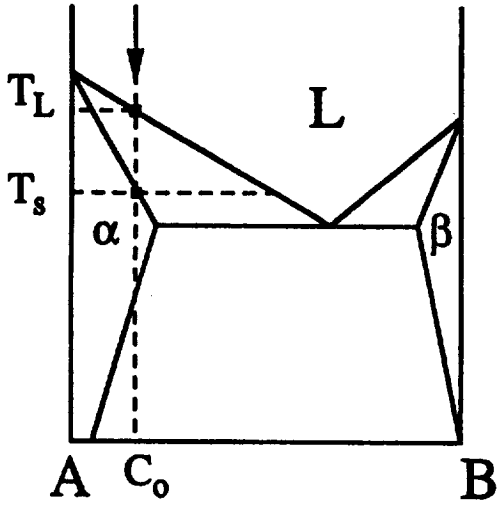

Jones
Uravova
Sahmen
Rogelber
Bagnoud and Feschotte
Sederman
Liquid
(Cu)
Mg
Mg2Cu
MgCu2
Temperature °C
Mg
Cu at%
Cu

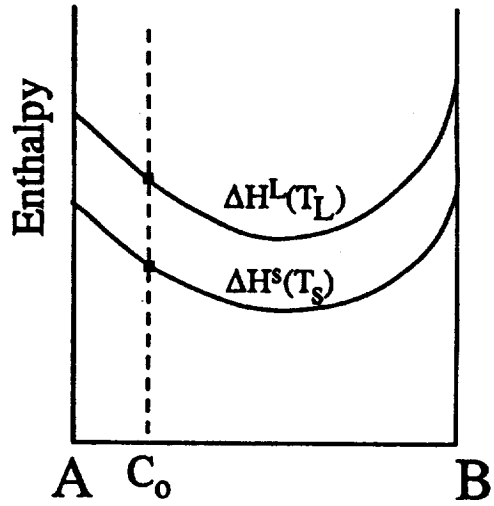

$\bar{\Delta G}_{mg}$ KJ/mol
0
-8
-16
-24
-32
-40
0
20
40
60
80
100
Al
at% Mg
Mg
This study
Saunders
Belton and Rao
Schneider and Stoll
Bhatt and Garg
Juneja et al.
Vyazner et al.
Tiwari

C3

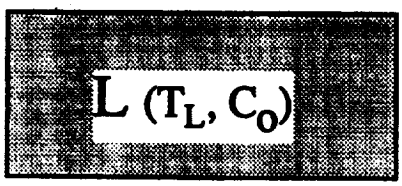
Enthalpy of Solidification

Case I: Equilibrium Solidification



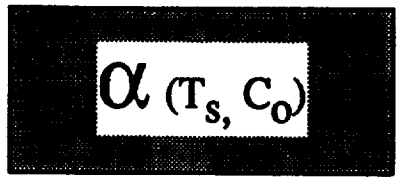


Before Solidification:



$\Delta H^L(T_L, C_o)$

After Solidification:

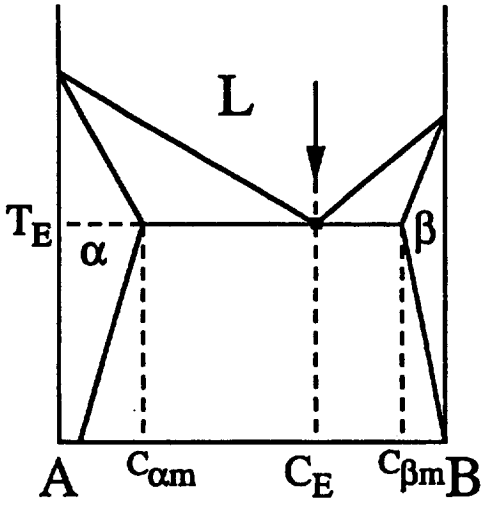


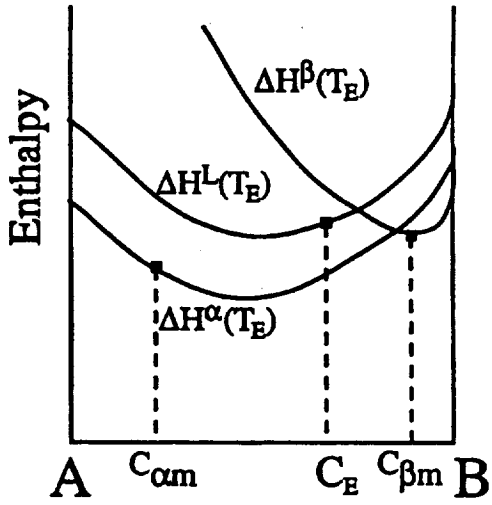
$\Delta H^S(T_S, C_o)$

Enthalpy of Solidification:

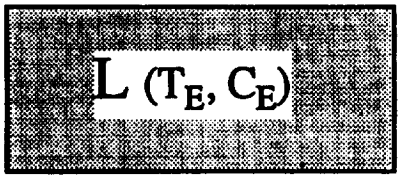
$$\Delta H = \Delta H^S(T_S, C_o) - \Delta H^L(T_L, C_o)$$

Case II: Eutectic Solidification



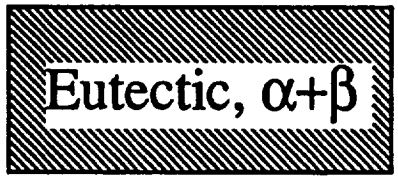


Before Solidification:



$\Delta H^{L}(T_E, C_E)$

After Solidification:

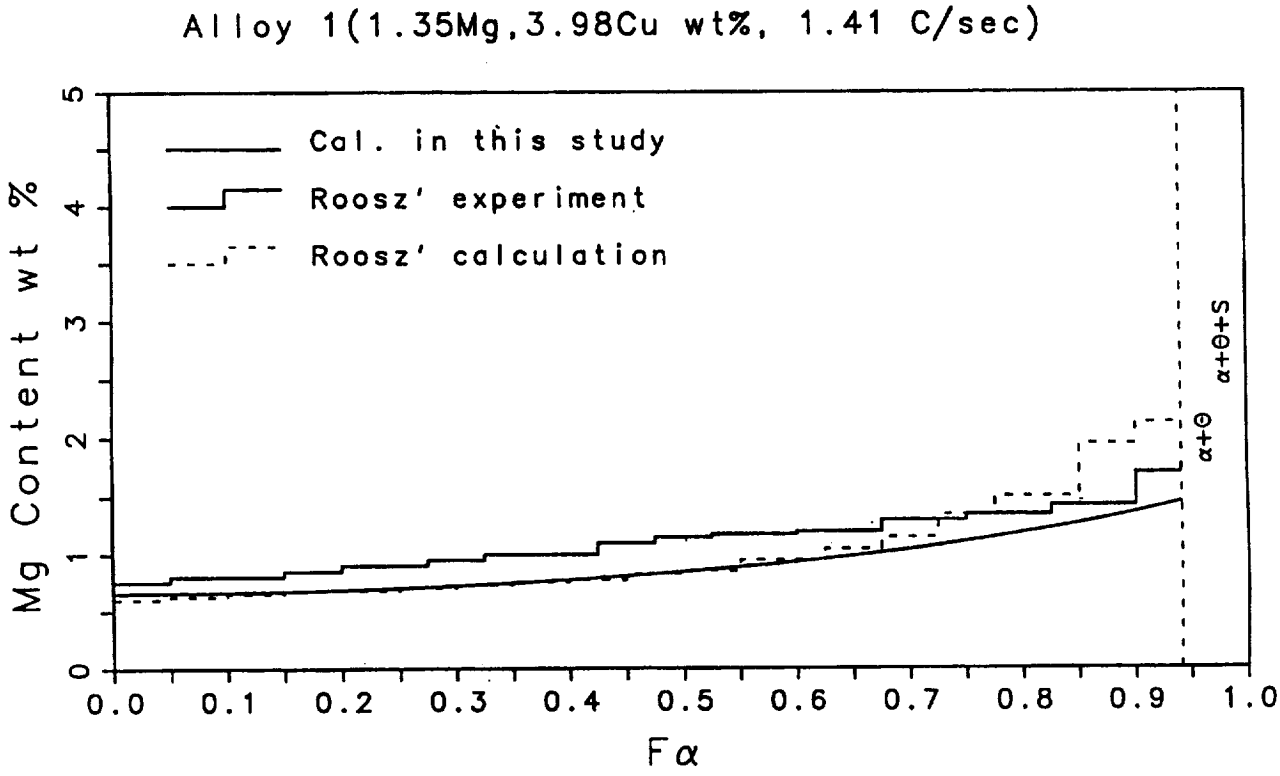


$\Delta H^{\alpha}(T_E, C_{\alpha m})$

$\Delta H^{\beta}(T_E, C_{\beta m})$

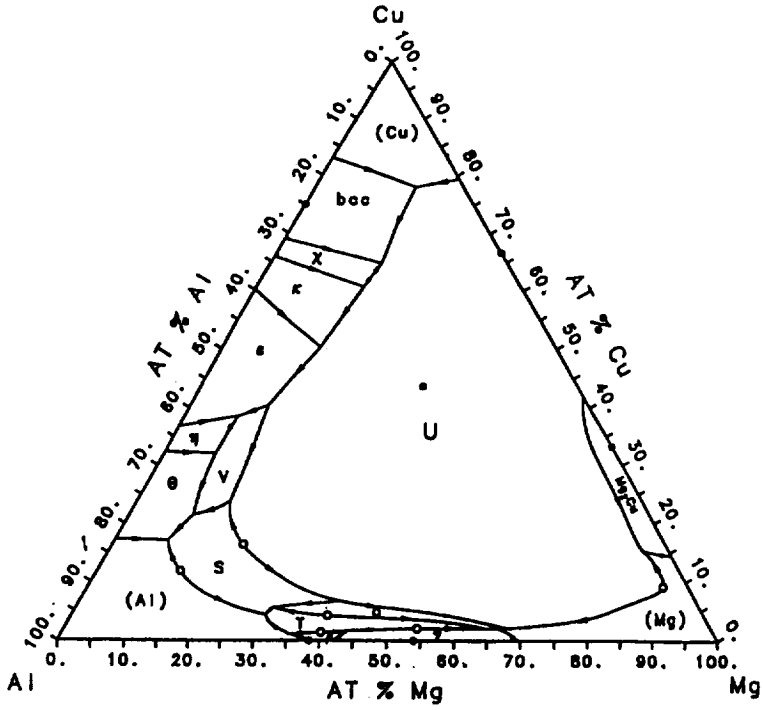
Enthalpy of Solidification:

$$\Delta H = [a\,\Delta H^{\alpha}(T_E, C_{\alpha m}) + b\,\Delta H^{\beta}(T_E, C_{\beta m})] - \Delta H^{L}(T_E, C_E)]$$

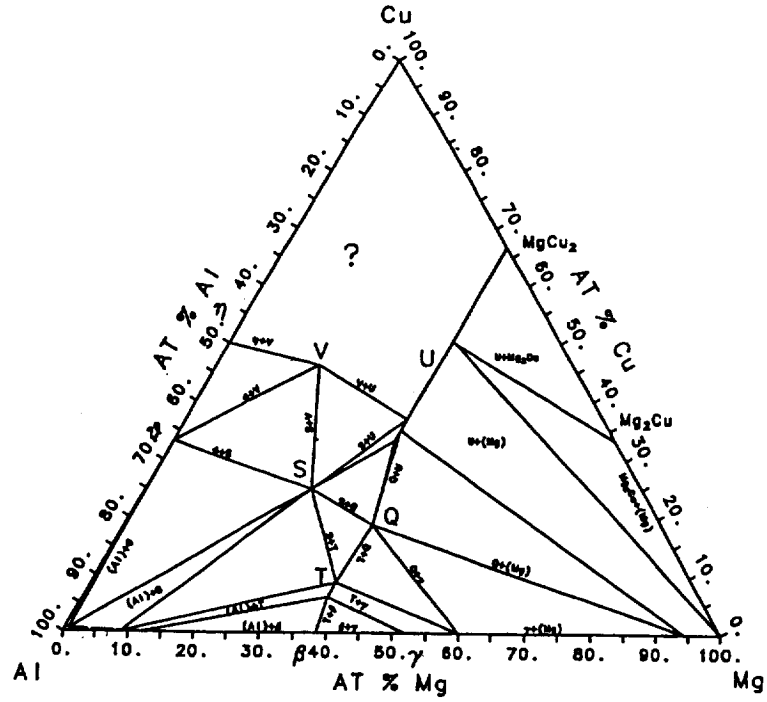


Enthalpy of Solidification

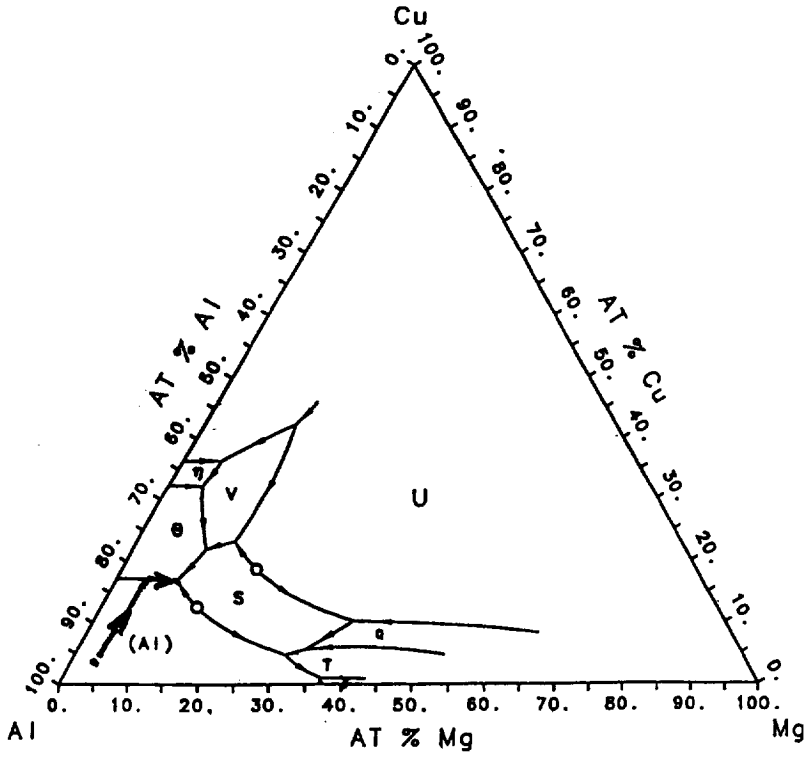
Experimental Liquidus Projection of Al-Mg-Cu



Calculated Isotherm of Al-Mg-Cu at 400 °C



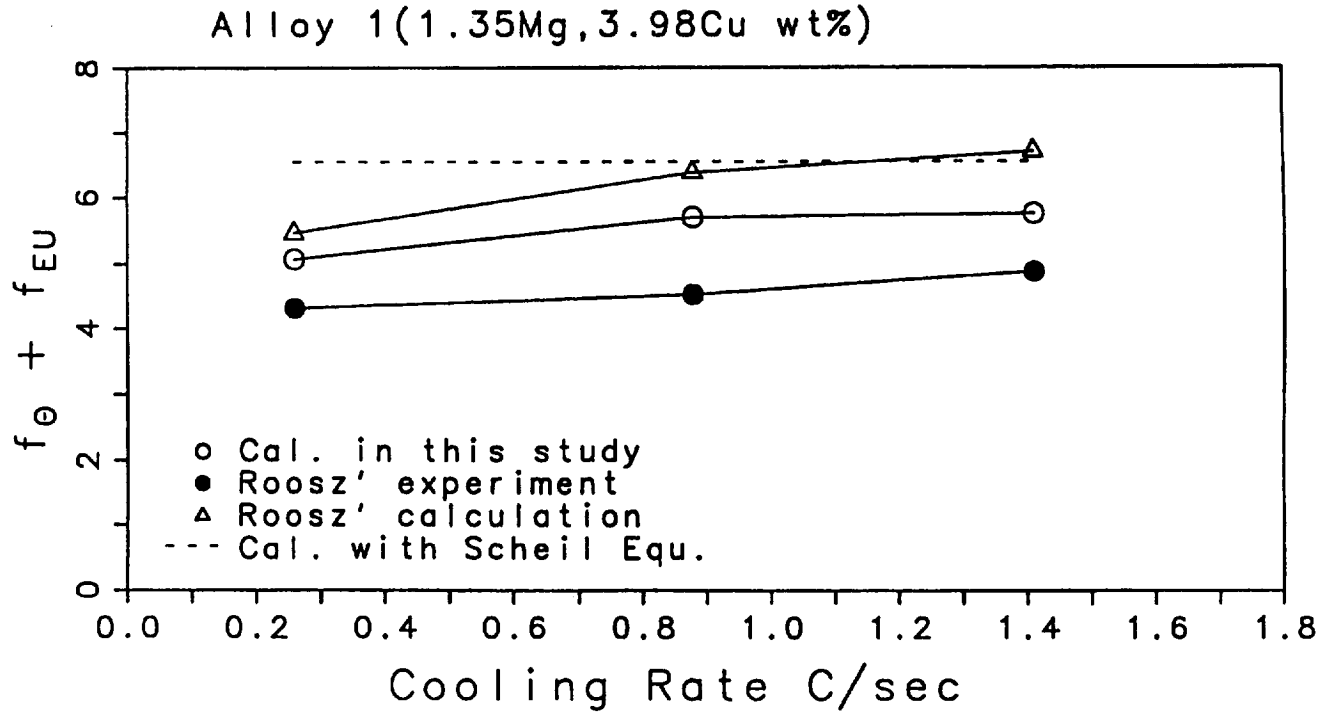
Calculated Liquidus Projection for the
Al-rich corner of Al-Mg-Cu

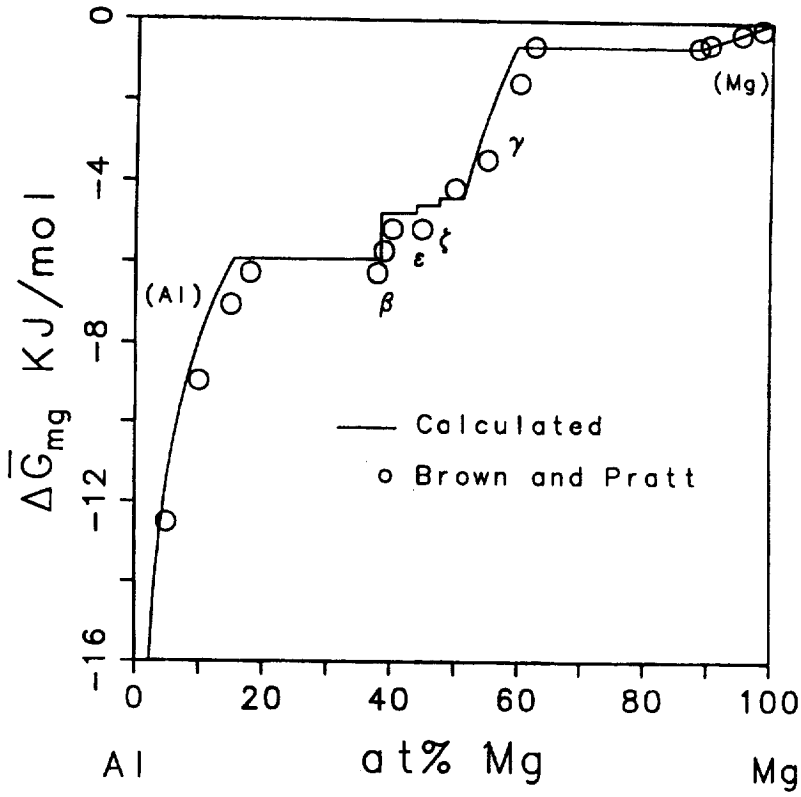


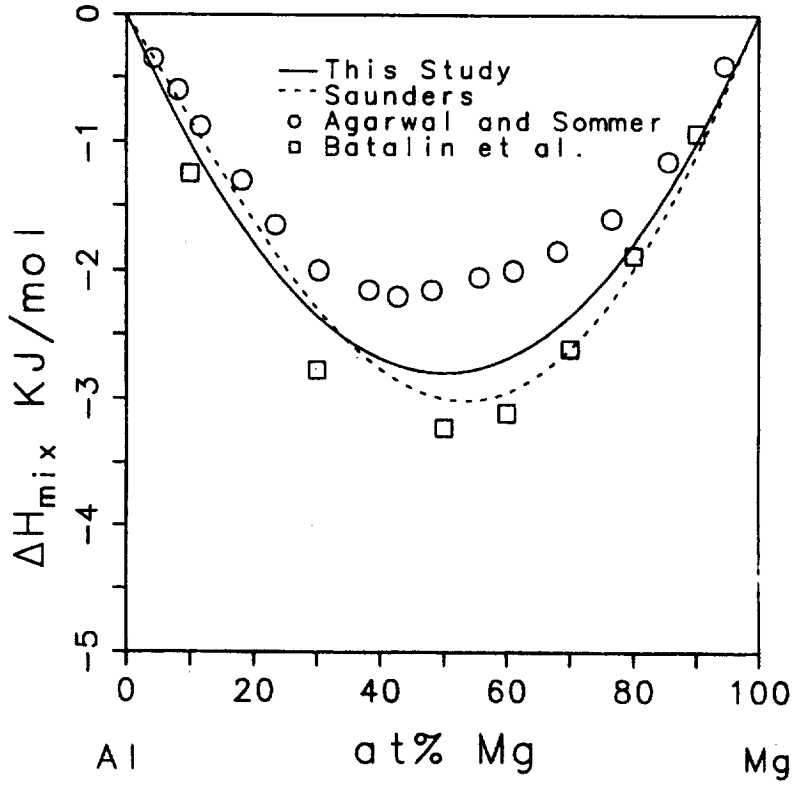
Demonstrate the Importance of Using Correct Distribution Coefficient, k

Comparison between the model proposed in this study and that by Roozs and Exner

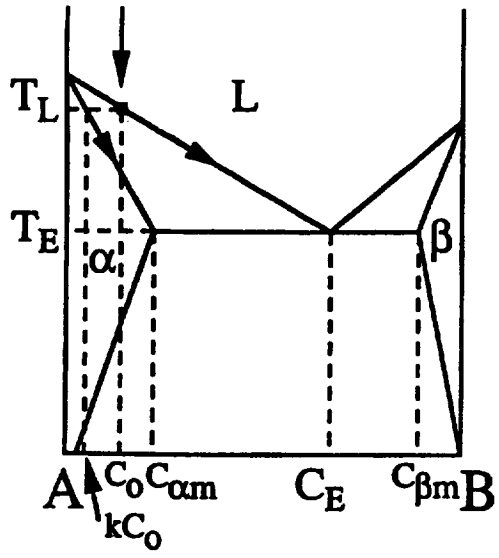
	Model of Roozs & Exner	Present model
Mass balance: Scheil equation with solid state diffusion	yes	yes
Distribution coefficient	Taken from binaries directly as constant	Computed from thermodynamic model
Heat balance	yes	Assumed constant cooling rate
Dendritic coarsening	Described by semi-empirical equation	no

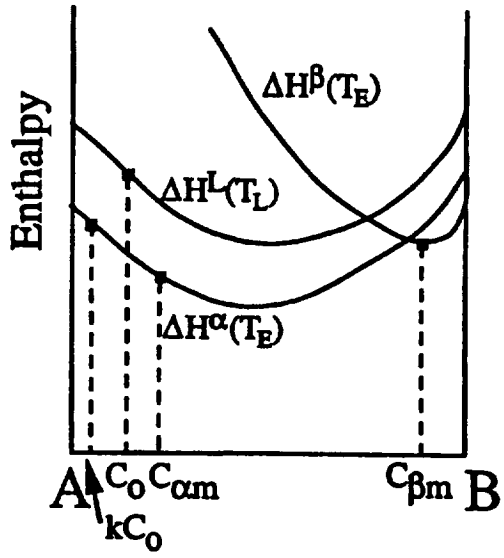



0
-4
-8
-12
-16
$\Delta\bar{G}_{mg}$ KJ/mol
(Al)
β
ε
ζ
γ
(Mg)
Calculated
Brown and Pratt
0
20
40
60
80
100
Al
at% Mg
Mg


0
-1
-2
-3
-4
-5
ΔH_{mix} KJ/mol
This Study
Saunders
Agarwal and Sommer
Batalin et al.
0
20
40
60
80
100
Al
at% Mg
Mg

Case III: Scheil Equation

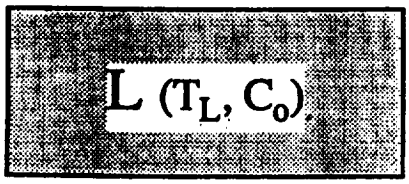




Scheil Equation:

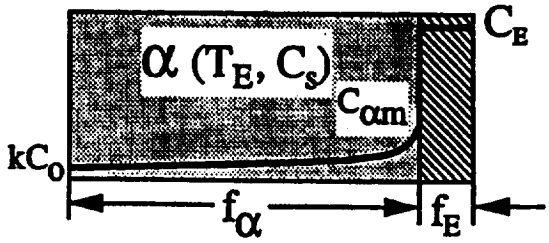
$$C_S^* = kC_O(1-f_S)^{(k-1)}$$

Before Solidification:



$\Delta H^L(T_L, C_o)$

After Solidification:



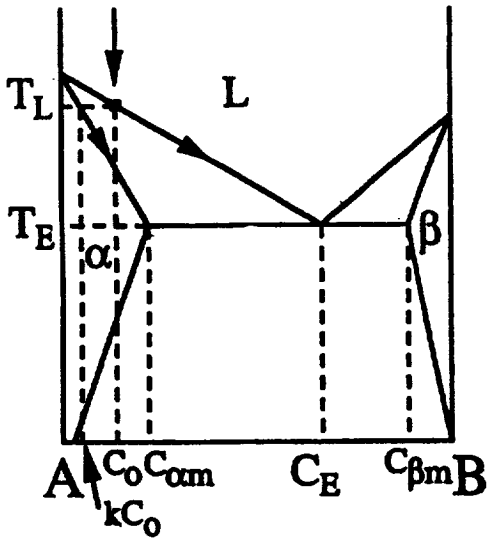
$$\Delta H^E = a\,\Delta H^{\alpha}(T_E, C_{\alpha m}) + b\,\Delta H^{\beta}(T_E, C_{\beta m})$$

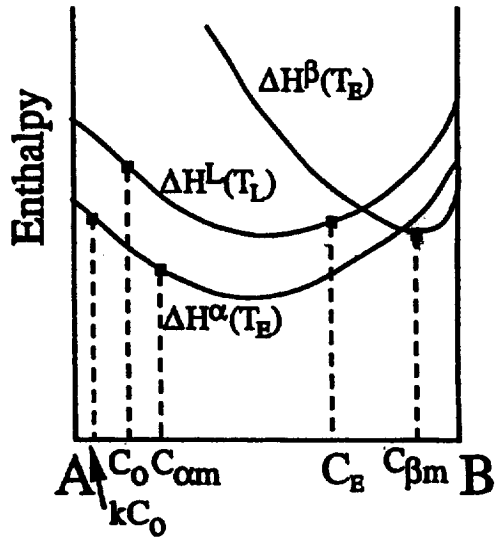
$$\Delta \overline{H}^{\alpha} = \left[\int_0^{f_\alpha} \Delta H^{\alpha}(T_E, C_s)\, df_\alpha\right] / f_\alpha$$

Enthalpy of Solidification:

$$\Delta H = (\Delta \overline{H}^{\alpha} f_\alpha + \Delta H^E f_E) - \Delta H^L (T_L, C_o)$$

Case III: Scheil Equation

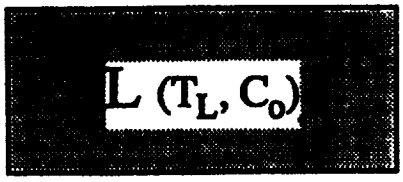




Scheil Equation:

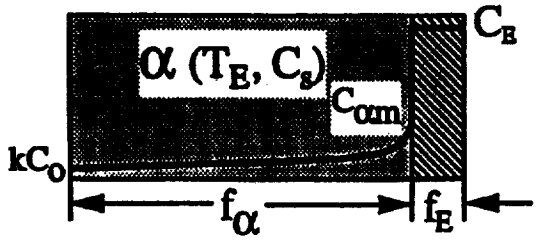
$$C_S^* = kC_O(1-f_S)^{(k-1)}$$

Before Solidification:



$\Delta H^L(T_L, C_o)$

After Solidification:



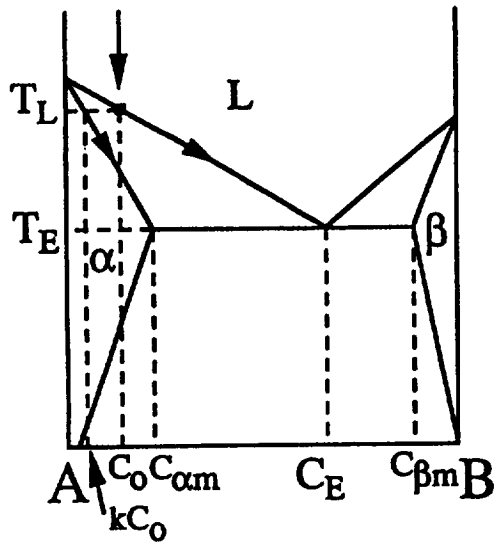
$$\Delta H^E = a\,\Delta H^{\alpha}(T_E, C_{\alpha m}) + b\,\Delta H^{\beta}(T_E, C_{\beta m})$$

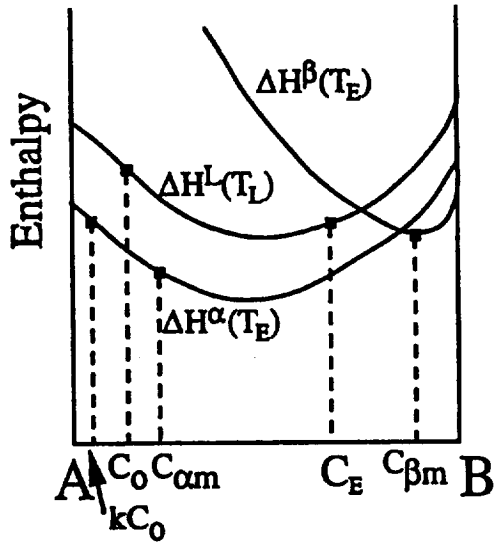
$$\Delta \overline{H}^{\alpha} = \left[\int_0^{f_\alpha} \Delta H^{\alpha}(T_E, C_s)\, df_\alpha\right] / f_\alpha$$

Enthalpy of Solidification:

$$\Delta H = (\Delta \overline{H}^{\alpha} f_\alpha + \Delta H^E f_E) - \Delta H^L (T_L, C_o)$$

Case III: Scheil Equation

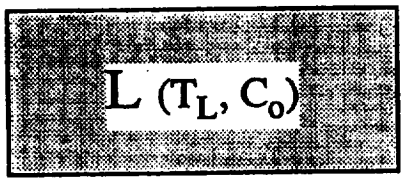




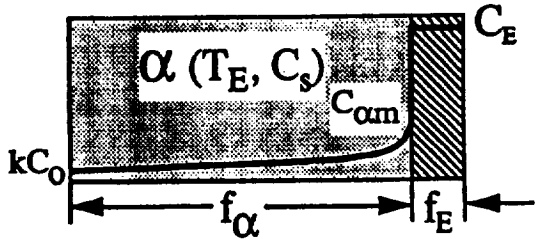
Scheil Equation:

$$C_S^* = kC_O(1-f_S)^{(k-1)}$$

Before Solidification:



After Solidification:



$\Delta H^L(T_L, C_o)$

$$\Delta H^E = a\,\Delta H^{\alpha}(T_E, C_{\alpha m}) + b\,\Delta H^{\beta}(T_E, C_{\beta m})$$

$$\Delta \overline{H}^{\alpha} = \left[\int_0^{f_\alpha} \Delta H^{\alpha}(T_E, C_s)\, df_\alpha\right] / f_\alpha$$

Enthalpy of Solidification:

$$\Delta H = (\Delta \overline{H}^{\alpha} f^{\alpha} + \Delta H^{E} f^{E}) - \Delta H^{L}(T_L, C_o)$$

Estimation of Cp

Yeum, Speiser & Poirier (1989)

Data Needed to Estimate Surface Tension (σ) of Binary Liquid Alloys

σ_A: Surface tension of the pure component A

σ_B: Surface tension of the pure component B

ρ_A: Density of the pure component A

ρ_B: Density of the pure component B

$\Delta^{XS}G$: Excess Gibbs energy of the liquid alloy

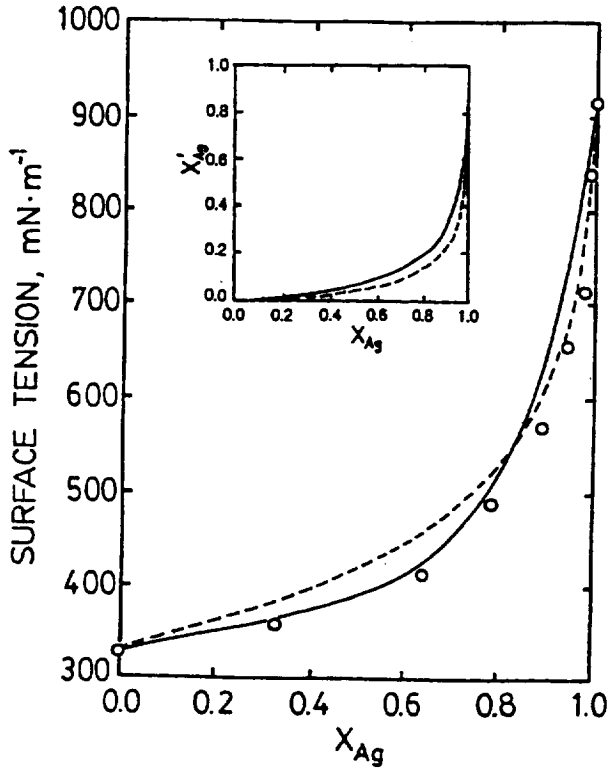
Surface Tension

10 Binary Liquid Alloy Systems were Evaluated

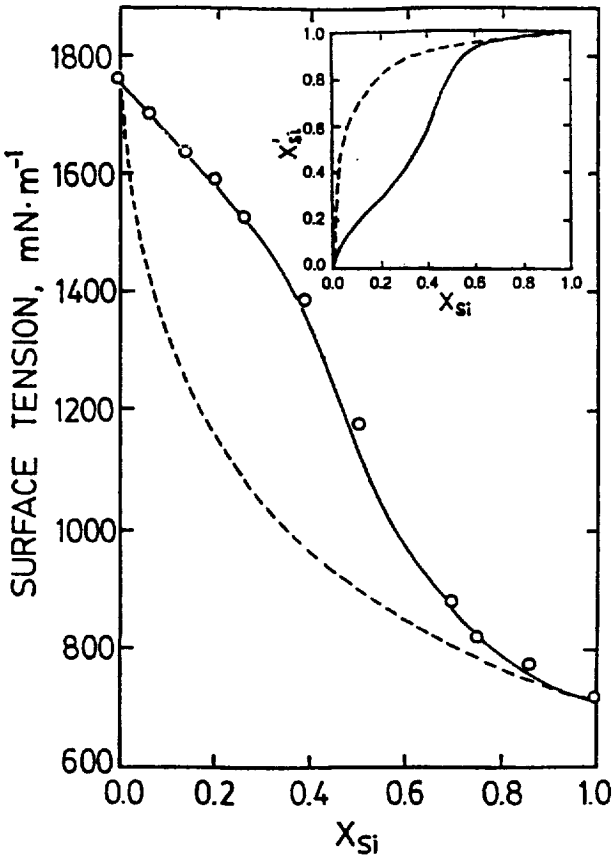
+ deviations from ideal behavior

- deviations from ideal behavior

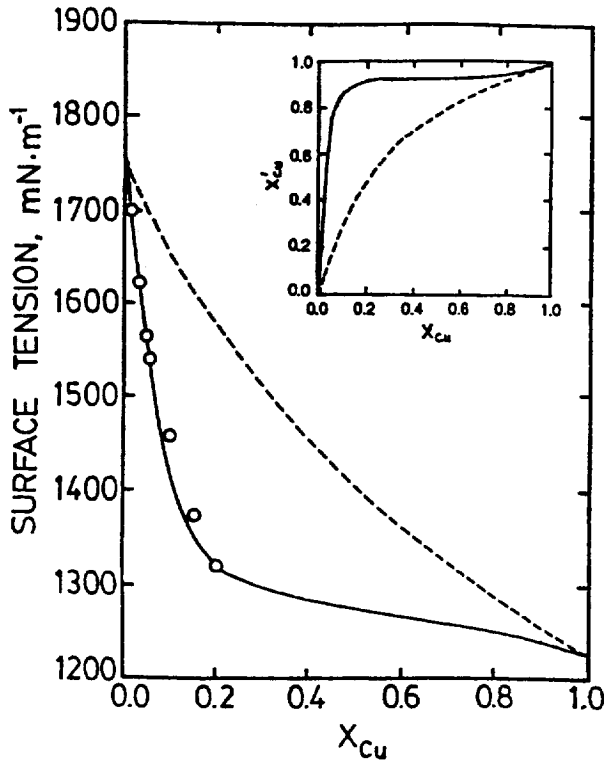
+,- deviations from ideal behavior



Surface tensions of Bi-Ag alloys at 1233 K: o = Metzger; ---- = ideal solution; and —— = calculated.



Surface tensions of Ni-Si alloys at 1823 K: o = Popel *et al.*; - - - = ideal solution; and —— = calculated.



Surface tensions of Fe-Cu alloys at 1823 K: o = Dyson; - - - = ideal solution; and —— =calculated.

Conclusions

1. A careful assessment of the thermodynamic and phase equilibrium data of binary and higher order systems is essential for developing a data base for engineering applications.

   Distribution Coefficients →
   Paths of Solidification
   Enthalpy of Fusion
   Enthalpy of Solidification
   Heat Capacity
   Surface Tension

2. A combined modelling / experimental approach is the best (perhaps the only realistic) approach to obtain a thermodynamic description of multi-component alloy systems.