The CALPHAD method and its uncertainty quantification challenge

Ursula R. Kattner
MSED, MML, NIST

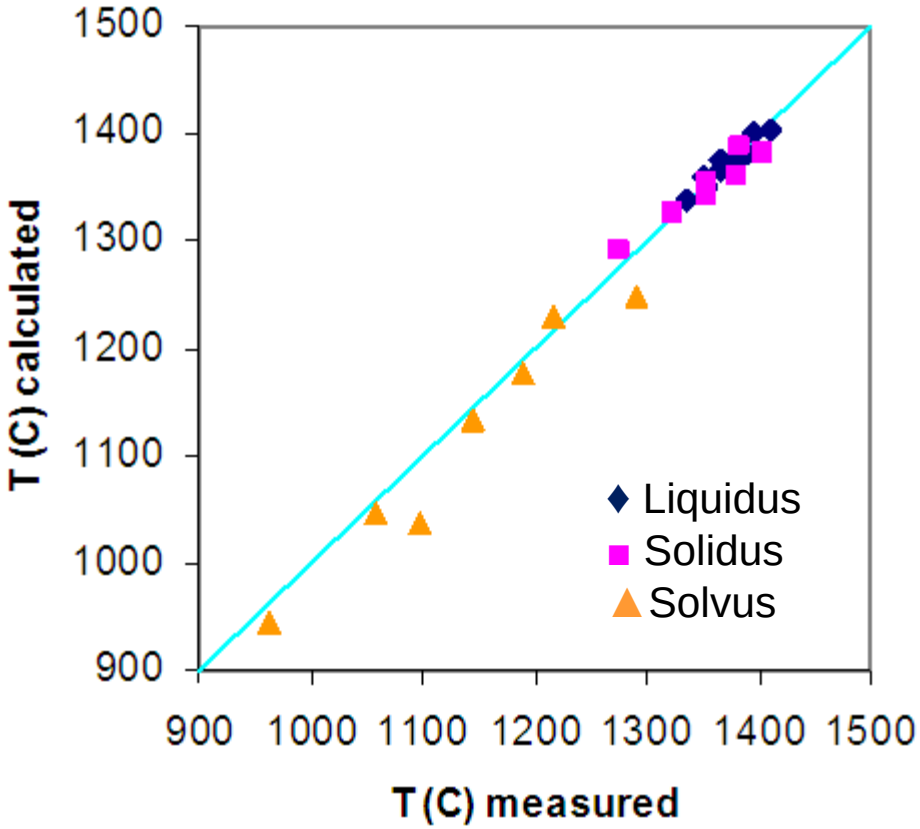
Workshop on Quantification of Uncertainties in Material Science
Gaithersburg, MD
January 15, 2016

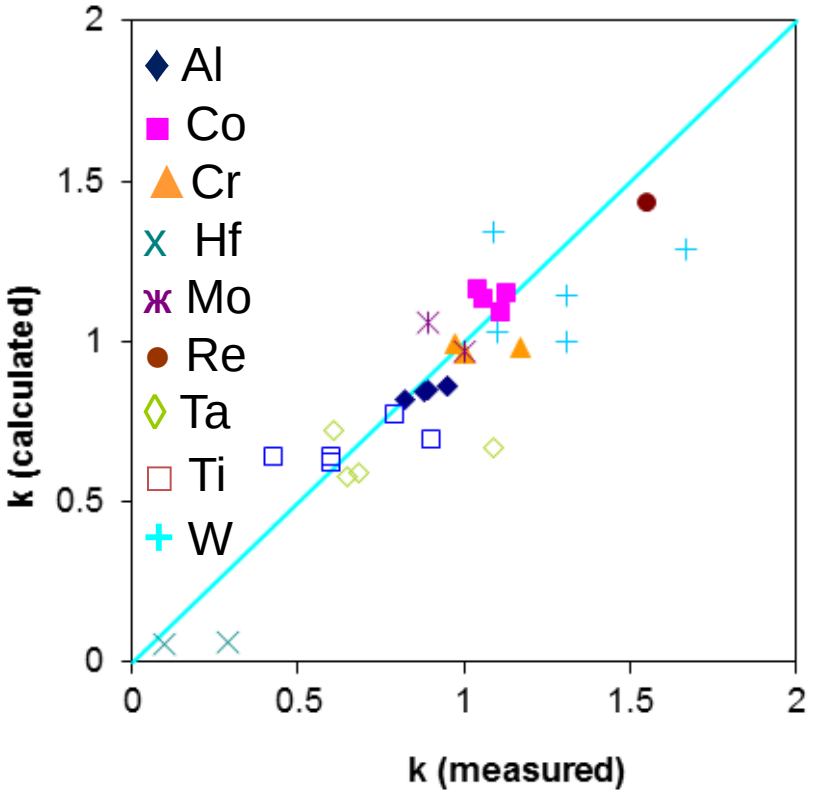
Why CALPHAD?

- **CAL**culation of **PHA**se **D**iagrams and more
- Currently only method for calculating multi-component, multiphase systems with solution phases
- Integrated Computational Materials Engineering, National Research Council, 2008:
  "… CALPHAD software is arguably the most important (and perhaps the only) generic tool available for ICME practitioners …"
- **BUT:** Practitioners need to be able to evaluate the uncertainty of results obtained from CALPHAD calculations for efficient materials and process development.

Comparison of measurement and calculation

Liquidus, solidus and solvus temperatures

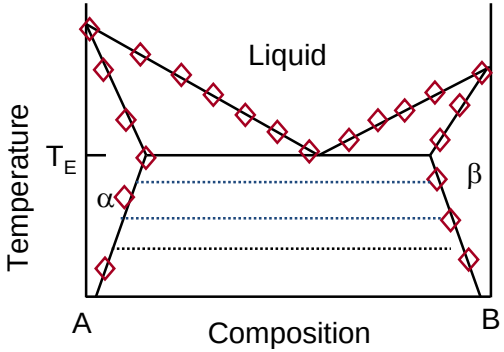




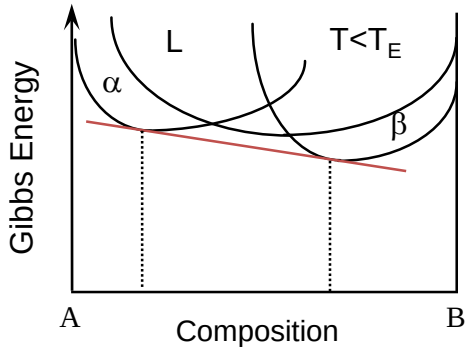
Partition ratios

Original CALPHAD approach

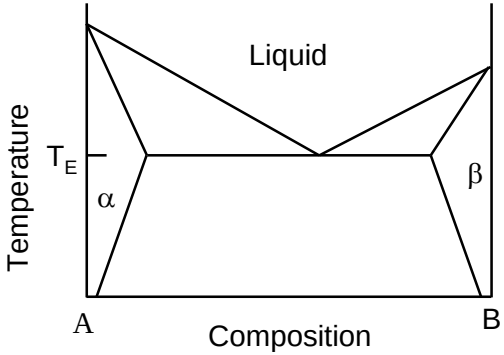
Experimental phase diagram and thermochemical data



Determine Gibbs energy functions for each phase: $G = f(x,T,P)$



Calculated phase diagram



$$G^{\phi} = G^{0} + G^{ideal} + G^{excess}$$

Binaries ⇨ Ternaries ⇨ Quaternaries ⇨ n^{th} Order Systems

True quaternary compounds are rare in metallic systems

⇨Assessment of ternary systems is usually sufficient for the description of a multicomponent system

⇨Same methodolgy can be applied to the description of other property data

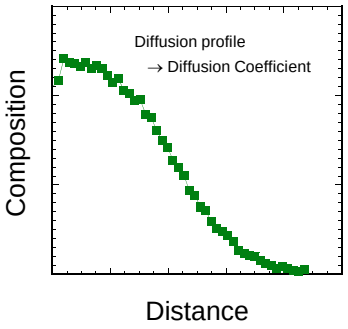
CALPHAD method and diffusion

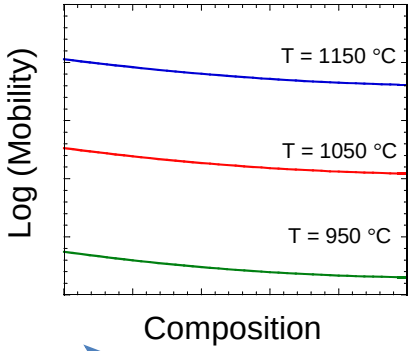
$$D_{kj}^{L} = x_k M_k \frac{\partial \mu_k}{\partial x_j}$$

use CALPHAD method to describe diffusion mobilities, M_k

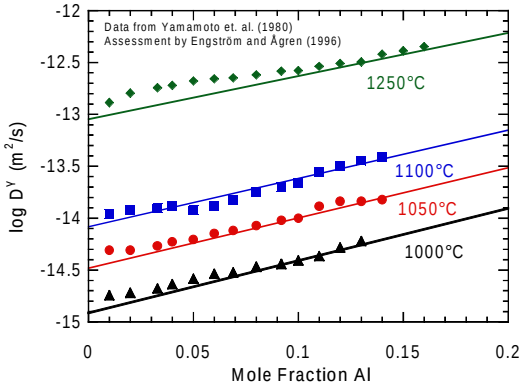
thermodynamic factor

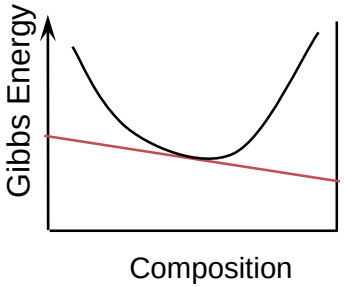
Experimental diffusion data → Determine diffusion mobility, $M = f(x,T)$ → Diffusion process simulations



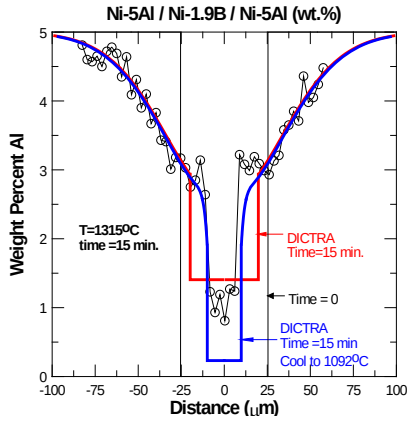


$\rightarrow M_i$





$\rightarrow \dfrac{\partial^2 G}{\partial x_i \partial x_j}$



Binaries → Ternaries → Quaternaries → n^{th} order Systems

CALPHAD models

- Describe properties as function of
  - **Temperature**
  - Pressure
  - **Composition**
  - Gibbs energy models with internal equilibrium may result in an implicit temperature dependence of the property
- Should describe phases as physically as possible
- Functions are not just “curves” that are fitted!
- Composition model used for thermodynamics defines composition model for other properties

Assessments and databases

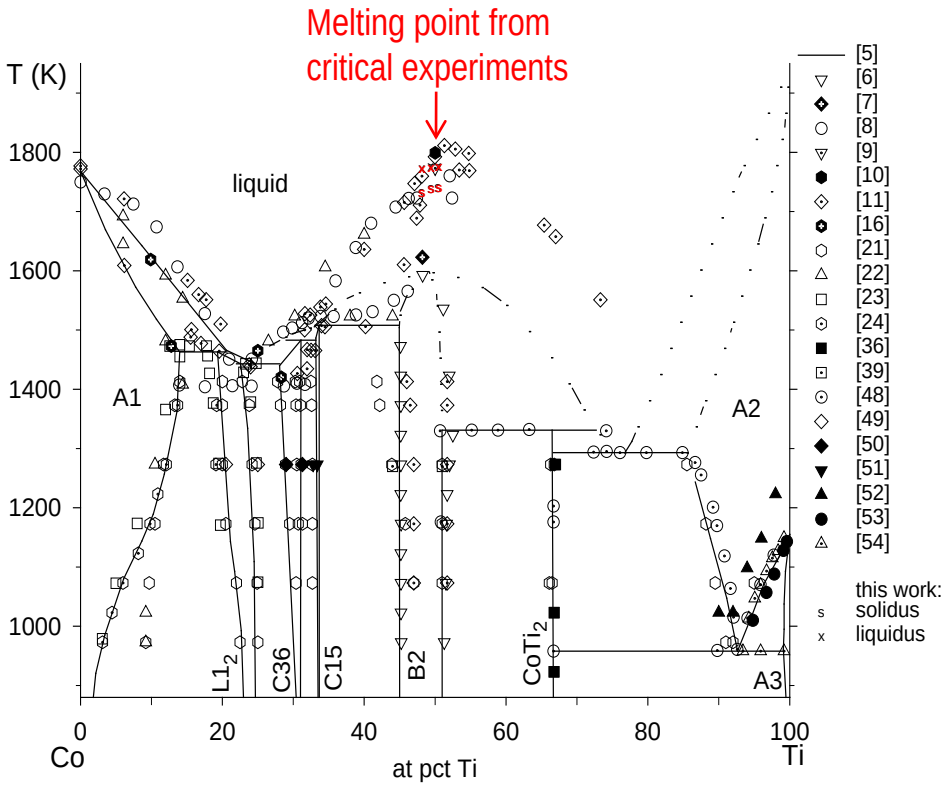
- Assessment of a system
  - Primarily binary and ternary systems
  - Selection of model descriptions for individual phases
  - Critical evaluation of experimental data
  - Adjustment of model parameters to experimental data
- Databases
  - At least 4 components (=*"multicomponent"*)
  - Critical evaluation of available thermodynamic descriptions of constituent binary and ternary subsystems
  - Model parameters that are not determined by the constituent binary and ternary subsystems are fit to experimental data

Data for model parameter assessment

- Phase diagram data
  - Thermal analysis (TA), differential thermal analysis (DTA), differential scanning calorimetry (DSC)
  - Phase analysis: Microstructure, diffraction and spectroscopy methods
  - Diffusion couples and multiples: electron probe microanalysis (EPMA)
  - Thermogravimetry, dilatometry, …
- Thermochemical data
  - Calorimetry: solution, drop, reaction, …
  - Electromotive force measurements (emf)
  - Vapor pressure measurements (Knudsen, …)
- Data from atomistic methods (DFT, …)

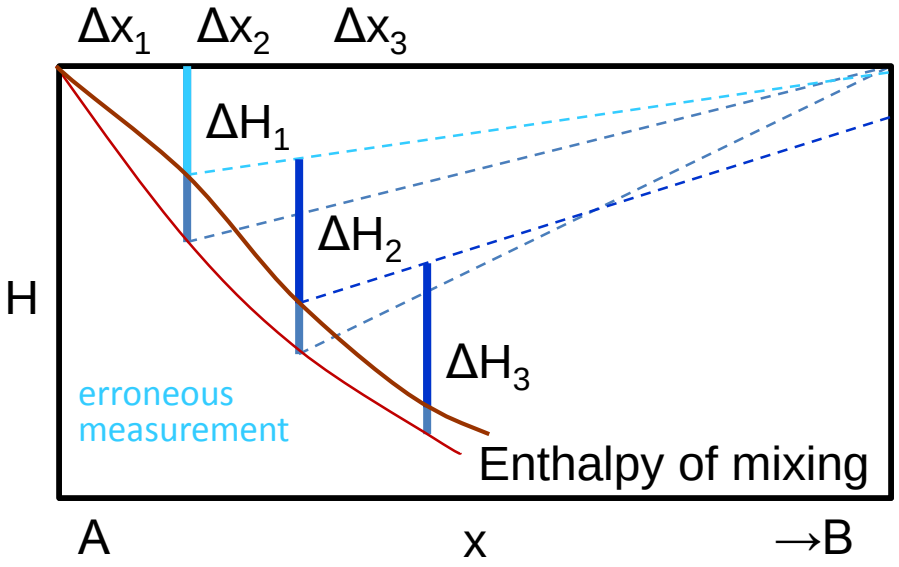
Evaluation of data from different sources

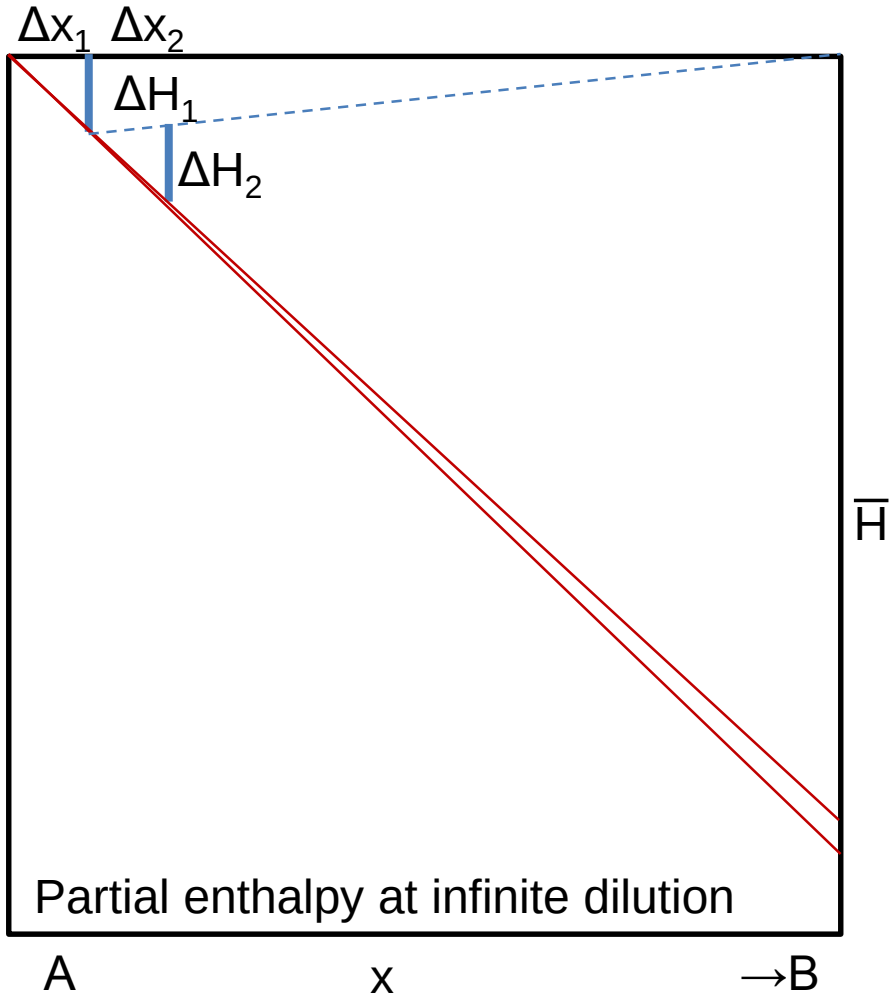
- Differences larger than individual experimental error
- Averaging is usually not acceptable



Experimental data and diagram evaluated by Murray (BAPD, 1982)

Solution calorimetry

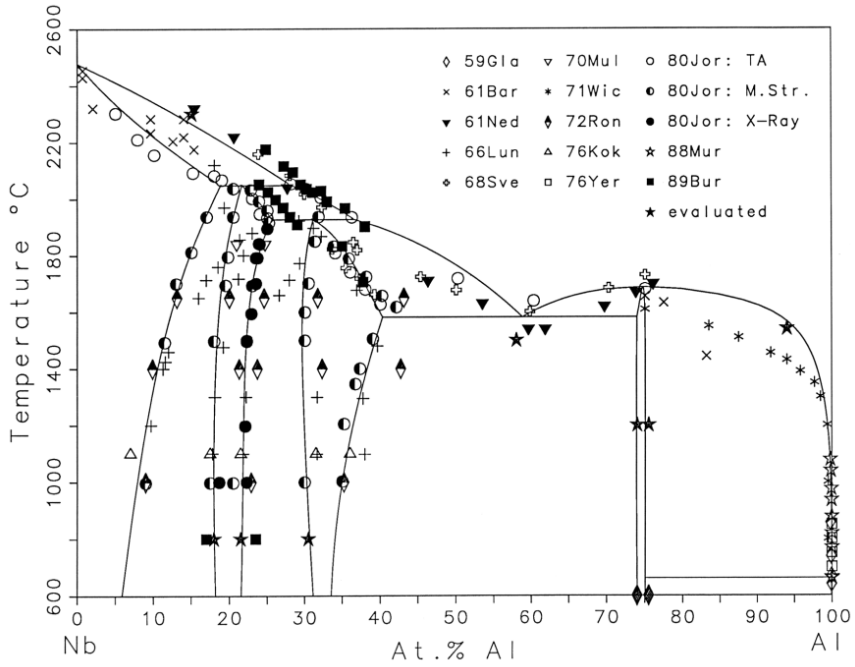




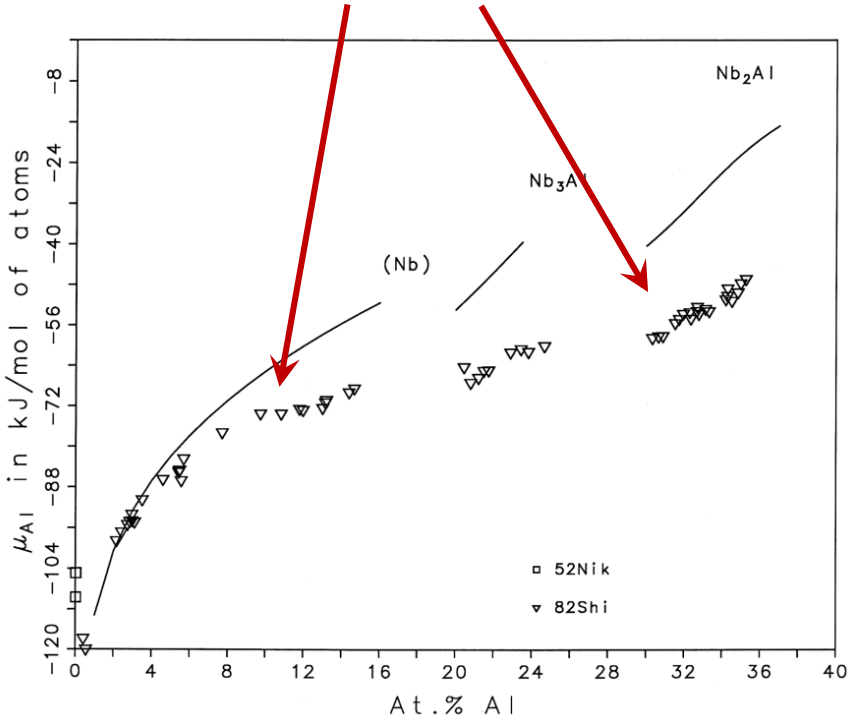
- Errors from individual measurements are propagated through entire series

Evaluation of different kinds of data

- Data inconsistencies may not be obvious



observed P_{Al} from Knudsen cell experiments lower than calculated by a factor of 2 to 6

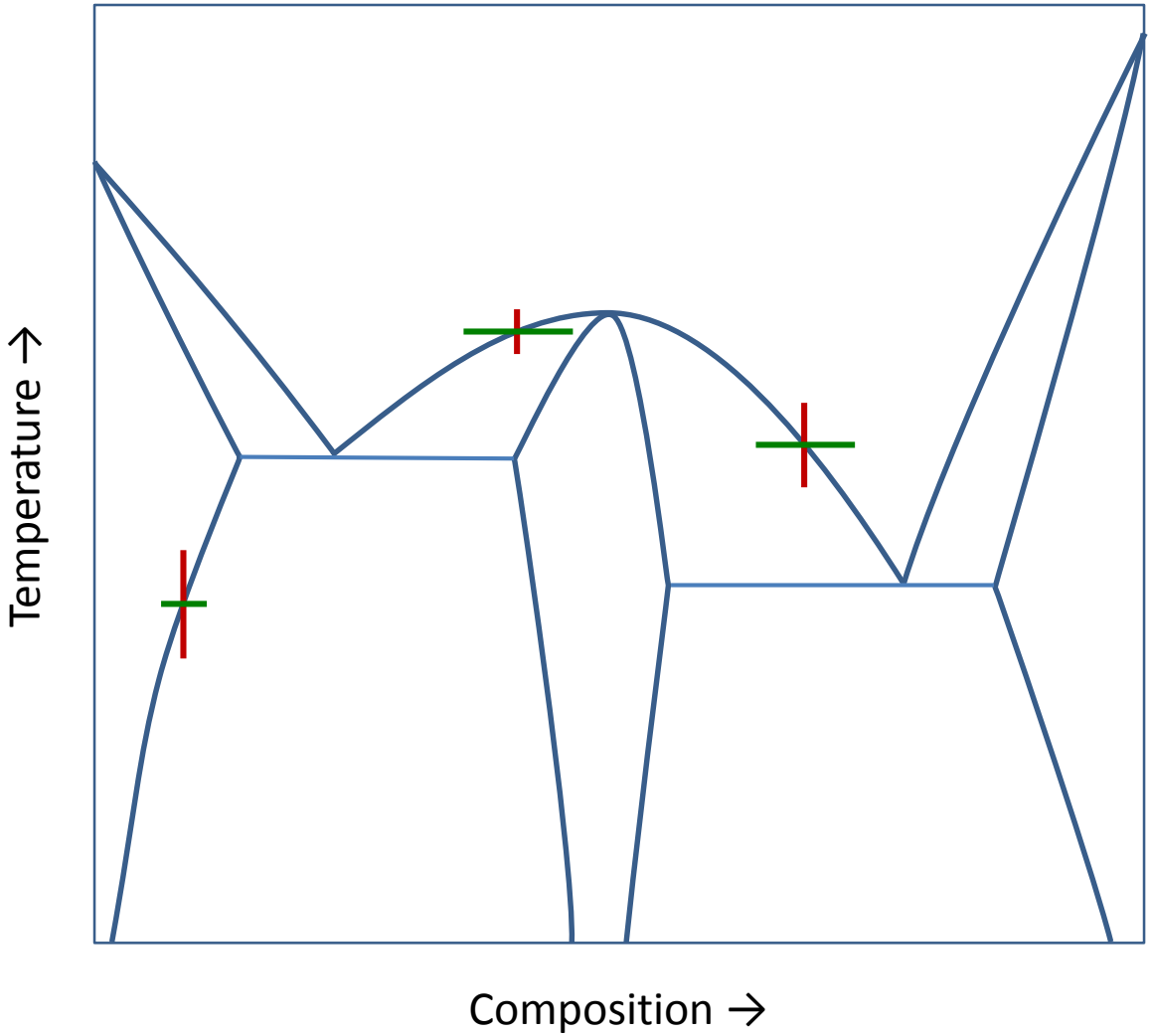


- Inconsistency can only be found during assessment

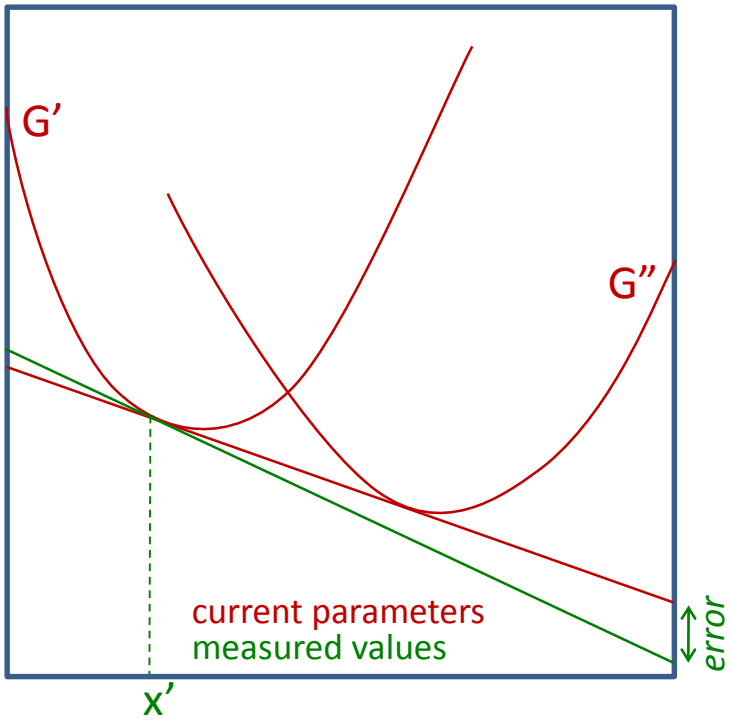
Assignment of “error” and weight

- Magnitude of error(s) assigned to a data point creates an implicit weight
- Relative magnitude of errors assigned to different quantities of a data point may influence optimization process and results
- Optimizers may provide different equations of error for the same kinds of data
- Weight of data points needs to be reevaluated during optimization process

Sensitivity of phase diagram errors

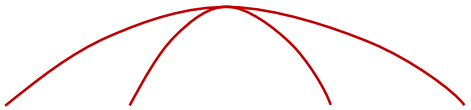


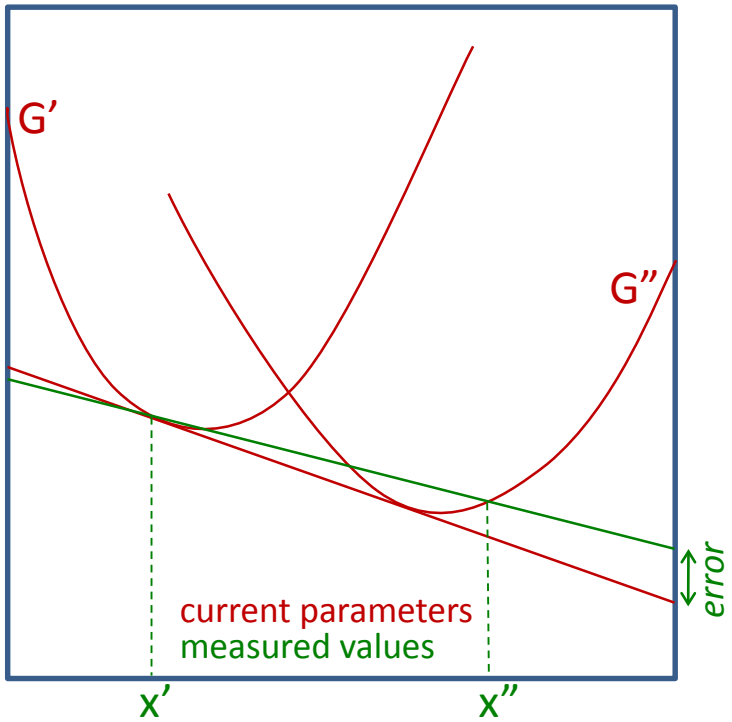
Partial Gibbs energy of a two phase equilibrium



$$\mu - {}^{\circ}G^{ref} - W = error$$

No solution if $T_{experiment}$ →

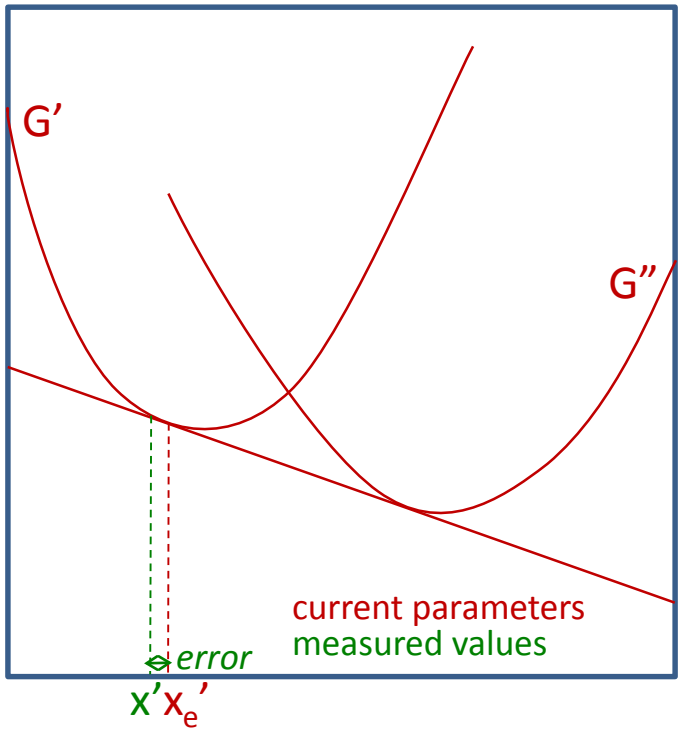


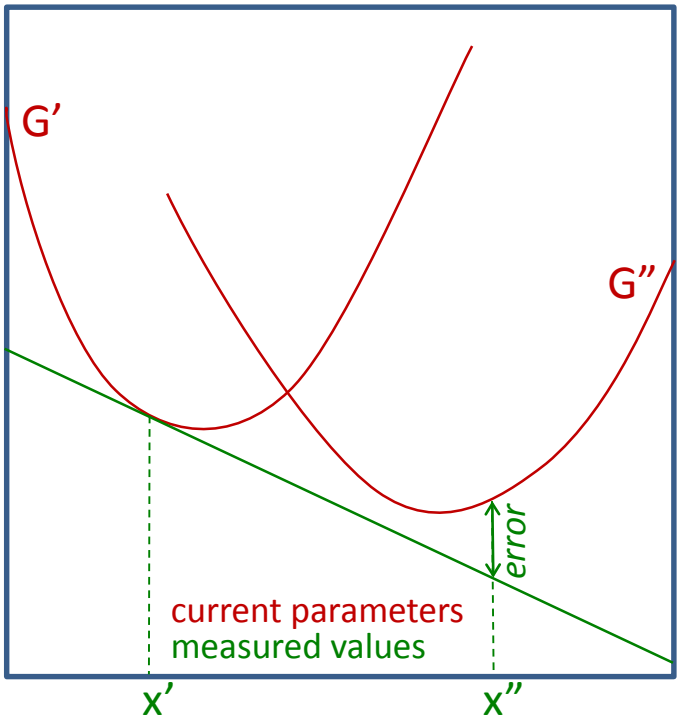


$$G' \frac{(x'' - 1)}{(x'' - x')} + G'' \frac{(x' - 1)}{(x' - x'')} - {}^{\circ}G^{ref} - W = error$$

Error depends on input for second phase

Compositions of a two phase equilibrium

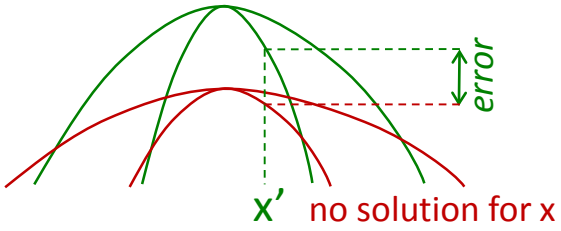




$$x'_e - x' = error$$

$$or$$

$$T_e - T = error$$



$$G' + (x' - x'')\frac{\partial G'}{\partial x} - G'' = error$$

Error depends on input for second phase

Result from an optimization

LAUF,IVERS,IALGOR,ITER,NMAX: 6 2 2 1 1, EPS = 1.00E-05
AUTHORS NOT USED : IM OS * **
MARQUARDT PARAMETER = 1.00D-06, CALCULATION WAS 1ST STEP
 979 VALUES, MEAN SQUARE OF ERROR = 16.8217

NO.	LINE	COLUMN	COEFFICIENT	CORRECTION	ERROR
1	4	1	-4906.699219	-4.199309	0.993784
2	4	2	4.302659	-0.002661	0.002249
3	5	1	-16474.871094	-0.870197	2.060547
4	5	2	-3.124728	0.000342	0.002908
5	6	1	-7283.138672	15.461390	1.592477
6	11	1	9896.750977	-101.649467	12.568715
7	11	2	-6.414345	-0.127765	0.010159
8	12	1	-44771.050781	-30.650499	19.183285
9	16	1	19089.398438	-6.902554	5.249254
10	20	1	5042.819824	-37.980129	4.898062
11	20	2	-8.171700	-0.118771	0.009219
12	21	1	-43159.507813	-106.110092	15.831768
13	24	1	-4095.636963	-18.737097	1.422898
14	24	2	1.865492	-0.023658	0.001674

Covariance (correlation) matrix

NO. CORRELATION MATRIX * 100000

1	100000												
2	53623	100000											
3	38797	3570	100000										
4	36739	57356	68243	100000									
5	-3409	-53926	61019	-3257	100000								
6	14497	28313	-6423	23863	-20462	100000							
7	11606	7280	-4213	10867	15716	40435	100000						
8	-7807	-44767	8860	-28759	51678	-67352	34866	100000					
9	400	-12208	3201	-5104	18672	-2168	6592	11082	100000				
10	35862	7881	10341	18715	-7775	21535	1564	-23022	767	100000			
11	12921	3681	-2295	9296	19967	39165	98621	36994	7516	2051	100000		
12	-8900	-30628	1155	-19252	46282	9880	77445	60521	11085	-45843	80462	100000	
13	13659	-32802	8509	-10849	51751	18993	74551	49615	14205	15418	78207	71960	100000
14	14026	-2964	-804	6529	28602	32542	85894	35661	9688	6417	87494	70989	92529	100000

Liquid

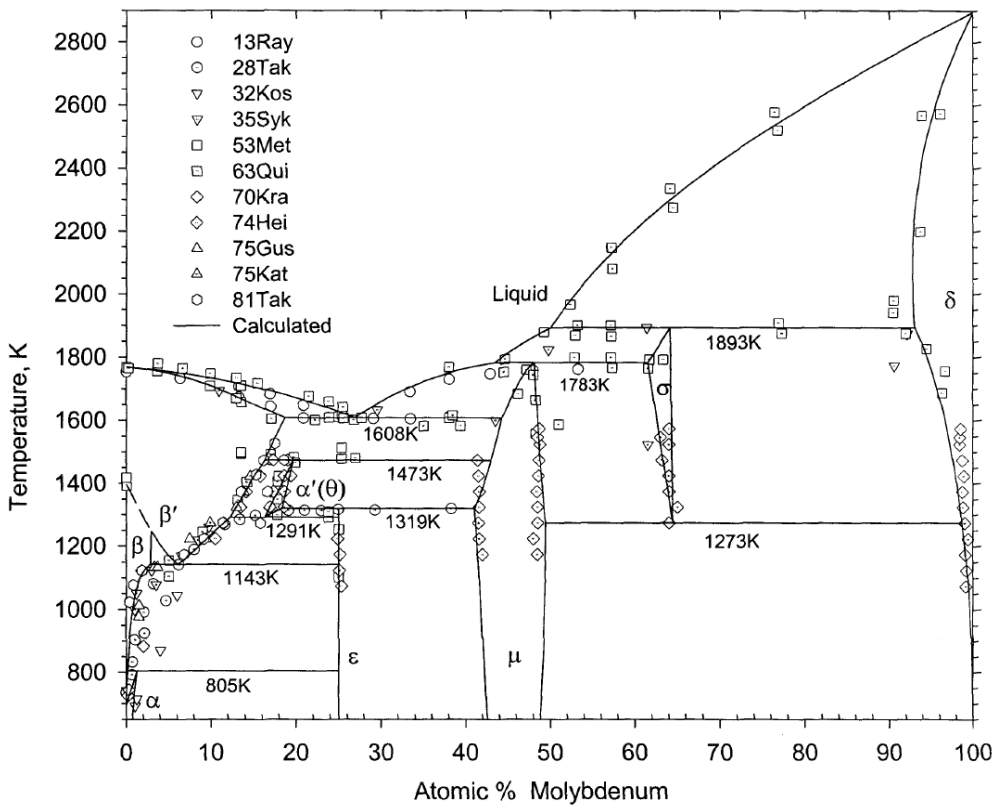
fcc-Ag

bct-Sn

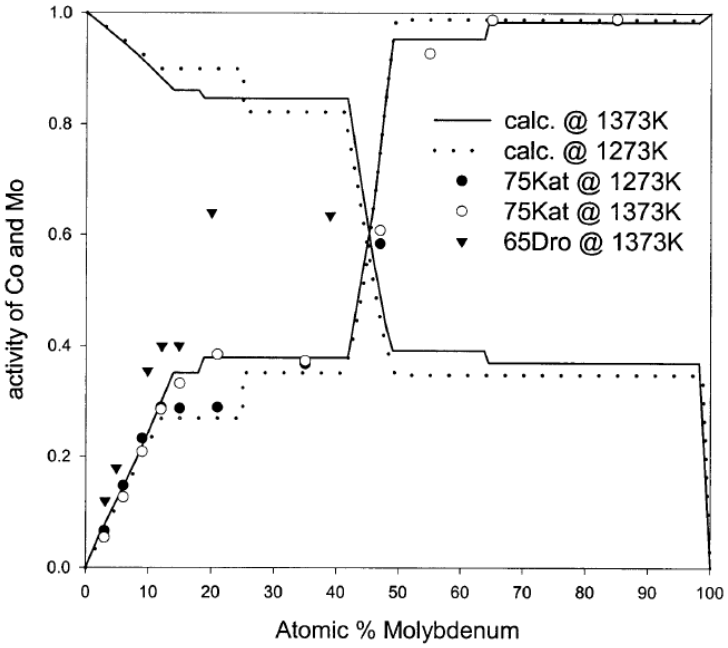
hcp-Ag,Sn

Ag_3Sn

Results from a binary CALPHAD assessment



Phase Diagram of the Co-Mo System



Thermodynamic Activities of Co and Mo at 1273 and 1373 K

Davydov & Kattner, J. Phase Equilibr. 20 (1999) 5

Malakhov, 1997: Covariance matrix

Covariance matrix obtained from least squares optimization

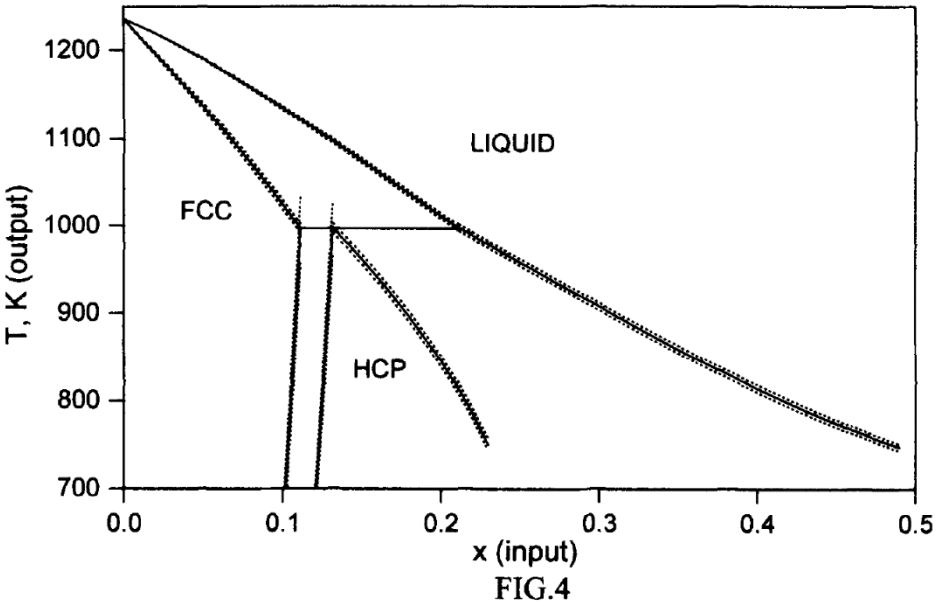


FIG.4

95% confidence intervals of calculated temperatures

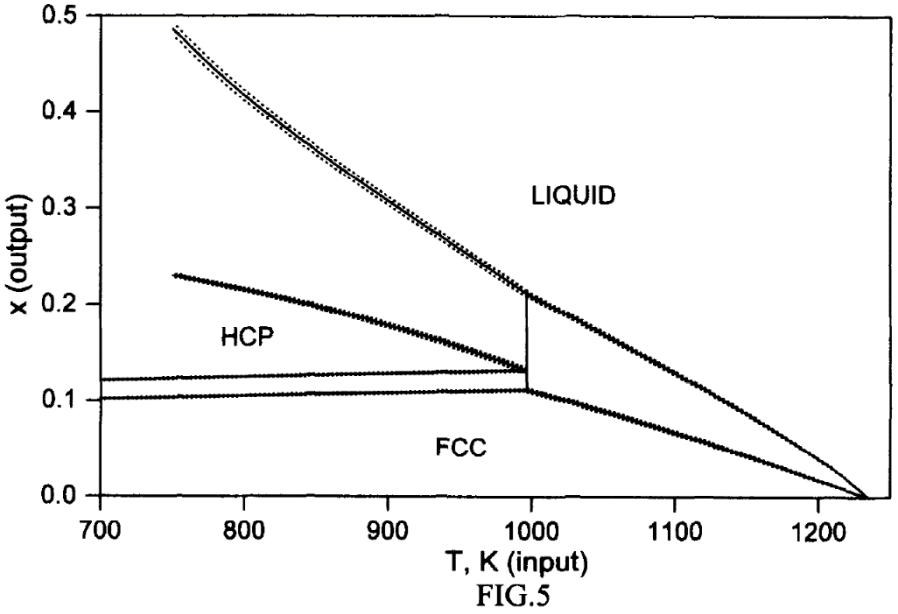


FIG.5

95% confidence intervals of calculated compositions

Stan & Reardon, 2003: Uncertainty bounds

Optimization using a genetic algorithm and Bayesian statistics

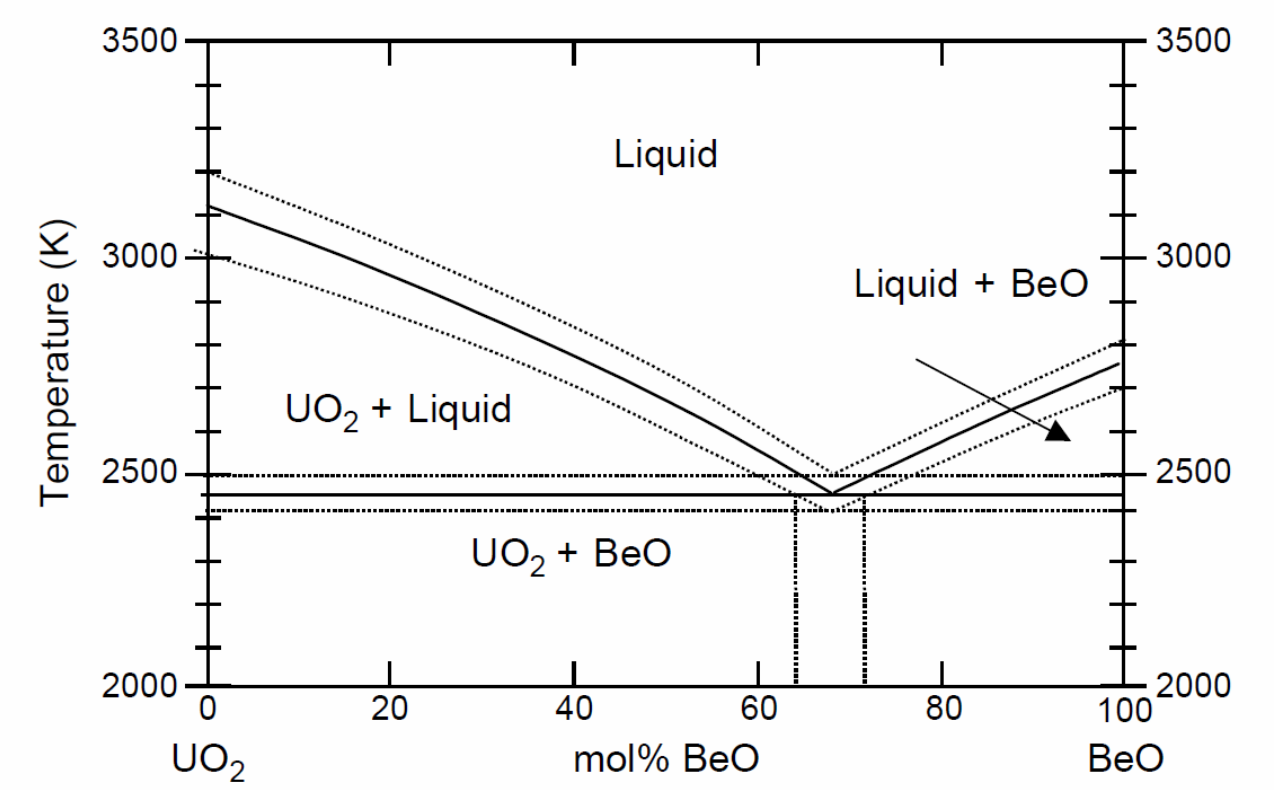
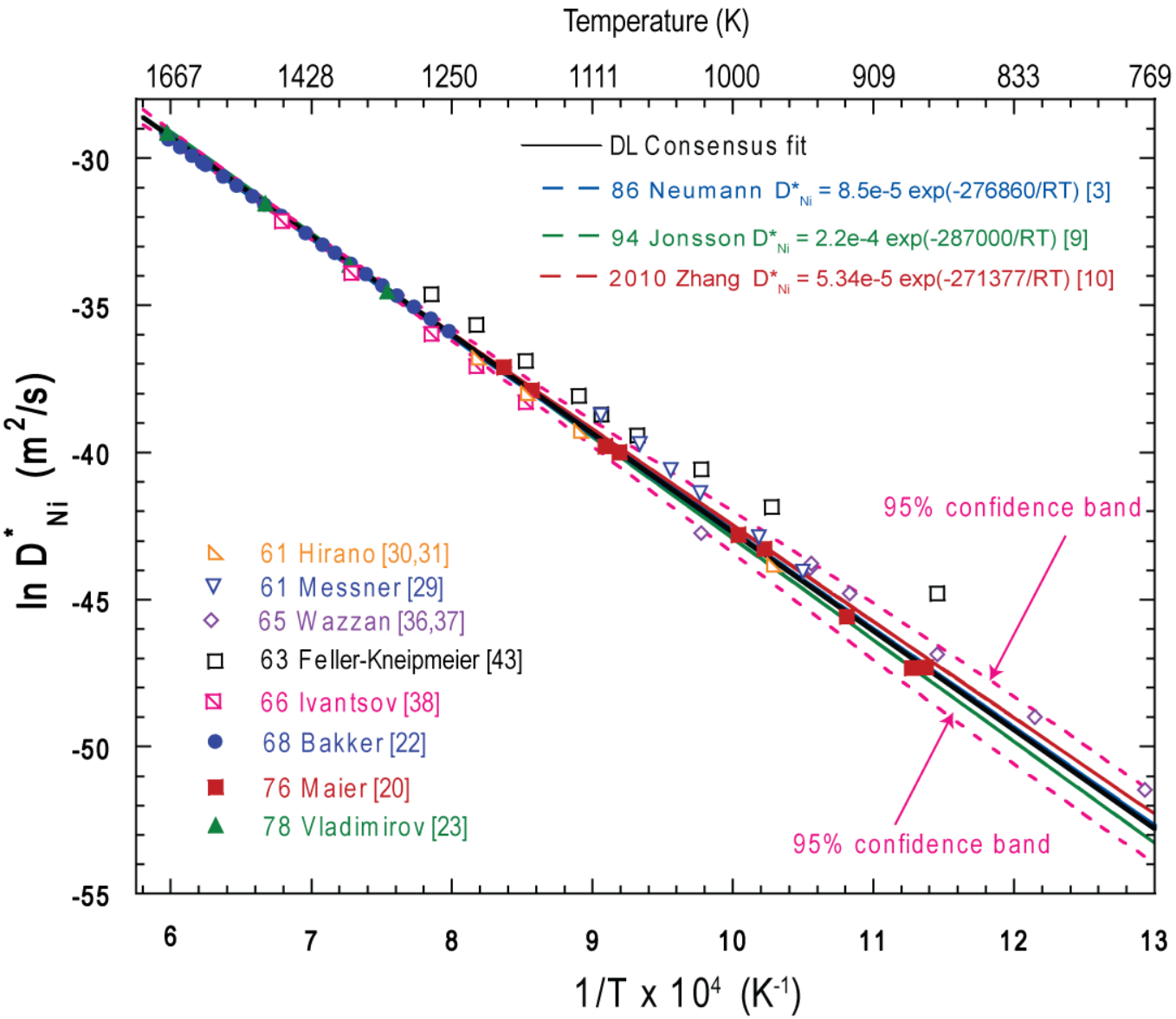


Fig. 2. The calculated UO_2–BeO phase diagram (solid lines) and the uncertainty intervals (dotted lines).

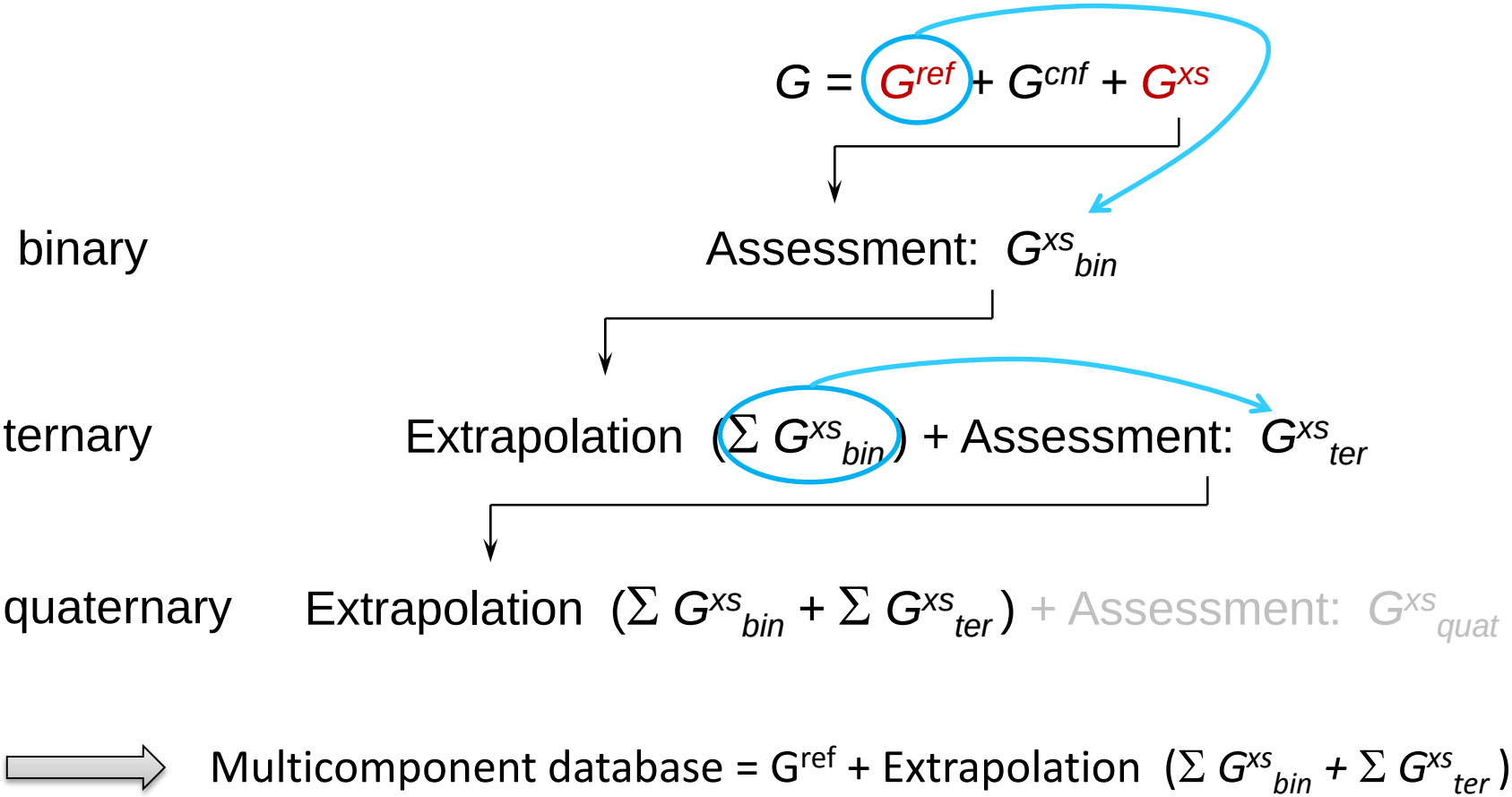
Campbell and Rukhin, 2011: Weighted means statistics



Tracer diffusion mobilities of Ni

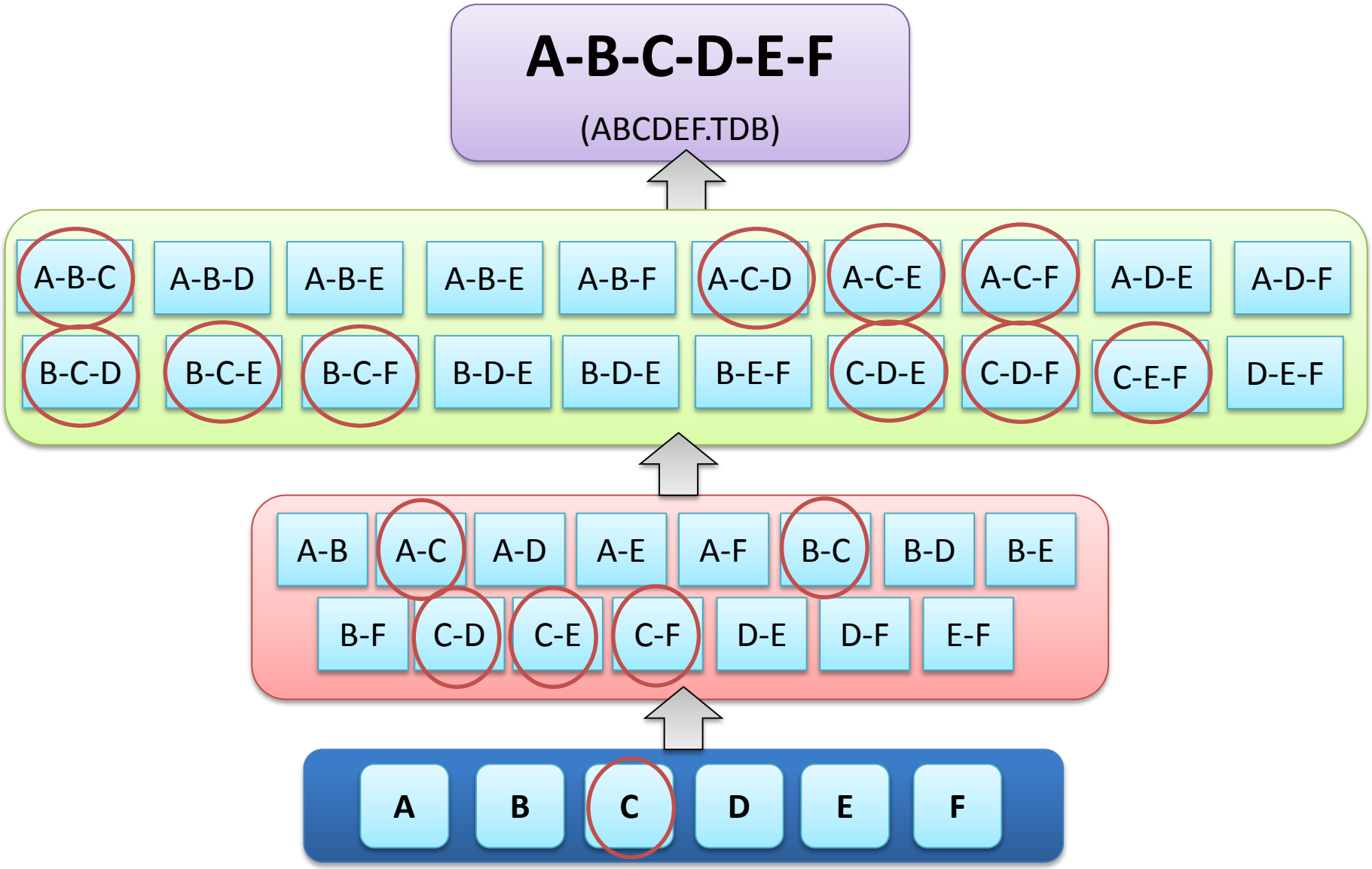
p = 3 data sets
N = 34 data points
***b** = 0 no-between studies effect*

CALPHAD methodology



BUT: How do the uncertainties propagate?

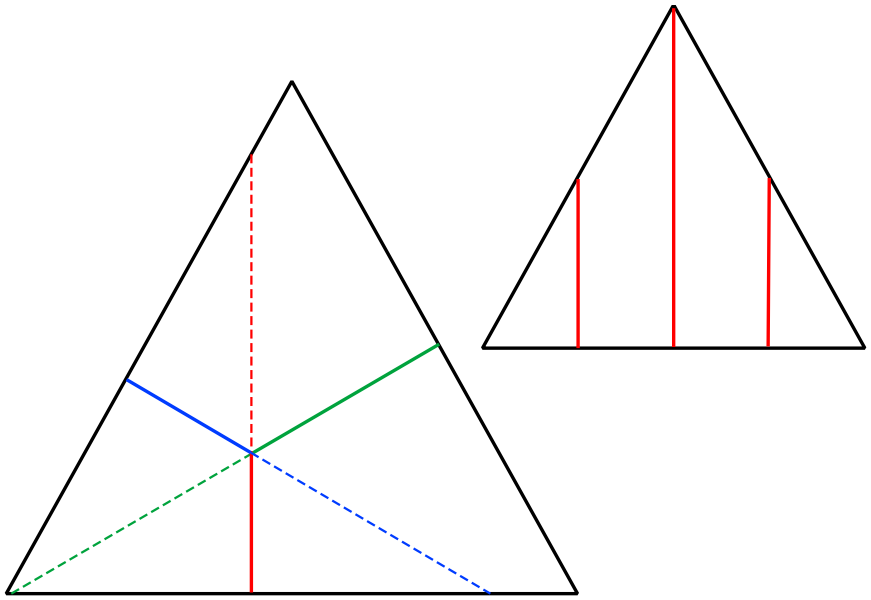
CALPHAD dependencies



Extrapolation of multicomponent systems

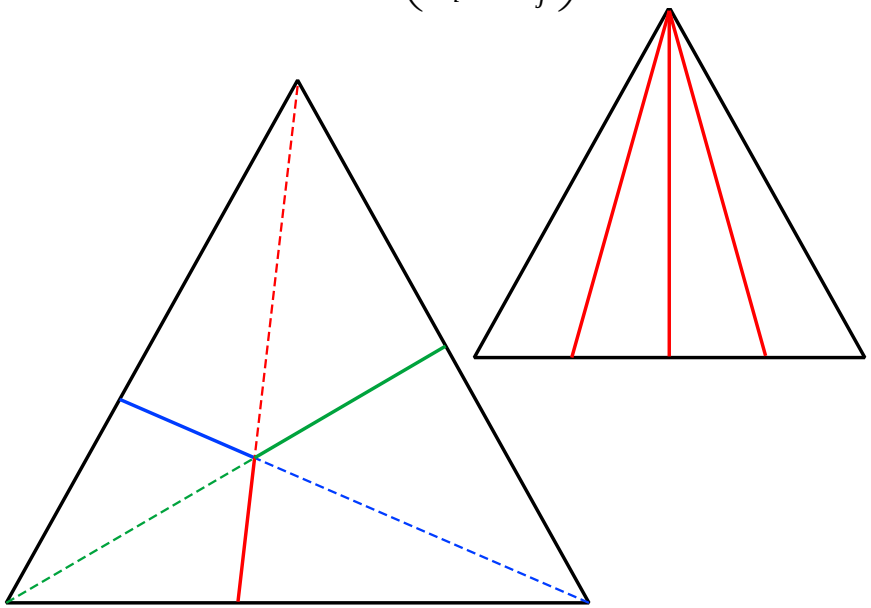
Muggianu formalism:

$$^{ex}G = \sum_{m}^{\frac{n(n-1)}{2}} x_i x_j \sum_{k}^{l_{ij}} L_k^{ij} \left(x_i - x_j\right)^k$$



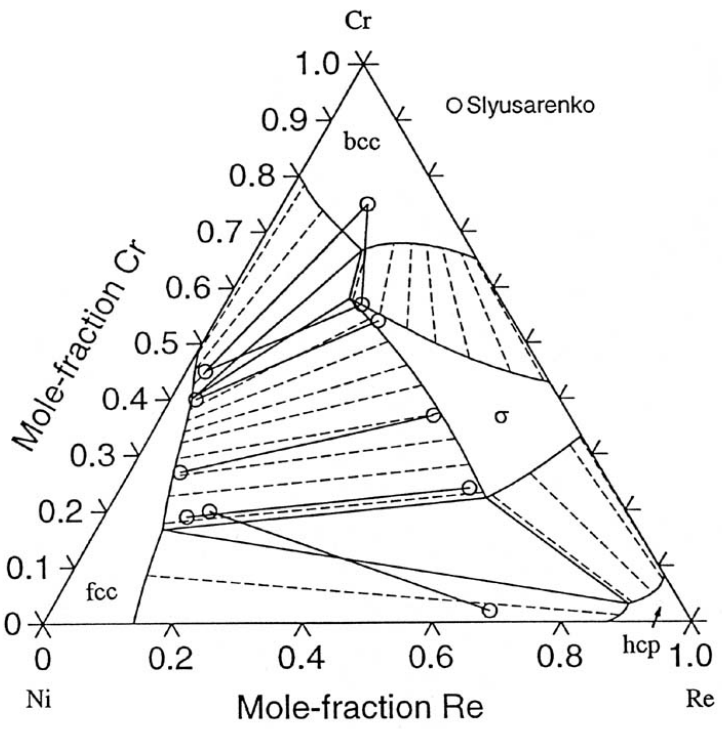
Kohler formalism:

$$^{ex}G = \sum_{m}^{\frac{n(n-1)}{2}} x_i x_j \sum_{k}^{l_{ij}} L_k^{ij} \left(\frac{x_i - x_j}{x_i + x_j}\right)^k$$

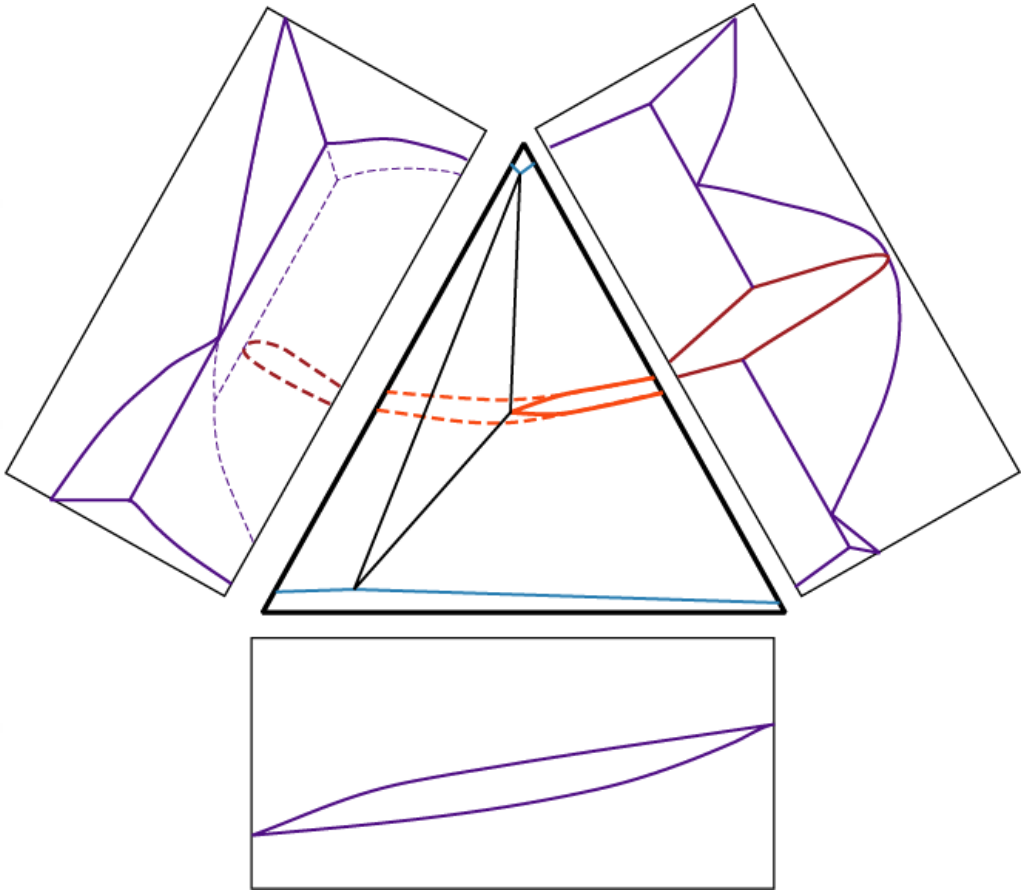


Muggianu formalism is most commonly used because it is easily generalized

Extrapolation of homogeneity ranges



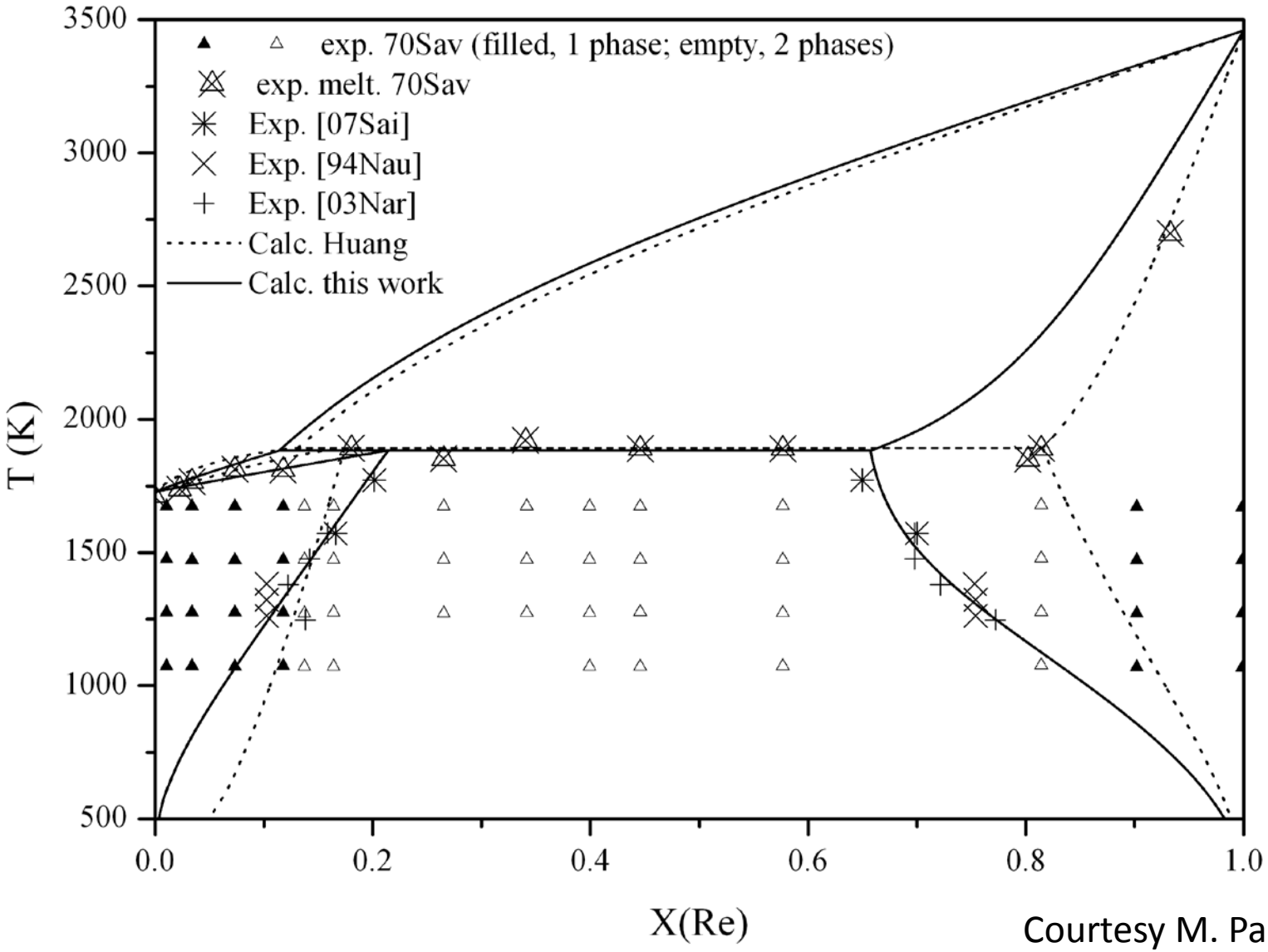
Huang and Chang
J. Alloys & Compds. 274 (1998) 209



Parameters are needed to describe hypothetical metastable end-member phases

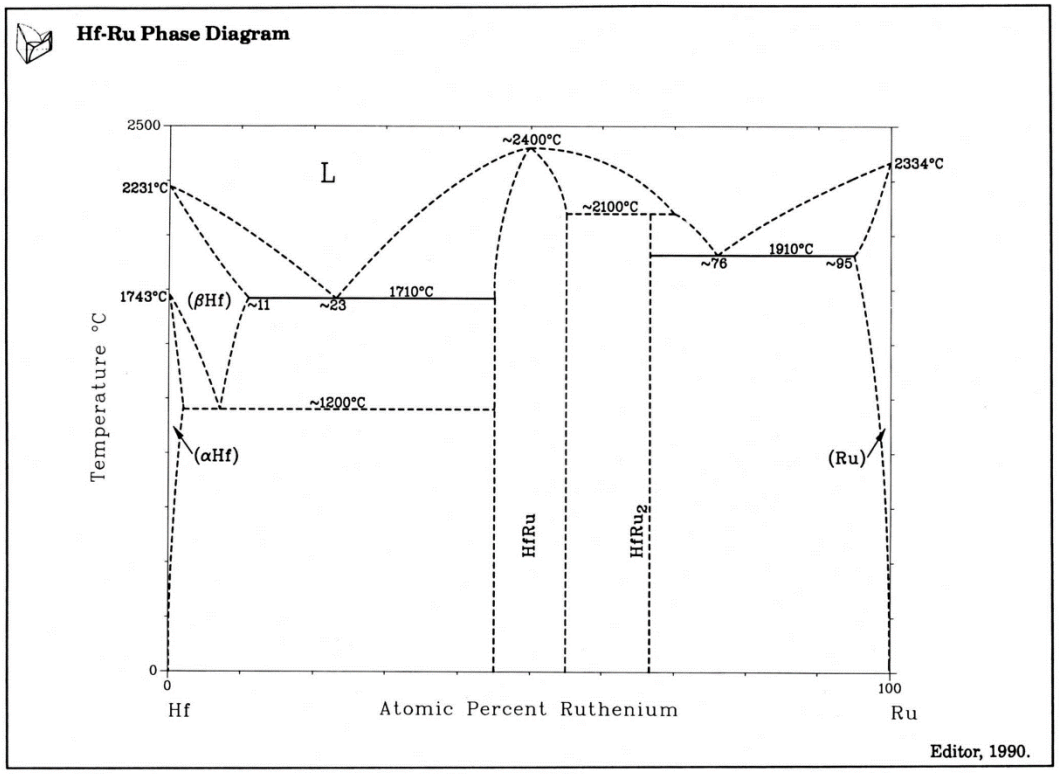
stable binary
metastable binary
stable ternary
metastable ternary

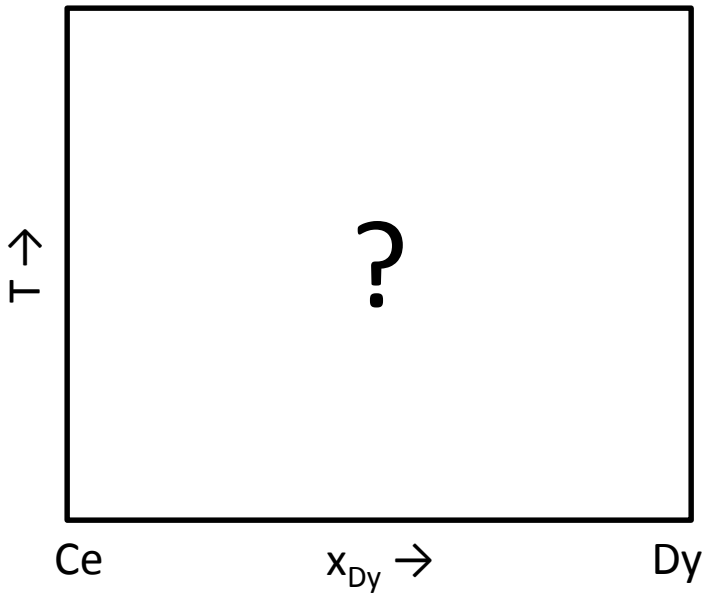
Few and contradictory data



Courtesy M. Palumbo

Almost no data - or no data at all





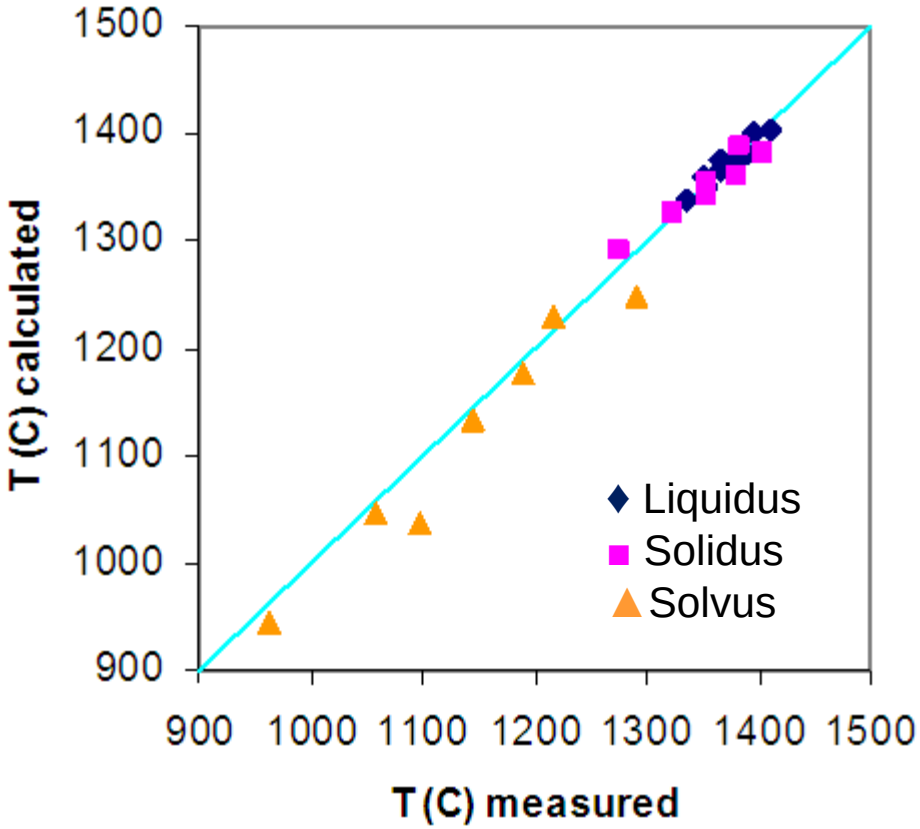
Development of a thermodynamic database for Ni-based superalloys

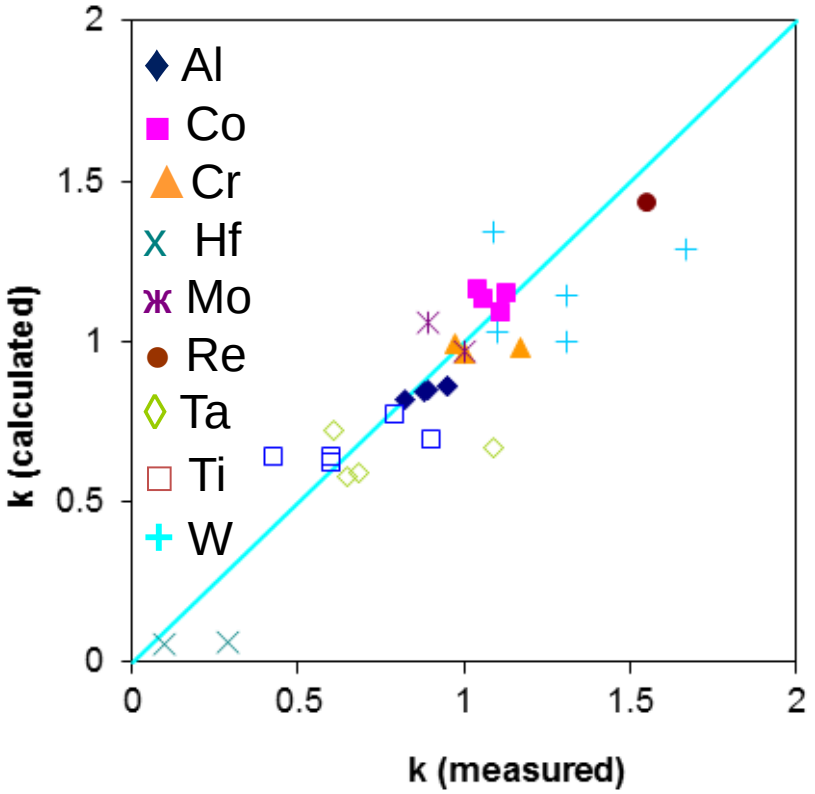
Available thermodynamic descriptions for the 10-component system Ni-Al-Co-Cr-Hf-Mo-Re-Ta-Ti-W

Constituent systems	Total number of systems	Available assessments **1996**	Available assessments **2000**
binary	45	28	42
ternary	120	11	20
Ni-base ternary	36	9	14
Ni-Al base ternary	8	4	8

Comparison of measurement and calculation

Liquidus, solidus and solvus temperatures



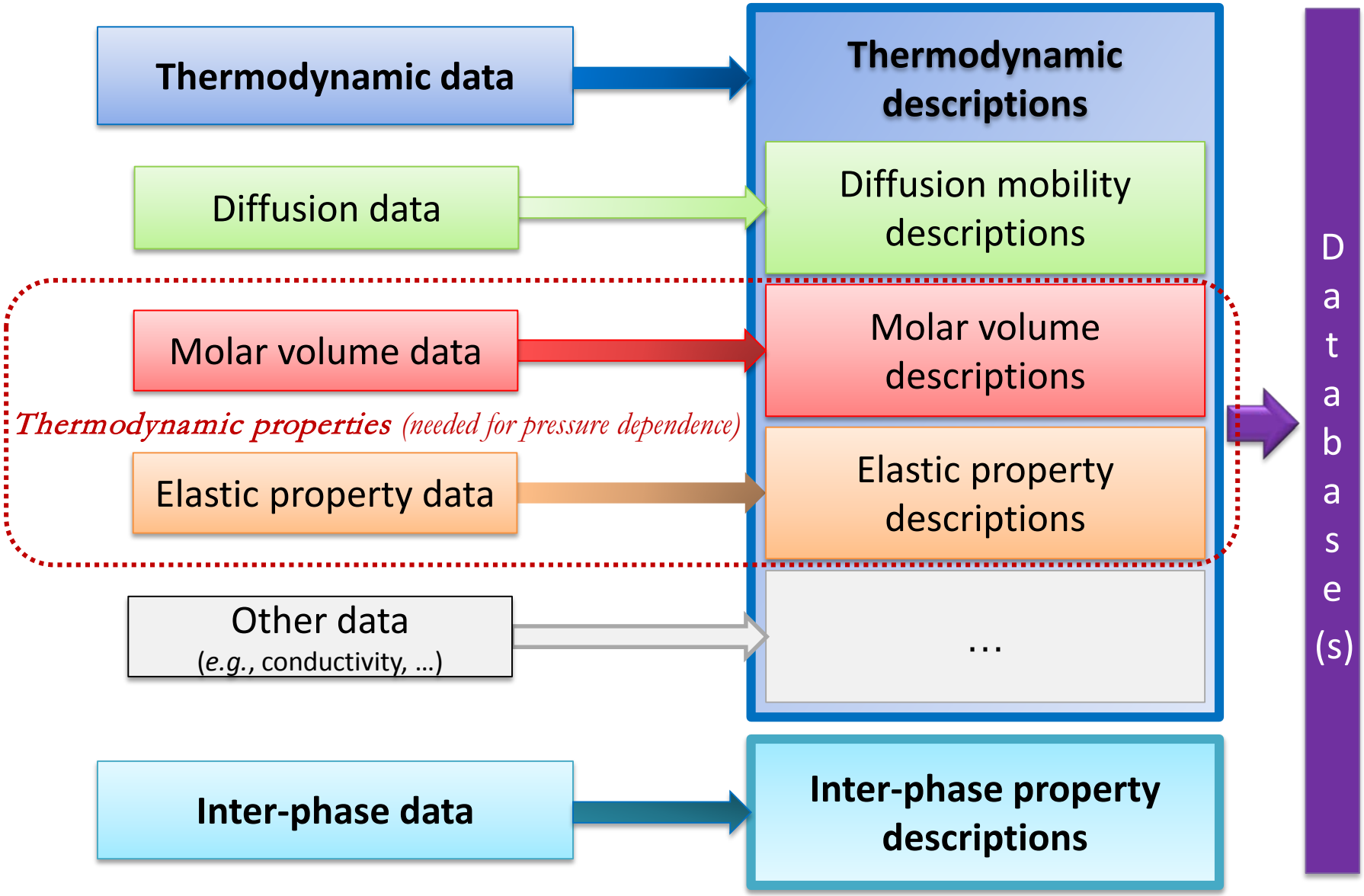


Partition ratios

CALPHAD challenge

- Development of a way to bring these “uncertainties” together to evaluate reliability of predictions from extrapolations of multicomponent systems
- Weighting scheme to evaluate “incomplete” databases?
  - D. Miracle, 2015: Evaluation of databases for projected reliability for predicting high entropy alloys
    - Fraction of assessed binaries: $FAB = \sum_i \kappa_i^B / TB$ of total systems TB
    - Fraction of assessed ternaries: $FAT = \sum_i \kappa_i^T / TT$ of total systems TT with κ_i^S level of assessment of system S
      - = 1: complete thermodynamic
      - = 0.1: partial thermodynamic description
      - = 0: no thermodynamic description

CALPHAD and phase-based data



Uncertainties for the derivatives

Gibbs energy	$G = g(T, P, N_i)$
Entropy	$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N_i}$
Enthalpy	$H = G - T\left(\frac{\partial G}{\partial T}\right)_{P,N_i}$
Heat capacity	$C_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N_i}$
Chemical potential	$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{P,T,N_{j\neq i}}$
Volume	$V = \left(\frac{\partial G}{\partial P}\right)_{T,N_i}$
Thermal expansion	$\alpha = \frac{1}{V}\left(\frac{\partial^2 G}{\partial P \partial T}\right)_{N_i}$
Isothermal compressibility	$\kappa = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,N_i}$
Bulk modulus	$K = \frac{1}{\kappa}$
Intrinsic diffusivity	${}^{i}D_{jk} = N_j M_j \frac{\partial \mu_j}{\partial N_k}$

Only if included in Gibbs energy description and not treated as independent properties

M_j = Mobility
(not a thermodynamic quantity)

Thank you for your attention!

Questions?