Insights into the development of standard reference databases

Alan Dinsdale

National Physical Laboratory, UK

(also SGTE)

NIST Diffusion Workshop

25-26 March 2009

Outline

- SGTE
- What do we mean by “Standard Reference data” ?
- Experience with thermodynamics
- Standard reference data of importance to diffusion

What is SGTE ?

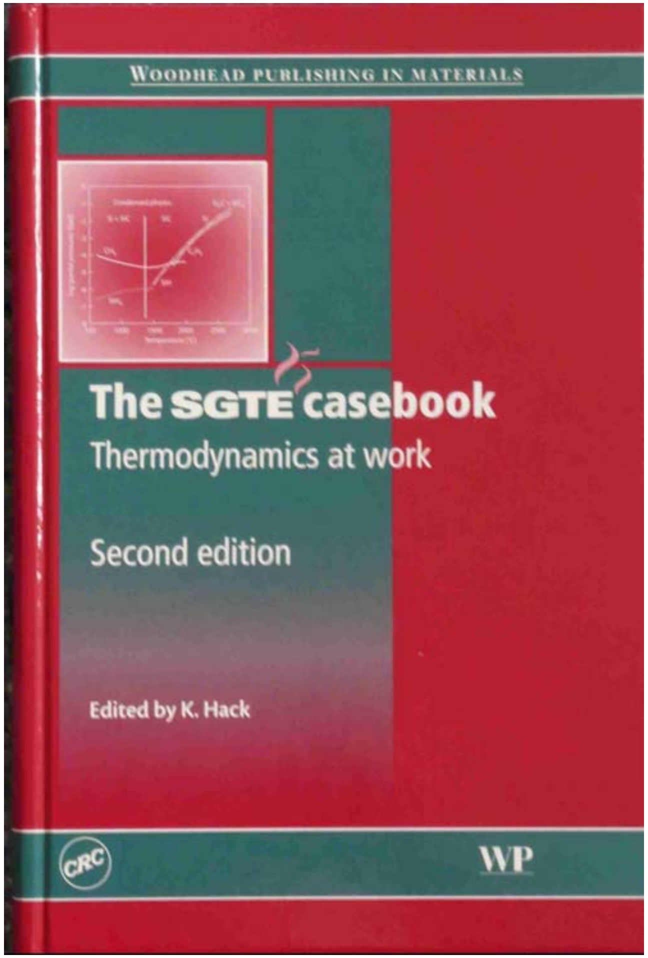
- Consortium of 15 leading Worldwide Centres involved in:
  - The provision, maintenance and expansion of high quality databases, that enable the user to undertake complex calculations of chemical equilibrium efficiently and reliably
  - Cooperation in a broader international effort to unify thermodynamic data and assessment methods; also to promote collaborative efforts
  - To promote the application of thermochemical data

SGTE members

- Canada
  - ThermFact (Montreal)
- France
  - Institute National Polytechnique (LTPCM), Grenoble.
  - Association THERMODATA, Grenoble.
  - Arcelor Research, Maizières-les-Metz.
  - University of Montpellier
- Germany
  - Department of Materials Chemistry, RWTH, Aachen.
  - Max Planck Institut für Metallforschung, PML, Stuttgart.
  - GTT Technologies, Hertzogenrath.
  - Technical University, Freiberg
  - Research Centre, Julich
- Sweden
  - Department of Materials Science and Engineering, Royal Institute of Technology, Stockholm.
  - Thermo-Calc Software AB Stockholm.
- United Kingdom
  - National Physical Laboratory, Teddington.
- USA
  - NIST
  - The Spencer Group, Ithaca

What are the aims of SGTE ?

- SGTE tries to be at the forefront of providing critically assessed thermodynamic data for alloys
- Use of the expertise of SGTE members in inorganic chemistry and materials science
- Development of standard reference data for the elements - used worldwide
- Promotion of guidelines for modelling of data for phases
- Development of self-consistent and inter-consistent databases
- Use of well-defined quality procedures
- Promotion of workshops to explore future needs and developments



WOODHEAD PUBLISHING IN MATERIALS

The SGTE casebook

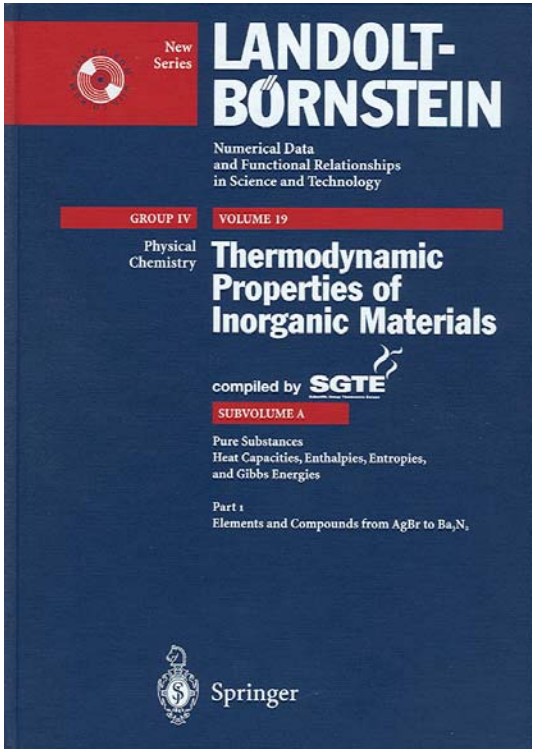
Thermodynamics at work

Second edition

Edited by K. Hack

CRC

WP



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Heat Capacities, Enthalpies, Entropies,
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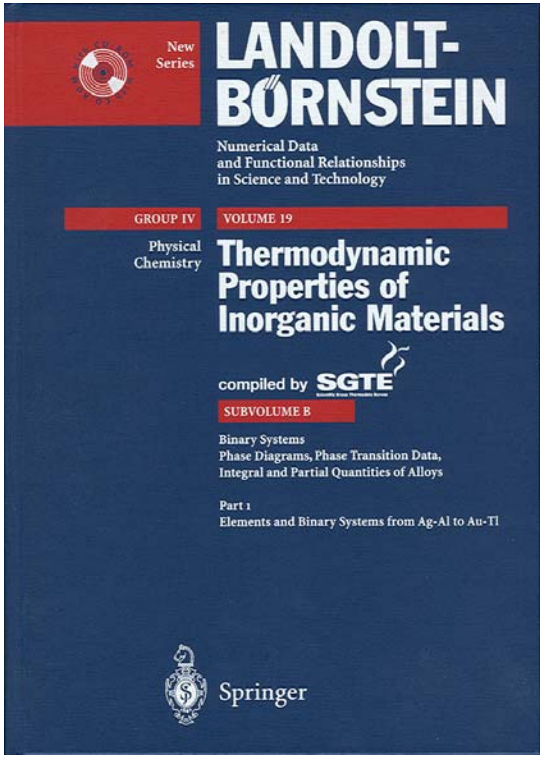

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SUBVOLUME B

Binary Systems
Phase Diagrams, Phase Transition Data,
Integral and Partial Quantities of Alloys

Part 1
Elements and Binary Systems from Ag-Al to Au-Tl

Springer

What do we mean by “Standard Reference data” ?

- “*Scientific Data in the 21st Century - NIST Standard Reference Data and CODATA*”: John Rumble (1999)
  - “Standard Reference Data is a key resource within the sciences. It provides critical evaluation of measurement data, giving a reliable basis for the work of scientists, engineers and the general public. Data users are not experts on how the data are generated, and they do not know the quality of the data that has been published.”
- US Congress document
  - The term “standard reference data” means quantitative information, related to a measurable physical or chemical property of a substance or system of substances of known composition and structure, which is critically evaluated as to its reliability under section 290b of this title.

Some examples of Standard Reference Data

- Fundamental constants
- International Temperature Scale
- Atomic weights
- Atomic energy levels
- Nuclear half life data
- Force field data (Molecular dynamics)
- Wave function and basis set database (*ab initio*)

Sources of Standard Reference Data: Thermodynamics

- CODATA Key Values for Thermodynamics, 1989 (J.D. Cox, D.D. Wagman, V.A. Medvedev)
- CODATA Thermodynamic Tables Selections for Some Compounds of Calcium and Related Mixtures: A Prototype Set of Tables, 1989 (D. Garvin, V.B. Parker, H. J. White Jr.)
- Selected Values of Chemical Thermodynamic Properties, NBS Technical Notes 270/1 - 8, 1965 - 1981 (D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S. M. Bailey, R. Schumm)
- Thermochemical Constants of Substances, Parts 1 to 10, Academy of Sciences, Moscow 1965 - 1981 (V. P. Glushko, V.A. Medvedev)
- JANAF Thermochemical Tables, 1971-1985 (M W Chase et al)
- Thermodynamic Properties of Individual Substances, 1978-1994 (L.V. Gurvich et al)
- Selected Values of the Thermodynamic Properties of the Elements, 1973, (Hultgren et al)
- Selected Values of Thermodynamic Properties of Binary Alloys, 1973 , (Hultgren et al)
- SGTE Data for the elements, 1991

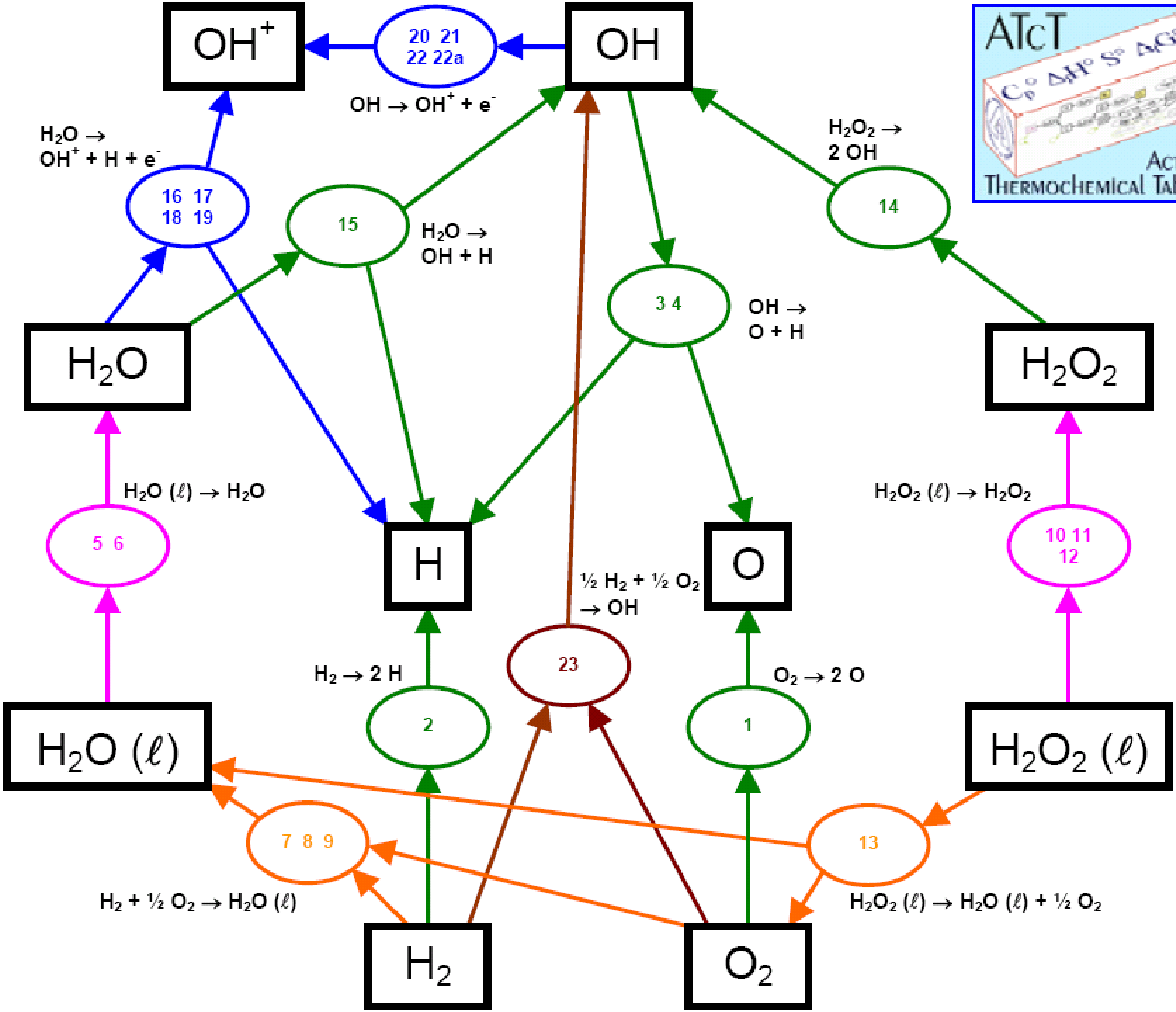
Sources of Standard Reference Data: Phase Diagrams

- M. Hansen and K. Anderko, 1958
- R. P. Elliott, 1965
- F. A. Shunk, 1969
- R.B. Massalski et al, 1990
- Various volumes for multicomponent systems, or specific types of materials

Do other sources of data rely on these ?

Issues *(more to follow later)*

- Hierarchy of standard reference data
  - Basic: eg Fundamental constants, International Temperature Scale, Atomic weights
  - Foundation: CODATA Key Values, Unary data, Data for key binary systems
  - Derived: Result of individual assessments (could be changed with no knock on effects) eg quaternary assessment, phase diagram. However each assessment must be self-consistent.
- Infrequent updates eg lifetime of version of database
  - Fundamental constants updated every 10 years
  - (Argonne active thermochemical tables: “Thermochemistry for the 21st Century”)



ATcT

ACTIVE THERMOCHEMICAL TABLES

Thermodynamic standard reference data

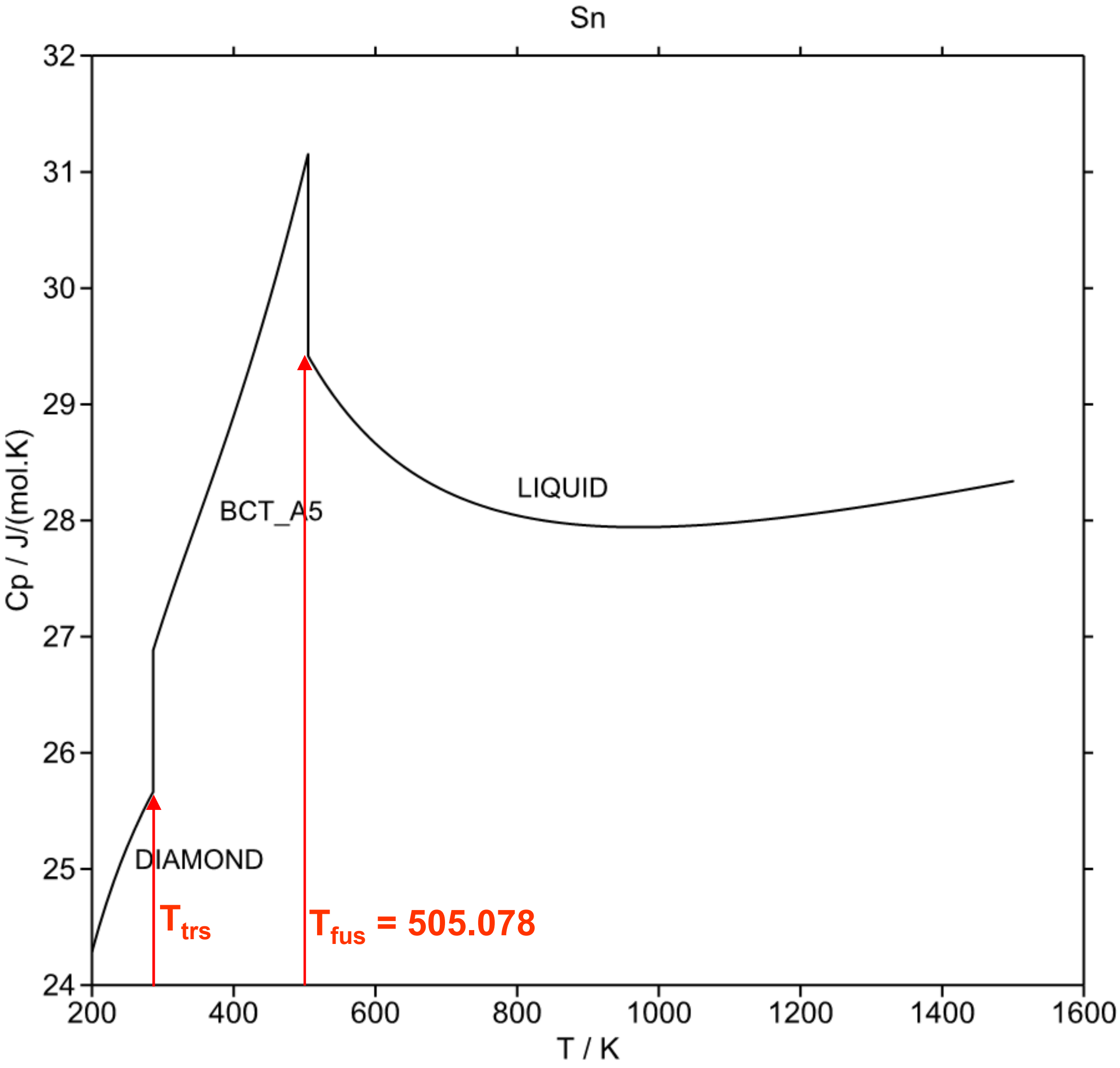
- Linked to a large number of experimental quantities
  - Enthalpies of formation
  - Enthalpies of transition
  - Heat capacities
  - Vapour pressures
  - Phase and chemical equilibria
  - Mass spectroscopic studies
  - UV, visible and IR spectra
  - Emf studies

SGTE Pure Element Transformation Data

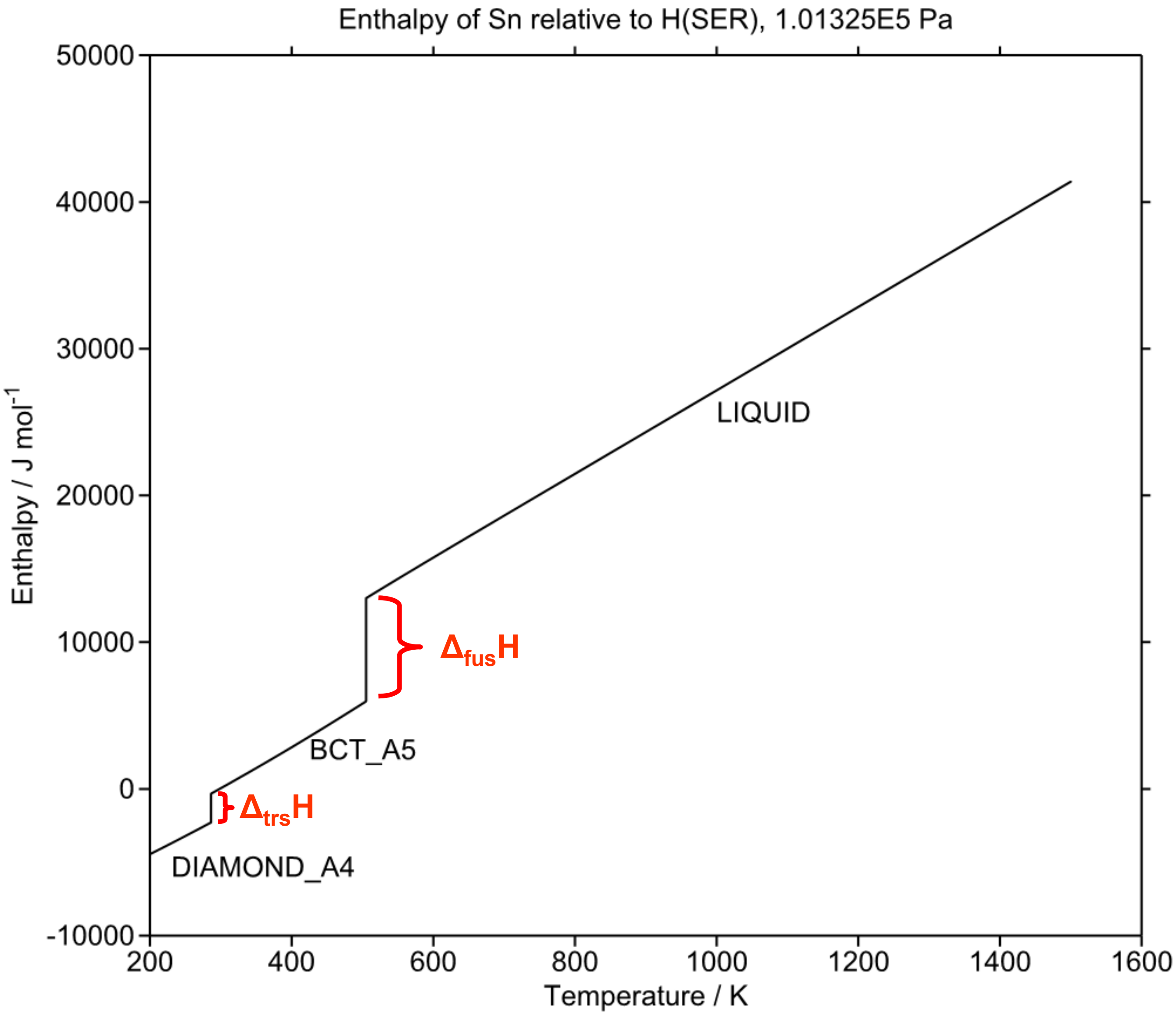
Compiled by A.T. Dinsdale
Division of Materials Metrology
National Physical Laboratory
Teddington, Middlesex, UK

Element	Symmetry(a)	Strukturbericht designation	Atomic weight	Enthalpy $H(298)-H(0)$, J/mol	Entropy $S(298)$, J/mol · K	Transformation temperature, K	Enthalpy $\Delta_{trs}H$, J/mol	Entropy $\Delta_{trs}S$, J/mol · K	Heat capacity $\Delta_{trs}C_p$, J/mol · K
Ag	fcc	*A1*	107.8682	5744.632	42.5513	1235.08	11 296.8	9.1466	1.5388
Al	fcc	*A1*	26.98154	4577.296	28.3215	933.60	10 711.04	11.4728	−2.2082
Am	dcph	...	243	6407	55.396	1042	870	0.8349	−2.7811
	fcc	*A1*				1350	5 862	4.3422	1.2898
	bcc	*A2*				1449	14 393	9.933	2.092
As	rho	*A7*	74.922	5117.032	35.6895	1090	24 442.9	22.4247	0
Au	fcc	*A1*	196.9665	6016.592	47.4884	1337.58	12 552	9.3841	0
B	tet	...	10.81	1222	5.9	2348	50 200	21.3799	0.8362
Ba	bcc	*A2*	137.33	6910	62.5	1000	7 120	7.12	−4.345
Be	cph	*A3*	9.01218	1932	9.44	1527	6 849	4.4853	−1.892
	bcc	*A2*				1560	7 895	5.0608	−1.212
Bi	rho	*A7*	208.9804	6426.624	56.735	544.52	11 296.8	20.7463	0.6538
C	hex	*A9*	12.011	1054	5.7423	4765.3	117 369	24.63	0
Ca	fcc	*A1*	40.08	5736	41.588	716	928.85	1.2973	−1.2332
	bcc	*A2*				1115	8 539.54	7.6588	−8.2257
Cd	cph	*A3*	112.41	6250.896	51.7979	594.26	6 192.32	10.4202	0.166
Ce	fcc	*A1*	140.12	7280.16	69.4544	999	2 991.56	2.9946	−0.1165
	bcc	*A2*				1071	5 460.12	5.0982	0.02
Co	cph	*A3*	58.9332	4765.567	30.04	694.99	427.59	0.6153	0
	fcc	*A1*				1768	16 200	9.1629	0.8962
Cr	bcc	*A2*	51.996	4050	23.5429	2180	21 004.00	9.6349	−10.7118
Cs	bcc	*A2*	132.9054	7711	85.2281	301.59	2 096	6.9498	0.1128
Cu	fcc	*A1*	63.546	5004.064	33.1498	1358.02	13 263.28	9.7666	1.5383
Dy	cph	*A3*	162.50	8865.896	75.563	1659	3 882.75	4.184	−0.0381
	bcc	*A2*				1684	10 782.17	6.4027	−0.2929

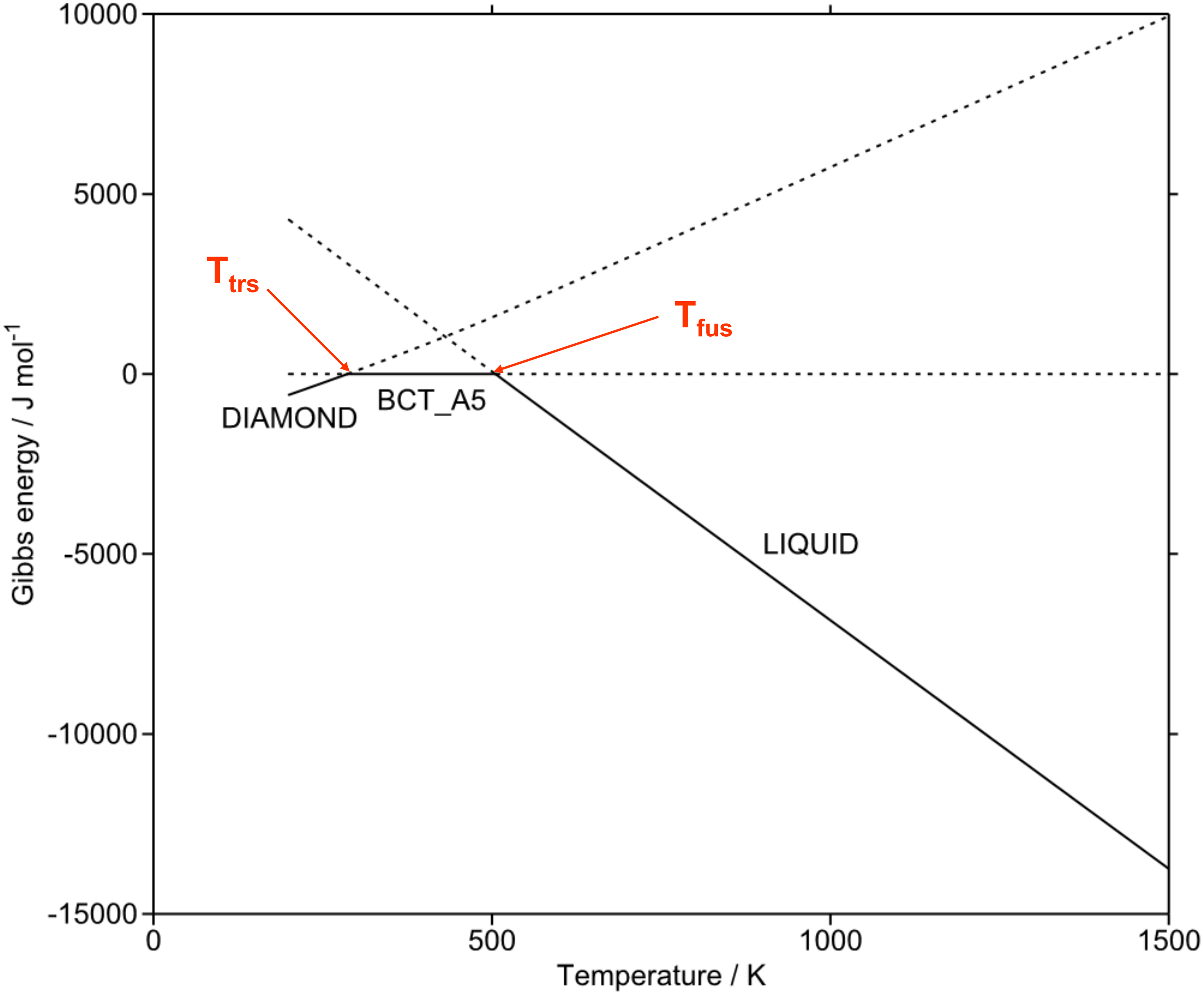
Heat capacity of Sn for different phases



Enthalpy of Sn relative to 298.15 K



Gibbs energy of phases of Sn relative to BCT

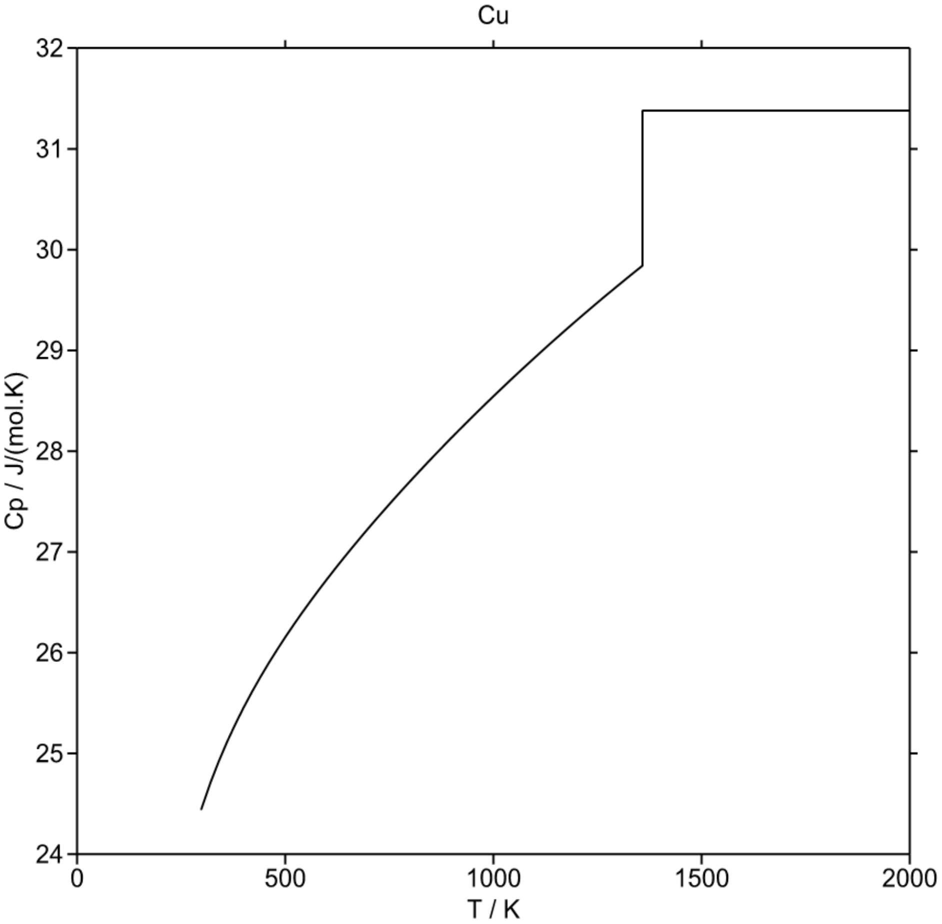


Thermodynamic standard reference data

- Also ab initio calculations
  - Gas phase (atom centred wave functions)
  - Crystalline phase (plane wave functions)
  - Molecular dynamics (force field data)
- And empirical relationship and correlations for data between phases and systems
- Thermodynamics requires rigorous consistency between these experimental and calculated properties
- However we need phenomenological models to express variation with temperature, pressure and composition
  - Based on Gibbs energy, but its derivatives have physical meaning

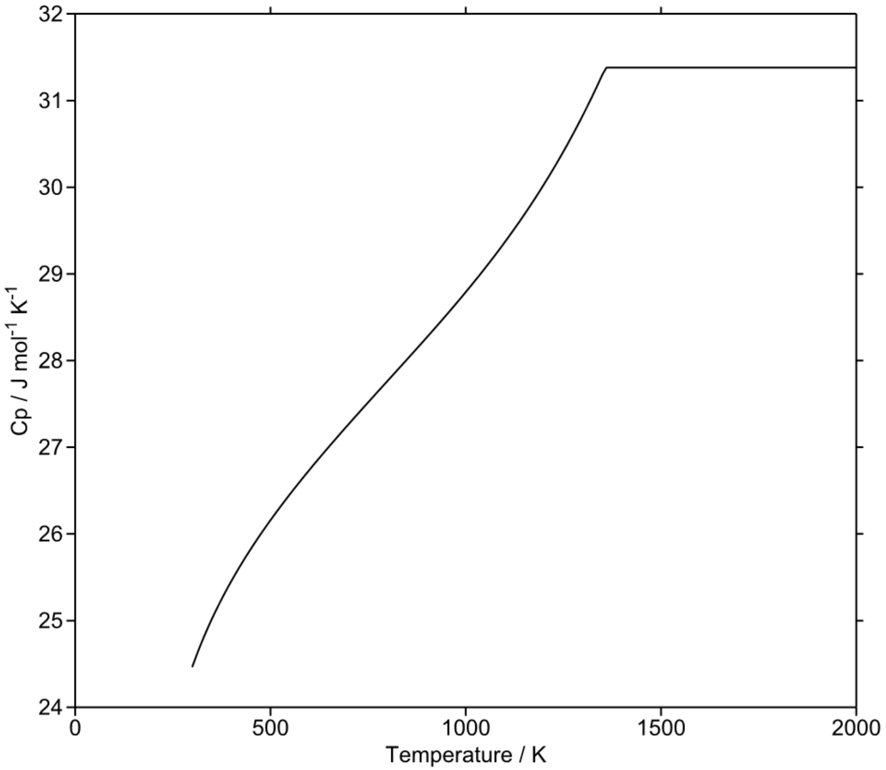
Traditional lattice stability approach

- All phases have the same heat capacity
- Gives discontinuities in values for Cp
- Can’t be used to calculate heat capacity of real materials
- Unphysical



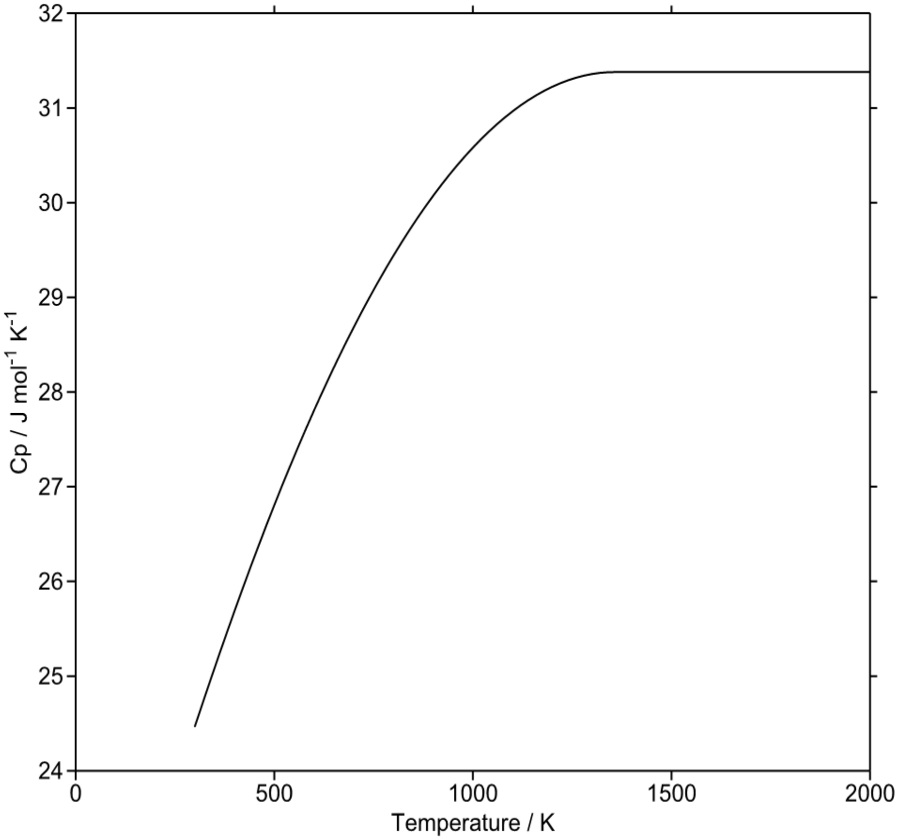
"SGTE extrapolation"

- Terms in T^7 and T^{-9} in G
- Heat capacities are continuous but discontinuities in gradient (kinks)
- Inherited by binary and higher order systems
- Can be used to calculate heat capacity of real materials with care
- Unphysical

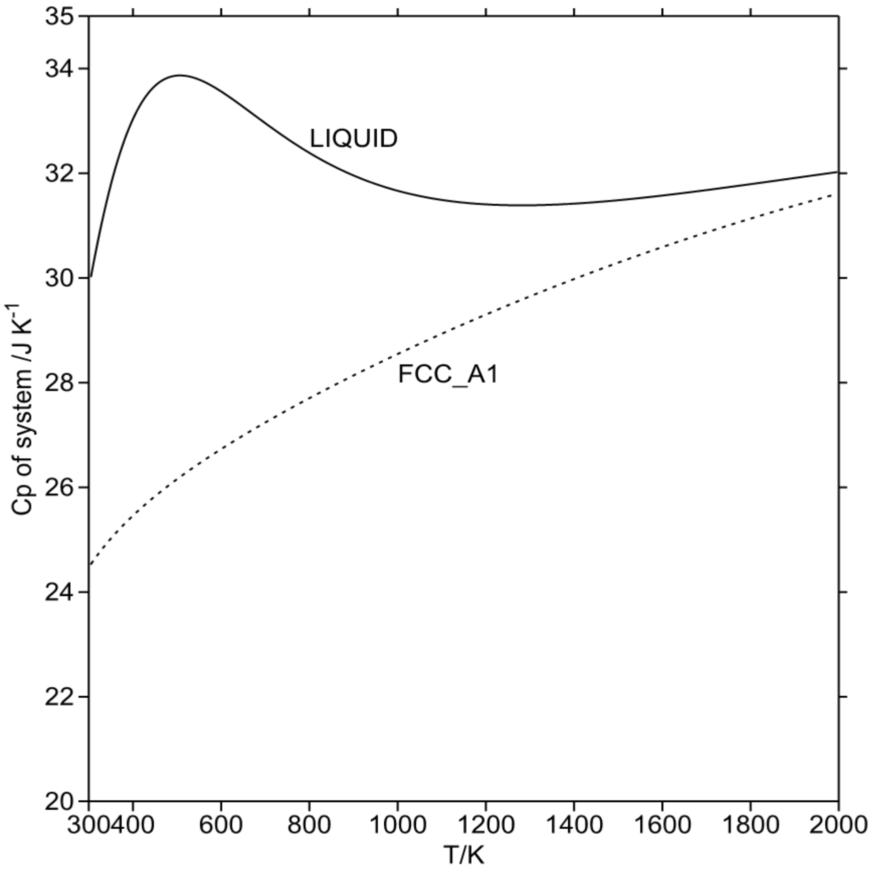


Alternative SGTE method

- Smooth variation of heat capacity – heat capacity and gradient fixed at melting point and at defined lower temperature
- Gives odd coefficients
- Can be used to calculate heat capacity of real materials
- Unphysical



We would like to use another liquid model



- Two state model
- Reproduce experimental heat capacities for liquid
  - above melting point
  - below melting point where available
- Heat capacity should approach that of stable crystalline phase at low temperatures
- Probably a maximum in liquid heat capacity
- Large investment required
- Need defined and agreed methodology

NPL National Physical Laboratory

Issues *(continued)*

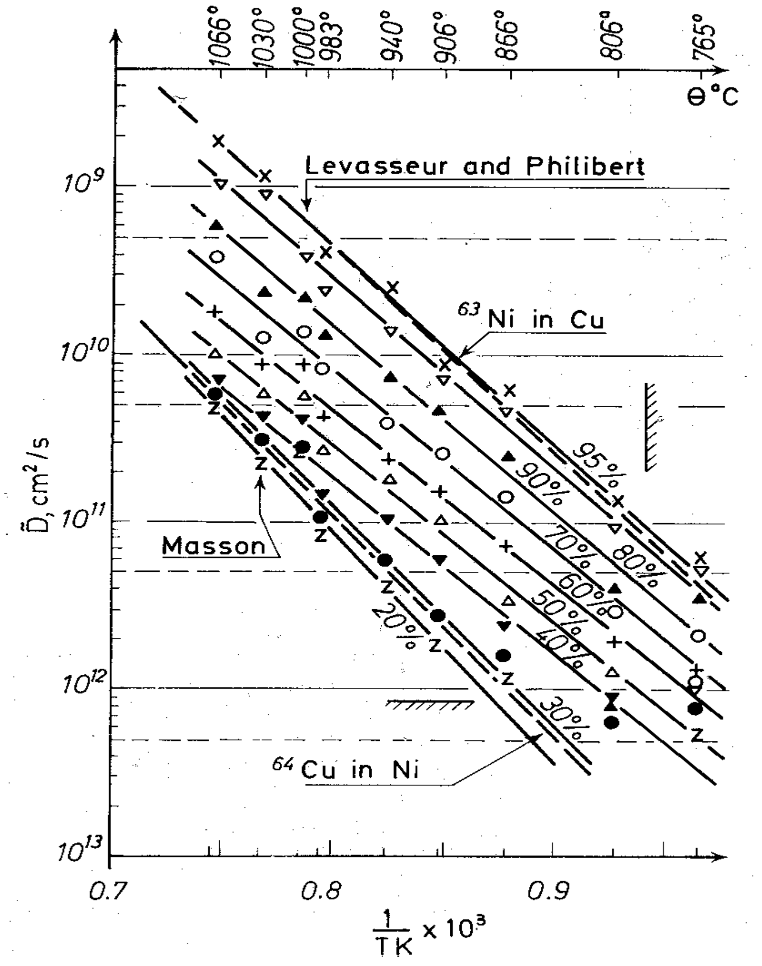
- Standard Reference Data need to be international and authoritative
  - Need to have agreed management with long term funding and continuity
  - Don’t underestimate the effort involved in maintaining standards
  - Does act as a stimulus for collaboration
- Need to define scope and aspiration
  - Element data initially was for an SGTE project
- Are you happy with the models ?
  - Is your approach consistent across range of phases? Phase names
  - Anisotropy ?
  - Do you need to introduce extra standards to be associated with the models
- How mature are your standard reference data ?
  - Are you likely to want to polish them again next week ?

Issues *(continued)*

- Standard Reference Data must be published
  - Publication needs to be seen to have backing from key users and developers
  - Should include description of the models you have used
  - Implemented for a range of software
- People are generally just very happy you have defined a comprehensive set of data
- Be prepared for the criticism
  - and to be ignored by other disciplines eg geochemists
- Beware of divergence (Sn fcc/ hcp)
- Large investment required makes it difficult
  - to correct errors eg Cr melting point
  - to introduce new, possibly, better models
  - Could actually stifle progress

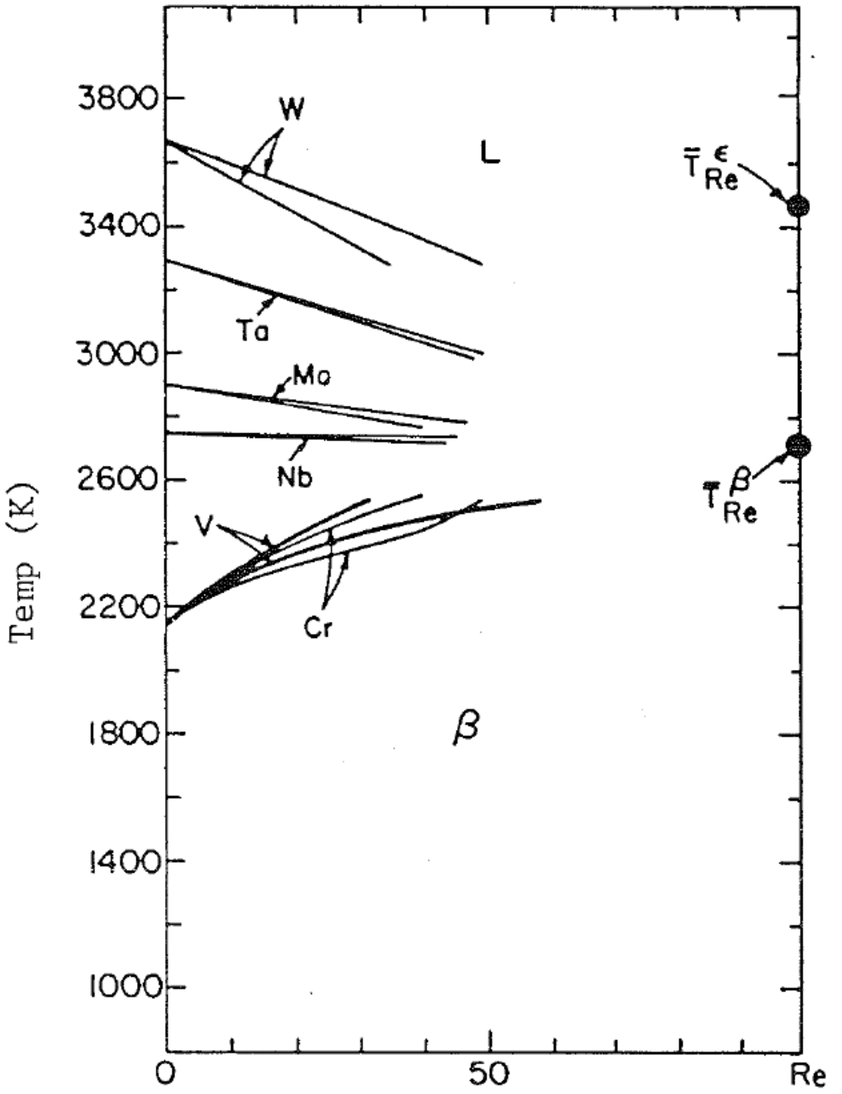
Chemical diffusion data

- Assume we are considering bulk diffusion ?
- Mobility database relies on standard reference thermodynamic database
- Are there possibilities for cross checking of information between different sorts of experiments ?
- Need models to express variation with temperature and composition
- Does the model for diffusion really relate to sublattice occupancy ?



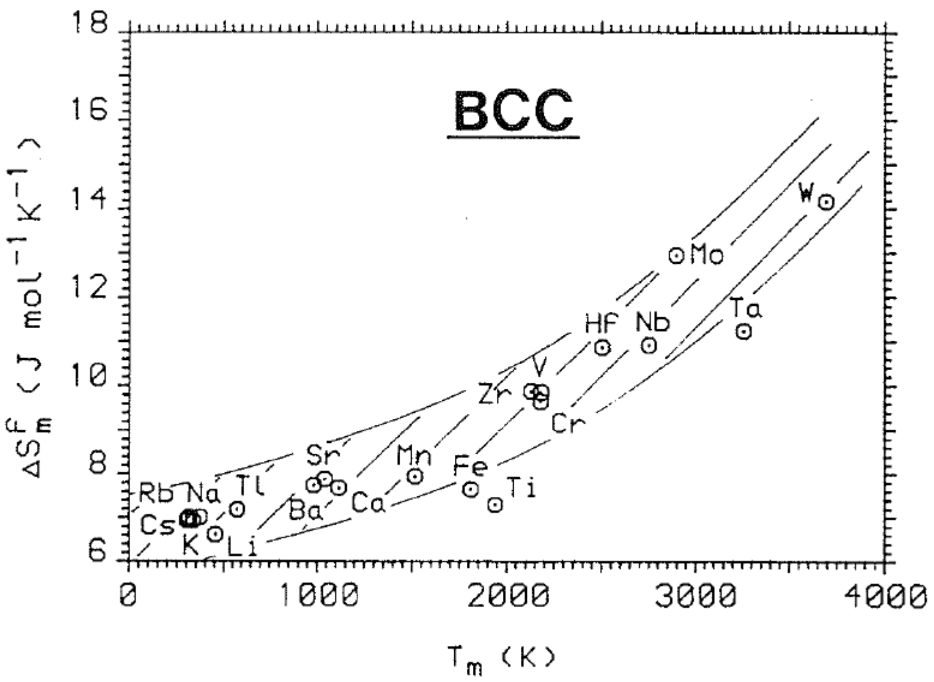
Chemical diffusion data

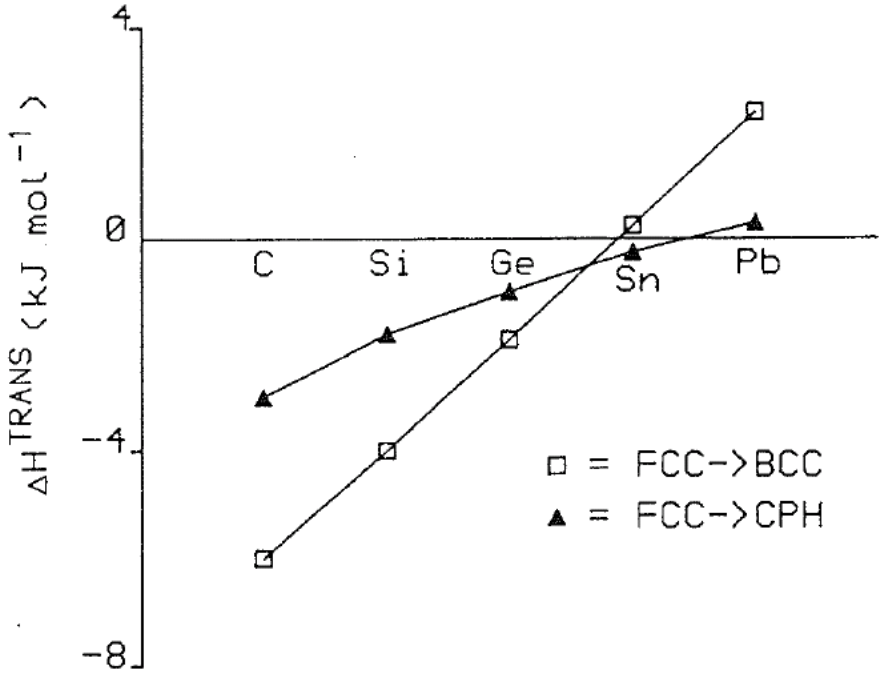
- Is there any possibility to derive data by extrapolation for a number of systems ?



Chemical diffusion data

- Correlations
  - From phase to phase
  - From element to element



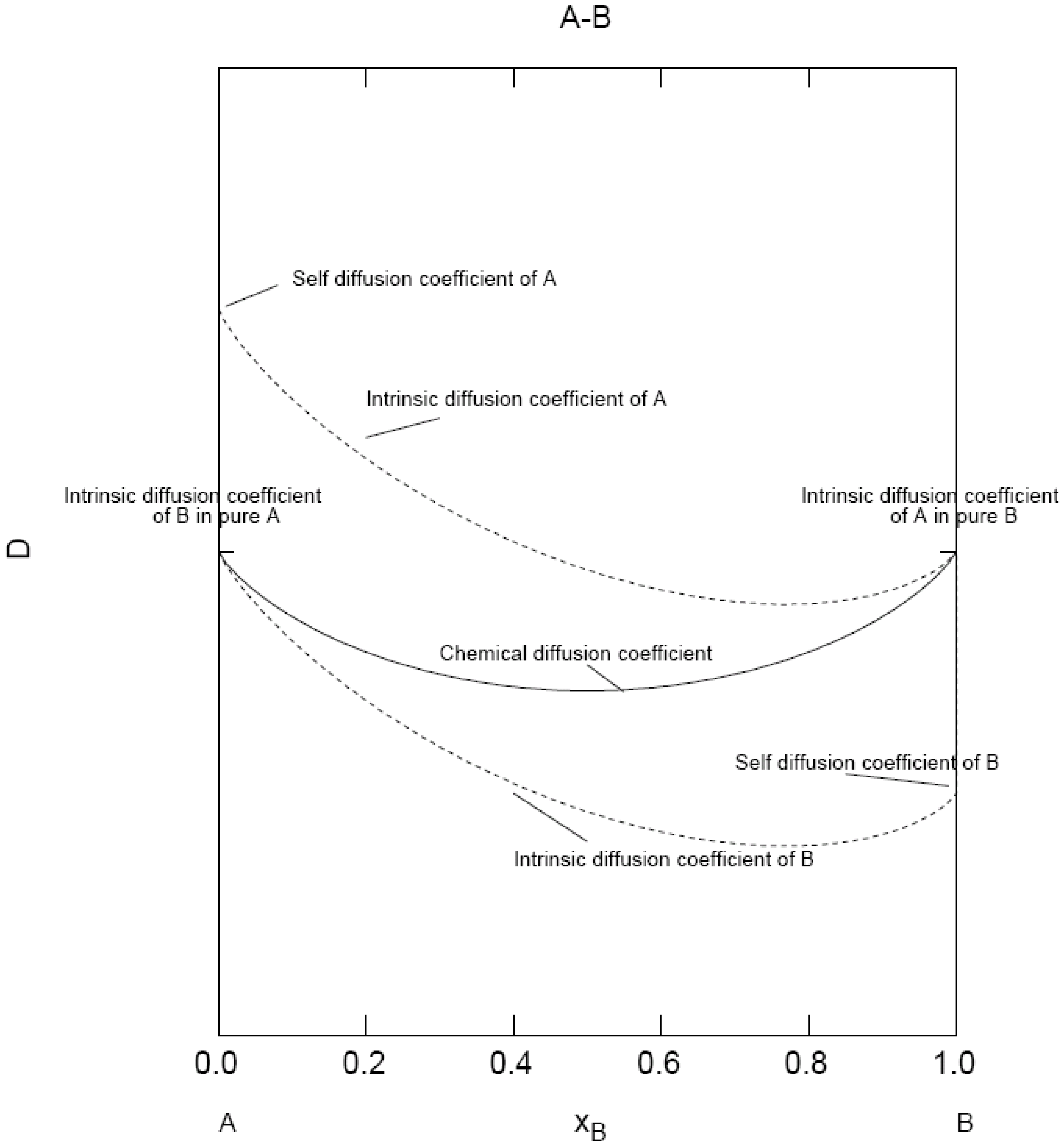


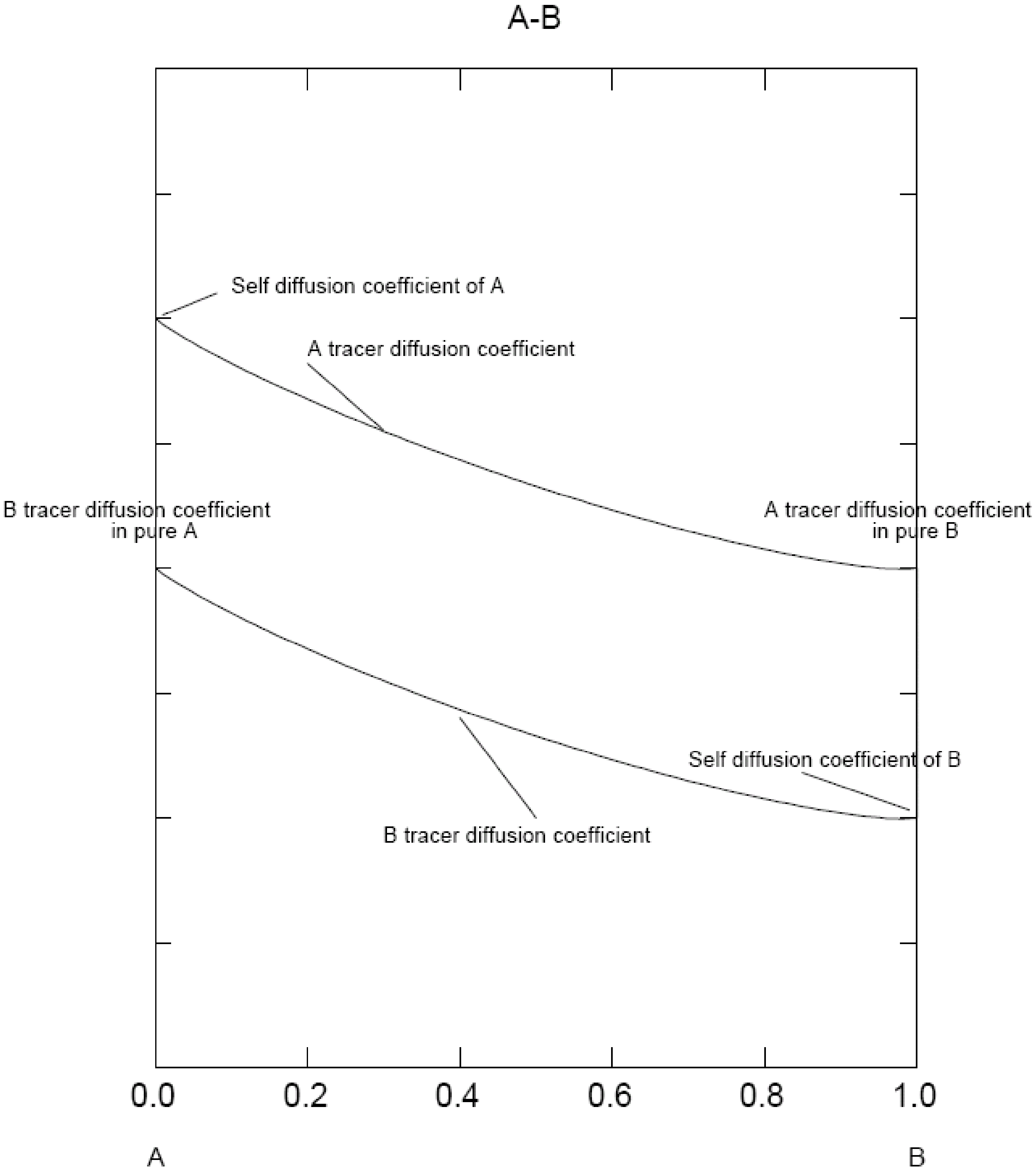
Chemical diffusion data

- Standard reference data hierarchy
  - Based on a mobility database
    - But relies on reference thermodynamic data for system
      - Relies on standard reference data for elements etc
    - Need “fixed” self diffusion data for the elements
      - in all appropriate phases
    - Assessed mobility data for key systems, binaries and ternaries
    - Implied set of agreed models
    - anisotropy
- How often are you going to release revisions ?
- Better to have wrong data than different sets of data

Modelling of Chemical Diffusion Data

- $(n-1)^2$ chemical diffusion coefficients are required for multicomponent system (n components)
- Chemical diffusion coefficients can be calculated directly from mobilities if thermodynamic data are known
- Mobilities are closely related to the tracer diffusion coefficients
- Only n mobilities are required for the multicomponent system each of which are then represented as a function of temperature and composition
- Data for self mobilities can be thought of as standard reference data
- Do you need standard models to go alongside any standard reference data


A-B
Self diffusion coefficient of A
Intrinsic diffusion coefficient of A
Intrinsic diffusion coefficient of B in pure A
Intrinsic diffusion coefficient of A in pure B
D
Chemical diffusion coefficient
Self diffusion coefficient of B
Intrinsic diffusion coefficient of B
0.0
0.2
0.4
0.6
0.8
1.0
A
x_B
B

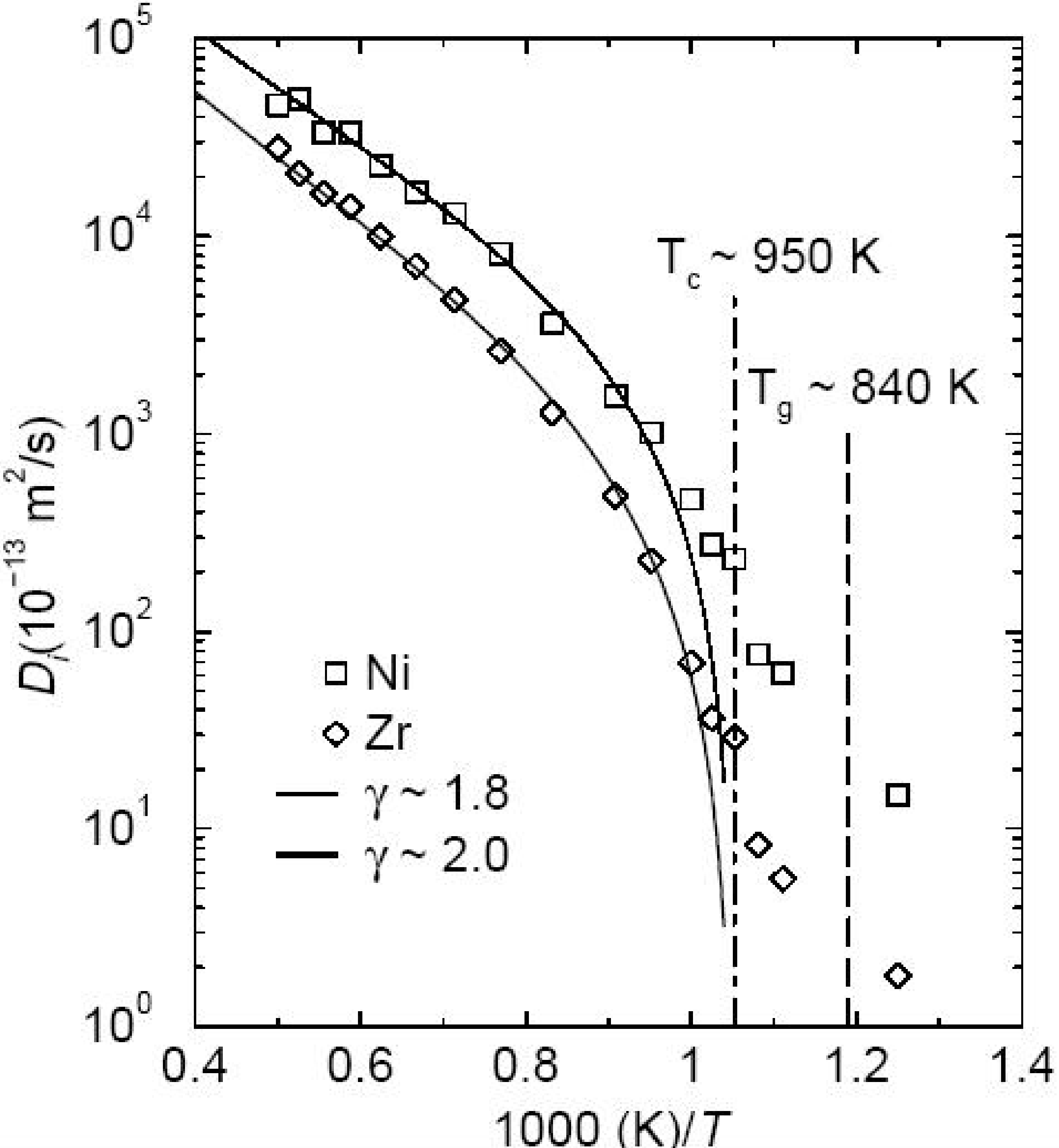

A-B
Self diffusion coefficient of A
A tracer diffusion coefficient
B tracer diffusion coefficient in pure A
A tracer diffusion coefficient in pure B
Self diffusion coefficient of B
B tracer diffusion coefficient
0.0
0.2
0.4
0.6
0.8
1.0
A
B

Chemical diffusion data

- Is there a link to other sorts of properties eg bulk modulus, viscosity, surface tension ? Can this be exploited ?
- Can mobilities be calculated from ab initio or molecular dynamics ?
  - Various talk later this morning (ab initio)
  - Mikhail Mendelev (molecular dynamics on Zr)

Molecular dynamics studies (quick google search)

- Carbon diffusion in cementite
- Carbon diffusion in austenite
- Gases
- Liquids especially organic
- Self diffusion in MgO as a function of pressure
- Mg diffusion in GaN crystal
- Ni-Zr glass forming system
- Diffusion in supercooled Cu-Zr alloys
- Diffusion in B2 phase in Al-Ni system
- Self diffusion in Ni_2Y
- Defects in semiconductors
- Al diffusion in quasicrystals Al-Ni-Co, Al-Cu-Co
- Si diffusion in $TiSi_2$
- Diffusion of B in Si



T_c ~ 950 K
T_g ~ 840 K
□ Ni
◇ Zr
γ ~ 1.8
γ ~ 2.0
$D_i (10^{-13}\ m^2/s)$
10^0
10^1
10^2
10^3
10^4
10^5
0.4
0.6
0.8
1
1.2
1.4
1000 (K)/T

Conclusions

- Need to define scope and aspiration
  - Element data initially was for an SGTE project
- Maintenance of standards does cost
  - Don’t underestimate the effort involved
- How mature are your reference data ?
- Are you happy with the models ?
  - Is your approach consistent across range of phases?
- Large investment make it difficult
  - to correct errors eg Cr melting point
  - to introduce new, possibly, better models
- People are generally just very happy you have defined a comprehensive set of data
- Be prepared for the criticism
- Publication needs to be seen to have backing from key users and developers