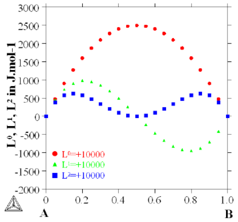
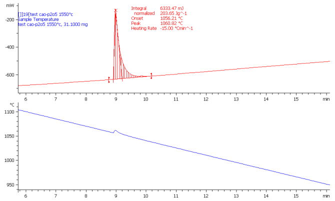
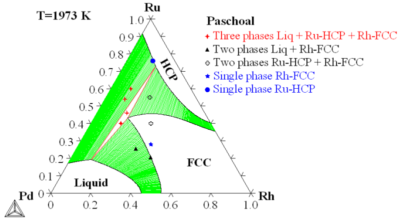
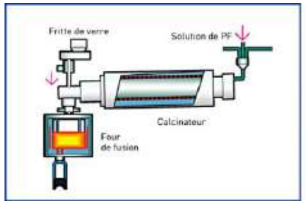








Modélisation thermodynamique de fontes verrières complexes selon la méthode Calphad (Calculation of Phase Diagrams) : avancées et perspectives

Exemple d'application à la compréhension du comportement des éléments platinoïdes dans les matrices de borosilicate élaborées en creuset froid

Stéphane Gossé, Christine Guéneau

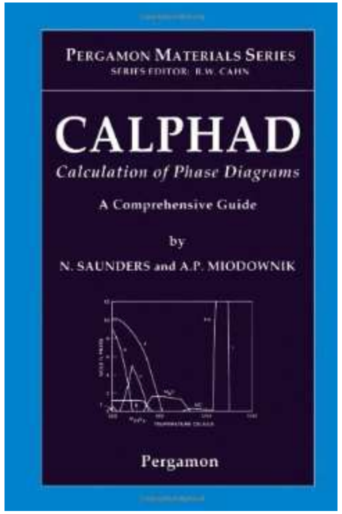
Atomistic Simulation, Thermodynamics & Thermochemistry Laboratory
Physico-Chemistry Department, Nuclear Energy Division
CEA – Centre de Saclay, 91191 Gif-sur-Yvette, France

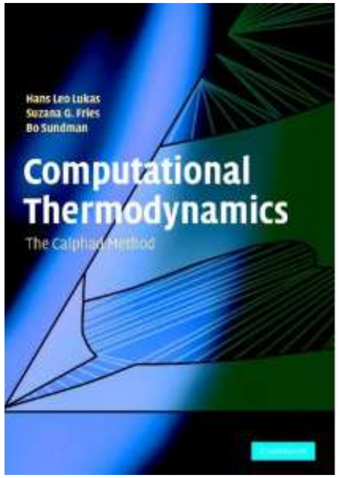
In collaboration with:

Bo Sundman
INSTN/UEINE
CEA – Centre de Saclay, 91191 Gif-sur-Yvette Cedex, France

The Calculation of Phase Diagram (Calphad) Method
Introduction

Une technique semi-empirique de modélisation et de calcul de diagrammes de phases…





In the early **seventies** computational thermodynamics started with the pioneering work of **Dr. Larry Kaufman**, evolving to what is known today as the **CALPHAD** method. The method is based on the concept of deriving the thermodynamic functions of a system **from all available experimental data**. The thermodynamic functions are expressed as polynomials of temperature and chemical composition. The numerical values of the polynomial coefficients are obtained using numerical optimization techniques.

The CALPHAD method is based on the fact that a phase diagram is a representation of the thermodynamic properties of a system. Thus, if the thermodynamic properties are known, it would be possible to calculate the multi-component phase diagrams. Thermodynamic descriptions of lower-order systems (**e.g., the Gibbs energy of each SOLID, LIQUID, GAS phase**) are combined to extrapolate higher-order systems.

The **Gibbs energy of a phase** is described by a model that contains a relatively small number of experimentally optimized variable coefficients. Examples of experimental information used include melting & transformation temperatures, solubilities, as well as **experimental** (heat capacities, enthalpies of formation, and chemical potentials) and **calculated** (DFT, MD) thermodynamic properties.

… également adaptée pour calculer les fonctions thermodynamiques de systèmes chimiques complexes (multiéléments, multiphasés)

The Calculation of Phase Diagram (Calphad) Method
Definitions

Definition : www.calphad.com

Elements: Those from the periodic chart
Species: An element or a combination of elements that forms an entity: H_2O, CO_2, Fe^{+2}
Constituents: Species that exist in a phase, **a constituent can be real or fictitious**
Components: Irreducible subset of the Species

Each phase is modelled separately:

- Phases with no compositional variation has just a G(T,p) expression.
- Phases with a small compositional variation can be very difficult to model as one should take into account the different types of defects that cause the non-stoichiometry (Vacancies, Interstitials)

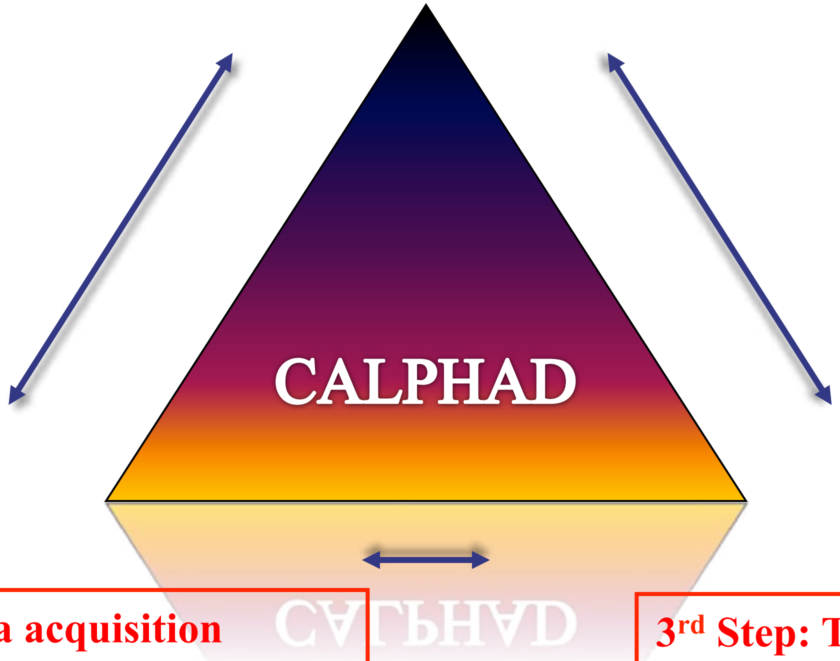
Softwares: Factsage, Thermocalc, Pandat, MT Data, Gemini…

The Calculation of Phase Diagram (Calphad) Method
Modelling Procedure

1st Step: Critical review of the experimental data

Binary systems
Ternary systems

CALPHAD IS NOT A PREDICTIVE METHOD



2nd Step: Experimental data acquisition
Phase diagram transitions by Heat Treatments, DTA
ΔH_f, Cp(T), H(T)-H(298K) by **Calorimetry, DSC**
Activities by HTMS (Knudsen Cell), EMF
Δ H (at 0 K) by DFT calculations

3rd Step: Thermodynamic Modelling

Definition of the models
Data selection
Optimization Step

1st step: modelling of the binary systems
2nd step: modelling of the ternary systems
➡ Extrapolation to n-ary systems

Applications: Phase Diagrams & Thermodynamic Calculations

The Calculation of Phase Diagram (Calphad) Method
Gibbs energy for pure elements, end members & stochiometric compounds

For pure elements and stoichiometric compounds, the following model is most commonly used:
Relation used by the Scientific Group Thermodata Europ (SGTE)

$$^{\circ}G_i\,(T) - {}^{\circ}H_i^{SER}\,(298.15K) = a + bT + cT\ln T + \sum d_n T^n$$

where G_i - H_iSER is the Gibbs energy relative to a Standard Element Reference state (SER), H_iSER is the enthalpy of the element in its stable state at the temperature of 298.15 K and the pressure of 10^5 Pascal (1 bar). ***a***, ***b***, ***c***, and ***d_i*** are the model parameters.

L'expression de l'énergie de Gibbs permet de calculer les fonctions thermodynamiques :

$$H(T) = -T^2\left(\frac{\partial\left(G/T\right)}{\partial T}\right)_p = \int_0^T C_P\,dT = a - c\,T - \sum_2^n (n-1)\,d_n T^n$$

$$S(T) = -\left(\frac{\partial G}{\partial T}\right)_p = \int_0^T \frac{C_P}{T}\,dT = -b - c - c\,\ln T - \sum_2^n n\,d_n T^{n-1}$$

$$C_p(T) = T\left(\frac{\partial S}{\partial T}\right)_P = -c - \sum_2^n n(n-1)d_n T^{n-1}$$

The Calculation of Phase Diagram (Calphad) Method
Gibbs energy in databases

Exemple de description de l'énergie de Gibbs du Si (Element pur)

PHASE DIAMOND_A4 % 1 1 !
CONSTITUENT DIAMOND_A4 : Si : !
PARAMETER G(DIAMOND_A4,Si;0) 298.15 +GHSERSi; 3600 N Ref1 !
FUNCTION GHSERSi 298.15 -8162.609+137.236859*T-22.8317533*T*Ln(T)-.001912904*T^{2}-3.552E-09*T^{3}+176667*T^{-1}; 1687 Y
-9457.642+167.281367*T-27.196*T*Ln(T)-4.20369E+30*T^{-9}; 3600 N !

Exemple de description de l'énergie de Gibbs de SiO_2 (Quartz stoechiométrique)

PHASE QUARTZ % 1 1 !
CONSTITUENT QUARTZ : SiO2 : !
PARAMETER G(QUARTZ,SiO2;0) 298.15 +GSiO2S; 6000 N Ref0 !

FUNCTION GSIO2S 298.15
-900936.64-360.892175*T+61.1323*T*Ln(T)-.189203605*T^{2}+4.9509742E-05*T^{3}-854401*T^{-1}; 540 Y
-1091466.54+2882.67275*T-452.1367*T*Ln(T)+.428883845*T^{2}-9.0917706E-05*T^{3}+12476689*T^{-1};
770 Y
-1563481.44+9178.58655*T-1404.5352*T*Ln(T)+1.28404426*T^{2}-2.35047657E-04*T^{3}+56402304*T^{-1}; 848 Y
-928732.923+356.218325*T-58.4292*T*Ln(T)-.00515995*T^{2}-2.47E-10*T^{3}-95113*T^{-1}; 1800 Y
-924076.574+281.229013*T-47.451*T*Ln(T)-.01200315*T^{2}+6.78127E-07*T^{3}+665385*T^{-1}; 2960 Y
-957997.4+544.992084*T-82.709*T*Ln(T); 6000 N !

The Calculation of Phase Diagram (Calphad) Method
Gibbs energy for substitutional solutions (solid or liquid)

For a solution, the Gibbs energy per mole is :

$$G = G^{\circ} + {}^{id}G_{mix} + {}^{xs}G_{mix}$$

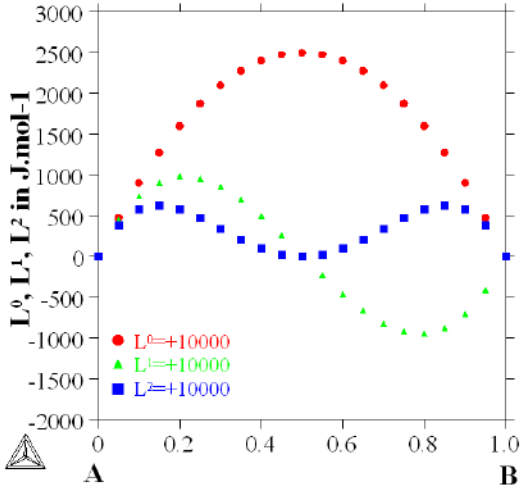
$$G^{\circ} = \Sigma_i\, c_i \cdot G^{\circ}_i$$

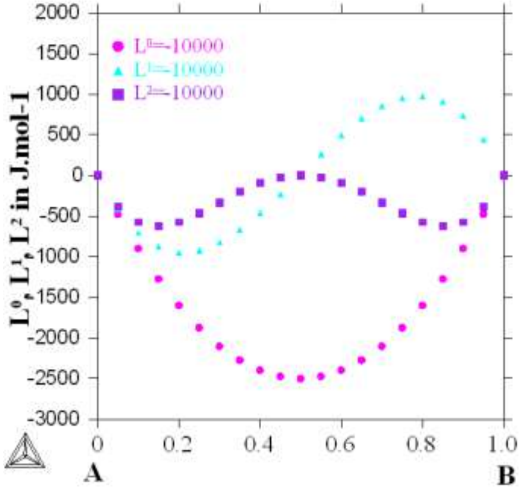
$${}^{id}G_{mix} = R \cdot T \cdot \Sigma_i\, c_i \cdot \ln(c_i)$$

$${}^{xs}G_{mix} = \Sigma_i\, \Sigma_{j>i}\, c_i \cdot c_j \cdot \Sigma_k\, L^k_{i,j} \cdot (c_i - c_j)^k$$

c_i and c_j are the mole fraction of species i and j,
$L^k_{i,j}$ is a binary interaction parameter between species i and j.

0 order: ${}^{xs}G^0_{i,j\ mix} = c_i \cdot c_j \cdot L^0_{i,j}$
1^{st} order: ${}^{xs}G^1_{i,j\ mix} = c_i \cdot c_j \cdot (c_i - c_j)^1 L^1_{i,j}$
2^{nd} order: ${}^{xs}G^2_{i,j\ mix} = \ldots$

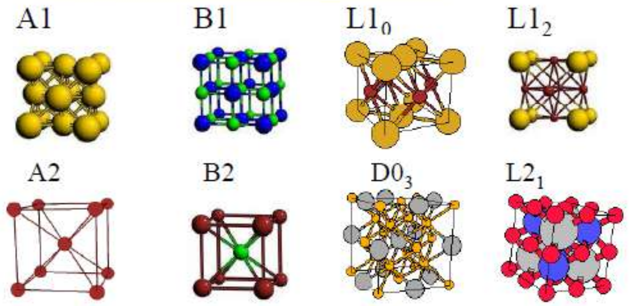




G° = Gibbs energy due to the mechanical mixing of the constituent of the phase
${}^{id}G_{mix}$ = Ideal mixing contribution (Configuration entropy)
${}^{xs}G_{mix}$ = Excess Gibbs energy of mixing

The Calculation of Phase Diagram (Calphad) Method
Experimental Data

http://cst-www.nrl.navy.mil/lattice/



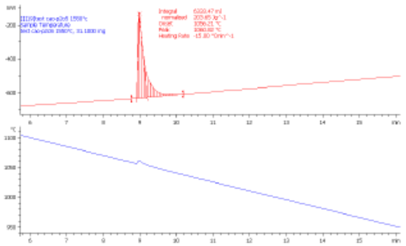
Crystallographic data

- Defects for non-stoichiometric compounds
- Structure of the phases in the system
- Sublattices for different constituents

Phase diagram data

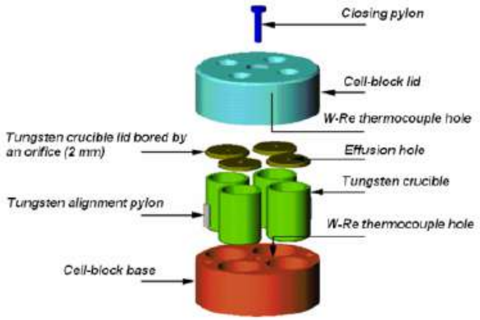
- Thermal analysis: start/end temperatures of transformations
- Microscope: phase identification, determining phase amounts
- X-ray: phase identification, lattice parameters
- Microprobe: phase identification, phase compositions (tie-lines)
- X-ray and neutron diffraction: site occupancies

CaO (55%)-P_2O_5 (45%)



Thermochemical data

- Calorimetric data: Enthalpy of formation, transformation, mixing
- EMF, Knudsen cell data: chemical potentials, activities
- Partial pressure: activities
- DSC: heat content, heat capacity, enthalpy of transformation
- DFT & MD Calculations



Multiple Knudsen cell

EXEMPLES
&
APPLICATIONS

The Calculation of Phase Diagram (Calphad) Method
The Tremendous role of the LITERATURE

Thèse R. Mathieu, Septembre 2009

INSTITUT NATIONAL POLYTECHNIQUE DE LORRAINE

Ecole Doctorale Ressources Procédés Produits Environnements (RP2E)

THESE DE DOCTORAT

Présentée pour obtenir le grade de

Docteur de l'Institut National Polytechnique de Lorraine en Géosciences

Présentée par

Romain MATHIEU

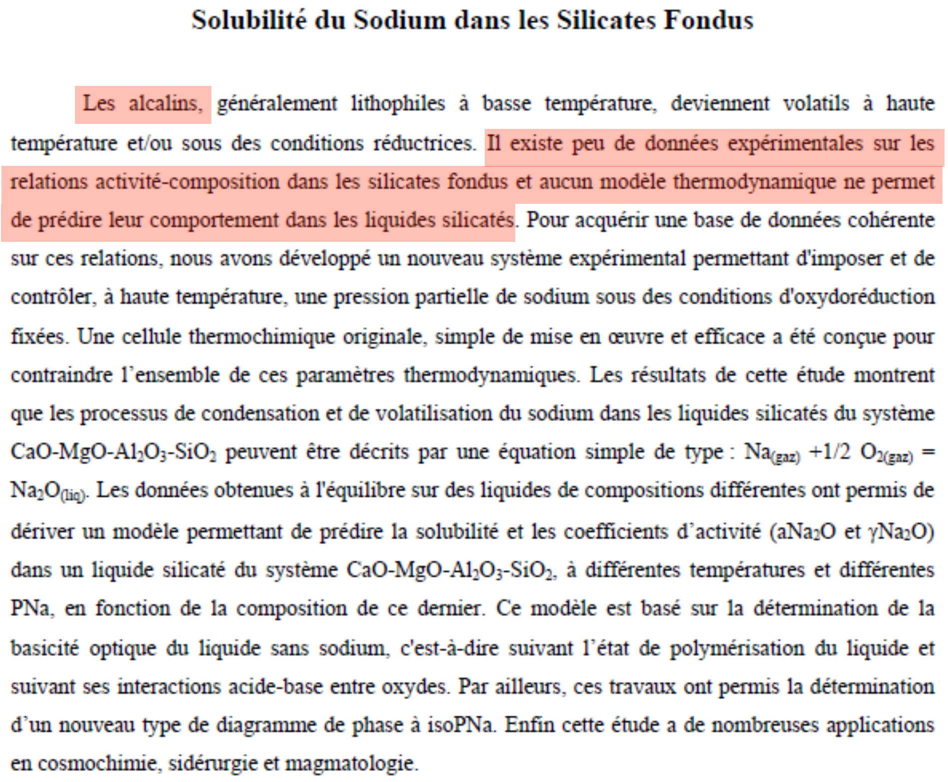
Solubilité du sodium dans les silicates fondus

Soutenue publiquement le 04 septembre 2009, à Vandoeuvre les Nancy;
devant le jury composé de:

Rapporteurs:	Dr. Bruno Scaillet, ISTO-CNRS, Orléans Pr. Andreas Pack, Georg-August-Universitat, Gottingen, Allemagne
Examinateurs:	Pr. Christophe Rapin, LCSM, Nancy Université Dr. Jean Lehmann, Arcelor-Mittal, Maizières les Metz Pr. Roger Hewins, MNHN, Paris et Rutgers University, USA
Directeurs de thèse:	Pr. Guy Libourel, CRPG-CNRS-ENSG, Nancy Université Dr. Etienne Deloule, CRPG-CNRS, Nancy Université

Centre de Recherches Pétrographiques et Géochimiques, Vandoeuvre les Nancy

Résumé



Solubilité du Sodium dans les Silicates Fondus

Les alcalins, généralement lithophiles à basse température, deviennent volatils à haute température et/ou sous des conditions réductrices. Il existe peu de données expérimentales sur les relations activité-composition dans les silicates fondus et aucun modèle thermodynamique ne permet de prédire leur comportement dans les liquides silicatés. Pour acquérir une base de données cohérente sur ces relations, nous avons développé un nouveau système expérimental permettant d'imposer et de contrôler, à haute température, une pression partielle de sodium sous des conditions d'oxydoréduction fixées. Une cellule thermochimique originale, simple de mise en œuvre et efficace a été conçue pour contraindre l'ensemble de ces paramètres thermodynamiques. Les résultats de cette étude montrent que les processus de condensation et de volatilisation du sodium dans les liquides silicatés du système CaO-MgO-Al_2O_3-SiO_2 peuvent être décrits par une équation simple de type : $Na_{(gaz)} + 1/2\ O_{2(gaz)} = Na_2O_{(liq)}$. Les données obtenues à l'équilibre sur des liquides de compositions différentes ont permis de dériver un modèle permettant de prédire la solubilité et les coefficients d'activité (aNa_2O et γNa_2O) dans un liquide silicaté du système CaO-MgO-Al_2O_3-SiO_2, à différentes températures et différentes PNa, en fonction de la composition de ce dernier. Ce modèle est basé sur la détermination de la basicité optique du liquide sans sodium, c'est-à-dire suivant l'état de polymérisation du liquide et suivant ses interactions acide-base entre oxydes. Par ailleurs, ces travaux ont permis la détermination d'un nouveau type de diagramme de phase à isoPNa. Enfin cette étude a de nombreuses applications en cosmochimie, sidérurgie et magmatologie.

The Calculation of Phase Diagram (Calphad) Method
The Tremendous role of the LITERATURE

PAS DE RÉSULTATS EXPÉRIMEN **AD**

CALPHAD is not SCIENCE,
CALPHAD is ART…

YES. CALPHAD CAN !!!

The Calculation of Phase Diagram (Calphad) Method
The Tremendous role of the LITERATURE

MODELING THE CHARGE COMPENSATION EFFECT
IN SILICA-RICH Na_2O-K_2O-Al_2O_3-SiO_2 MELTS

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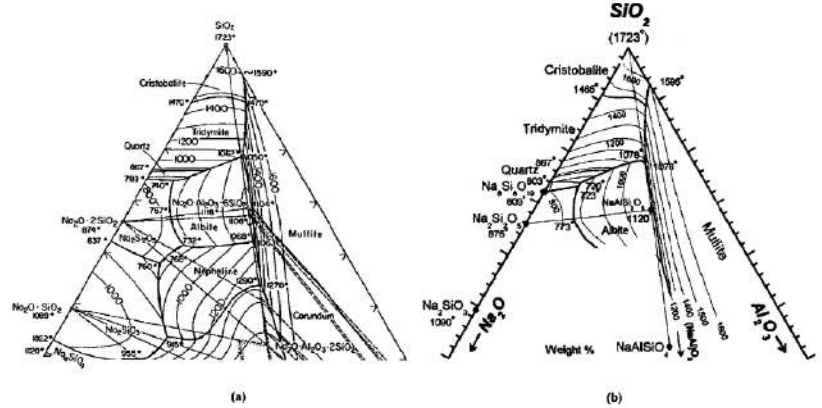
P. O. Box 6079, Station "Downtown"
Montreal, Québec H3C 3A7
Canada

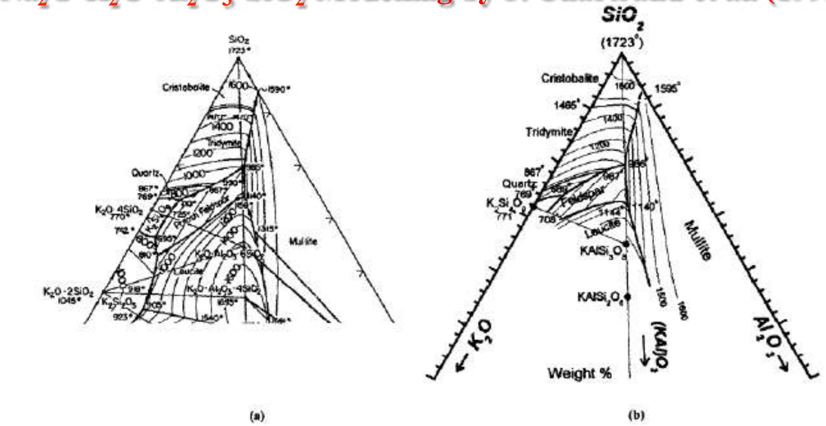
(Presented at CALPHAD XXVIII, Grenoble, France, May 1999)



(a) (b)

Figure 3: Liquidus surface of the Na_2O-Al_2O_3-SiO_2 system in the SiO_2-rich region: (a) as reported by Osborn and Muan[20]; (b) calculated. (composition in weight%; T in °C)

Na_2O-K_2O-Al_2O_3-SiO_2 Modelling by P. Chartrand et al. (1999)



(a) (b)

Figure 7: Liquidus surface of the K_2O-Al_2O_3-SiO_2 system in the SiO_2-rich region: (a) as reported by Osborn and Muan[20]; (b) calculated. (composition in weight%, T in °C)

Available online at www.sciencedirect.com
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Computer Coupling of Phase Diagrams and Thermochemistry 30 (2006) 270–276
www.elsevier.com/locate/calphad

Critical thermodynamic evaluation of oxide systems relevant to fuel ashes and slags. Part 1: Alkali oxide–silica systems

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Received 23 December 2005; received in revised form 8 March 2006; accepted 18 March 2006
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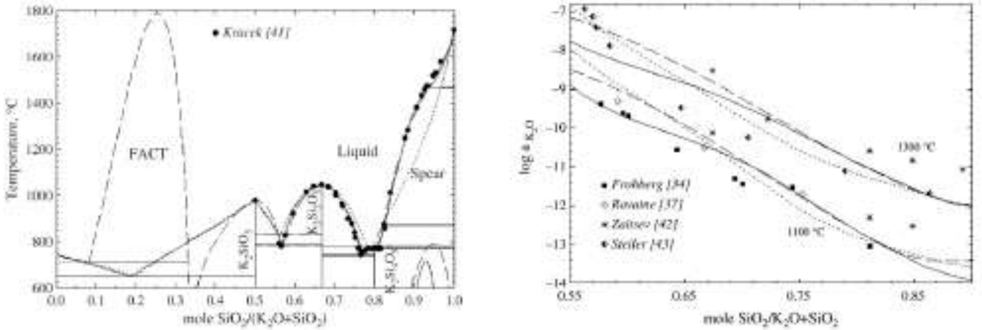
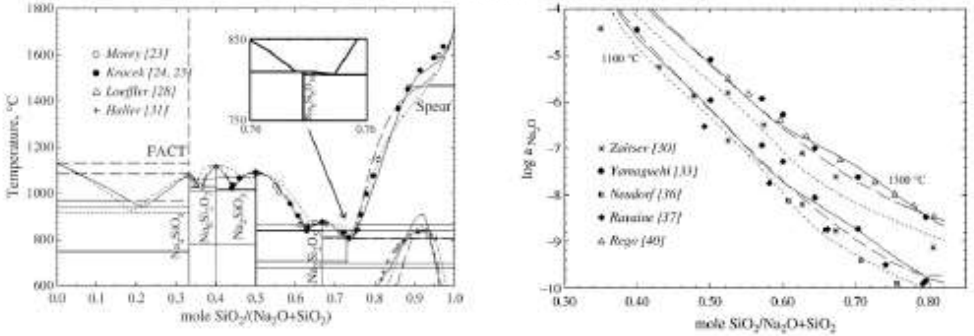
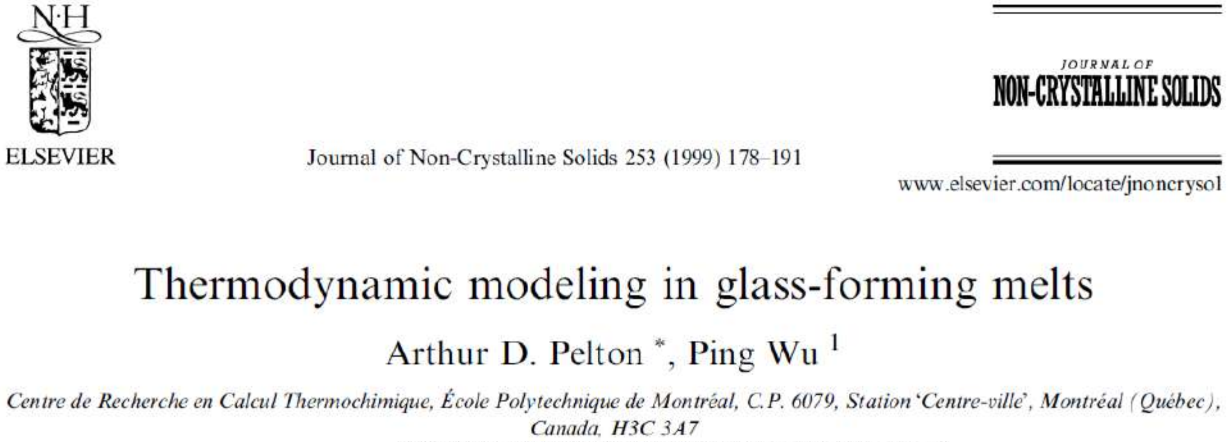


Na_2O-K_2O-SiO_2 Modelling by E. Yazhenskikh et al. (2006)
Activities at 1100°C & 1300°C



The Calculation of Phase Diagram (Calphad) Method
Ex 1: Thermodynamic modelling of the Na_2O-CaO-SiO_2 System



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Journal of Non-Crystalline Solids 253 (1999) 178–191

JOURNAL OF NON-CRYSTALLINE SOLIDS

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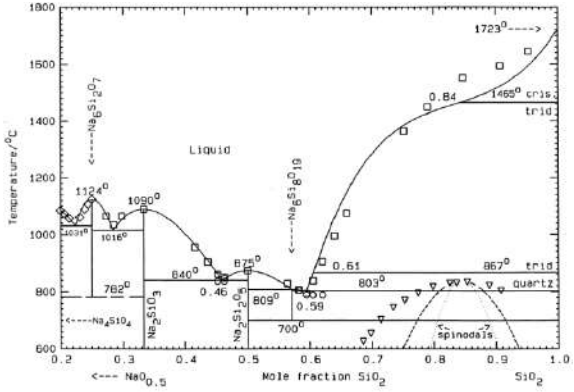
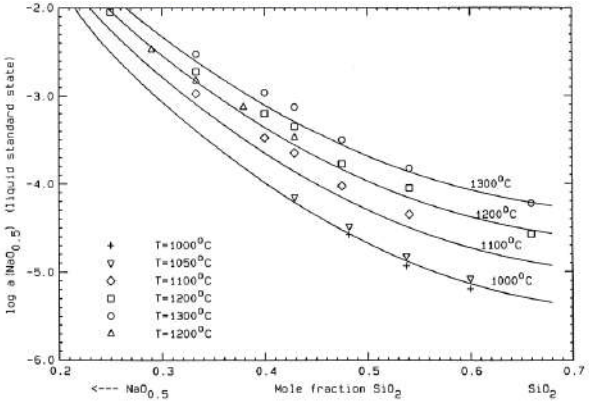
Thermodynamic modeling in glass-forming melts

Arthur D. Pelton *, Ping Wu [1]

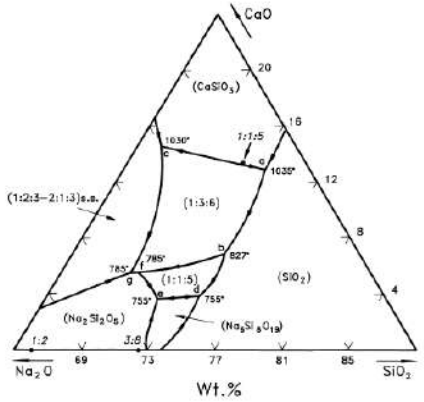
Centre de Recherche en Calcul Thermochimique, École Polytechnique de Montréal, C.P. 6079, Station 'Centre-ville', Montréal (Québec), Canada, H3C 3A7



Na_2O-SiO_2 System



$NaO_{1/2}$ activity in the liquid



Liquidus in the rich SiO_2 domain

Modélisation des systèmes binaires et extrapolation au niveau ternaire

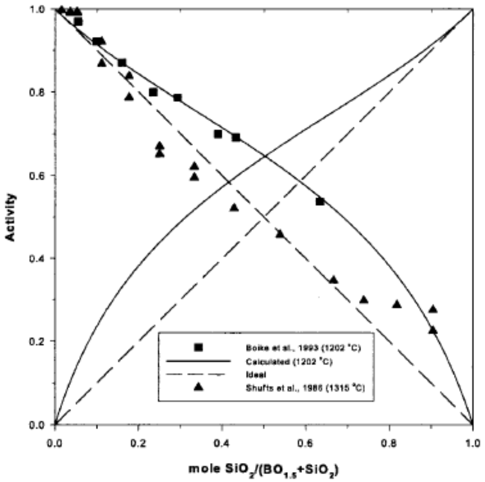
Calcul des propriétés thermodynamiques (activité chimique)

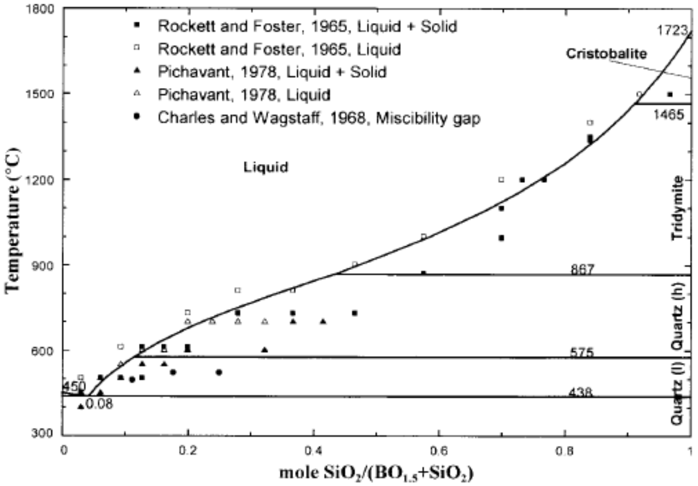
Possibilité de prendre en compte la solubilité des gaz dans le liquide (Sulfates, Phosphates…)

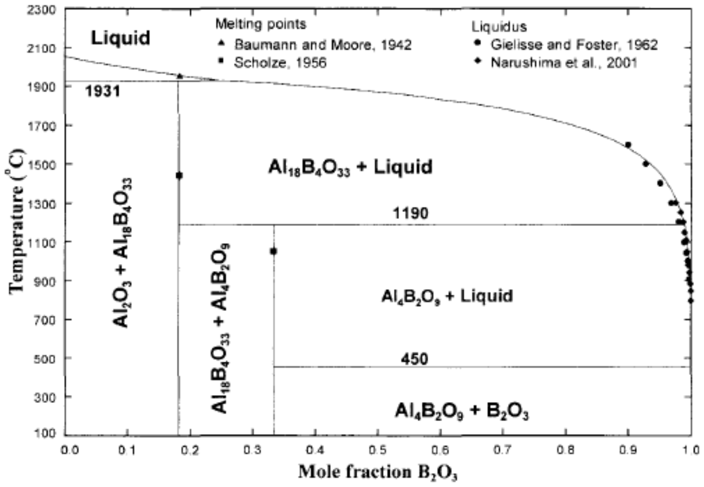
The Calculation of Phase Diagram (Calphad) Method
Ex 2: Thermodynamic modelling of the B_2O_3-SiO_2 & B_2O_3-Al_2O_3 Systems

Sergei A. Decterov[a], Varghese Swamy[b], In-Ho Jung[c]
[a]Center for Research in Computational Thermochemistry, Department of Chemical Engineering, École Polytechnique de Montréal, Montréal, Canada
[b]Department of Materials Engineering, Monash University, Victoria, Australia
[c]Research Institute of Industrial Science and Technology, Pohang, South Korea

Thermodynamic modeling of the $B_2O_3-SiO_2$ and $B_2O_3-Al_2O_3$ systems



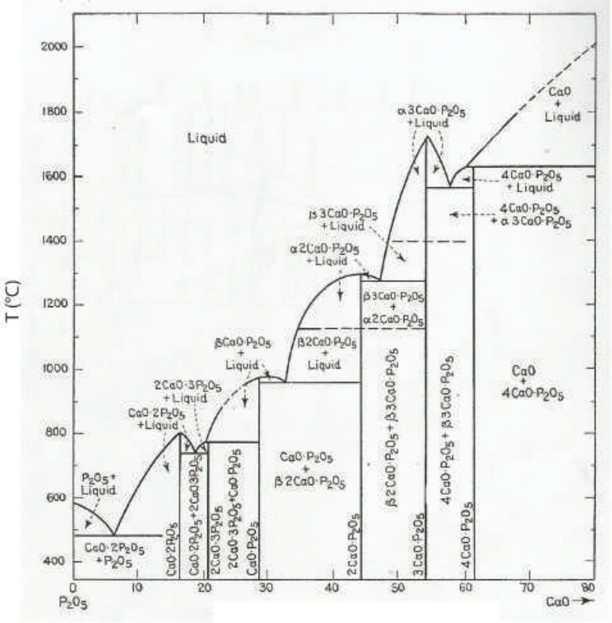


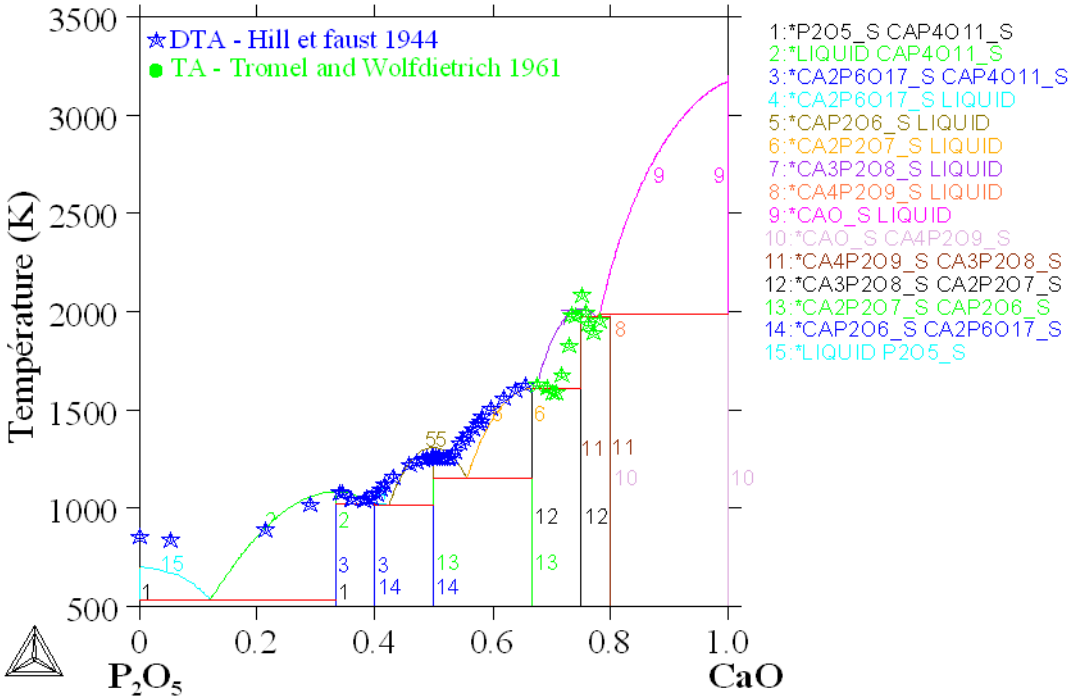


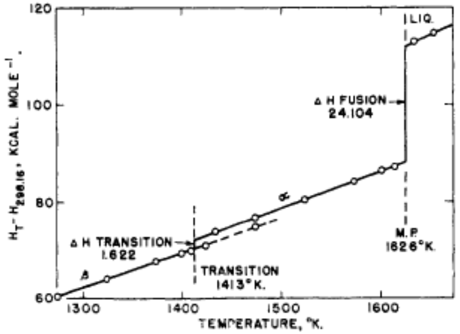
Modélisation des systèmes binaires, représentation des équilibres liquide/oxydes
Calculs des activités de SiO_2 et de B_2O_3
La description thermodynamique dépend de la qualité et de la cohérence des données exp

The Calculation of Phase Diagram (Calphad) Method
Ex 3: Modelling of the CaO-SiO_2 & P_2O_5-SiO_2 binary systems

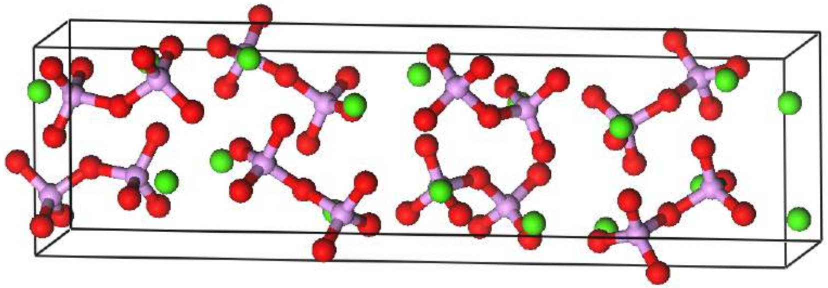
CaO-P_2O_5 phase diagram



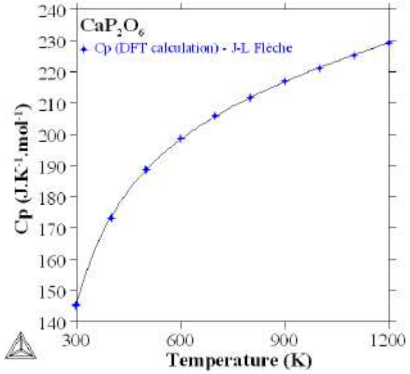




$Ca_2P_2O_7$ H_t-H_{298} (Kcal.mol^{-1})



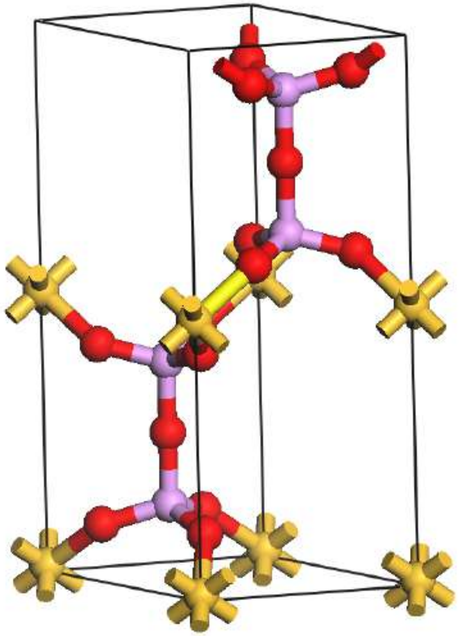
Calcul **DFT de la structure $Ca_2P_2O_7$**

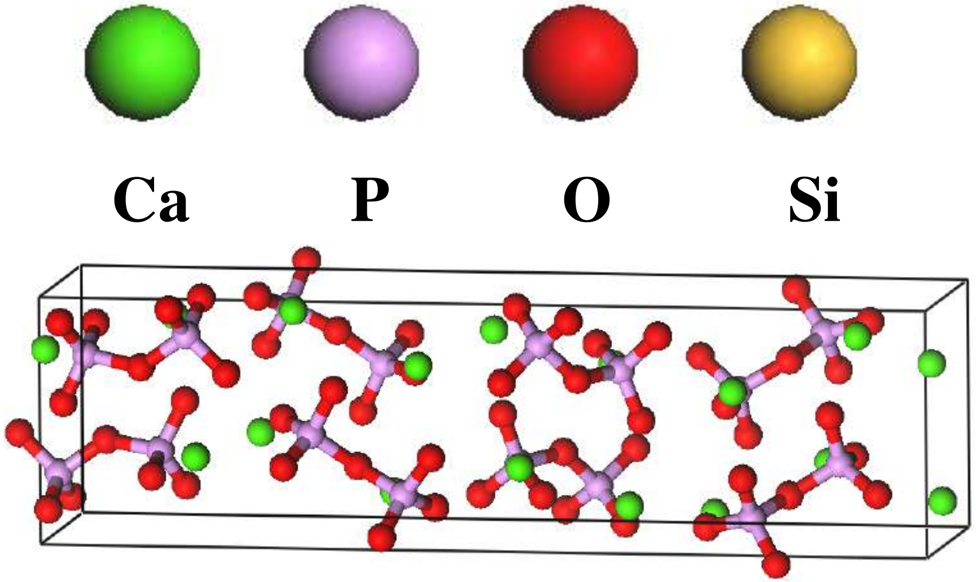


Calcul **du Cp de CaP_2O_6**

Calcul ab initio des fonctions thermodynamiques de $Ca_2P_2O_7$ et SiP_2O_7

Méthode : Phys. Rev. B65,245116(2002)
Code CASTEP (ACCELRYS Inc.) : DFT+ ondes planes + pseudopotentiel
J. Phys.: Cond. Mat. 14 (2002)



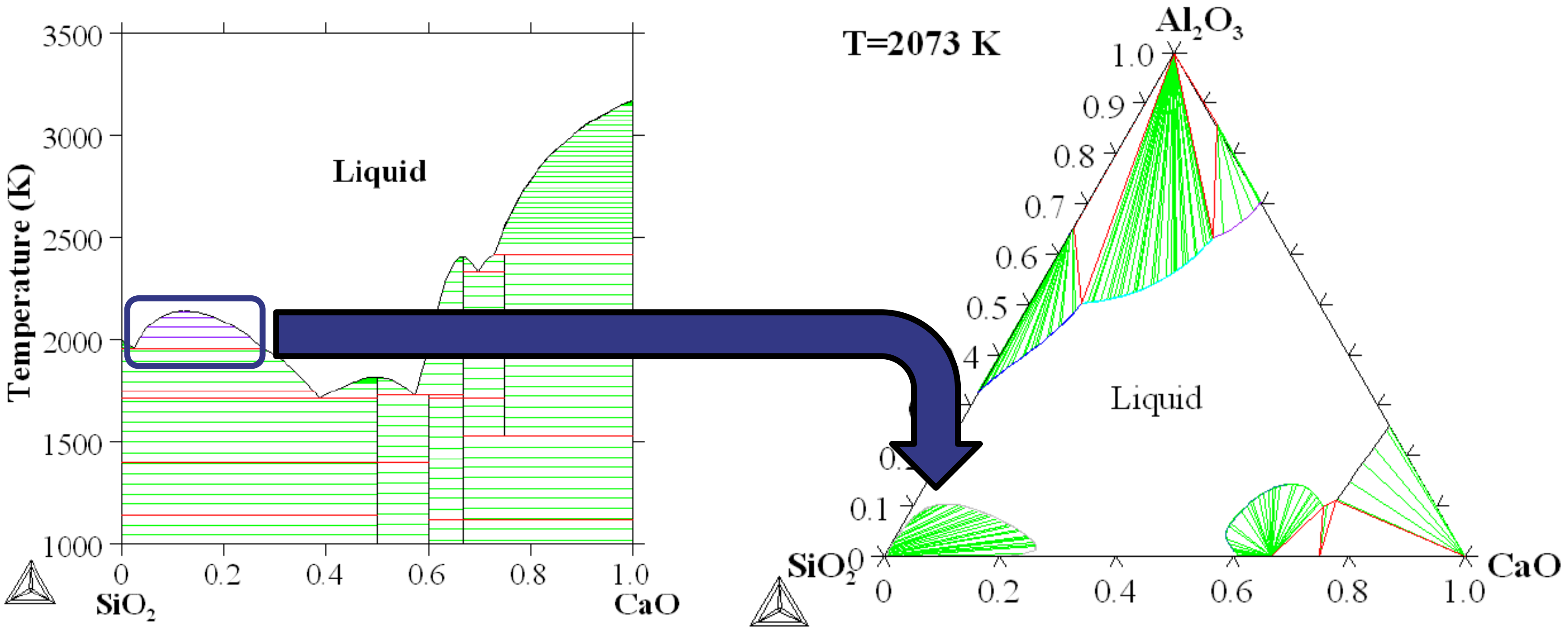


SiP_2O_7 (P63)	a	b	c
mesures	4.7158	4.7158	11.917
ab initio	4.7829	4.7829	12.064

$Ca_2P_2O_7$ (P41)	a	b	c
mesures	6.6858	6.6858	24.147
ab initio	6.7593	6.7593	24.454

The Calculation of Phase Diagram (Calphad) Method
Ex 4: Miscibility Gaps in the liquid phase

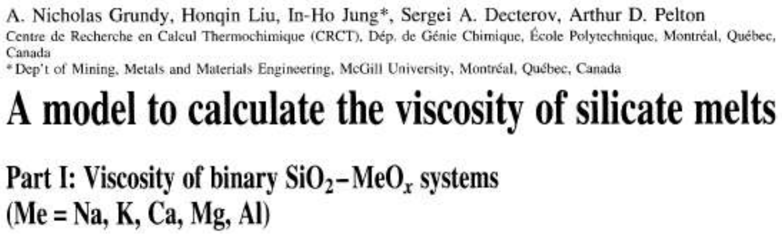
SiO_2-CaO System **Al_2O_3-SiO_2-CaO System**



La méthode Calphad est adaptée pour décrire la thermodynamique du liquide (melt, slag) :

- *Les lacunes de miscibilité entre deux liquides oxydes*
- *Les lacunes de miscibilité entre un liquide oxyde et un liquide métallique*

The Calculation of Phase Diagram (Calphad) Method
Ex 5: Modelling the viscosity of silicate melts



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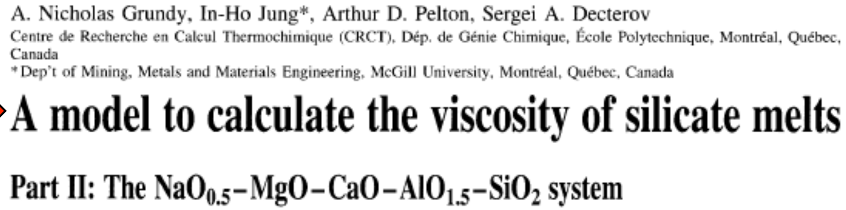
A model to calculate the viscosity of silicate melts

Part I: Viscosity of binary SiO_2–MeO_x systems
(Me = Na, K, Ca, Mg, Al)



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A model to calculate the viscosity of silicate melts

Part II: The $NaO_{0.5}$–MgO–CaO–$AlO_{1.5}$–SiO_2 system

Relation entre la thermodynamique de la phase liquide et sa viscosité :

- La viscosité est modélisée en optimisant des paramètres représentatifs de la structure du liquide
- Utilisation du Modèles Quasi Chimique Modifié (Modélisation de l'ordre à courte distance, SRO)

The viscosity η of the unary systems as a function of temperature is given by an Arrhenius equation:

$$Ln\left(\eta_{SiO_2}\right) = A^*_{SiO_2} + A^E_{SiO_2} + \frac{E^* + E^E}{RT} \qquad Ln\left(\eta_{MeOx}\right) = A + \frac{E}{RT}$$

Dans les binaires la viscosité de SiO_2 est modélisée par 4 paramètres, sans réseau (SiO^{4-} isolé) et avec réseau et celle des autres oxydes par 2 paramètres…

Comment ???

Modélisation des populations en O^{2-} libres, O^- non-pontant et O^0 pontant dans SiO_2 liquide. Dans le cas d'un système binaire MeO-SiO_2 ou $MeO_{0.5}$-SiO_2 (Ca, Na=oxydes basiques), chaque SiO_2 entre dans le réseau sous la forme orthosilicate SiO^{4-}…. POLYMERISATION

Le nombre d'oxygènes pontants est calculé dans la population totale d'oxygène $n(O)_{tot}$

$$n(O)_{tot} = \frac{1}{2}X(MeO_{0.5}) + X(MeO) + \frac{3}{2}X(Al_2O_3) + \frac{3}{2}X(B_2O_3) + 2X(SiO_2)$$

Aux basses températures, la déviation de la viscosité par rapport à la loi d'Arrhenius n'est pas considérée : Modèle établi pour les hautes températures

The Calculation of Phase Diagram (Calphad) Method
Ex 5: Modelling the viscosity of silicate melts

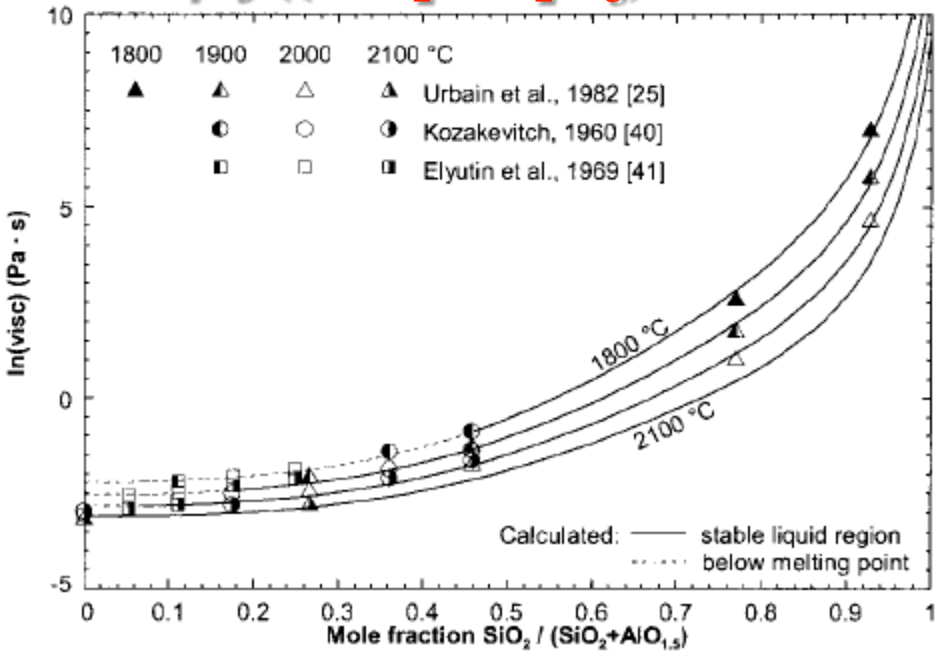
Concept de Q^i-Species : ou i représente le nombre d'oxygène pontant par atome de Si

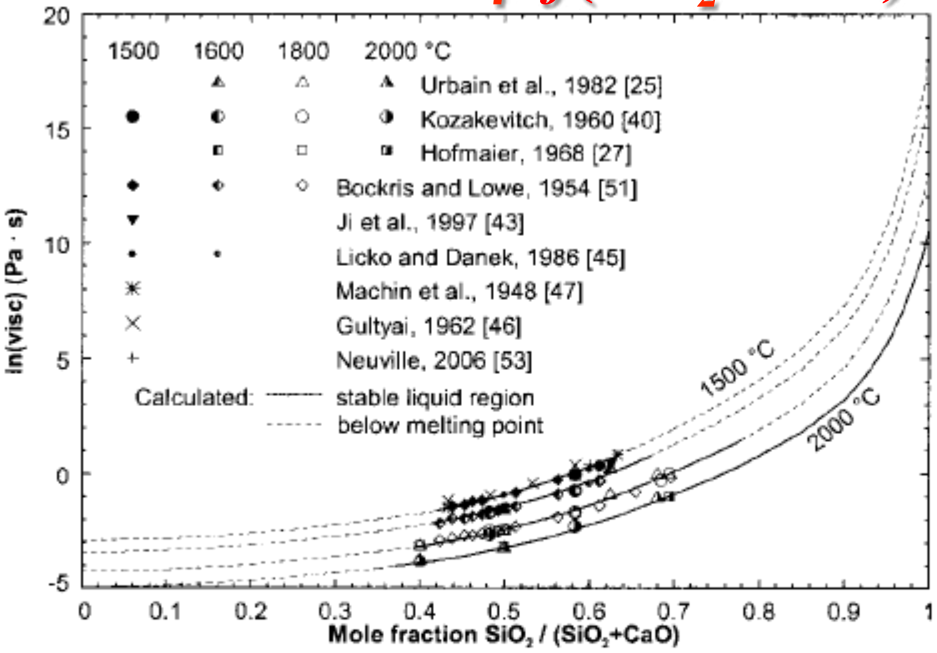
Ex : Dans SiO_2, chaque O autour d'un Si est pontant donc la fraction de Q^4-species=1

Un Si dans une chaine est une Q^2-species car 2 de ses atomes d'O sont pontants

"Qi -species in a melt (in-situ measurement) or in a quenched glass can be determined using Raman spectroscopy or nuclear magnetic resonance (NMR) measurements…

$Ln\ \eta = f(SiO_2+Al_2O_3)$ **(1 Pa.s = 1 poiseuille = 10 poises)** **$Ln\ \eta = f(SiO_2+CaO)$**





Modèle prédictif des viscosités pour des systèmes SiO_2 + Oxyde (Al_2O_3, CaO, MgO, Na_2O, K_2O)

Dans le cas des alcalins, le modèle s'applique dans le domaine $0.4<X(SiO_2)<0.7$, les très faibles viscosités ne sont pas modélisées

The Calculation of Phase Diagram (Calphad) Method
Application to glasses…

La méthode CALPHAD peut décrire la thermodynamique des systèmes oxydes

La thermodynamique du liquide (melt, slag) est modélisée, d'autres propriétés peuvent également l'être (Viscosité)

Dans ces bases, le verre est décrit en extrapolant les propriétés thermodynamiques du liquide vers les basses températures

La transition vitreuse n'est donc pas considérée

Et le verre ???

The Calculation of Phase Diagram (Calphad) Method
Application to glasses…

Du point de vue thermodynamique, la transition vitreuse peut être considérée comme une transition du 2^{nd} ordre (saut de Cp, H et S restent continues)

Verres

Aspects théoriques

par **Jean PHALIPPOU**

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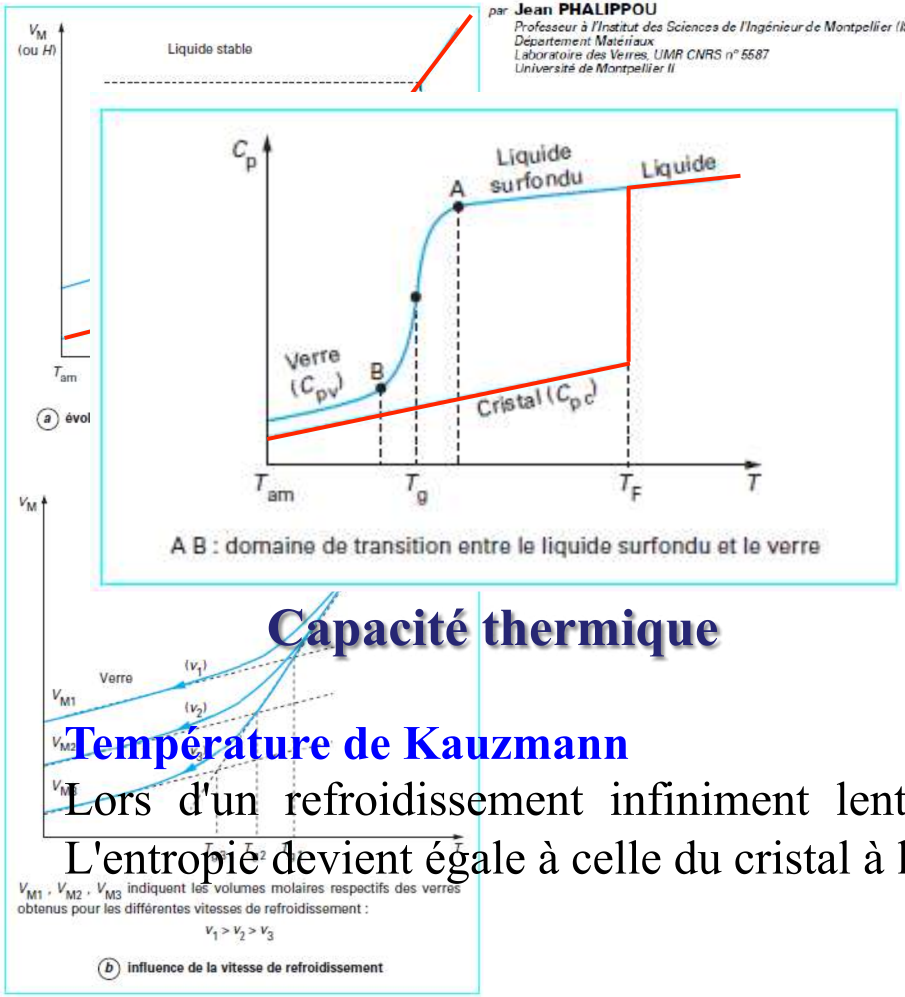
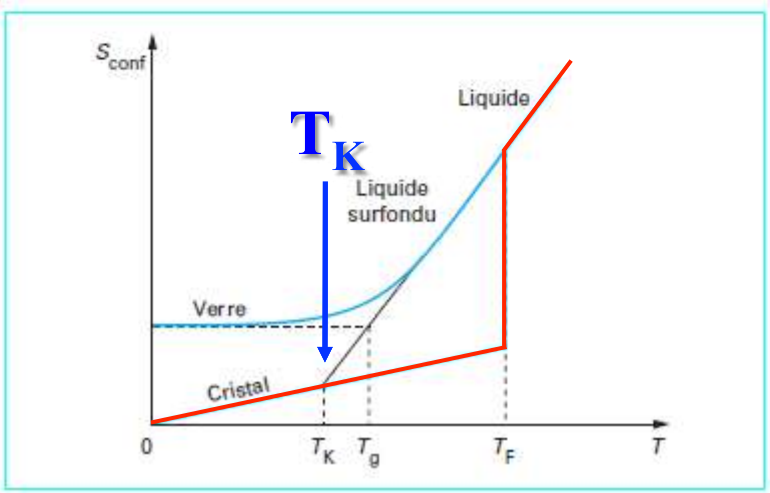


A B : domaine de transition entre le liquide surfondu et le verre

V_{M1}, V_{M2}, V_{M3} indiquent les volumes molaires respectifs des verres obtenus pour les différentes vitesses de refroidissement :
$v_1 > v_2 > v_3$

(b) influence de la vitesse de refroidissement

Capacité thermique



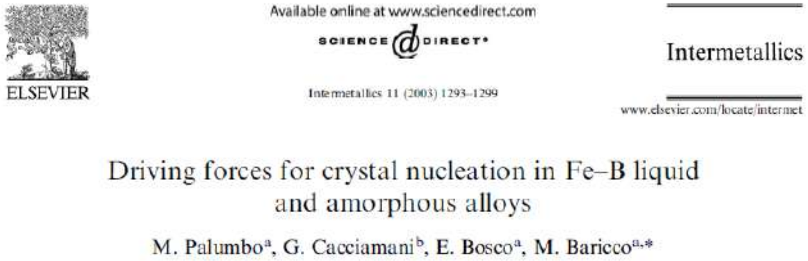
Entropie de configuration

Température de Kauzmann

Lors d'un refroidissement infiniment lent, le liquide surfondu ne peut pas cristalliser. L'entropie devient égale à celle du cristal à la température T_K

The Calculation of Phase Diagram (Calphad) Method
CALPHAD Modelling of Amorphous Alloys

Certains systèmes métalliques ont la capacité de former des alliages métalliques amorphes (Fe-B, Cu-Zr, Ni-Zr,Cu-Mg-Y)



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Driving forces for crystal nucleation in Fe–B liquid and amorphous alloys

M. Palumbo[a], G. Cacciamani[b], E. Bosco[a], M. Baricco[a,*]

JOURNAL OF APPLIED PHYSICS — VOLUME 88, NUMBER 7

Prediction of amorphous phase stability in metallic alloys

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(Received 31 March 2000; accepted for publication 28 June 2000)

The glass transition is considered as a 2nd order phase transformation from liquid phase

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Intermetallics 13 (2005) 409–414

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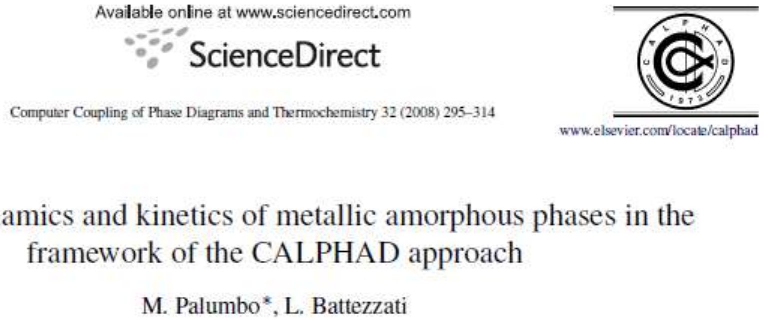
Glass forming ability of multi-component metallic systems

G. Shao*, B. Lu[1], Y.Q. Liu[2], P. Tsakiropoulos



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Computer Coupling of Phase Diagrams and Thermochemistry 32 (2008) 295–314

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Thermodynamics and kinetics of metallic amorphous phases in the framework of the CALPHAD approach

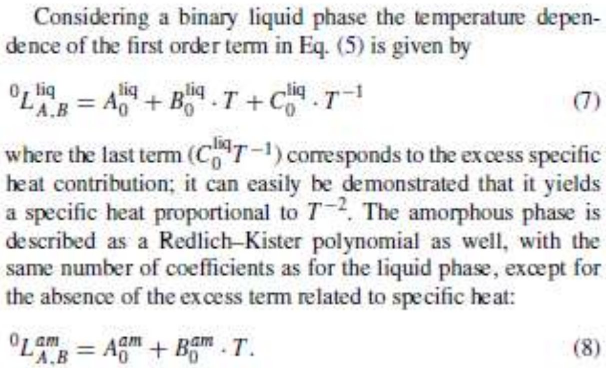
M. Palumbo*, L. Battezzati

These formalisms can be applied to oxide glasses !!!

The Calculation of Phase Diagram (Calphad) Method
CALPHAD Modelling of Amorphous Alloys

To model the glass transition (L→Am) as a second order transformation, the Gibbs energy of the amorphous solid needs to be formalised in such a way that ***the change in entropy ($\Delta S_{L\to Am}$) and free energy ($\Delta G_{L\to Am}$) become zero above T_g****. Below T_g, $\Delta S_{L\to Am}$ approaches the maximum entropy change ΔS_{max} and $\Delta G_{L\to Am}$ approaches ΔH_{max} at $T=0$ K*

Bormann's Model



Considering a binary liquid phase the temperature dependence of the first order term in Eq. (5) is given by

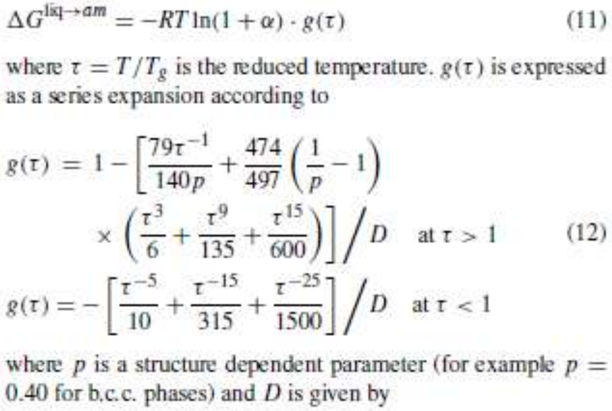
$$^{0}L^{liq}_{A,B} = A^{liq}_0 + B^{liq}_0 \cdot T + C^{liq}_0 \cdot T^{-1} \qquad (7)$$

where the last term ($C^{liq}_0 T^{-1}$) corresponds to the excess specific heat contribution; it can easily be demonstrated that it yields a specific heat proportional to T^{-2}. The amorphous phase is described as a Redlich–Kister polynomial as well, with the same number of coefficients as for the liquid phase, except for the absence of the excess term related to specific heat:

$$^{0}L^{am}_{A,B} = A^{am}_0 + B^{am}_0 \cdot T. \qquad (8)$$

Ne peut pas être appliqué quand T→ 0K

Shao's Approach
Magnetic Transition (T Curie)



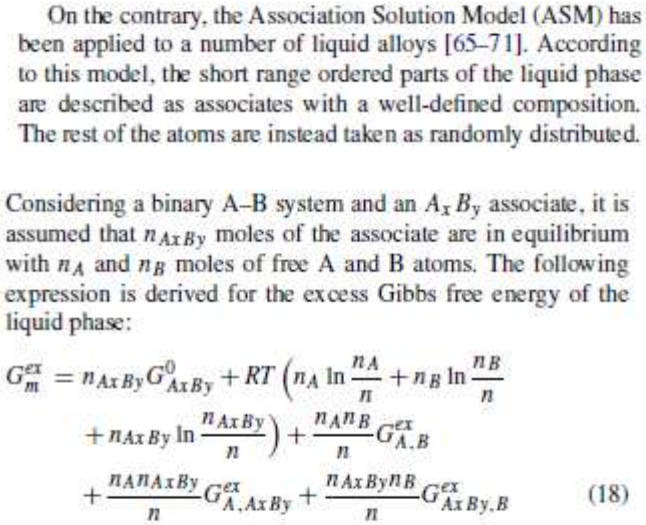
$$\Delta G^{liq\to am} = -RT\ln(1+\alpha)\cdot g(\tau) \qquad (11)$$

where $\tau = T/T_g$ is the reduced temperature. $g(\tau)$ is expressed as a series expansion according to

$$\begin{aligned} g(\tau) &= 1 - \left[\frac{79\tau^{-1}}{140p} + \frac{474}{497}\left(\frac{1}{p} - 1\right)\right.\\ &\quad \left.\times\left(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600}\right)\right]\Big/ D \quad \text{at } \tau > 1 \qquad (12)\\ g(\tau) &= -\left[\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500}\right]\Big/ D \quad \text{at } \tau < 1 \end{aligned}$$

where p is a structure dependent parameter (for example $p = 0.40$ for b.c.c. phases) and D is given by

Association Solution Model



On the contrary, the Association Solution Model (ASM) has been applied to a number of liquid alloys [65–71]. According to this model, the short range ordered parts of the liquid phase are described as associates with a well-defined composition. The rest of the atoms are instead taken as randomly distributed.

Considering a binary A–B system and an $A_x B_y$ associate, it is assumed that n_{AxBy} moles of the associate are in equilibrium with n_A and n_B moles of free A and B atoms. The following expression is derived for the excess Gibbs free energy of the liquid phase:

$$\begin{aligned} G^{ex}_m &= n_{AxBy} G^0_{AxBy} + RT\left(n_A \ln\frac{n_A}{n} + n_B \ln\frac{n_B}{n}\right.\\ &\quad \left. + n_{AxBy}\ln\frac{n_{AxBy}}{n}\right) + \frac{n_A n_B}{n} G^{ex}_{A,B}\\ &\quad + \frac{n_A n_{AxBy}}{n} G^{ex}_{A,AxBy} + \frac{n_{AxBy} n_B}{n} G^{ex}_{AxBy,B} \qquad (18) \end{aligned}$$

M. Palumbo, L. Battezzati / Computer Coupling of Phase Diagrams and Thermochemistry 32 (2008) 295–314

The Calculation of Phase Diagram (Calphad) Method
Conclusion

Méthode de calcul thermodynamique par minimisation de l'énergie libre d'un système chimique

Trouve sont intérêt dans les systèmes complexes ternaires, quaternaires, quinaires… *N*aires (plus de 15 éléments dans la base thermodynamique FUELBASE en cours de développement au CEA)

En général, modélisation jusqu'au niveau ternaire puis extrapolation aux niveaux supérieurs

Permet de confronter des données pour valider leur cohérence dans un système chimique f(T, compo)

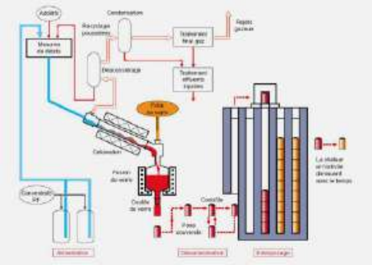
Fort besoin de données mesurées ou calculées

Le principe réside sur l'étude de systèmes chimiques simples, ensuite extrapolés vers des systèmes plus complexes
L'inverse ne correspond plus à la méthode Calphad

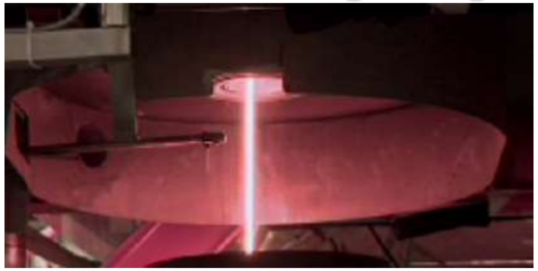
Platinoid Thermodynamics in Nuclear Waste Glasses

Glass frit

Calcinate



Glass melt during cooling



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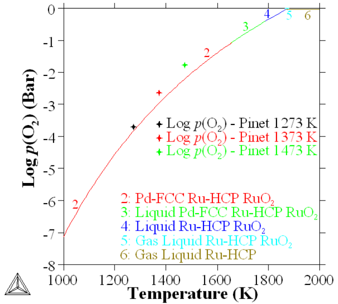
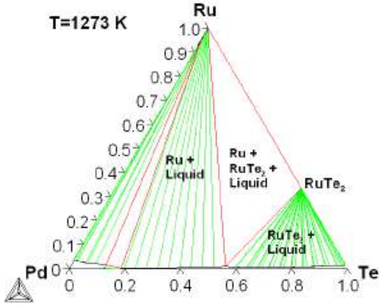
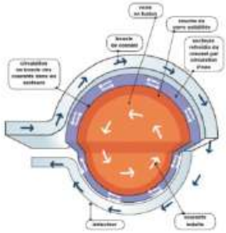
High-level Waste glass

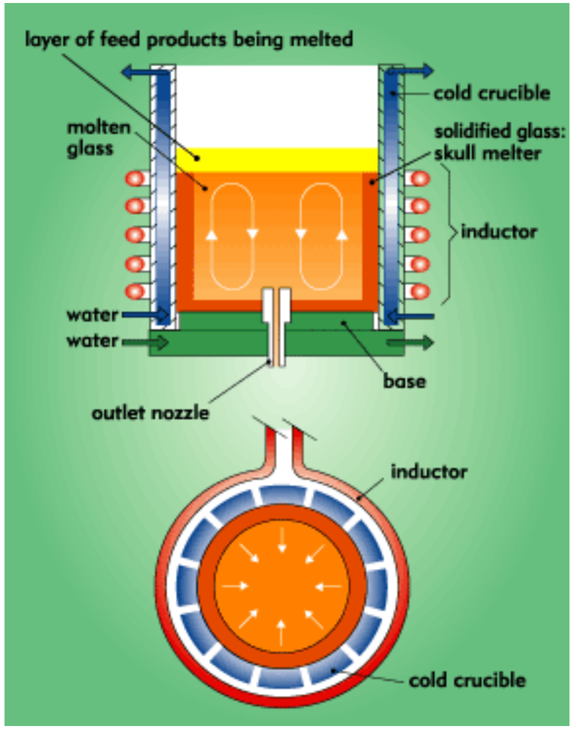






PlatinoidsThermodynamics in Nuclear Waste Glasses
The direct-induction cold-crucible vitrification process

http://www.areva.com/EN/activites-3400/activites-l-ensemble-du-cycle-nucleaire-et-les-energies-renouvelables.html
http://www.cea.fr/var/cea/storage/static/gb/library/Clefs46/pagesg/clefs46_42.html



In the cold crucible process, electric currents are induced directly in the material to be melted by an electromagnetic field. The melter load must be conductive to allow induction to occur. Glass is an insulating material at room temperature, but once melted its electrical resistivity drops and allows induction.

The advantages of the direct-induction cold crucible are mainly due to the formation of a layer of glass that solidifies upon contact with the cold melter walls to form a "skull melter". The skull prevents direct contact between the molten product and the cooled wall and creates a thermal insulation barrier.

From the nuclear waste-reprocessing standpoint, the main advantage is the very long melter service life that reduces maintenance requirements and the quantity of secondary technological waste to be managed

This process allows higher temperatures to be reached, generally leading to improved waste loading and therefore more effective volume reduction. It has been opened in 2010 at La Hague waste reprocessing facility

PlatinoidsThermodynamics in Nuclear Waste Glasses
Approach

During the vitrification process, slightly soluble Pd-Rh-Ru platinoids precipitate in the vitreous matrix of High Level Waste containment glasses. These platinoids precipitate into Pd-Rh-Te intermetallics, Rh(Ru)-FCC or Ru-HCP metallic particles and $(Ru,Rh)O_2$ or Rh_2O_3 oxide phases

Understanding the formation of metallic inclusions in the glass

Investigation of the low temperature eutectics and of the solubility limits in the solid solutions

Development of a thermodynamic database on the Pd-Rh-Ru-Te system

- CalPhaD modelling of all the Pd-Rh, Pd-Te, Rh-Te, Pd-Ru, Rh-Ru, Ru-Te binary systems
- Pd-Ru-Te & Rh-Ru-Te: Description of the phase diagrams by extrapolating the binaries
- **Pd-Rh-Ru & Pd-Rh-Te: Use of ternary interaction parameters to model the phase diagrams**

Application to Laboratory Nuclear Waste Glasses

Improvement of the understanding of the Pd-Rh-Ru-Te alloys formation in the glass

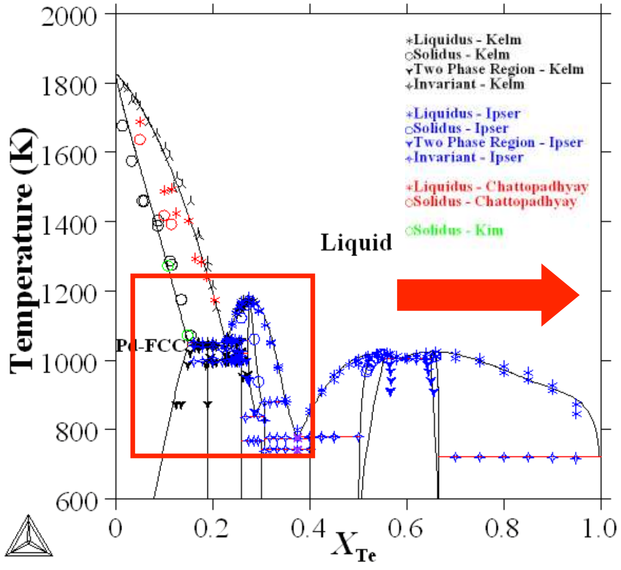
- Calculation of solidification pathways with the same platinoids amounts as in laboratory glasses
- Calculation of the chemical activities considering the oxygen potential of the glass through the oxide phases
- Experimental work on the solubility limits of platinoids in the Te rich liquid by DTA (SEM+XRD Analyses)
- Temperature measurements of the solid/liquid transitions in the ternary systems

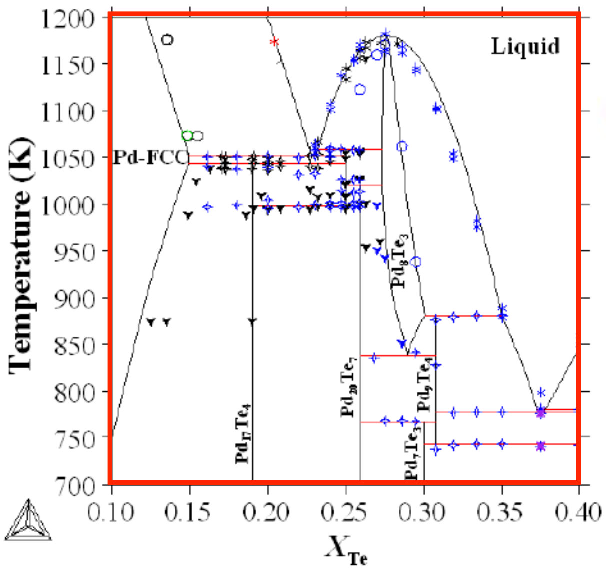
Parce que les platinoïdes sont insolubles dans la matrice de verre, il est possible de modéliser leurs propriétés thermodynamiques indépendamment de celles du verre
Le verre n'est modélisé qu'au travers du rôle tampon du potentiel d'oxygène

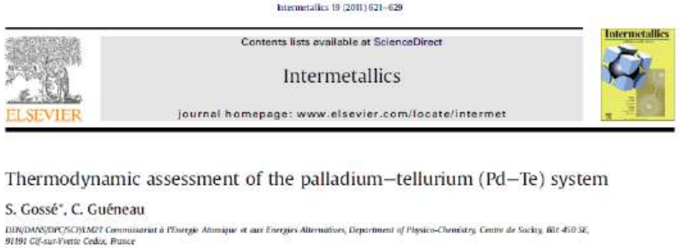
PalladiumThermodynamics in Nuclear Waste Glasses
Thermodynamic study of the Pd-Te system (1)

The Pd-Te diagram is made up of 9 intermetallic phases:
$Pd_{17}Te_4$, Pd_3Te, $Pd_{20}Te_7$, Pd_8Te_3, Pd_7Te_3, Pd_9Te_4, Pd_3Te_2, PdTe and $PdTe_2$

Phase	$Pd_{17}Te_4$	Pd_3Te	$Pd_{20}Te_7$	Pd_8Te_3	Pd_7Te_3	Pd_9Te_4	Pd_3Te_2	PdTe	$PdTe_2$
Structure Type	$Pd_{10}Te_3$	W	$Pd_{20}Sb_7$	…	…	Pd_9Te_4	Pd_3Te_2	AsNi	CdI_2
Space Groupe	$F\bar{4}3m$	$Im\bar{3}m$	$R\bar{3}$	…	…	$mP52$	$Cmcm$	$P6_3/mmc$	$P\bar{3}m1$
Parameters (Å)	a=12.678	a=3.226	a=11.797 c=11.172 γ=120°	a=12.843 b=15.126 c=11.304	a=7.444 b=13.918 c=8.873	a=7.458 b=13.938 c=8.839	a=3.858 b=12.687 c=7.900	a=4.20 c=5.79 γ=120°	a=4.0365 c=5.1262 γ=120°
Reference	[Kim]	[Bhan]	[Wopersnow]	[Kim]	[Kim]	[Matkovic]	[Matkovic]	[Kjekshus]	[Furuseth]






Intermetallics 19 (2011) 621–629

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Thermodynamic assessment of the palladium–tellurium (Pd–Te) system

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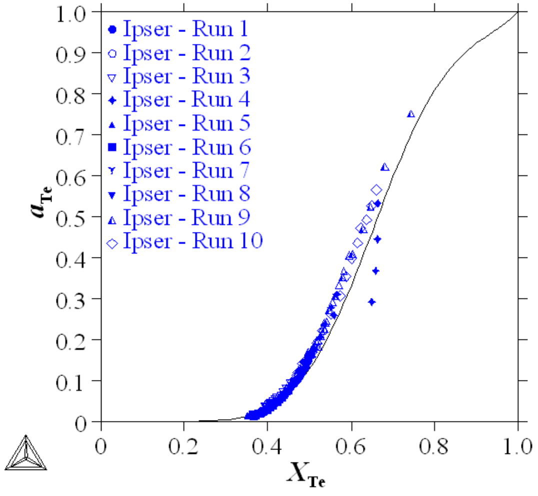
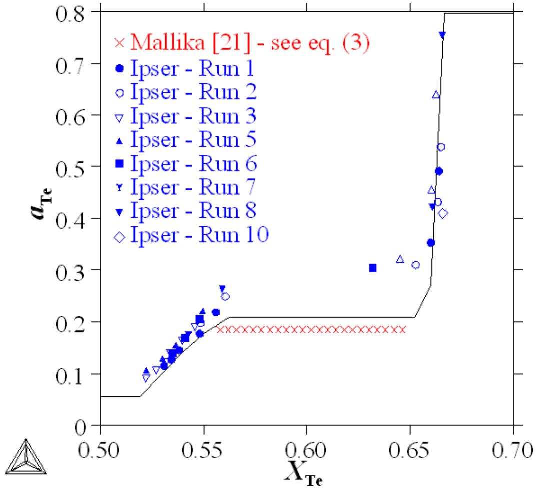
DEN/DANS/DPC/SCP/LM2T Commissariat à l'Energie Atomique et aux Energies Alternatives, Department of Physico-Chemistry, Centre de Saclay, Bât 450 SE, 91191 Gif-sur-Yvette Cedex, France

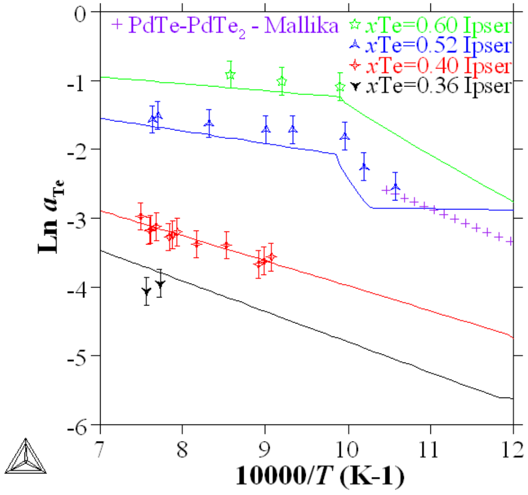
Results:

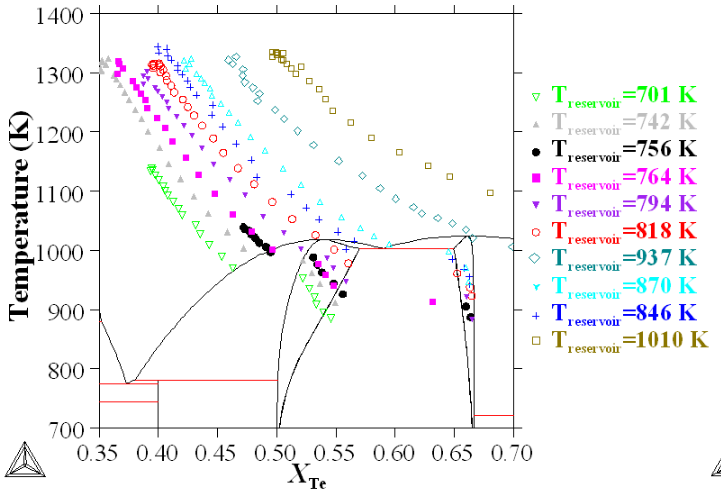
Good agreement between the calculated and the experimental phase diagram…

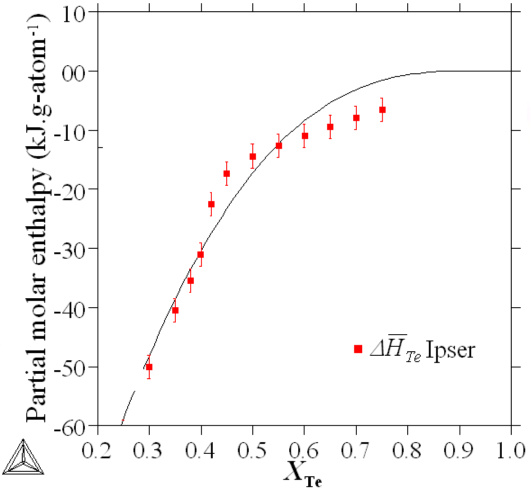
PalladiumThermodynamics in Nuclear Waste Glasses
Thermodynamic study of the Pd-Te system (2)

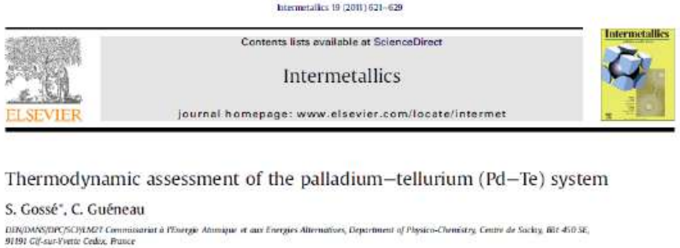












Intermetallics 19 (2011) 621–629

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Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Thermodynamic assessment of the palladium–tellurium (Pd–Te) system

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DEN/DANS/DPC/SCP/LM2T Commissariat à l'Energie Atomique et aux Energies Alternatives, Department of Physico-Chemistry, Centre de Saclay, Bât 450 SE, 91191 Gif-sur-Yvette Cedex, France

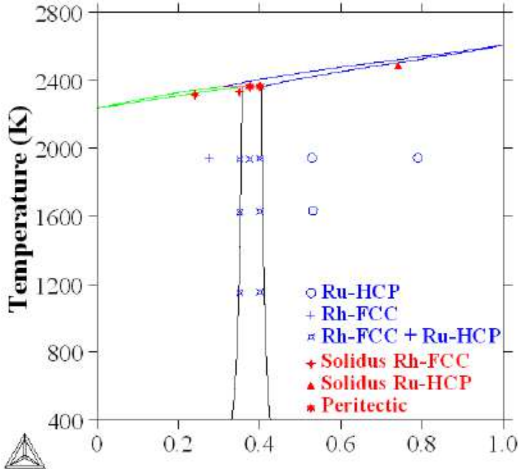
Results:

…The thermodynamic properties are well calculated too !

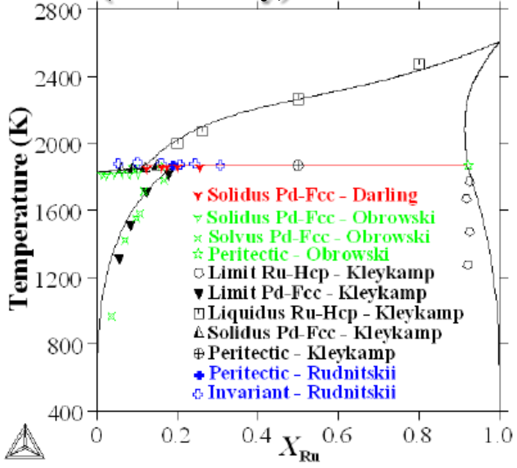
503 EXPERIMENTAL DATA USED TO MODEL THIS BINARY SYSTEM

PlatinoidsThermodynamics in Nuclear Waste Glasses
Modelling of the Pd-Rh-Ru system (Binary systems)

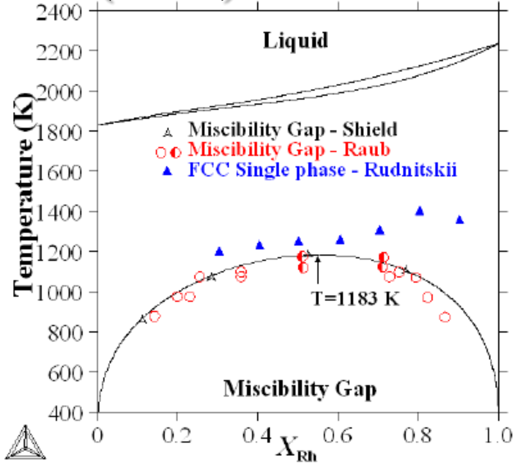
Rh-Ru Phase diagram
(This study)



Pd-Ru Phase diagram
(This study)



Pd-Rh Phase diagram
(Gürler)



Rh-Ru:
2 large solid solutions. No intermetallic phase, only one high temperature peritectic decomposition
Remark: No thermodynamic data

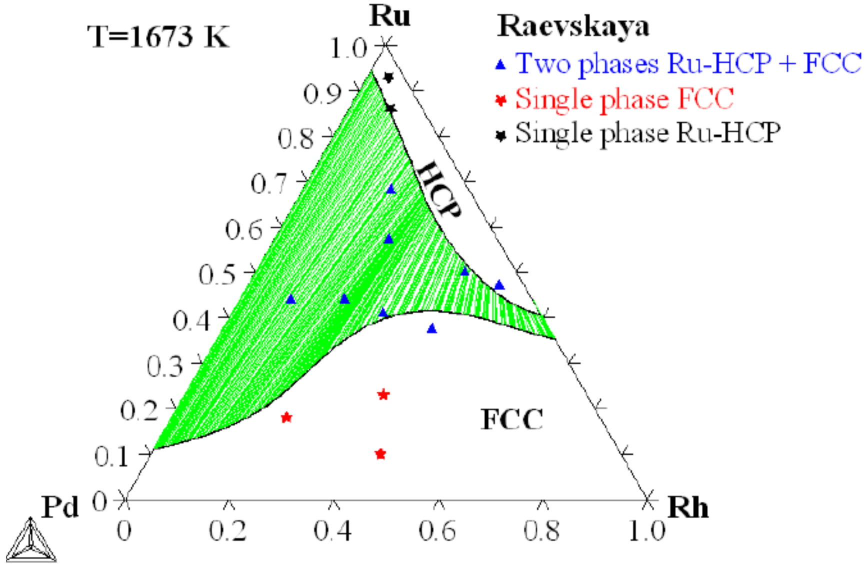
Pd-Ru:
No intermetallic phase , only one high temperature peritectic decomposition
Only one peritectic decomposition (15-20 at.% Ru)
Remark: The shape of the Pd limit in Ru-HCP by Kleykamp has not been considered

Pd-Rh:
No intermetallic phase, only one large miscibility gap between Pd-FCC and Rh-FCC
The thermodynamic modelling comes from Gürler et al.

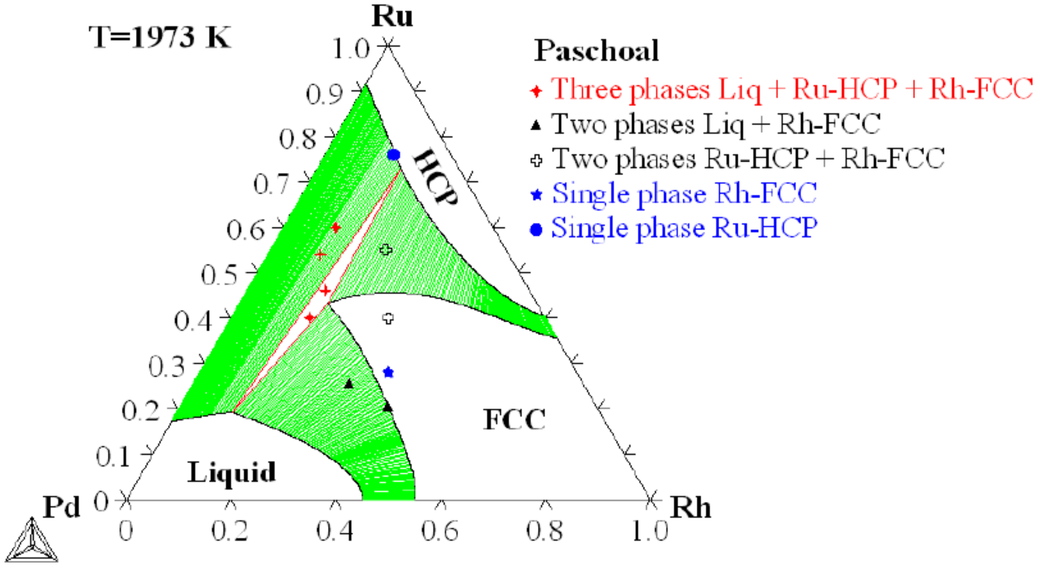
Due to the high temperature of the liquid formation, these systems are difficult to investigate

PlatinoidsThermodynamics in Nuclear Waste Glasses
Description of the Pd-Rh-Ru ternary system

Pd-Rh-Ru Phase diagram at 1673 K
Comparison with data from Raevskaya



Pd-Rh-Ru Phase diagram at 1973 K
Comparison with data from Paschoal

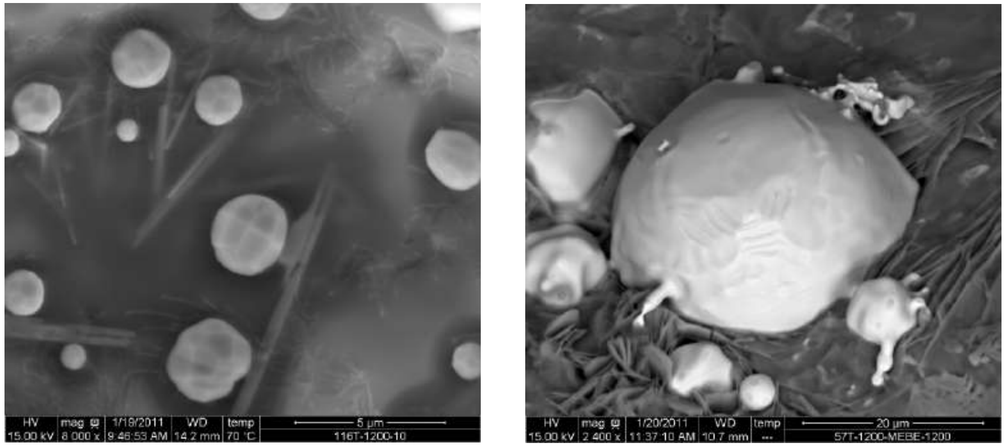


Two different sets of data make it possible to refine the thermodynamic modelling of the Pd-Rh-Ru systems:
R. Gürler, *J. of Nuc. Mat.* 199 (1992)
M. V. Raevskaya, V. V. Vasekin, I. G. Sokolova, *J. of the Less Com. Met.* 99 (1984)

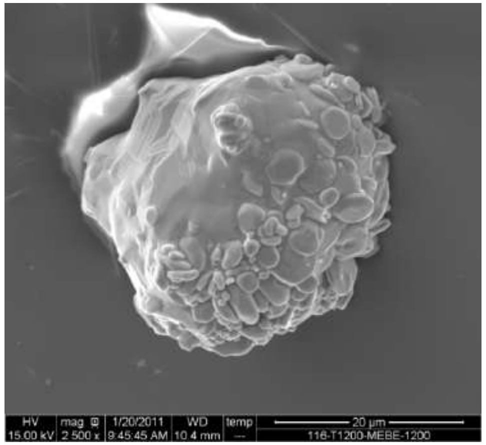
Difficult to calculate isothermal sections both consistent with 1673 K & 1973 K results

PlatinoidsThermodynamics in Nuclear Waste Glasses
SEM observation of the platinoid phases

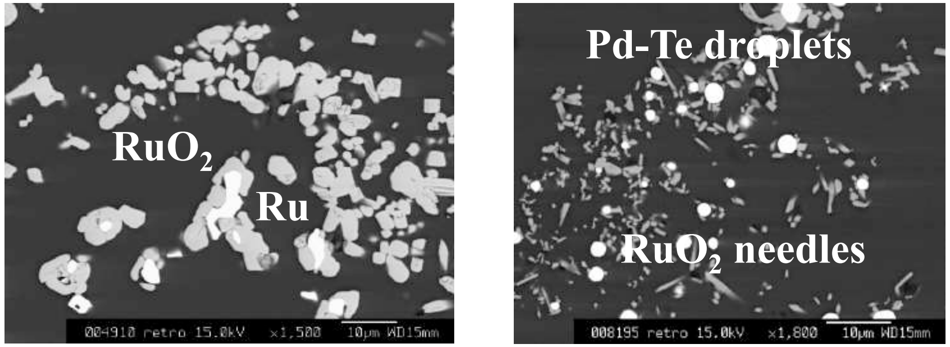
Pd-Te droplets inside the glass matrix



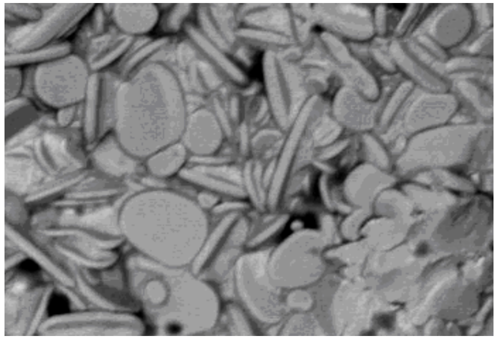
Ru, Pd-Te metallic inclusion



Morphologies of (Pd-Te, Ru) noble metals in a simulated nuclear waste glass



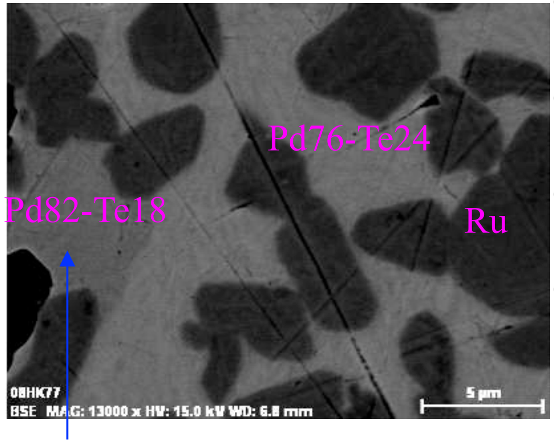
Rh-Ru inclusions in the glass



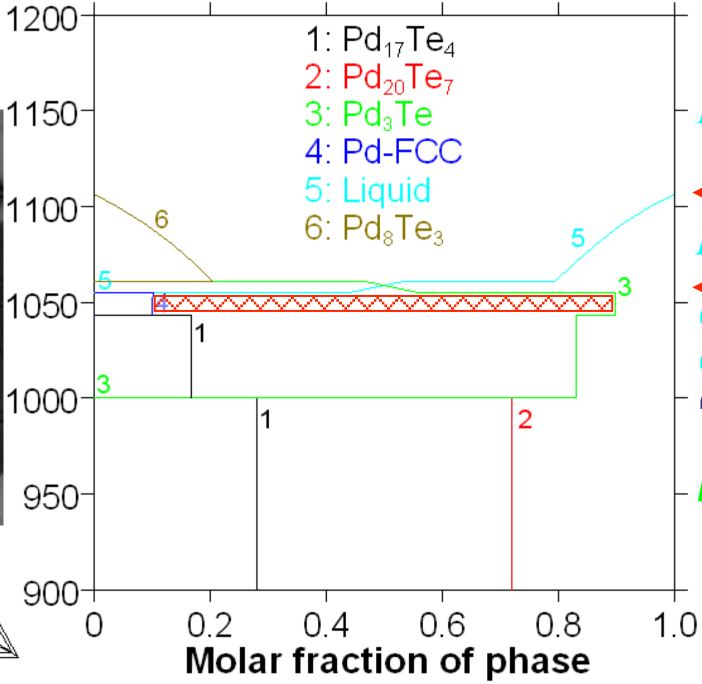
Platinoids Thermodynamics in Nuclear Waste Glasses
Application to borosilicate waste glasses

Explanation of the metallic alloy compositions: the Pd76-Te24 alloy (light grey)

Origin: Mean Pd-Te alloy in metallic clusters from high temperature gradient region



Pd-FCC Inclusion



Liq

1105

$Liq \rightarrow Liq + Pd_8Te_3$

1055

$Liq + Pd_8Te_3 \rightarrow Liq + Pd_3Te$

$Liq + Pd_3Te \rightarrow Liq + Pd_3Te + Pd$

$Pd + Pd_3Te \rightarrow Pd_3Te + Pd_{17}Te_4$

$Pd_3Te + Pd_{17}Te_4 \rightarrow Pd_{20}Te_7 + Pd_{17}Te_4$

At 1000 K, the last solid-solid reaction is: $Pd_3Te + Pd_{17}Te_4 \rightarrow Pd_{20}Te_7 + Pd_{17}Te_4$

For $T < 1000$ K the equilibrium phases should be $Pd_{20}Te_7$ and $Pd_{17}Te_4$ (respectively 26 at.% and 19 at.% Te)
But the Pd76-Te24 and Pd82-Te18 compositions match with (±1 at.% Te) :

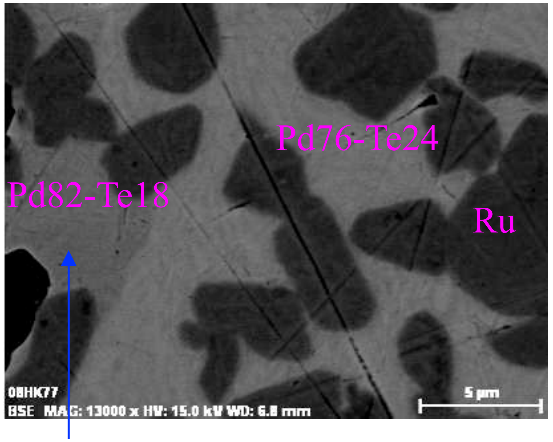
- **the Pd_3Te intermetallic compound**
- **the Pd-FCC solid solution (±15 at.% Te @ 1050 K)**

On the thermodynamic point of view, solidification of these alloys occurs between 1045 and 1055 K

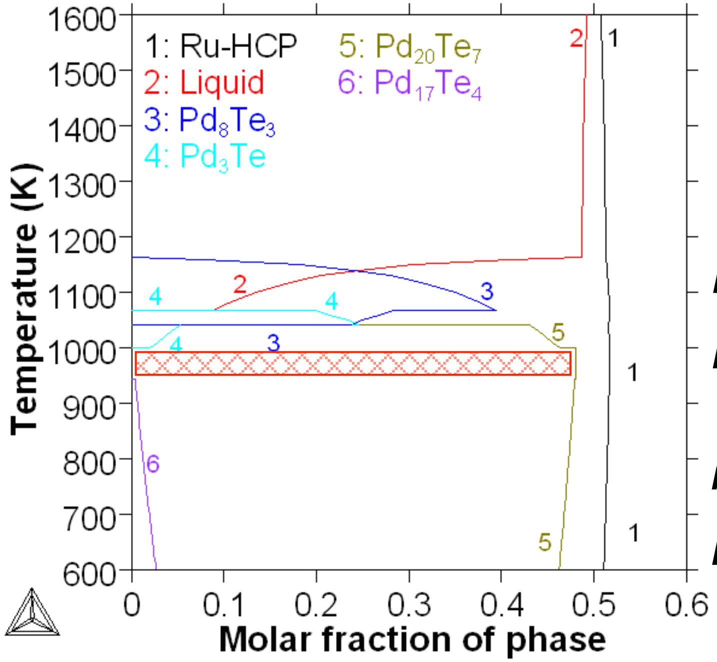
Platinoids Thermodynamics in Nuclear Waste Glasses
Application to borosilicate waste glasses

Explanation of the metallic alloy compositions: the Pd37.5-Ru50-Te12.5 alloy

Composition approximately equal to the mean integrated composition of the picture



Pd-FCC Inclusion



Ru+Liq

1160

Ru+Liq → Ru+Liq+Pd_8Te_3

1070

Ru+Pd_8Te_3+Liq → Ru+Pd_8Te_3+Pd_3Te

Ru+Pd_8Te_3+Pd_3Te → Ru+Pd_3Te+$Pd_{20}Te_7$

Ru+Pd_3Te+$Pd_{20}Te_7$ → Ru+$Pd_{17}Te_4$+$Pd_{20}Te_7$

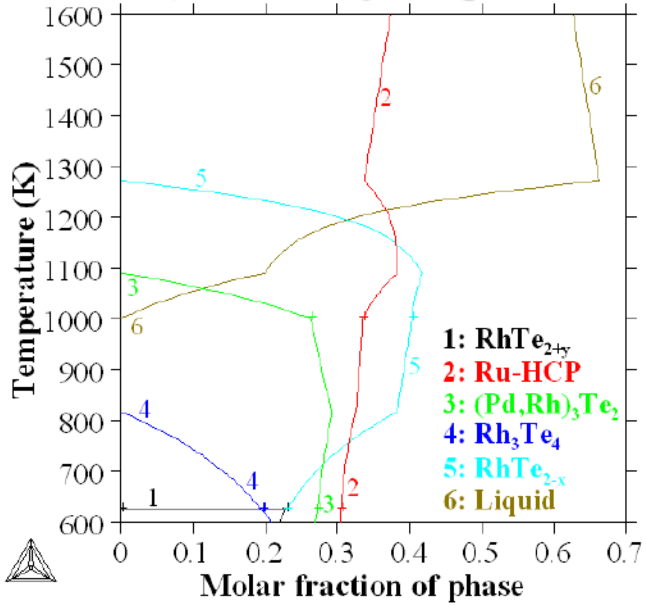
At 950 K, the last solid-solid reaction is: Ru + Pd_3Te + $Pd_{20}Te_7$ → Ru + $Pd_{17}Te_4$ + $Pd_{20}Te_7$

For T < 1160 K the mixture is made of 2 phases Ru-HCP + liquid (Ru solubility is about 1-2 at.%)
For T < 950 K the equilibrium phases should be Ru-HCP, $Pd_{20}Te_7$ and $Pd_{17}Te_4$
But the $Pd_{17}Te_4$ phase hasn't been observed in the simulated waste glasses

On the thermodynamic point of view, solidification occurs above the formation of $Pd_{17}Te_4$ (T > 950 K)

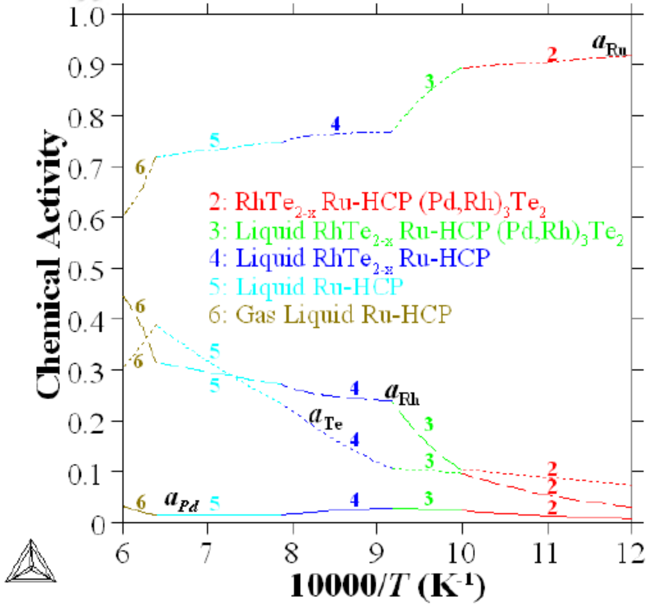
Platinoids Thermodynamics in Nuclear Waste Glasses
Study of the Pd-Rh-Ru-Te Metallic system

The considered composition is Pd_{08}-Rh_{25}-Ru_{30}-Te_{37}. It is representative of the relative platinoids (Pd-Rh-Ru) and tellurium amounts produced by an UO_2 fuel inside a LWR reactor (see H. Kleykamp, *J. Nuclear Mater.* 171 (1990))



$Pd_{08}Rh_{25}Ru_{30}Te_{37}$ Solidification pathway

Main formed phases are intermetallics and Ru-HCP



Pd, Rh, Ru and Te Activities and related equilibriums in function of the inverse of temperature (activities referenced to the pure element standard states)

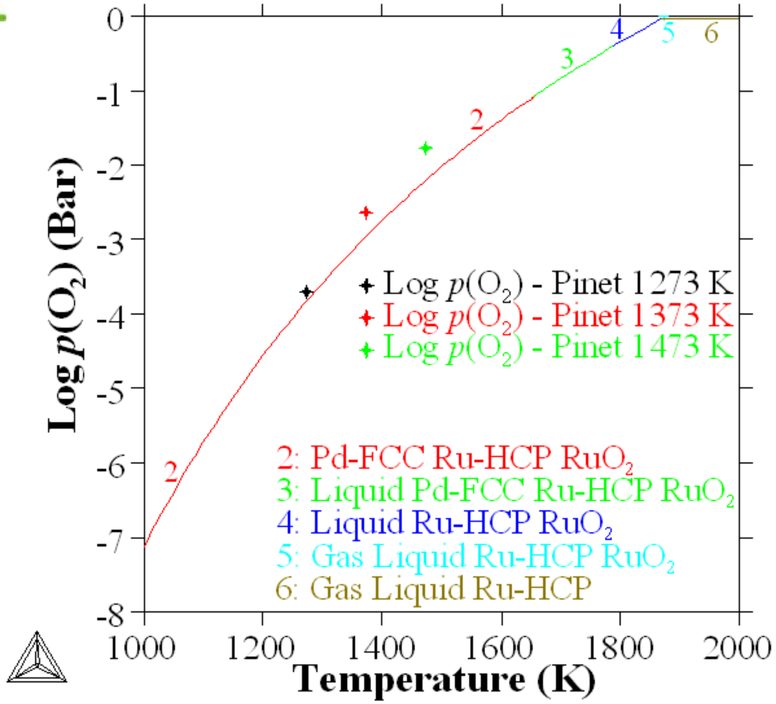
The solidification pathway is consistent with the formation of Pd-Rh-Te ternary phases also experimentally observed by Belyaev and by Krause in High-Level Nuclear Waste glasses:

A. V. Belyaev, *Journal of Structural Chemistry* 44, 1 (2003)

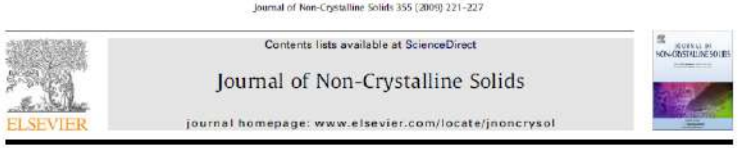
Ch. Krause, B. Luckscheiter, *Journal of Materials Research* 6, 12 (1991)

Platinoids Thermodynamics in Nuclear Waste Glasses
Study of the Pd-Ru-Te-(O) Oxide system

Calculation of oxygen partial pressure and of solidification pathways for a Pd-Ru-Te-O mixture
Normalised conditions for the calculation are $x(Pd)=2x(Ru)$, $x(Ru)=10x(Te)$ and $x(O)=0.09$



Evolution of Log $p(O_2)=f(T)$ for the Pd-Ru-Te-O mixture Comparison with measured oxygen partial pressure in a simplified nuclear waste glass by Pinet et al.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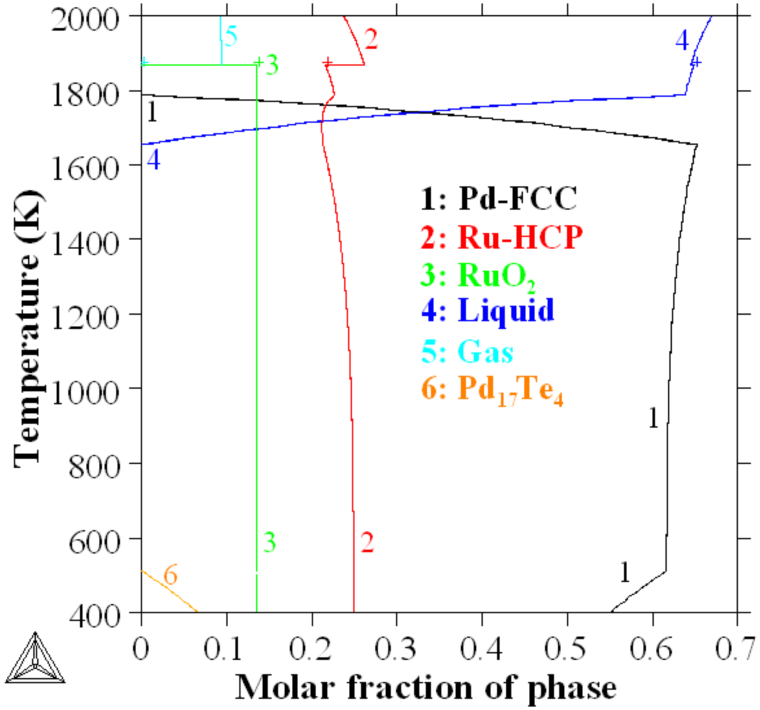
In both cases Log $p(O_2)=f(T)$ are nearly the same

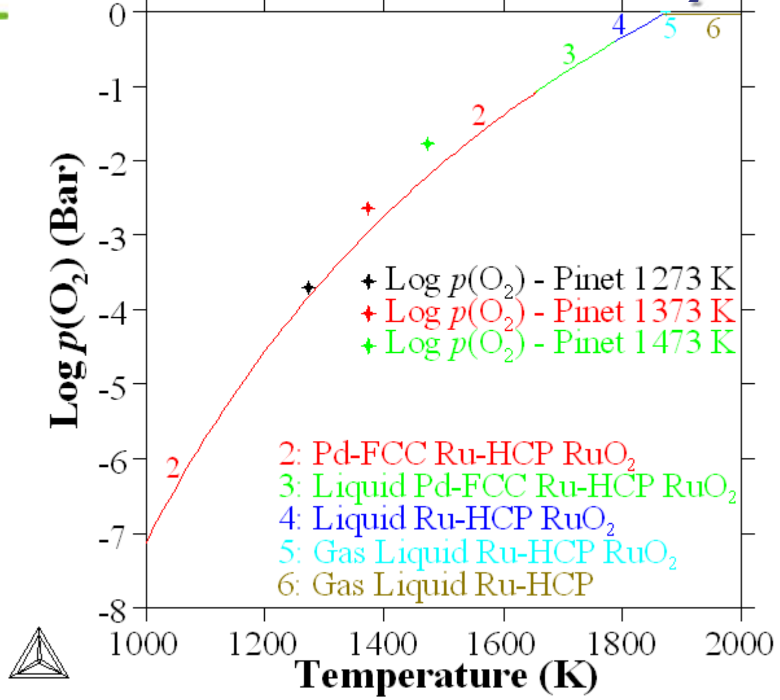


Solidification pathway for the same composition

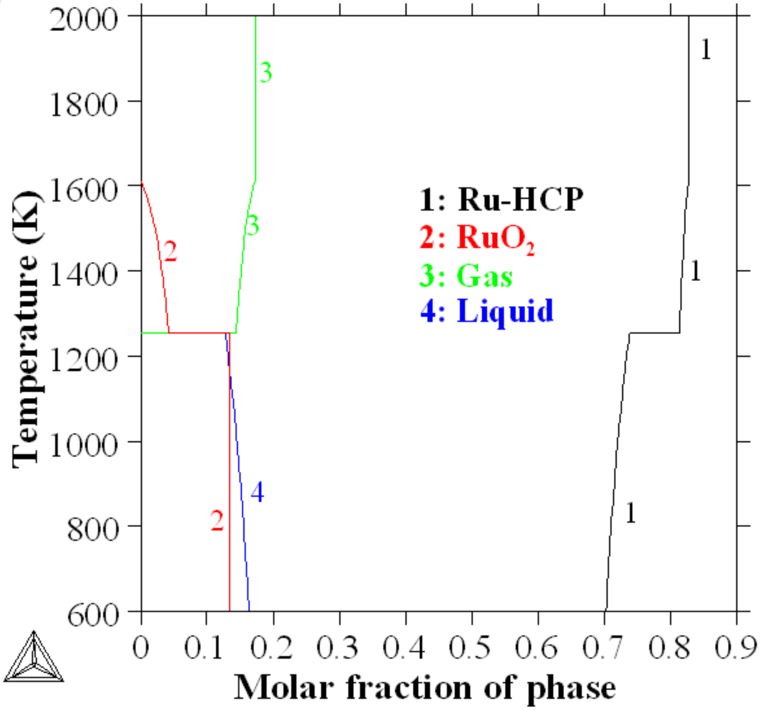
Nearly constant ratio between RuO_2 and Ru-HCP (Ru-HCP/RuO_2 ≈ 1.8)
Simultaneous existence of: (i) Ru-HCP and RuO_2 & (ii) $Pd_{17}Te_4$ and Pd-FCC phases

Platinoids Thermodynamics in Nuclear Waste Glasses
Study of the Ru-Te-(O) Oxide system

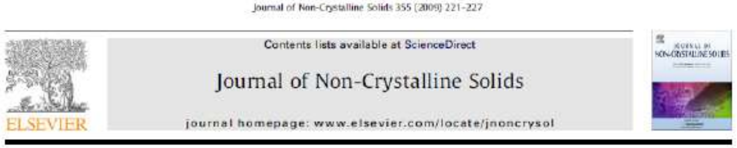
Calculation of oxygen partial pressure and of solidification pathways for a Ru-Te-O mixture (No Pd)
(Normalised conditions are x(Ru)=10x(Te) and x(O)=0.09)
The indirect effect of Pd on the Ru/RuO_2 ratio is highlighted by the Pd-FCC solid solution formation



Evolution of Log $p(O_2)$=f(T) for the Ru-Te-O mixture Comparison with measured oxygen partial pressure in a simplified nuclear waste glass by Pinet et al.



Solidification pathway for the same composition



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Ru-HCP over RuO_2 ratio is about Ru-HCP/RuO_2 ≈ 5 @ 1200 K
No direct effect of palladium on the oxygen potential
But, it can play an important role in the Ru-HCP/RuO_2 ratio

In both cases Log $p(O_2)$=f(T) are nearly the same

Platinoids Thermodynamics in Nuclear Waste Glasses
Conclusion

The thermodynamics of platinoid elements is studied in the framework of the vitrification process of High-Level Nuclear Waste. Using the Calphad method, a thermodynamic Fission-Products database is being developed on both metallic (Pd-Rh-Ru-Te) and oxide (O-Pd-Rh-Ru-Te) systems.

Assessed systems:

All the binary systems: Pd-Rh (Gürler), Pd-Te, Rh-Te, Pd-Ru, Rh-Ru, Ru-Te
Ternary systems described by extrapolation of the binaries: Pd-Ru-Te & Rh-Ru-Te
Ternary systems described with ternary interaction parameters: Pd-Rh-Ru & Pd-Rh-Te
For the time being, oxide phases come from the Ssub database by Dinsdale (SGTE)

Application to Laboratory Nuclear Waste Glasses

Better understanding of the Pd-Rh-Ru-Te-(O) alloys or oxide phases in the glass

- **Calculation of solidification pathways with the same platinoids amounts as in laboratory glasses**
- **Calculation of the chemical activities considering the oxygen potential of the glass through the oxide phases**

Comparison with experimental results in both Pd-Ru-Te-O and Ru-Te-O simplified compositions:

The calculations show the high affinity of Te for Pd
Te preferentially dissolves in the Pd-FCC solid solution or forms (Pd,Rh)Te intermetallic phases
The calculated pathways are consistent with the precipitated phases observed in nuclear waste containment glasses

Shortly, this database will be refined to predict thermodynamics of more complex systems:

1. **New FP or glass frit elements (Mo, Ni)**
2. **Ternary oxides (Na-Ru-O, Ca-Mo-O)**

Possible merger with the FUELBASE

THANK YOU FOR YOUR ATTENTION !