Incorporating CeO_2, Ce_2O_3, Cs_2O into the B_2O_3 -FeO_x-UO_x -ZrO_2 Oxide System

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MOTIVATION

Investigation of the behaviour of volatile radioactive species in case of severe nuclear accidents.

In case of nuclear accidents involving melt down of nuclear fuels at high temperatures, it is of considerable importance to accurately evaluate the highly-volatilizing behavior of fission products (FPs) over multicomponent debris.

Molten nuclear fuels (basically, UO_2-ZrO_2 system) will react with various kinds of surrounding materials in the fuel container (*e.g.* Fe in stainless steel) and the control rods (*e.g.* B_4C) to form multicomponent debris.

Work was initiated by the Japanese Government.

Contents of presentation

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- Addition of Cs_2O
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  - The Cs-Fe-O system
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  - The Cs_2O-ZrO_2 system
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  - The CeO_x-FeO_x system
  - The Ce-Fe-O system
  - The CeO_2-ZrO_2 phase diagram
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CeO_x-Cs_2O-B_2O_3-FeO_x-UO_x-ZrO_2 Oxide System

CeO_2 → **Ce_2O_3** → **Cs_2O** →

B_2O_3-FeO-Fe_2O_3-UO_2 -UO_3-ZrO_2 Oxide System

from TDNucl database

B_2O_3-Fe_2O_3 *The compound data from TDNucl improved a little to get better comparison with available experimental data [Makran, Touron,Loners, 1972] and [Vasaros, Jaklim, Pinter, 2004*].

B_2O_3-UO_2, B_2O_3-ZrO_2 *The slag data from TDNucl improved to get better comparison with available experimental data [Vasaros, Jaklim, Pinter, 2004*].

B_2O_3-UO_3 added by GTT.

UO_2-ZrO_2 done by GTT.

Introduction

The associate species containing Ce and Cs were added in order to describe the liquid phase in the B_2O_3-FeO_x-UO_x-ZrO_2 system.

System	*Associate species*	*Used data*
Ce-O	*Ce, CeO_2, Ce_2O_3*	*[06Zinkewich]*
Cs-O	*Cs, Cs_2O, CsO_2*	*SGPS*
B_2O_3-Cs_2O	*CsB_3O_5*	*GTT, H_{fus} [Marlor 1974]*
Cs_2O-FeO	*Cs_2FeO_2*	*GTT*
Cs_2O-Fe_2O_3	*$CsFeO_2$*	*GTT*
Cs_2O-ZrO_2	*Cs_2ZrO_3*	*GTT*

Contents of database

The database includes 93 stoichiometric phases,16 solid solution phases. Slag and the following 9 solid solution phases contain Ce and Cs.

Phase	Description	Properties
bcc-A2	$(Fe, U, Zr, Ce)_3(O,Va)$	The bcc-a2 phase.
fcc-A1	$(Fe, U, Zr, Ce)(O,Va)$	The fcc-a1 phase.
ZrO_2-LT	(ZrO_2, CeO_2)	ZrO_2-LT with solubility for CeO_2.
ZrO_2-MT	$(FeO, Fe_2O_3, UO_2, ZrO_2, CeO_2)$	ZrO_2-MT with solubility for CeO_2, UO_2, FeO_x.
MeO_2-MT	$(Ce^{+3}, Ce^{+4}, U^{+2}, U^{+4}, Zr^{+2}, Zr^{+4})(O^{-2}, Va)_2$	The phase $(Ce,U,Zr)O_2$-HT.
Ce_2O_3-LT	$(Ce^{+2},Ce^{+3})_2(O^{-2})_2(O^{-2},Va)_1$	The Ce_2O_3-LT phase.*
Ce_2O_3-MT	$(Ce^{+2},Ce^{+3})_2(O^{-2})_2(O^{-2},Va)_1$	The Ce_2O_3-MT phase.*
Ce_2O_3-HT	$(Ce^{+2},Ce^{+3})_2(O^{-2})_2(O^{-2},Va)_1$	The Ce_2O_3-HT phase.*
$Ce_{2-x}O_3$	$(Ce^{+3},Ce^{+4})_2(O^{-2})_3(O^{-2},Va)_1$	The $Ce_{2-x}O_3$ phase.*

** The assessment of the binary Ce-O system is taken from [06Zinkewich].*

Modelling of quasi-binary systems

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System	Phase	Description	Used data
B_2O_3-Cs_2O	$Cs_2B_2O_4$	stoichiometric	GTT
	$Cs_2B_4O_7$	stoichiometric	GTT
	$Cs_3B_7O_{12}$	stoichiometric	GTT
	$Cs_2B_6O_{10}$	stoichiometric	GTT
	$Cs_2B_8O_{13}$	stoichiometric	GTT
	$Cs_2B_{10}O_{16}$	stoichiometric	GTT
	$Cs_2B_{18}O_{28}$	stoichiometric	GTT
Cs_2O-FeO	$CsFeO_2$(s1)(s2)	stoichiometric	ΔHf [81Lindemer] H_{tr}, T_{tr} [2011Ali]
	Cs_2FeO_2	stoichiometric	ΔHf [81Lindemer]
	Cs_4FeO_3	stoichiometric	ΔHf [81Lindemer]
Cs_2O-Fe_2O_3	$CsFeO_2$(s1)(s2)	stoichiometric	ΔHf [81Lindemer] H_{tr}, T_{tr} [2011Ali]
	$CsFe_{11}O_{17}$	stoichiometric	GTT
Cs_2O-ZrO_2	Cs_2ZrO_3(s1)(s2)	stoichiometric	H_f [87Cordfunke],S_f[99Schramm]
	Cs_4ZrO_4	stoichiometric	GTT

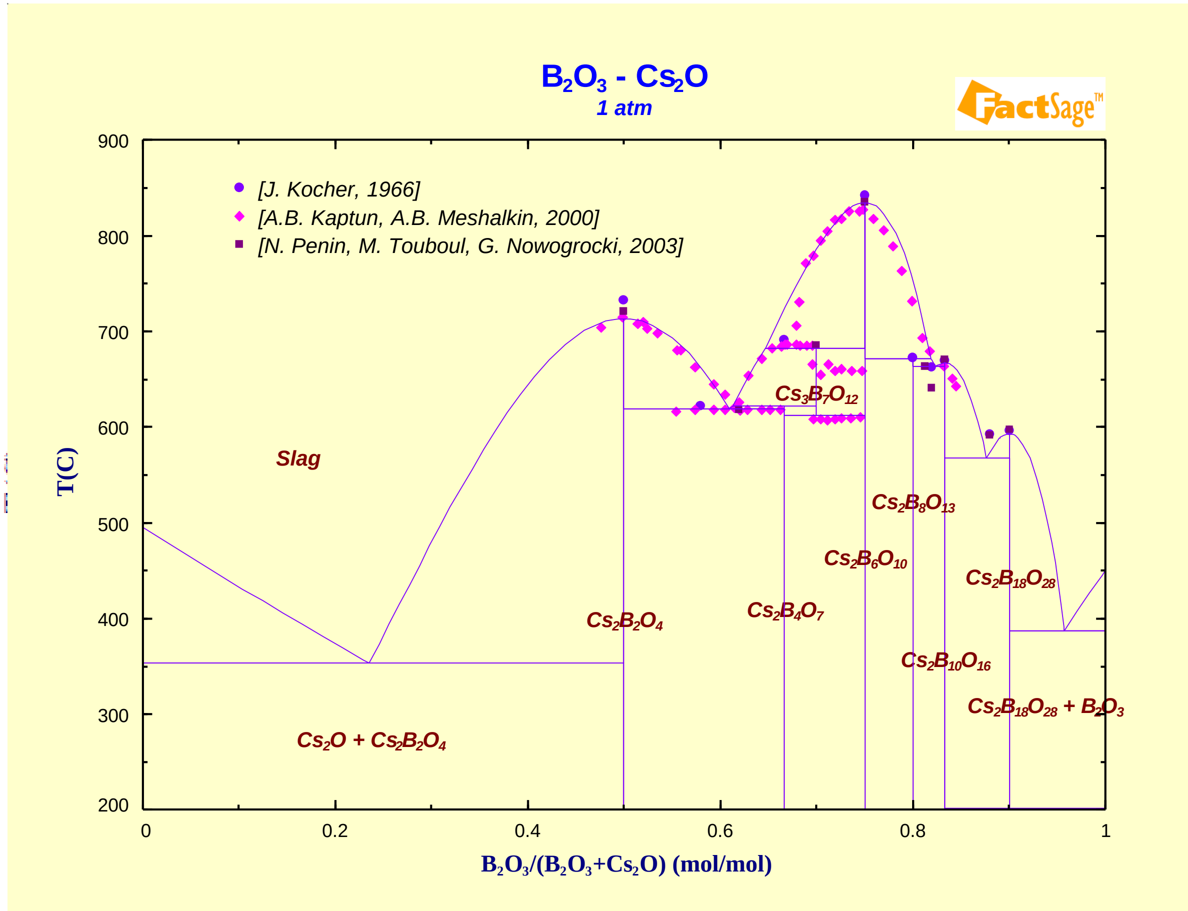
Modelling of quasi-binary systems with Cs_2O

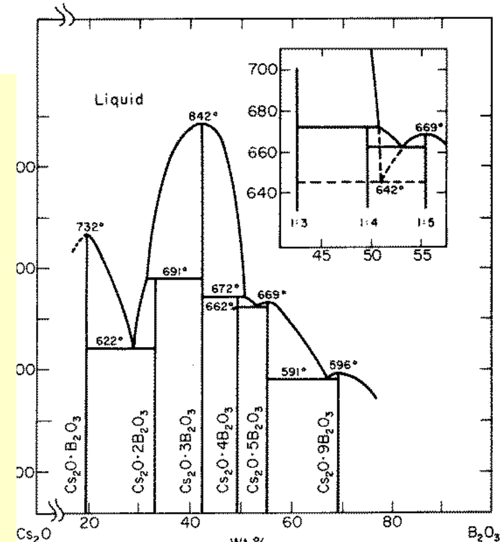
System	Phase	Description	Used data
Cs_2O-UO_3	$Cs_4U_2O_7$	stoichiometric	[81Lindemer]
	Cs_2UO_4	stoichiometric	[78Cordfunke and O'Hare]
	$Cs_2U_2O_7$	stoichiometric	[81Lindemer]
	$Cs_4U_5O_{17}$	stoichiometric	[81Lindemer]
	$Cs_2U_4O_{12}$	stoichiometric	[80Cordfunke,Westrum]
	$Cs_2U_4O_{13}$	stoichiometric	[81Lindemer]
	$Cs_2U_5O_{16}$	stoichiometric	[81Lindemer]
	$Cs_2U_6O_{18}$	stoichiometric	[81Lindemer]
	$Cs_2U_7O_{22}$	stoichiometric	[81Lindemer]
	$Cs_2U_9O_{27}$	stoichiometric	[81Lindemer]
CeO_2-FeO	$CeFeO_3$	stoichiometric	GTT

Modelling of systems containing CeO_x and added systems

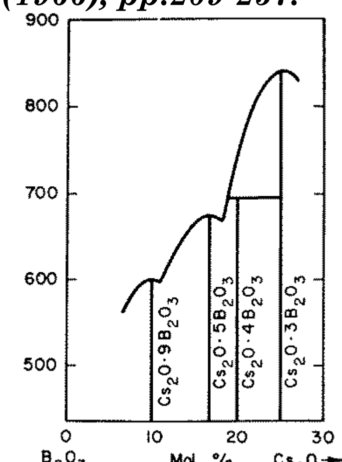
System	*Phase*	*Description*	*Used data*
CeO_2-ZrO_2	MeO2-HT ZrO2-MT ZrO2-LT	$(Ce^{3+},Ce^{4+},U^{2+},U^{4+})(O^{2-},Va)_2$ (ZrO_2, CeO_2) (ZrO_2, CeO_2)	GTT GTT GTT
Ce_2O_3-ZrO_2	$Ce_2Zr_2O_7$	stoichiometric	GTT
O-U	MeO2-HT U_4O_9	$(U^{2+},U^{4+})(O^{2-},Va)_2$ stoichiometric	GTT optimized to get T_m
	The rest of the system is identical with TDNucl-database.		
O-Zr	MeO2-HT	$(Zr^{2+},Zr^{4+})(O^{2-},Va)_2$	GTT
	The rest of the system is identical with TDNucl-database.		
UO_2-ZrO_2	MeO2-HT	$(U^{2+},U^{4+},Zr^{2+},Zr^{4+})(O^{2-},Va)_2$	GTT
B_2O_3-UO_3	UB_2O_6	stoichiometric	Hf [2006Chernorukov]

B_2O_3-Cs_2O phase diagram



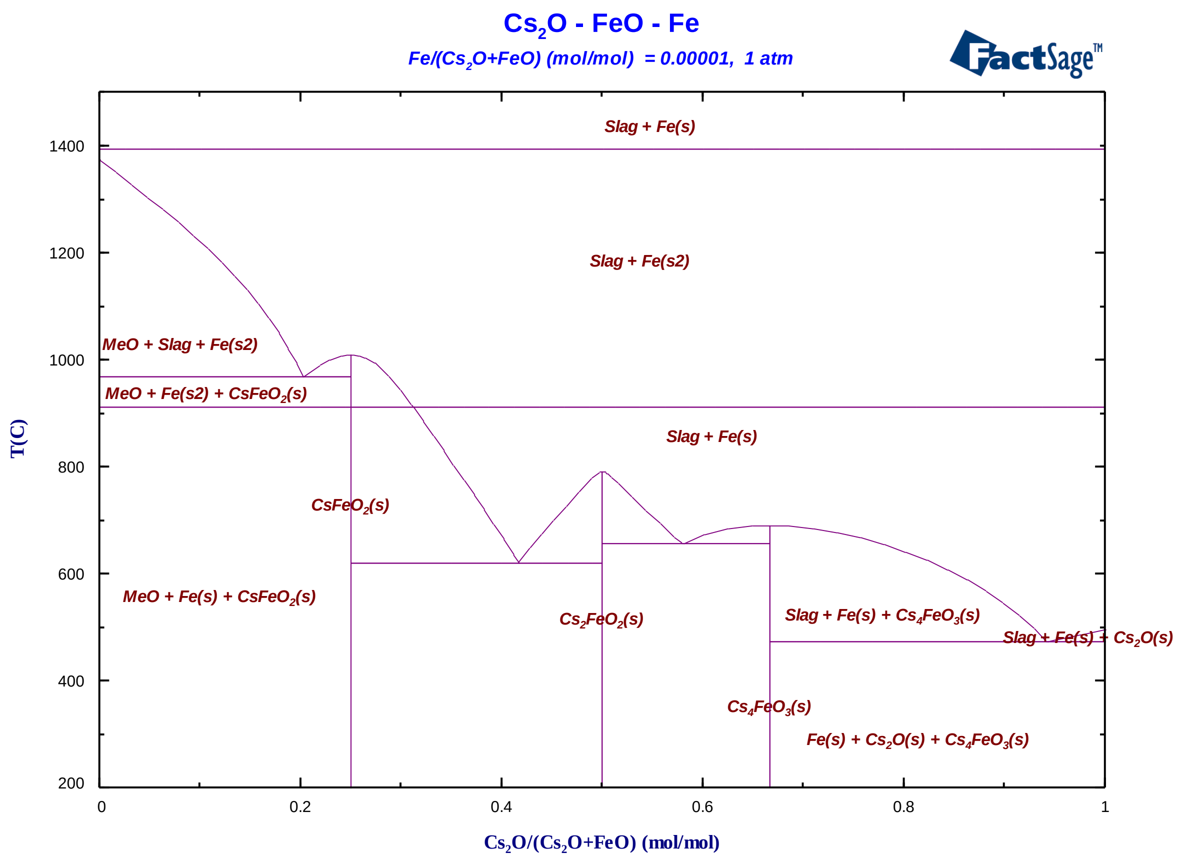


J. Kocher, Rev. Chim. Miner., 3[2], (1966), pp.209-257.



J. Krogh-Moe, Ark. Kemi., 12 [26], (1958), pp.247-249.

Cs_2O-FeO phase diagram in equilibrium with Fe



No phase diagram data are available. The present phase diagram is estimated comparing with K_2O-FeO and Na_2O-FeO.

Cs_2O-Fe_2O_3 phase diagram in air

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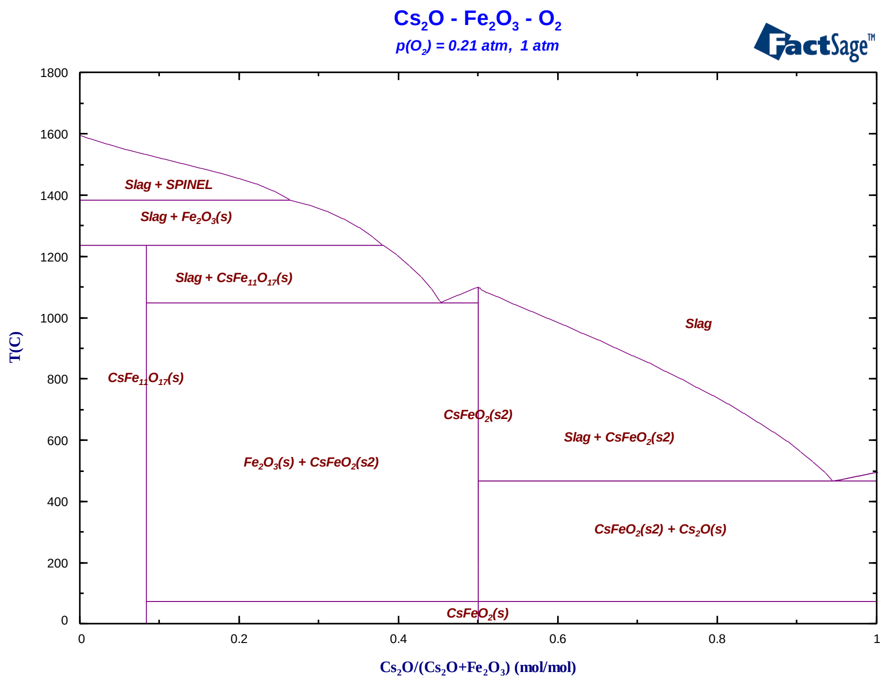
No phase diagram data are available.
The present phase diagram is estimated comparing with K_2O-Fe_2O_3 and Na_2O-Fe_2O_3.



73°C

$CsFeO_2$-LT→ $CsFeO_2$-HT [N.Z. Ali, 2011] H_{tr} =270 J/mol

The Cs-Fe-O phase diagram in solid state

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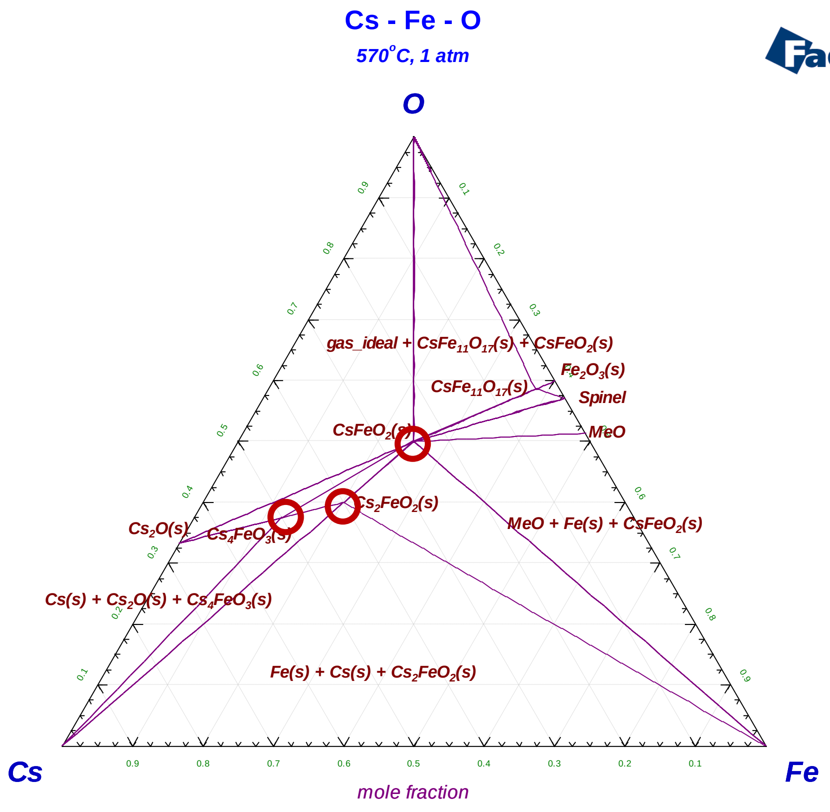


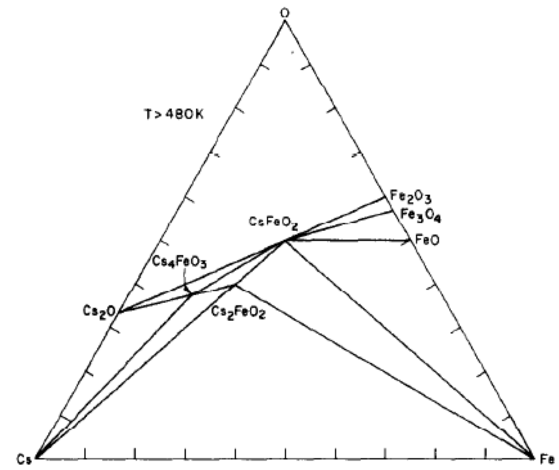
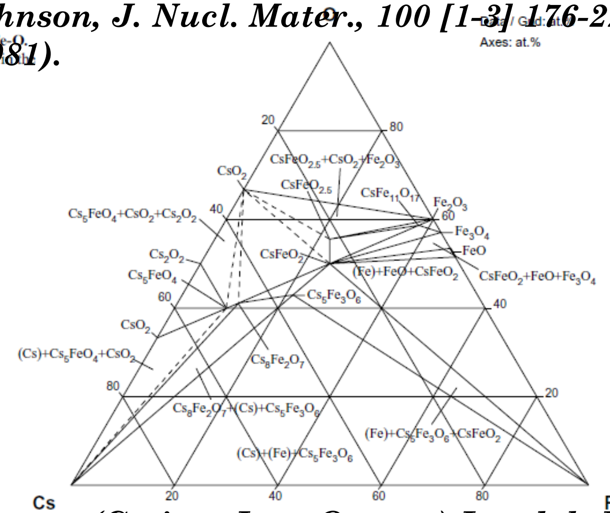


Fig. 29. Cs–Fe–O equilibrium diagram.

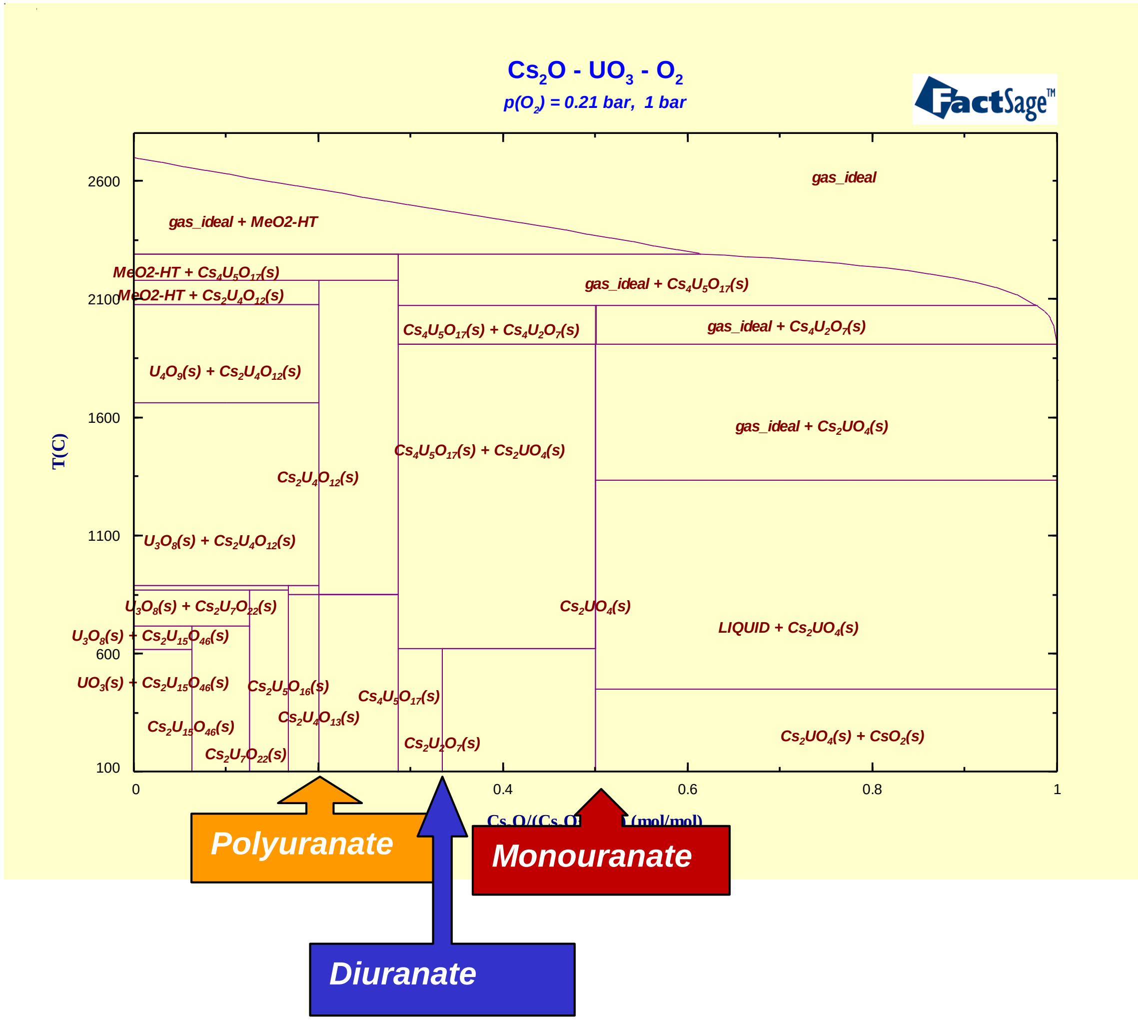
T. B. Lindemer, T. M. Besmann, and C. E. Johnson, J. Nucl. Mater., 100 [1-3] 176-226 (1981).

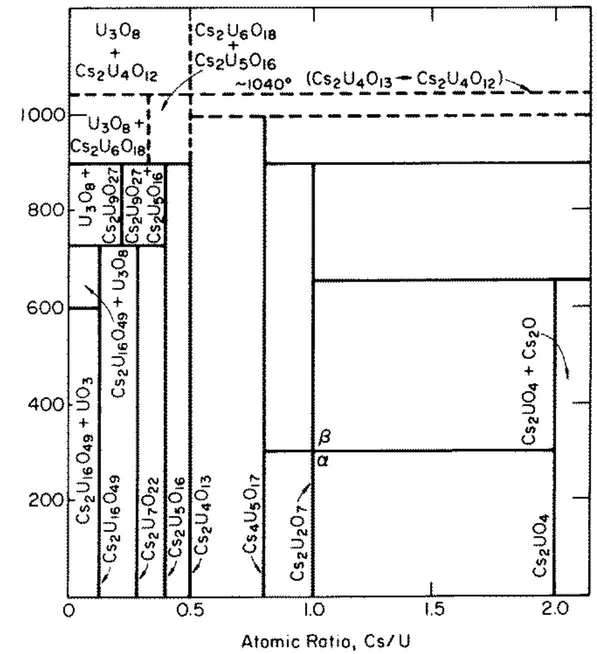
Fig. 1: Cs-Fe-O. The equilibria in the solid state



P. Perrot, (Cesium-Iron-Oxygen) Landolt-Börnstein, Non-Ferrous Metal Systems, Part 4, (2007), pp. 237-243.

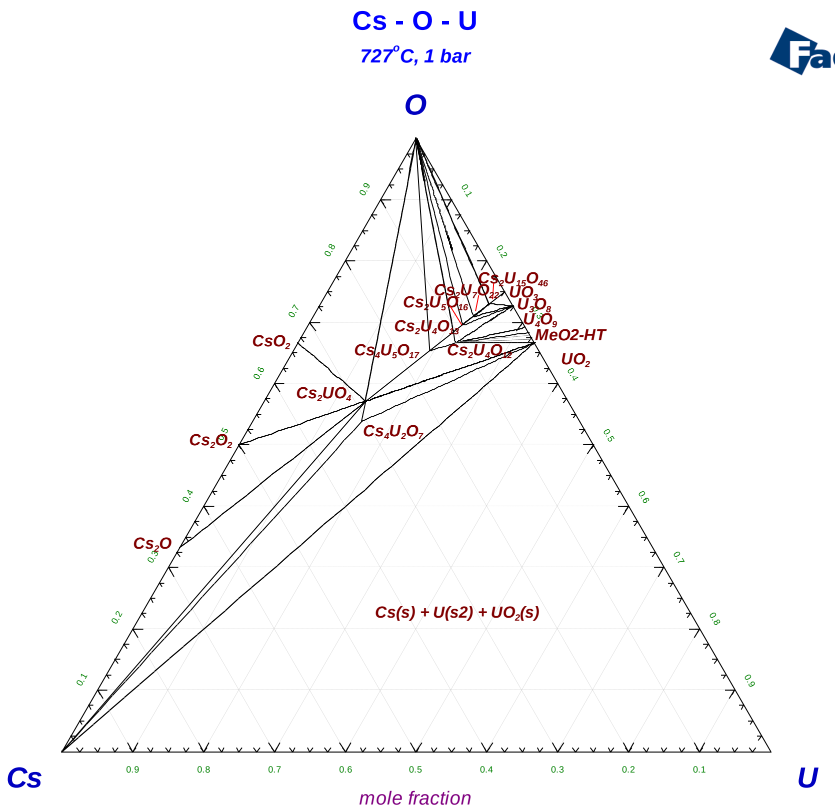
Cs_2O–UO_3 phase diagram

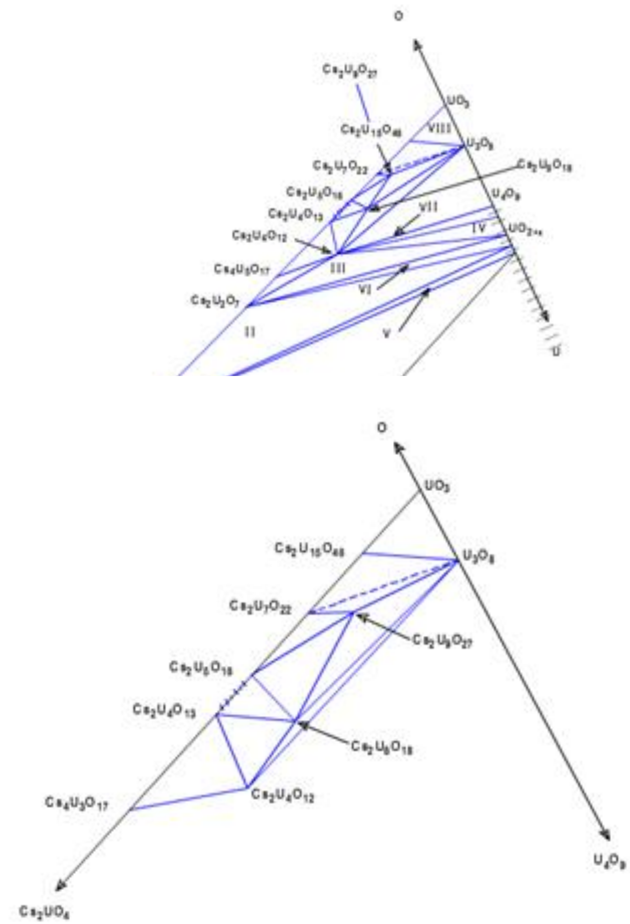




E. H. P. Cordfunke, A. B. Van Egmond, and G. Van Voorst, J. Inorg. Nucl. Chem., 37 [6] 1433-1436 (1975).

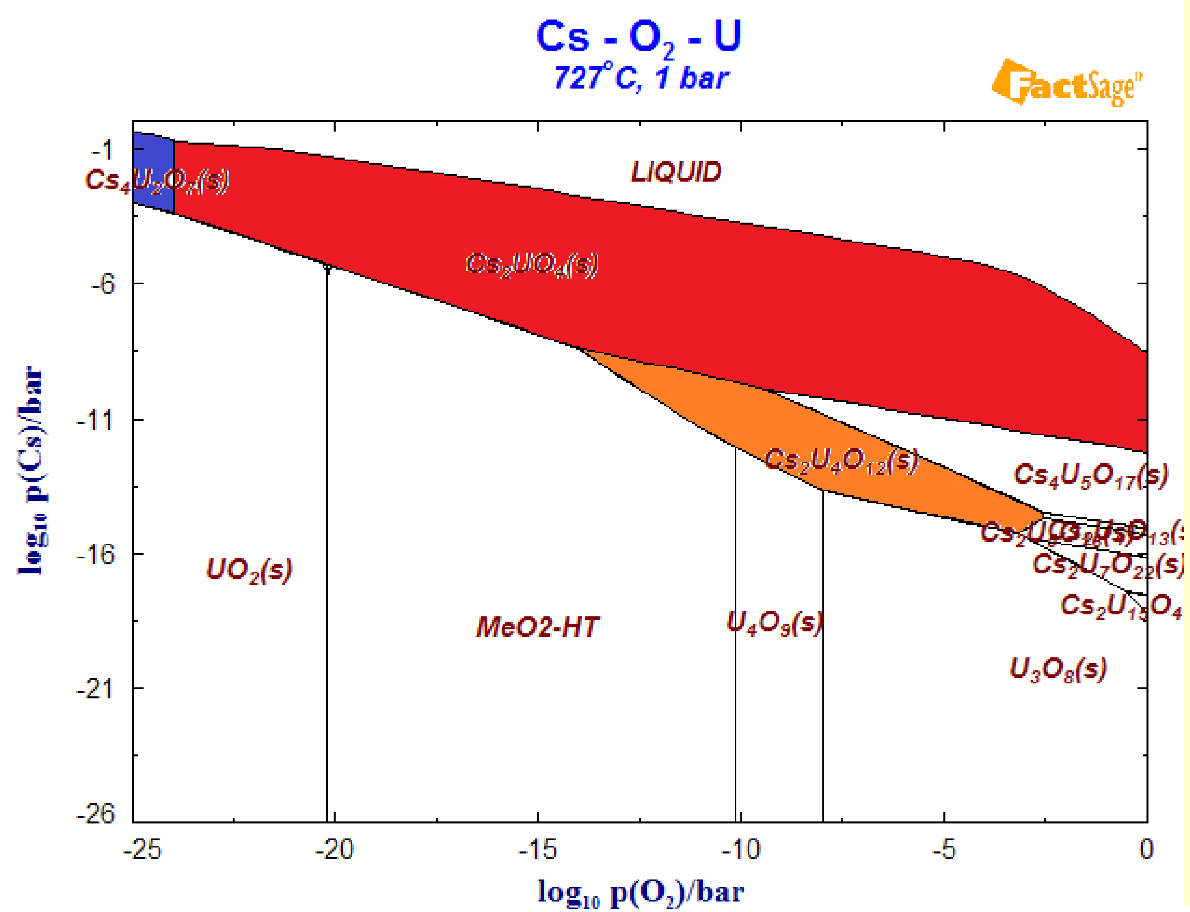
The Cs-U-O phase diagram in solid state



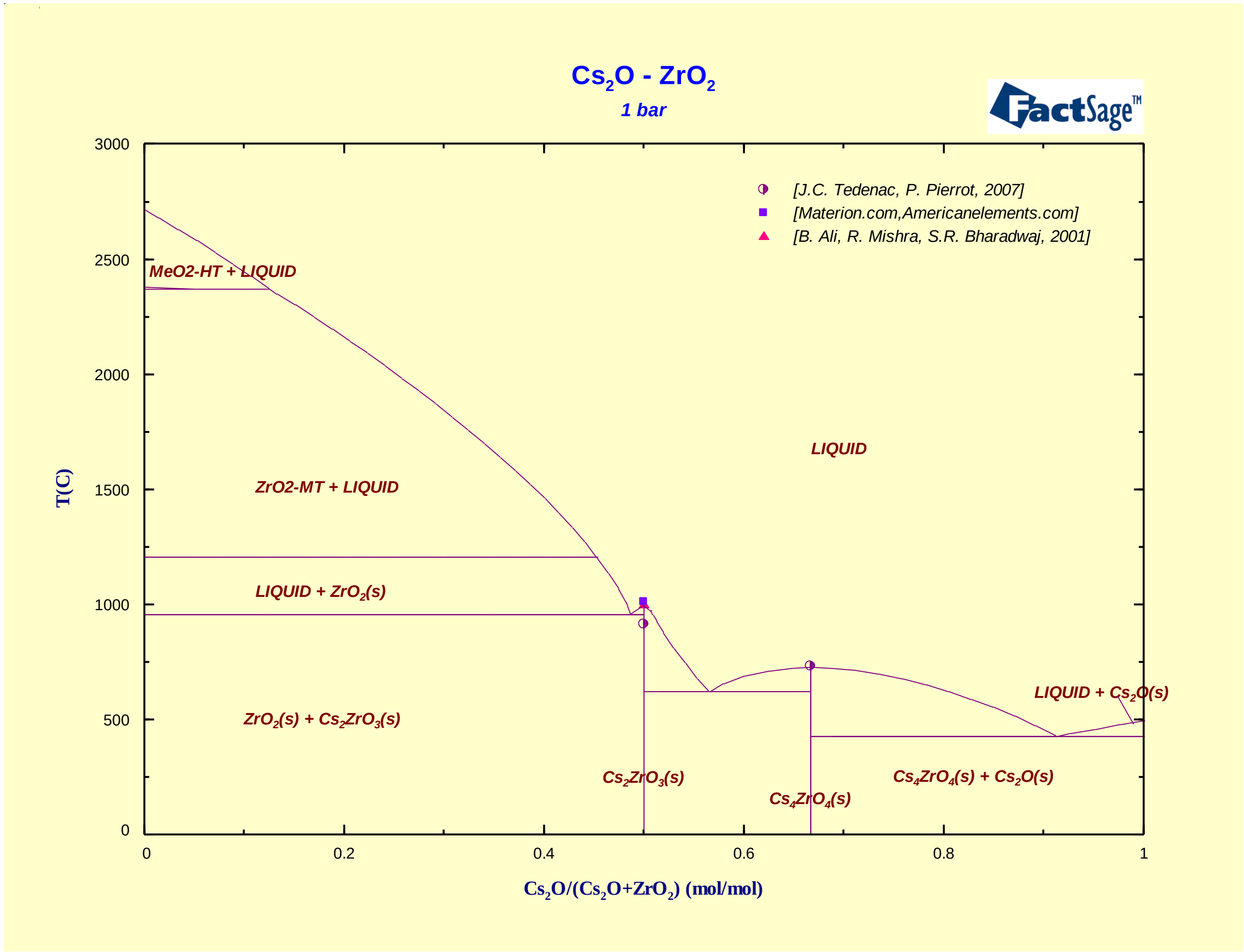


D. C. Fee and C. E. Johnson, J. Inorg. Nucl. Chem., 40 [7] 1375-1381 (1978).

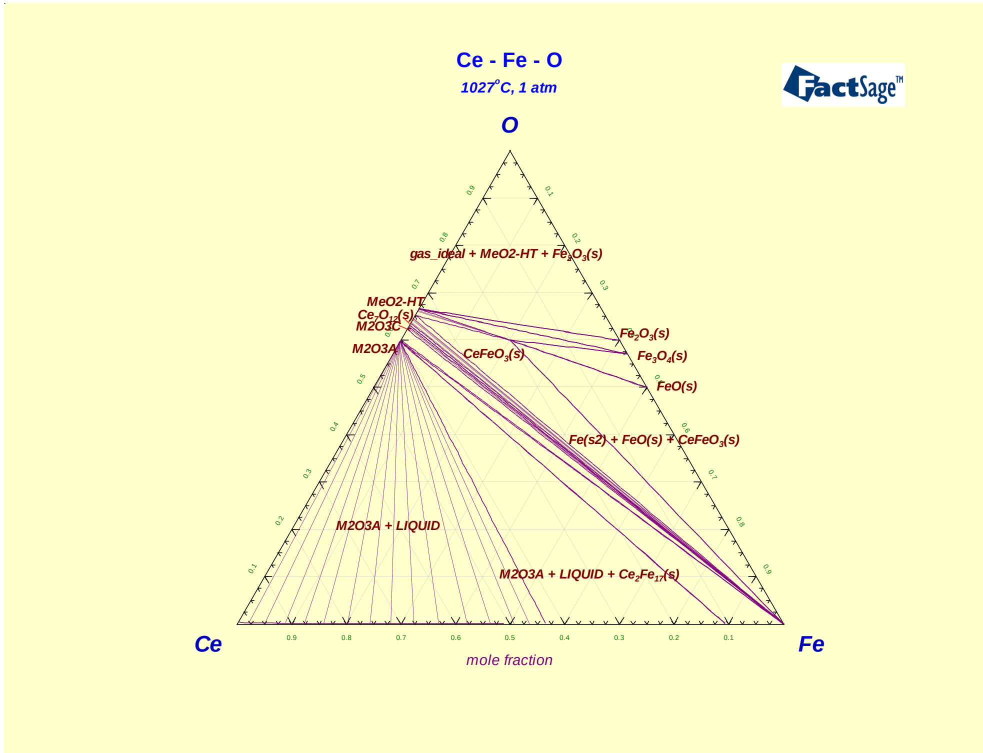
Stability of cesium uranates at 727ºC

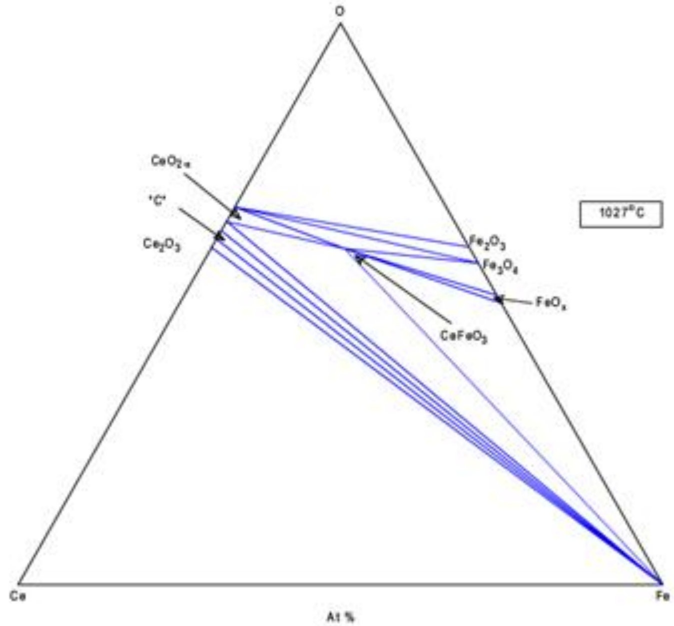


Cs_2O-ZrO_2 phase diagram



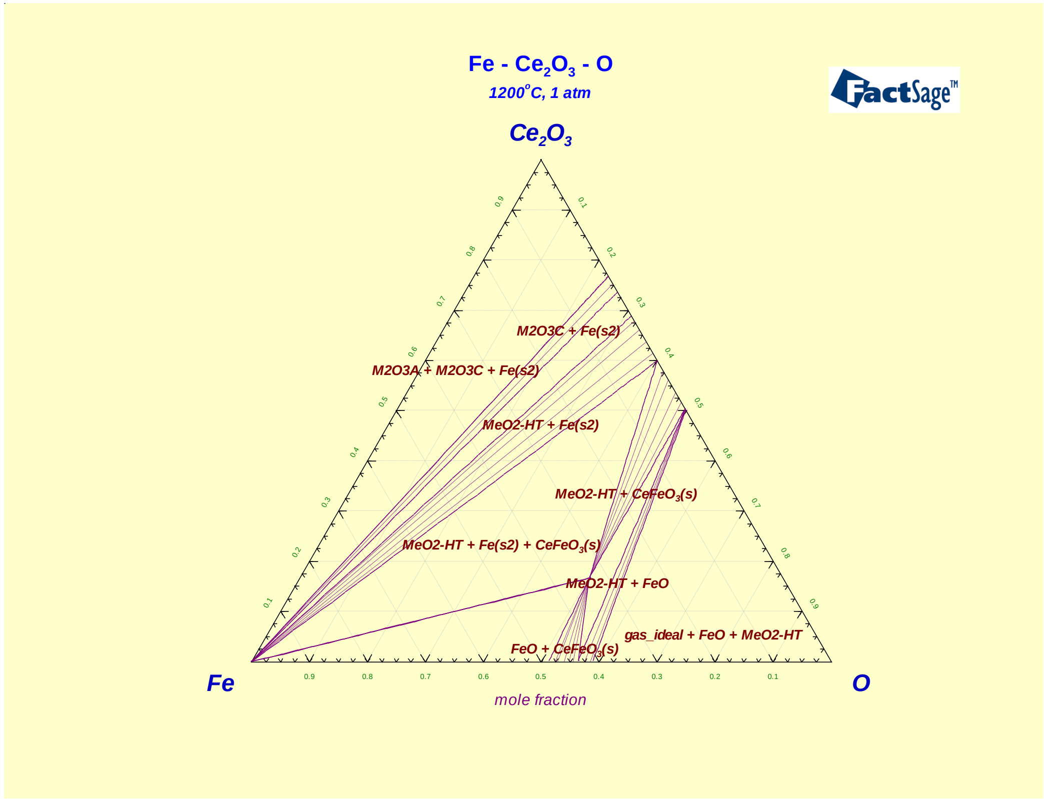
The isothermal section at 1027°C in Ce-Fe-O system

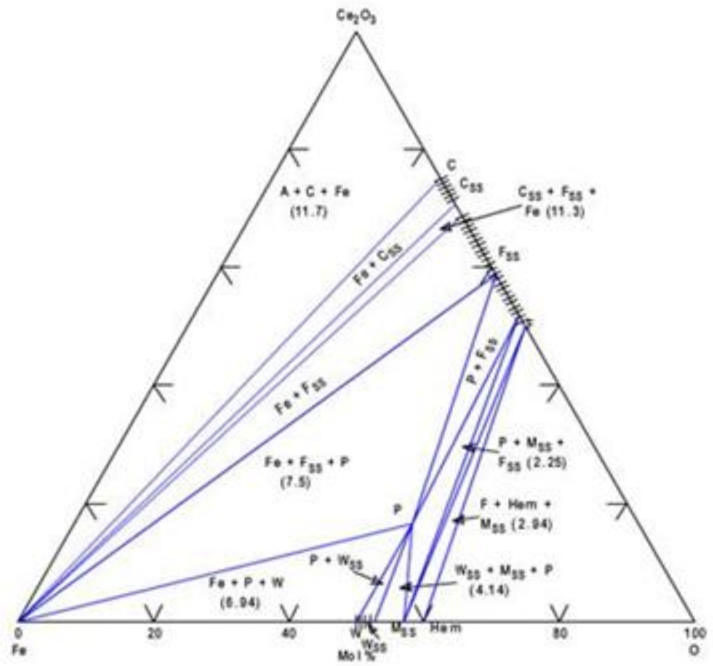




Yu. D. Tret'yakov, V. V. Sorokin, A. R. Kaul, and A. P. Erastova, J. Solid State Chem., 18 [3] 253-261 (1976).

The isothermal section at 1200°C in Ce-Fe-O system





K. Kitayama, K. Nojiri, T. Sugihara, and T. Katsura, J. Solid State Chem., 56 [1] 1-11 (1985).

The CeO_2-UO_2-ZrO_2 system

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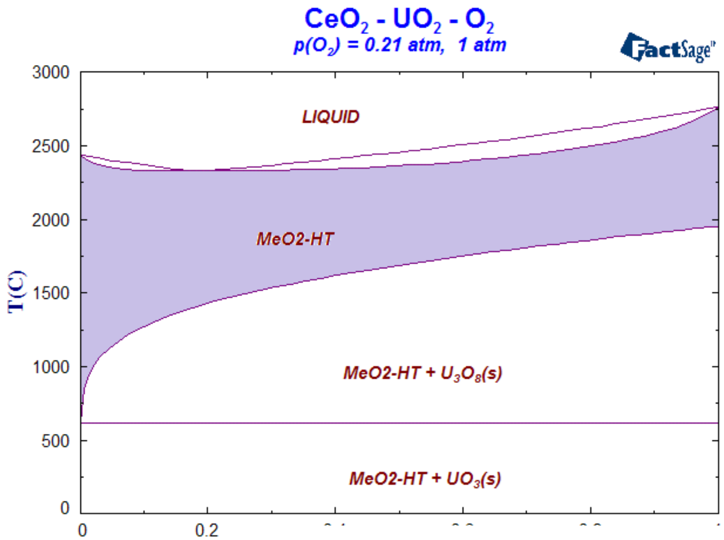
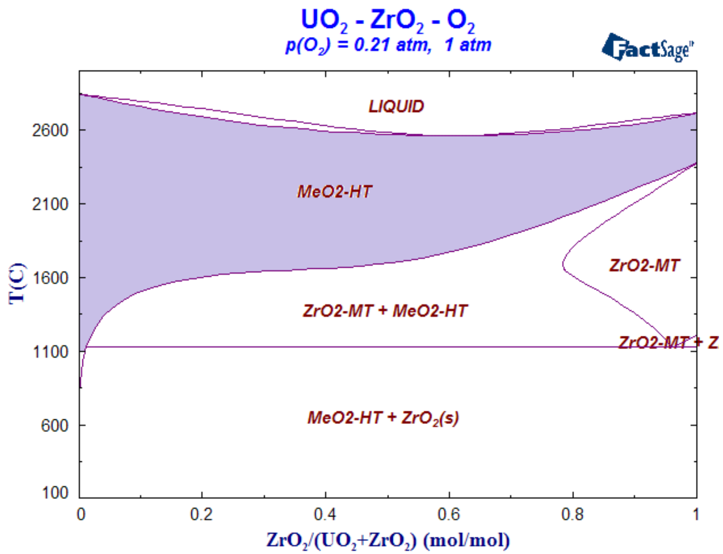
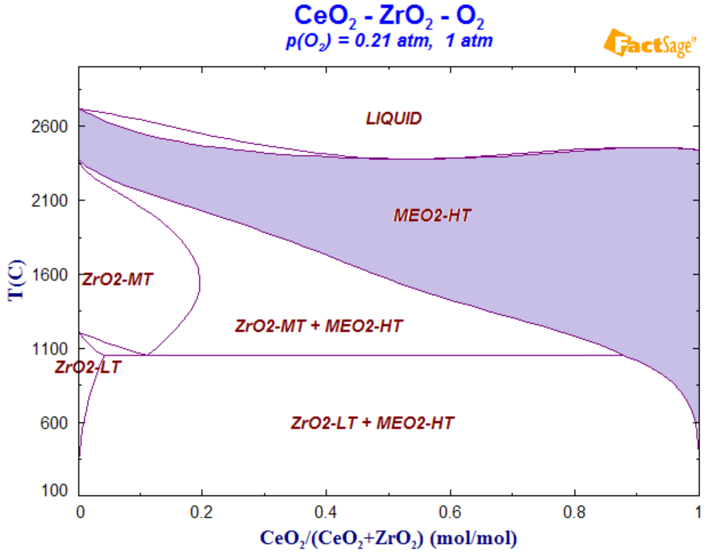
Oxide	Pearson Symbol	Space group	Prototype
CeO_2	cF12	225	CaF_2
UO_2	cF12	225	CaF_2
ZrO_2	cF12	225	CaF_2

MeO_2-HT

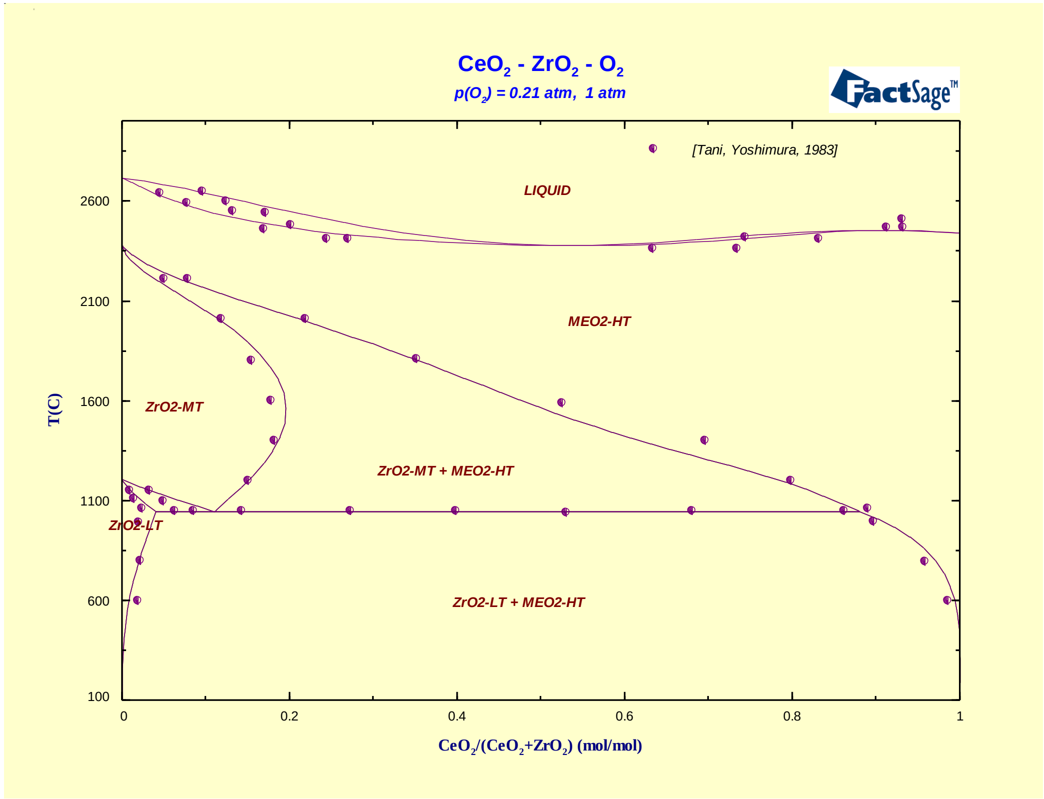
(Ce^{+3}, $\underline{Ce^{+4}}$, U^{+2}, $\underline{U^{+4}}$, Zr^{+2}, $\underline{Zr^{+4}}$) ($\underline{O^{-2}}$, Va)$_2$

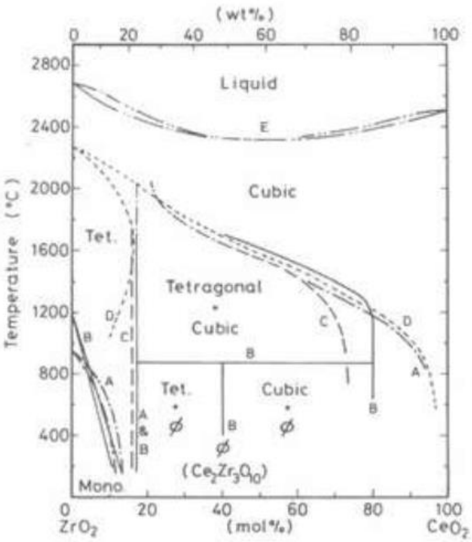






The CeO_2-ZrO_2 system in air





E.Tani, M.Yoshimura, S. Somiya, J.Am.Ceram.Soc., 66, (1983), pp.506-510.

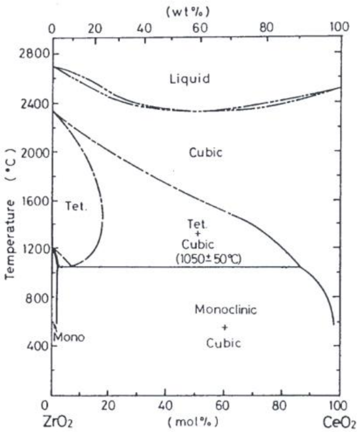
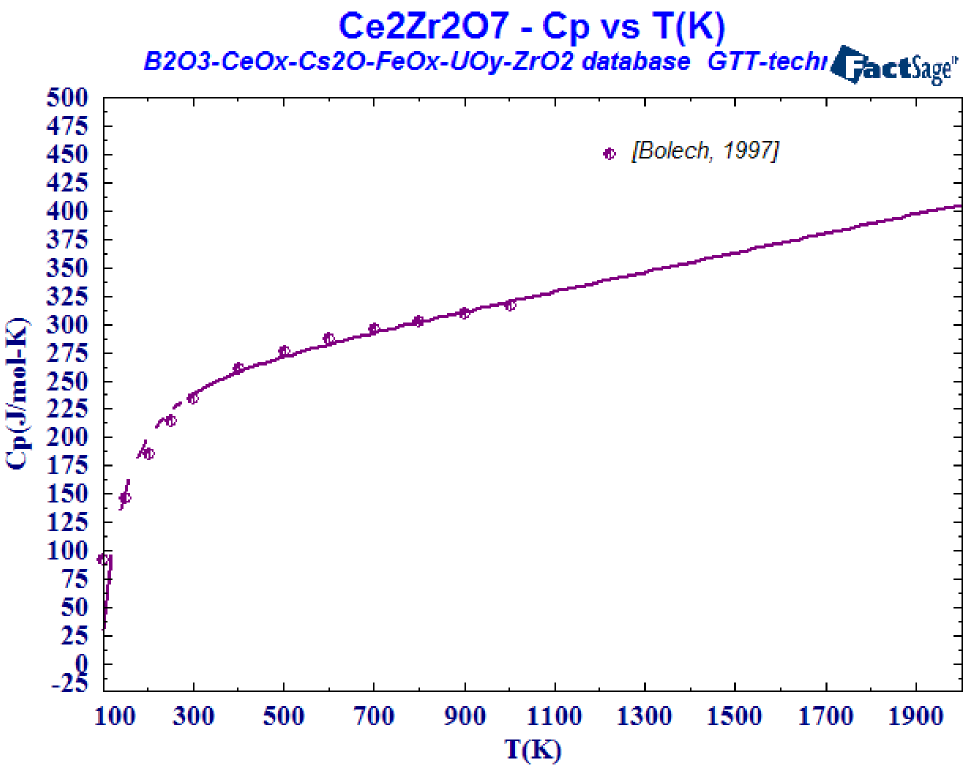
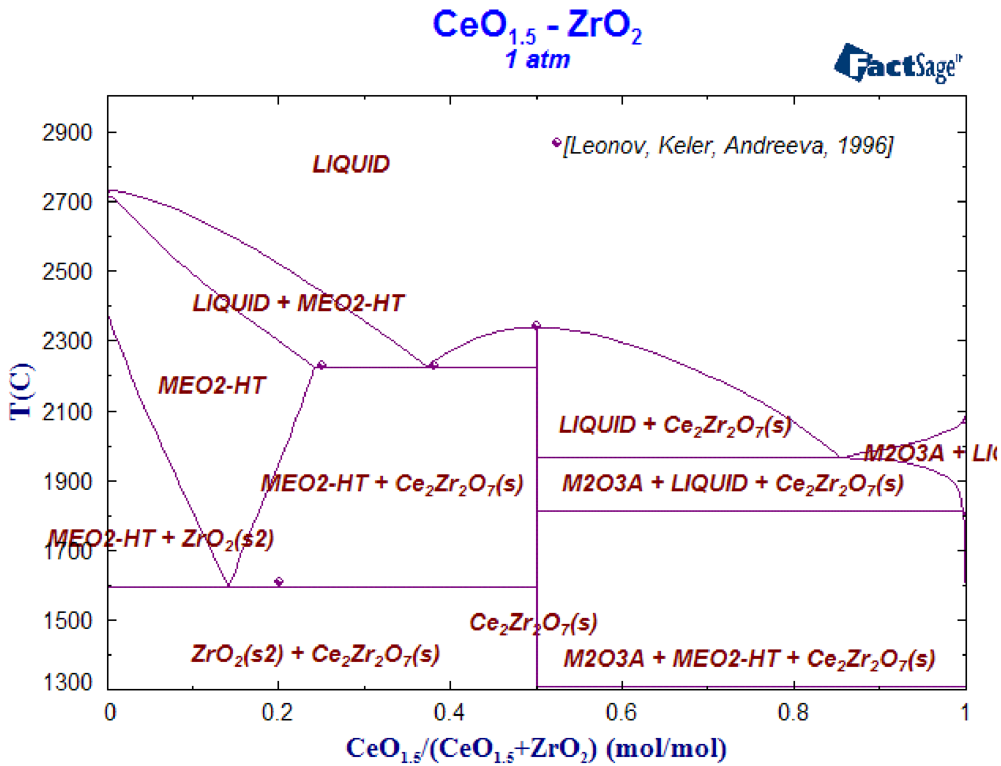


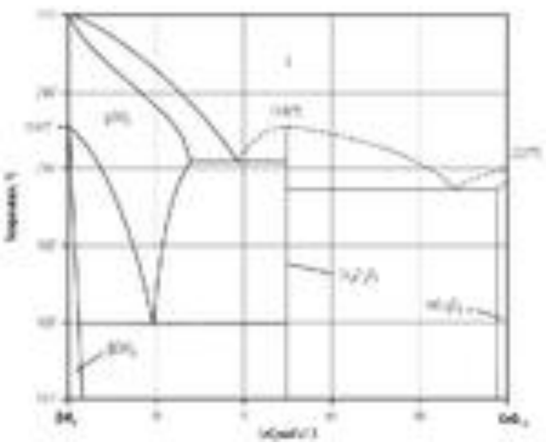
Figure 26. - Phase diagram for ZrO_2-CeO_2.[2,41] Reprinted by permission of the American Ceramic Society.

The heat capacity of $Ce_2Zr_2O_7$



The $CeO_{1,5}$-ZrO_2 system





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Conclusions

- The liquid phase in all subsystems was evaluated using the associate species model.
- 9 quasi-binary and 3 ternary systems were assessed using experimental phase diagram information.
- 27 stoichiometric phases containing Ce and Cs were incorporated.
- Data were employed for prediction of volatilisation behaviour of fission products by Osaka University.

Thanks for your attention

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