Vapour Pressure measurements of MSR Fuels

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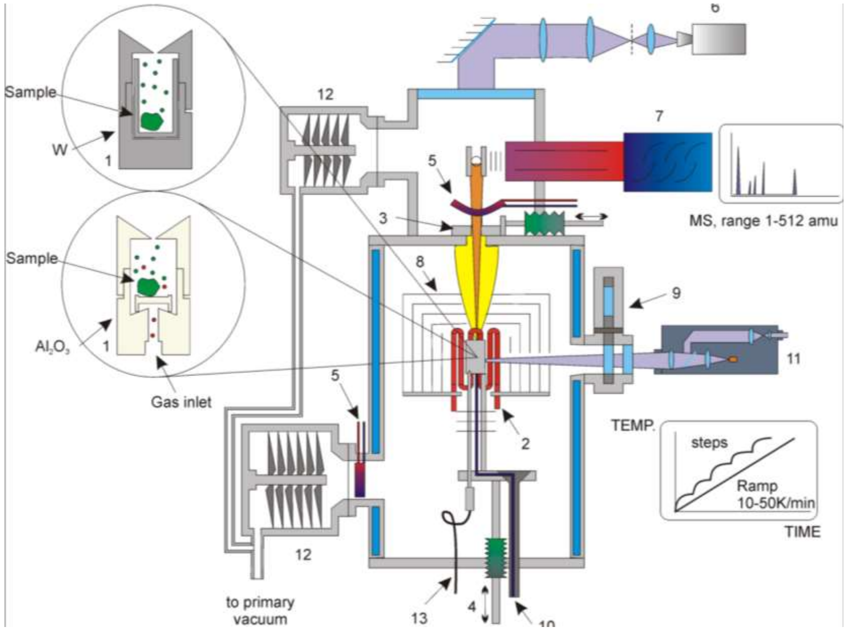
Outline

- KEMS Methodology
- Fundamental Vapour pressure data
- Fission Product Release from irradiated fuels
- Retention of Cs and I in MSR fuels

KEMS (Knudsen Effusion Mass Spectrometry)

- In house development with key commercial parts
- T max ~2800 K - complete vaporization of the fuel
- under vacuum conditions (or partial O_2 flow)
- In gamma-shielded GB
- Irradiated fuels suitable (<5 mg)



- T calibration on selected metals
- eV calibration by noble gases
- MS calibration in situ by Ag or Au
- Appearance potential correction

KEMS at JRC-Karlsruhe

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KEMS (Knudsen Effusion Mass Spectrometry)

2 Pillars of Studies

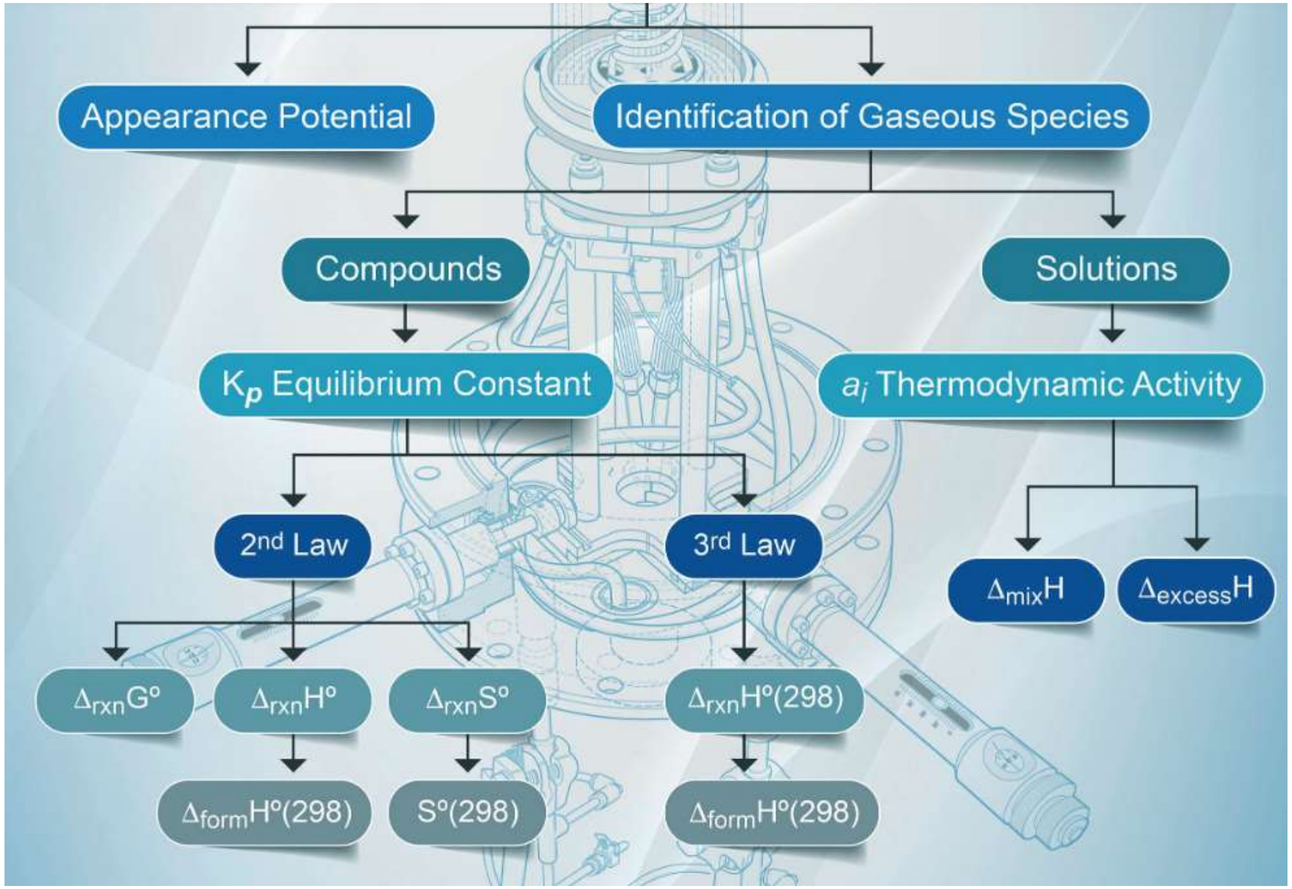
Fundamental Thermodynamic data

- Vapour pressures
- Boiling points
- Enthalpy of vaporization
- Activities (coefficients)

Post Irradiation Examination

- FP release
- FG quantification by Q-Games
- Retention capacity of MS

KEMS (Knudsen Effusion Mass Spectrometry)



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Rapid Communications in Mass Spectrometry WILEY

REVIEW ARTICLE

Knudsen effusion mass spectrometry: Current and future approaches

Nathan S. Jacobson[1] | Jean-Yves Colle[2] | Valentina Stolyarova[3,4] | Torsten Markus[5] | Ioana Nuta[6]

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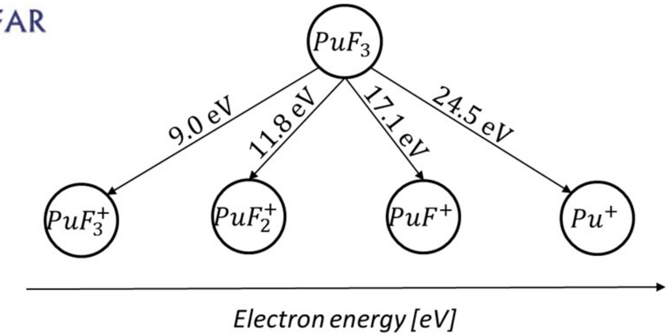
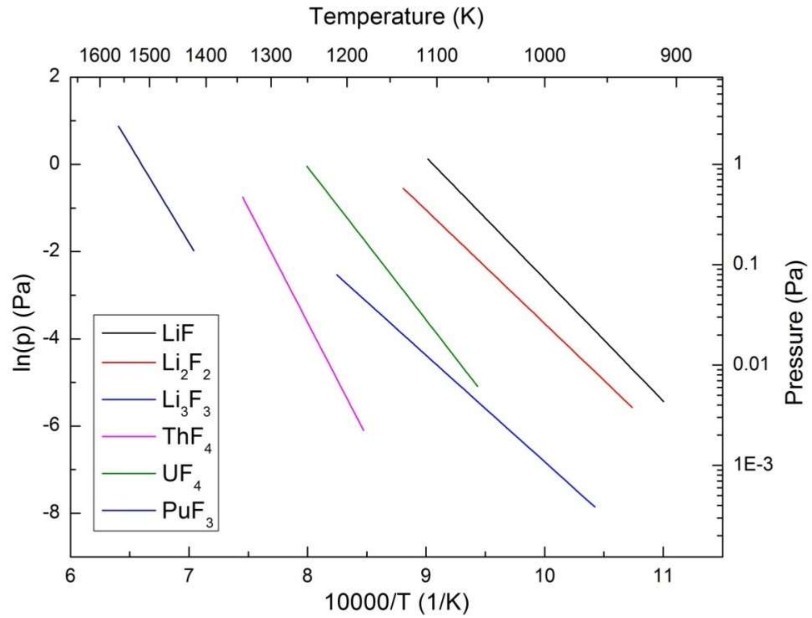
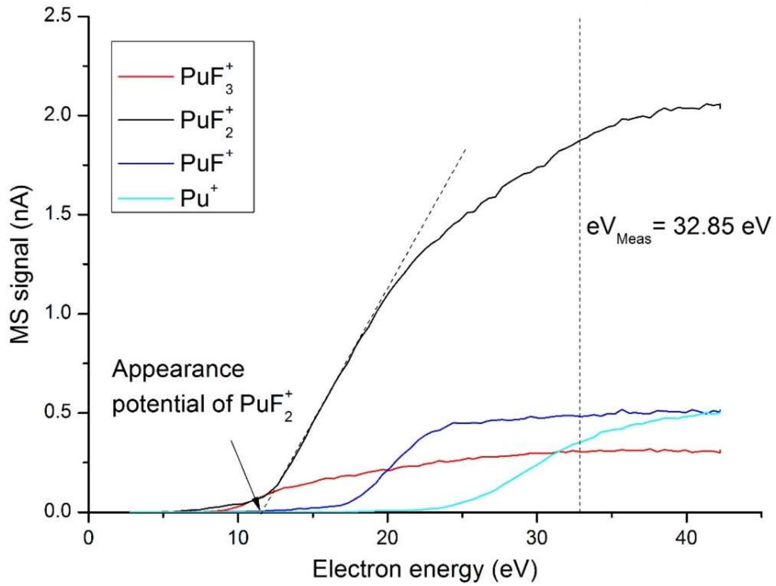
Fundamental Vapour Pressure Data

- *LiF-ThF$_4$-UF$_4$-PuF$_3$ (77.5-6.6-12.3-3.6 mol%)* MSFR fuel





Partial and total vapour pressures for the mixture LiF-ThF$_4$-UF$_4$-PuF$_3$ (77.5-6.6-12.3-3.6 mol%)



- Boiling point never reached (due to vacuum)
- Boiling point is very well extrapolated
- ... and correlated with JRCMSD database

B.p. = 1896 ± 20 K

Fundamental Vapour Pressure Data

- Funak Eutectic NaF-KF-UF_4 (50.4 – 23.2 – 26.4 mol%)

Open Access | Article

Thermophysical Properties of FUNaK (NaF-KF-UF_4) Eutectics

by Maxime Fache [1,2], Laura Voigt [1,2,3], Jean-Yves Colle [1], John Hald [2] and Ondřej Beneš [1,*]

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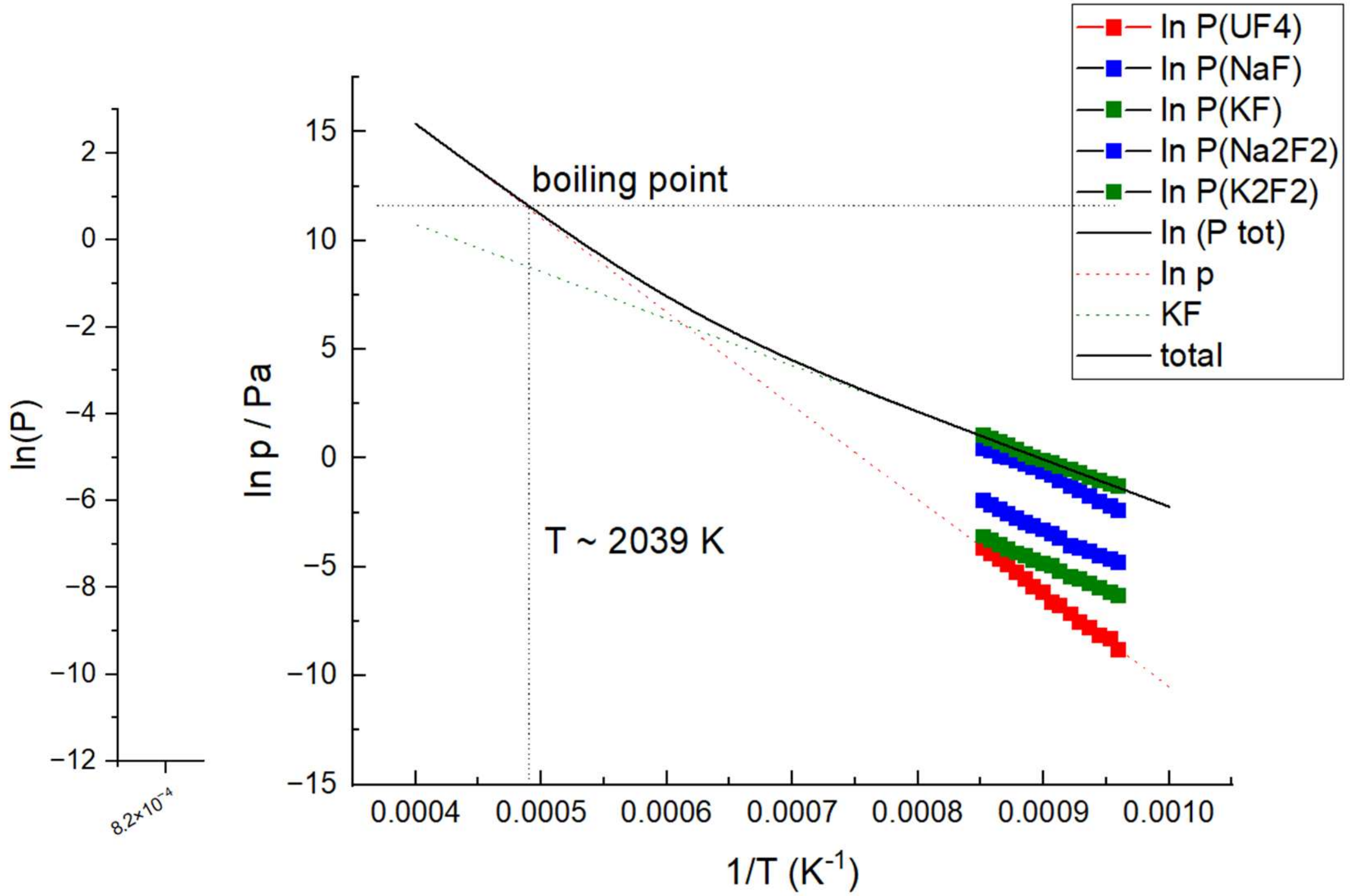
Materials **2024**, *17*(11), 2776; https://doi.org/10.3390/ma17112776



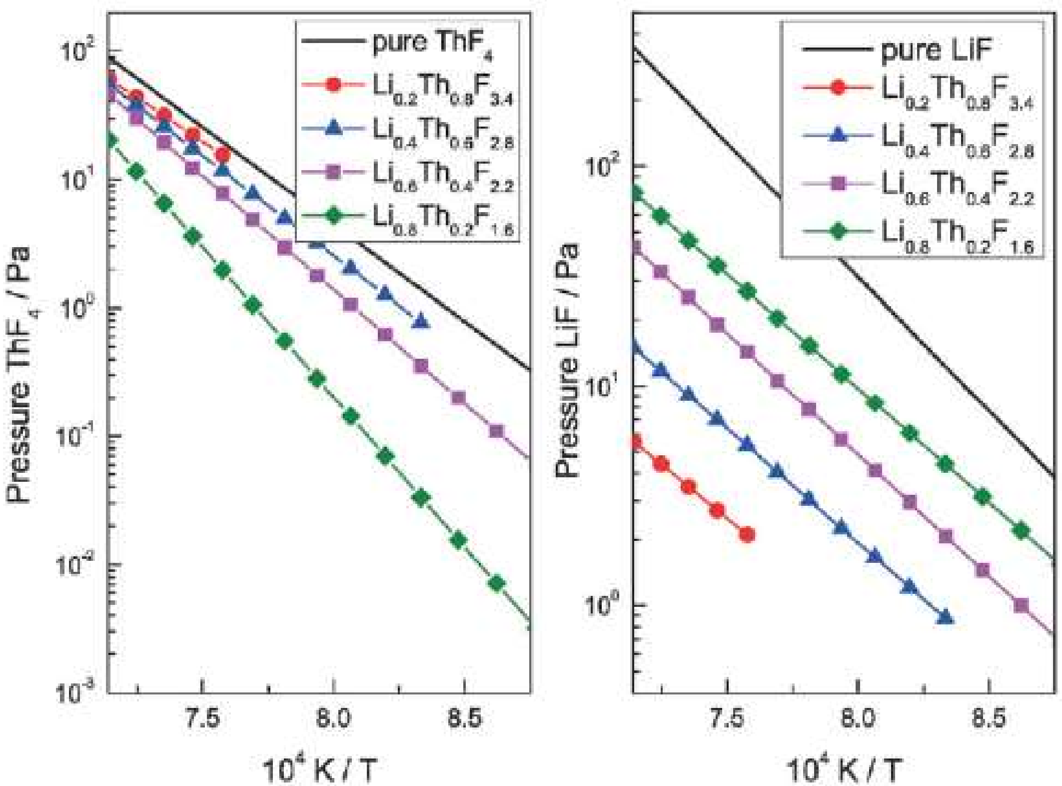
K - species

Na - species

U - species

Fundamental Vapour Pressure Data

Systematic investigation of LiF-ThF_4 vapour pressure: activity determination (excess Gibbs energy for Thermodynamic models)



Right graph: LiF vapour pressure (monomer) for the pure LiF liquid phase and for the $Li_xTh_{1-x}F_{4-3x}$ liquid solution.

Left graph: ThF_4 vapour pressure for the pure ThF_4 liquid phase and for the $Li_xTh_{1-x}F_{4-3x}$ liquid solution.

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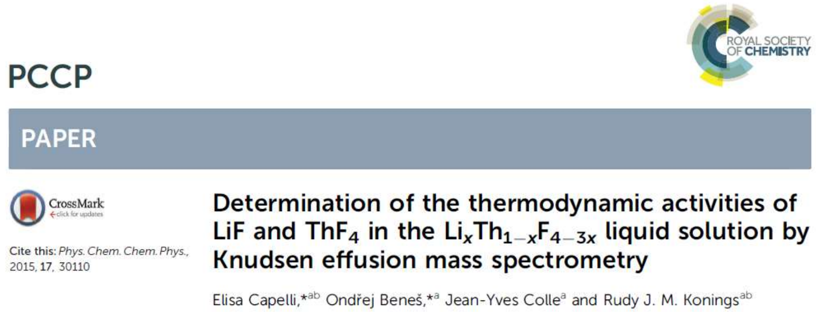
Fundamental Vapour Pressure Data

- LiF and ThF_4 activity
  Determined from the liquid-gas equilibria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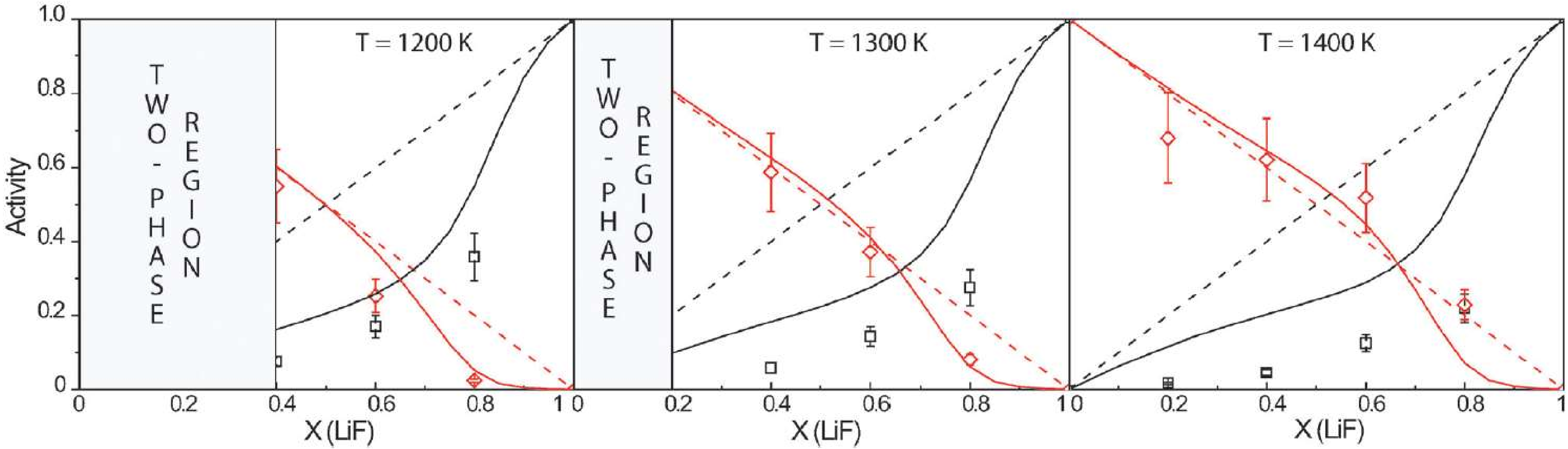
Cite this: *Phys. Chem. Chem. Phys.*, 2015, 17, 30110

Determination of the thermodynamic activities of LiF and ThF_4 in the $Li_xTh_{1-x}F_{4-3x}$ liquid solution by Knudsen effusion mass spectrometry

Elisa Capelli,*[ab] Ondřej Beneš,*[a] Jean-Yves Colle[a] and Rudy J. M. Konings[ab]



$$\Delta G(solution) = x_1G_1 + x_2G_2 + \Delta G_{mix}$$

$$\Delta G_{mix} = x_1RTln\mathbf{a_1} + x_2RTln\mathbf{a_2}$$

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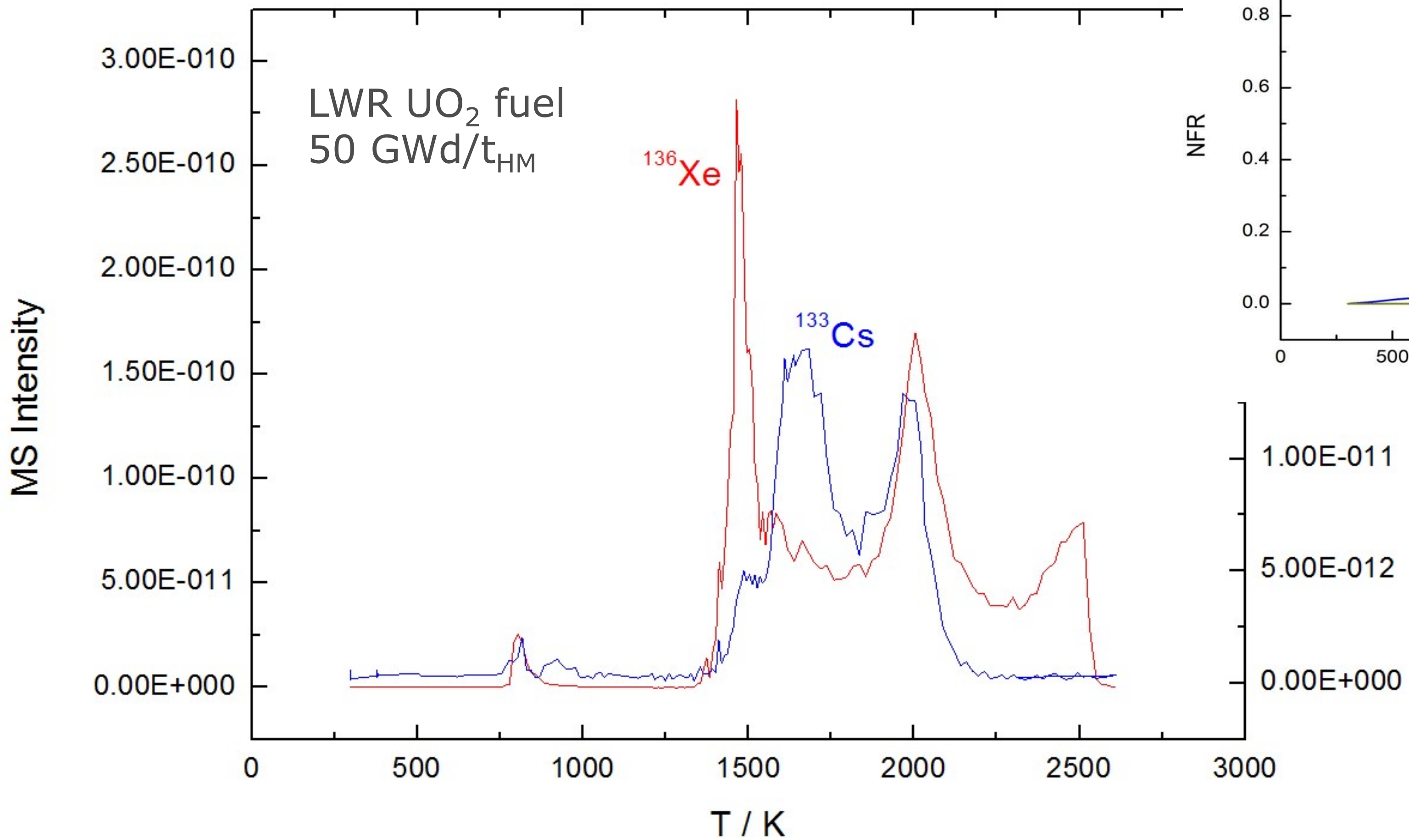
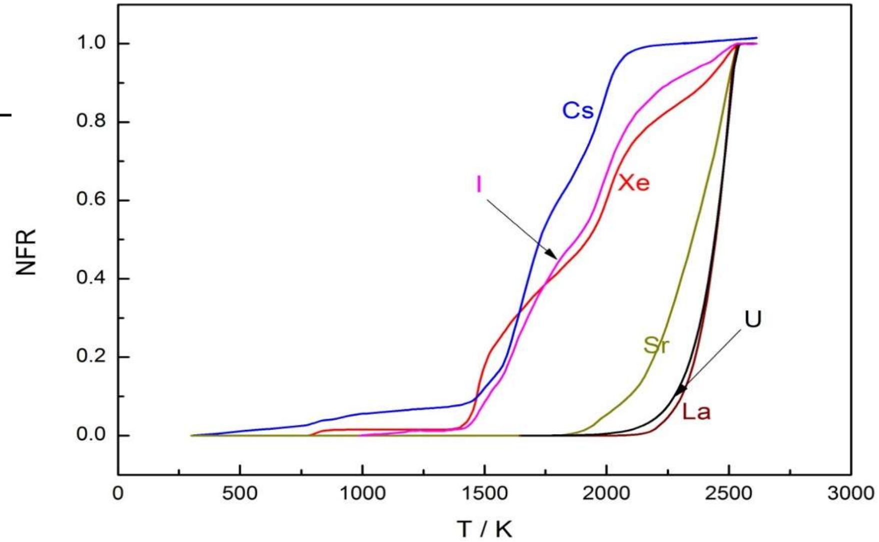
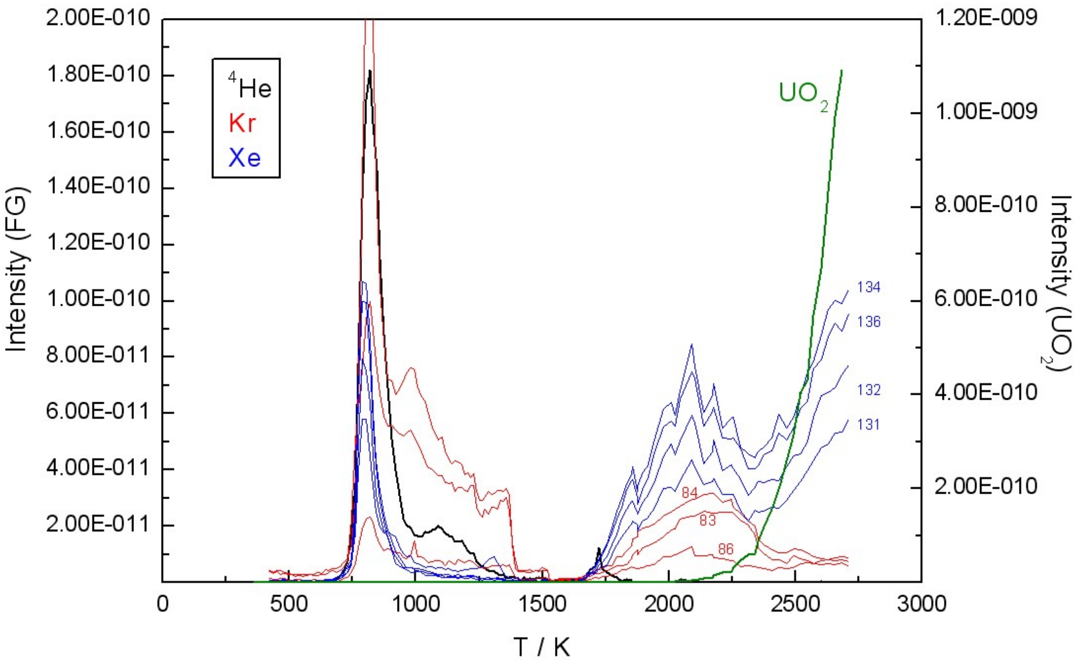
Fission Product Release from Irradiated fuels

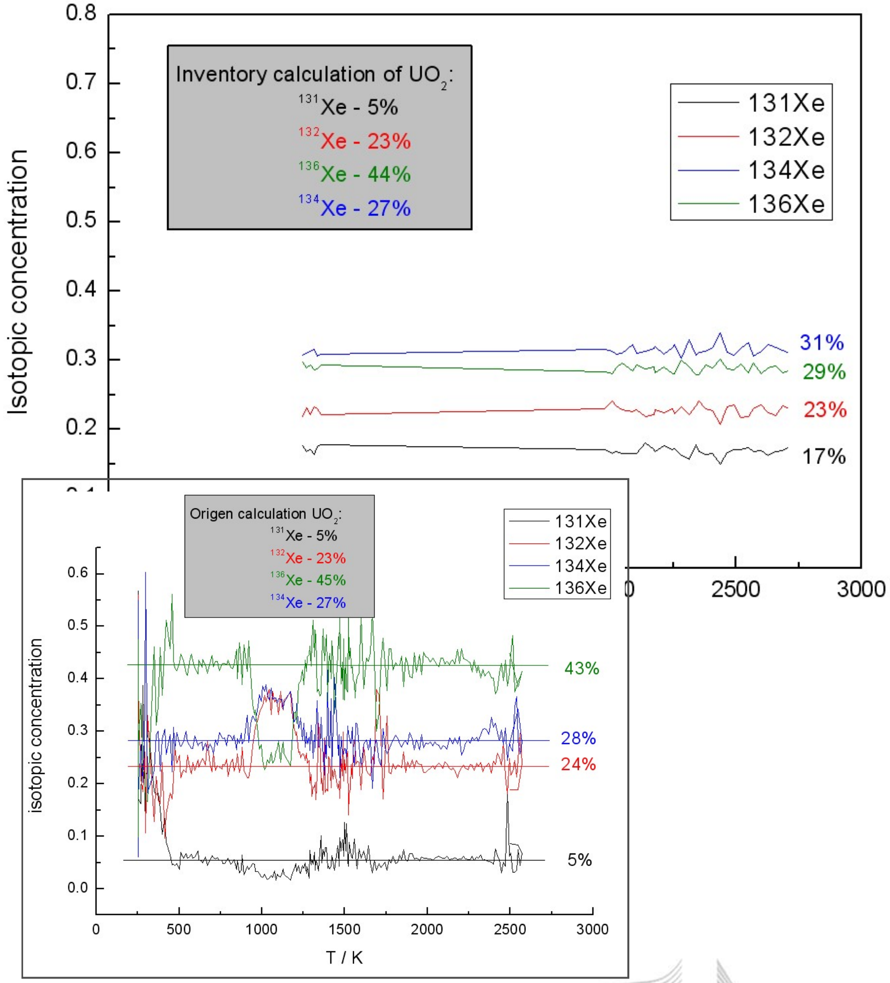




Fission Product Release from Irradiated fuels

Superfact – SF14 sample $(U_{0.6}Np_{0.2}Am_{0.2})O_2$





irradiated UO_2 (3.95% enrichment), 60GWd/t

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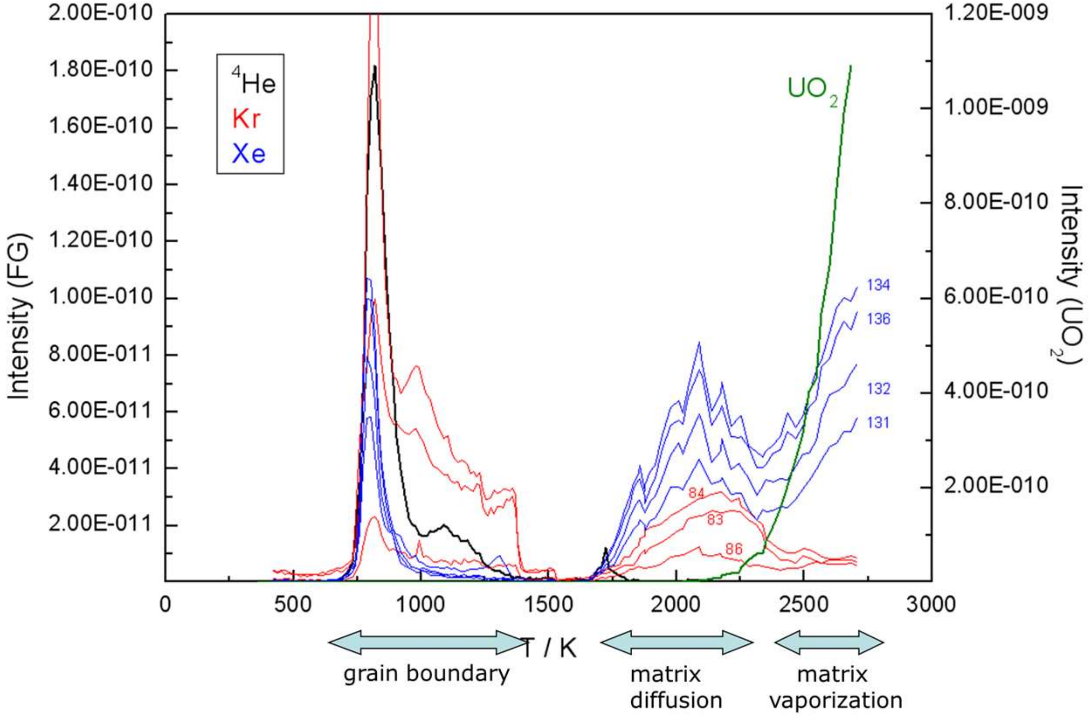
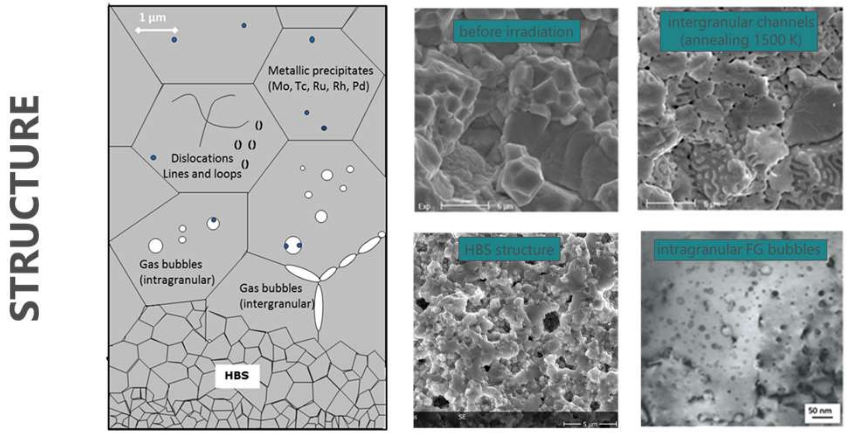
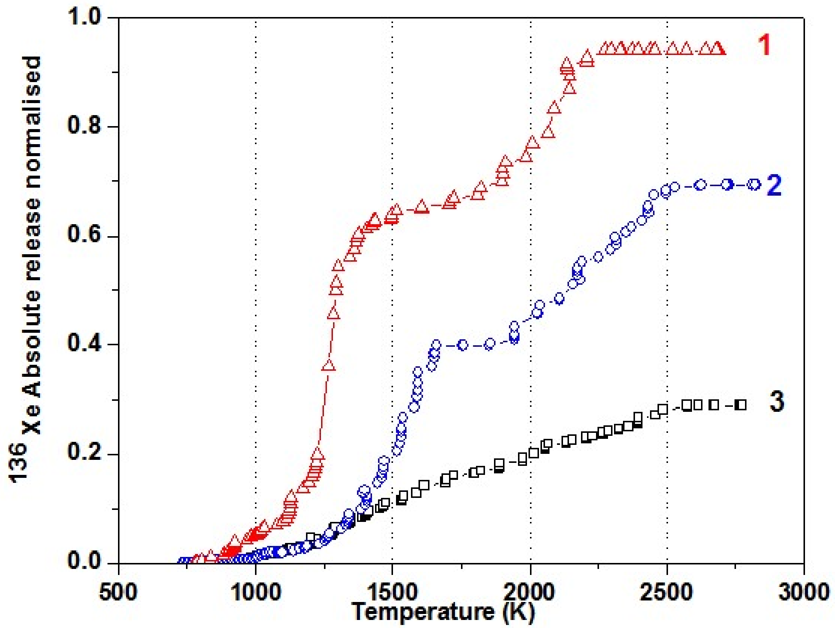
Fission Product Release from Irradiated fuels



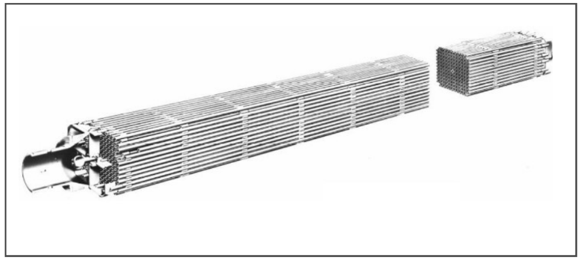


Fission Product Release from Irradiated fuels

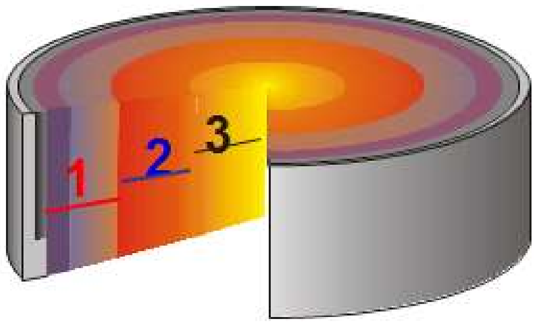
Effect of irradiation temperature



PWR fuel bundle



Sample size allows fuel pin region selection



Scheme of a fuel pin

Fission Product Release from Irradiated fuels

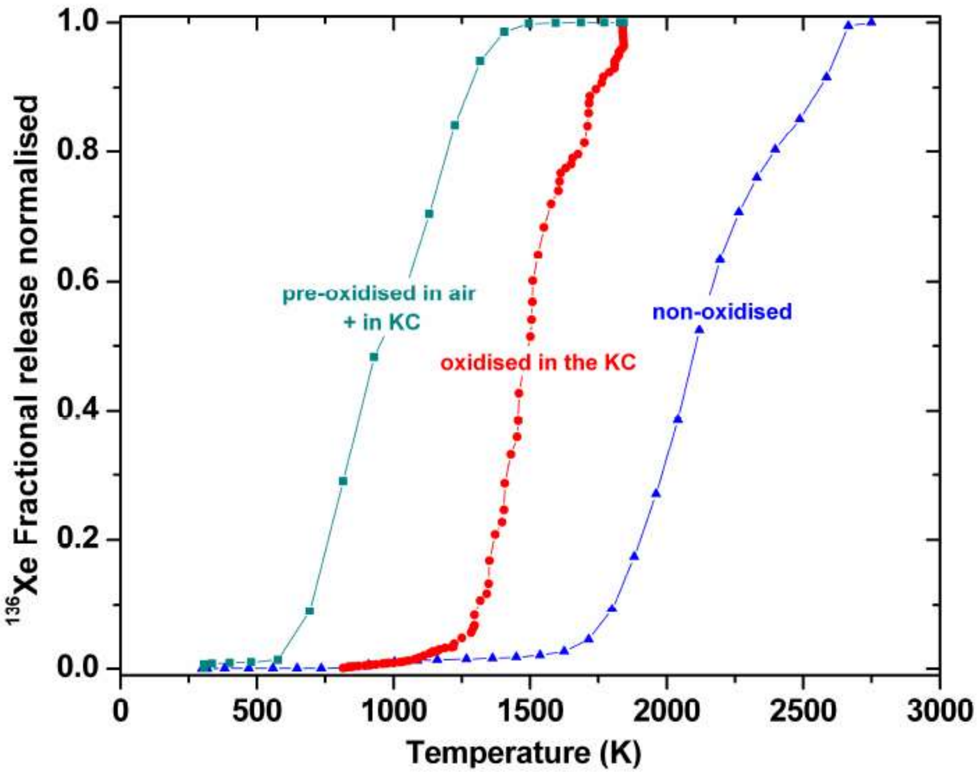
Effect of oxidation state of the fuel matrix

On picture: Release of ^{136}Xe from irradiated UO_2 sample (55 GWd/t)

non-oxidized ~ irr. UO_2 in vacuum

oxidized in KC ~ irr. UO_2 in O_2 (~1Pa)

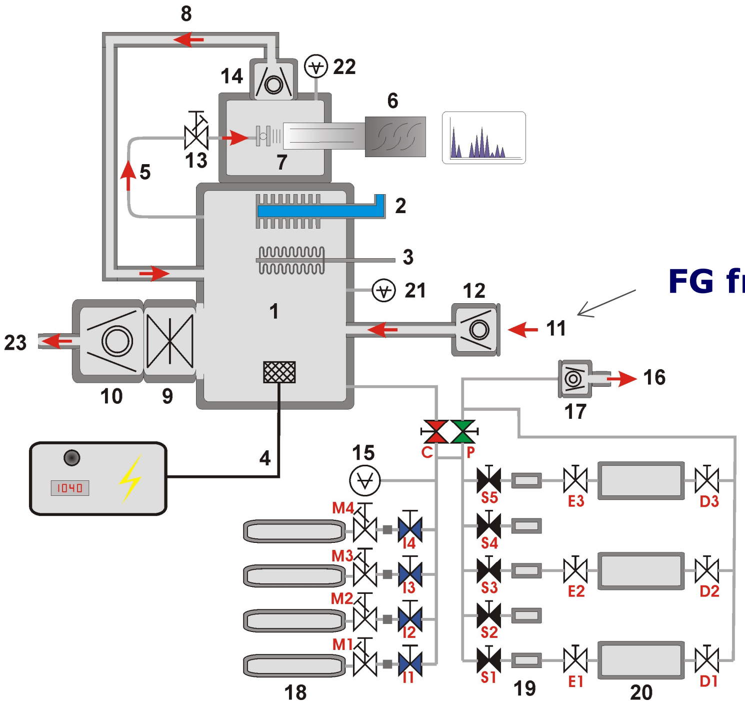
pre-oxidized in air + in KC
conditioned to U_3O_8 (8h, air, 550 K)
measured in O_2 (~1Pa)



Fission Product Release from Irradiated fuels

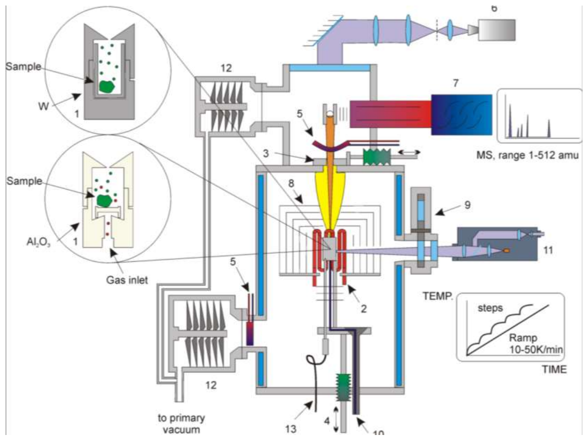
Quantification of Fission Gas released from irradiated fuel:

Q-GAMES device developed at ITU (Quatification-GAs MEasuring System)

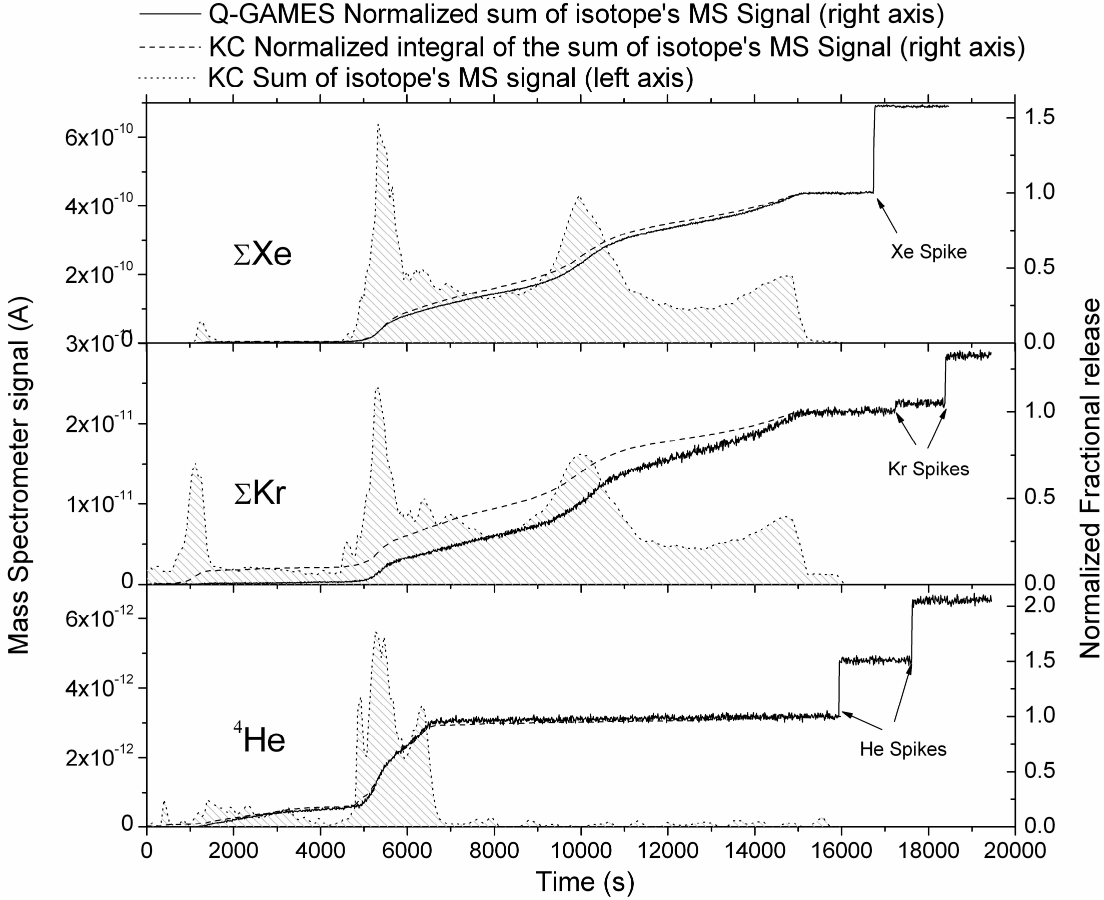


FG from KEMS

1 Sample chamber
2 Cold trap
3 Getter pump
4 Plasma generator
5 MS inlet
6 Quadrupole mass spectrometer
7 MS chamber
8 Feed back loop
9 Vacuum gate
10 Gas discharge pump
11 Sample gas inlet from desorbtion experiment
12 Compressing turbo pump
13 MS gas inlet μvalve
14 MS chamber pump
15 Absolute pressure transducer
16 Spike gas discharge
17 Spike gas discharge pump
18 Spike gas reserve
19 Spike calibrated volume
20 Calibrated expension vessel
21, 22 Full range vacuum gauge
23 Gas discharge



Fission Product Release from Irradiated fuels



Detection limit: 10^{-10} mol

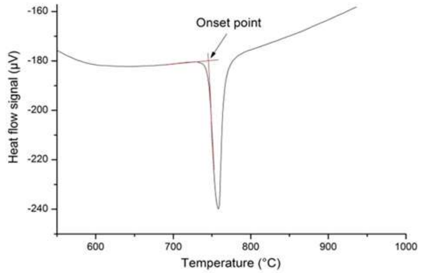
Fission Product Release from Irradiated fuels

SALIENT-03 project (follow-up of SALIENT-01)

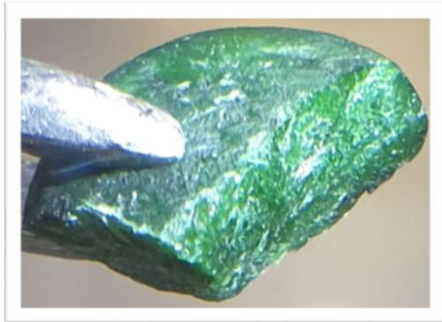
- 2nd European irradiation of molten salts at HFR, NRG, Petten (~5M€ project)
- Collaboration between JRC (KA, PT) and NRG
- Very challenging task (demand on purity, Quality control, ~100g of fuel mixture, encapsulation of plutonium fuel with no surface contamination)
- 4 different fuels (6 welded capsules) (^{7}LiF-ThF_4-UF_4-UF_3-PuF_3-(CrF_3) composition)

At JRC:

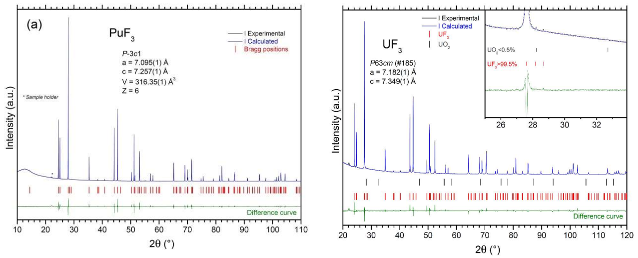
- Fuel synthesis and Encapsulation
- Safety analysis for HFR
- Post Irradiation Examination



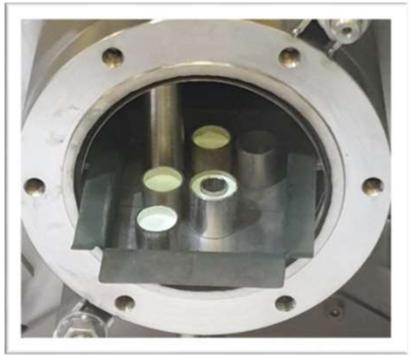
Melting point verification – Fuel 01



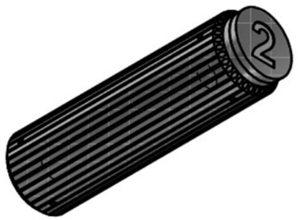
Solid ingots of frozen fuel of ~100% th. density



Purity analysis of all end-members



Densification of fuel by melting



Capsule 2 design (~6.5g fuel)

Optimized test weld

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Fission Product Retention

Fission Product retention of the MSR fuel

- 1 Determination of Fission product chemistry by simulation
- 2 Sim-fuel synthesis (CsI and CsF additives)
- 3 Measurement of CsF/CsI volatility using KEMS

Frame: HORIZON2020 Project SAMOFAR (2015-2019)


Issue 15, 2021

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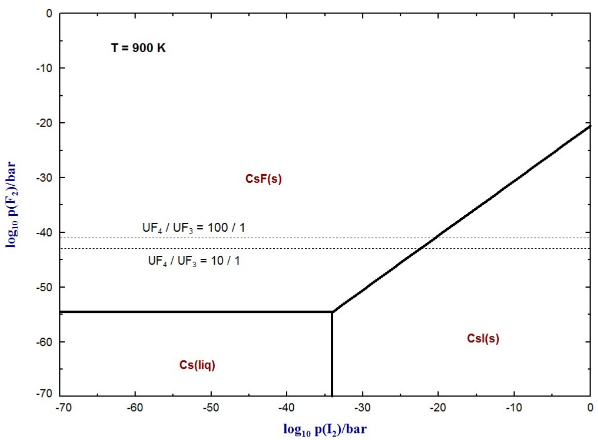
From the journal:
Physical Chemistry Chemical Physics

Cesium and iodine release from fluoride-based molten salt reactor fuel

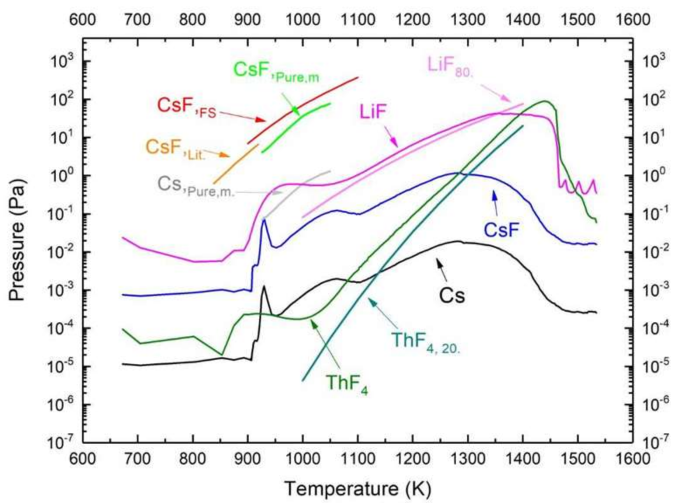
Check for updates

O. Beneš, E. Capelli, N. Morelová, J.-Y. Colle, A. Tosolin, T. Wiss, B. Cremer and R. J. M. Konings

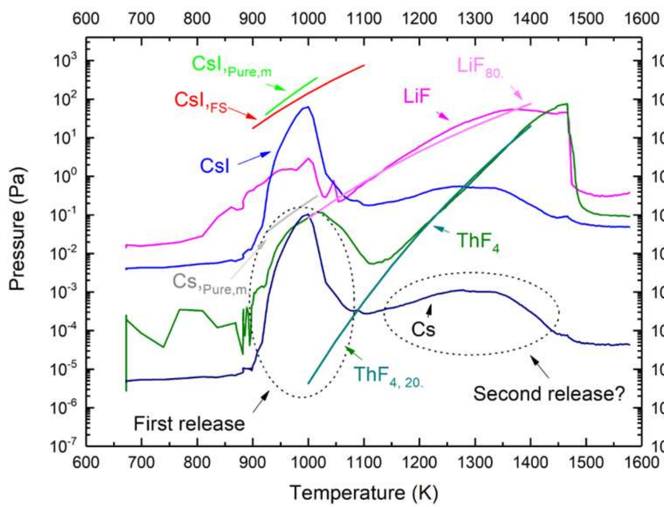
Calculation of Cs- and I- chemical forms



CsF release from LiF-ThF4



CsI release from LiF-ThF4



Conclusions:

- CsF dissolves and as consequnce decreases volatility of Cs >100000x (ref. Elemental form)
- CsI is highly immiscible, but formation of CsI compound causes ~3000x lower volatility (ref. Elemental form)

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Summary

- With KEMS you can do a lot!
- But, the more complex the system, the more exhaustive the data analysis is.
- Solid/liquid – gas equilibrium carries huge amount of highly relevant data:
  - Vapour pressures (total and partial)
  - Boiling point
  - Solubilities (e.g. FG solubility)
  - Enthalpy of vaporization
  - Activities of individual solution components
  - Retention capacity of molten salts
  - … and few more derived quantities

Contacts

- Ondrej Benes (Scientific lead)
- Jean-Yves Colle (Technical responsible)

Keep in touch

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Thank you