PennState
College of Engineering

NucE 497: Reactor Fuel Performance

Lecture 19: Fuel Chemistry

February 22, 2017

Michael R Tonks
Mechanical and Nuclear Engineering

Content taken from slides provided by ANT international

Today we will discuss fuel chemistry

- Module 1: Fuel basics
- Module 2: Heat transport
- Module 3: Mechanical behavior
- Module 4: Materials issues in the fuel
  - Property evolution and Intro to materials science
  - **Chemistry**
  - Grain growth
  - Fission products and fission gas
  - Densification, swelling, and creep
  - HBS
  - Fracture
  - Thermal conductivity
- Module 5: Materials issues in the cladding
- Module 6: Accidents, used fuel, and fuel cycle

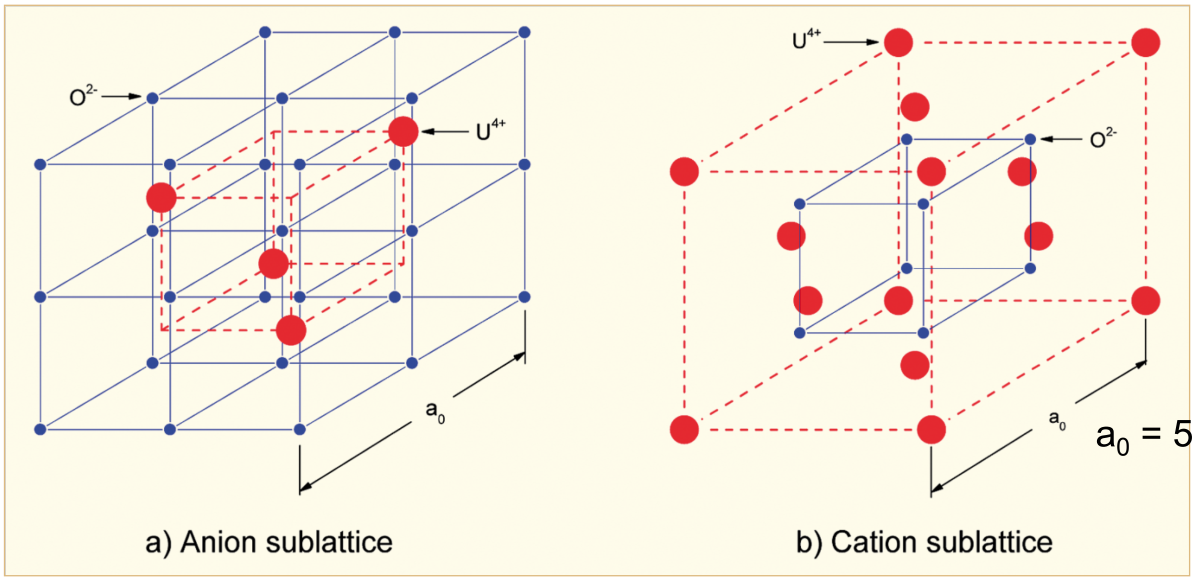
Here is some review from last time

- Which is a 2D planar defect?
  a) An interstitial impurity atom
  b) A dislocation loop
  c) A grain boundary
  d) A precipitate
- What is a fission product atom once it looses its energy and reaches a stable position?
  a) An impurity atom
  b) A dislocation loop
  c) A grain boundary
  d) A precipitate

UO_2 is an ionic compound that must have balanced charges

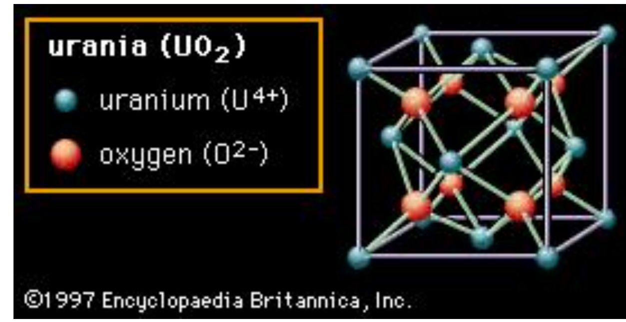
- What is the charge of a typical oxygen ion?
  - O^{2-}
- Uranium valance states
  - Possible: U^{3+}, U^{4+}, U^{5+}, U^{6+}
  - Most stable: U^{4+}, U^{5+}, U^{6+}
- What is the charge of uranium in UO_2?
  - U^{4+}

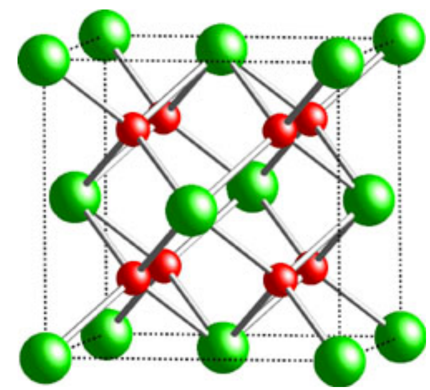
UO_2 has a cubic structure that is called the flourite crystal structure



a_0 = 5.47 Å

[after Olander, 1976]

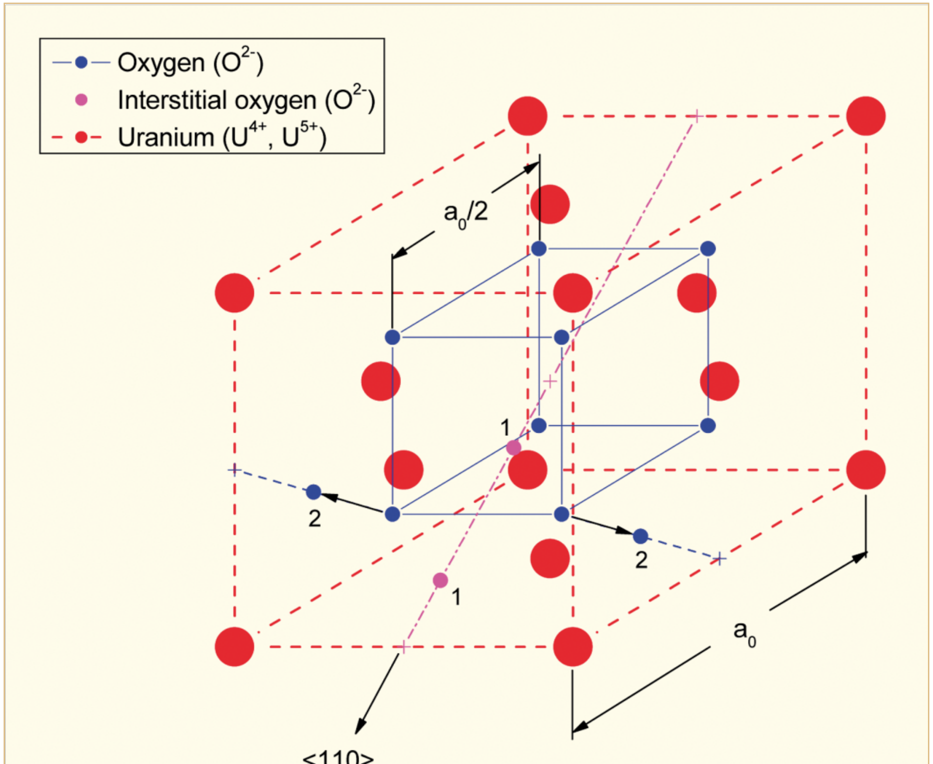




- The structure is very stable all the way up to the melting temperature and down to extremely low temperatures, even with irradiation damage
- There is space in the uranium lattice that can accommodate fission products

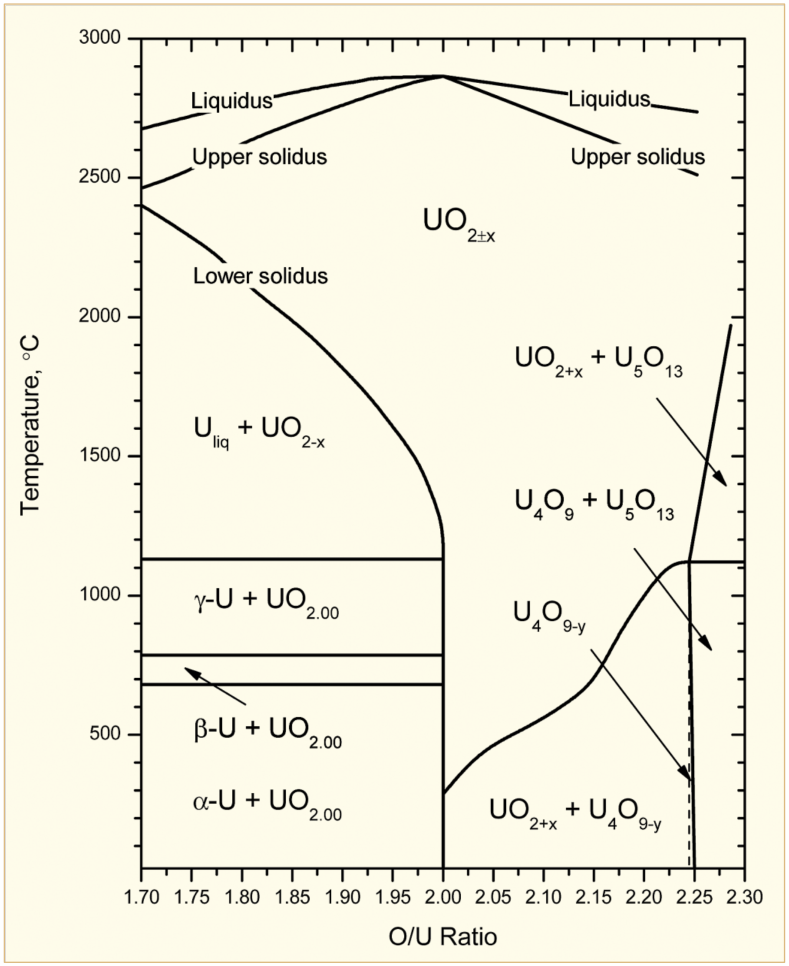
The crystal structure of UO_2 can also accommodate extra oxygen

- Excess oxygen resides at interstitial locations in vacant U sub-cells
- Oxygen in neighboring sites is displaced
- Cation valance increases to maintain electrical neutrality



[after Olander, 1976]

The ratio of oxygen to uranium metal (O/M ratio) can vary. We call this the stoichiometry.

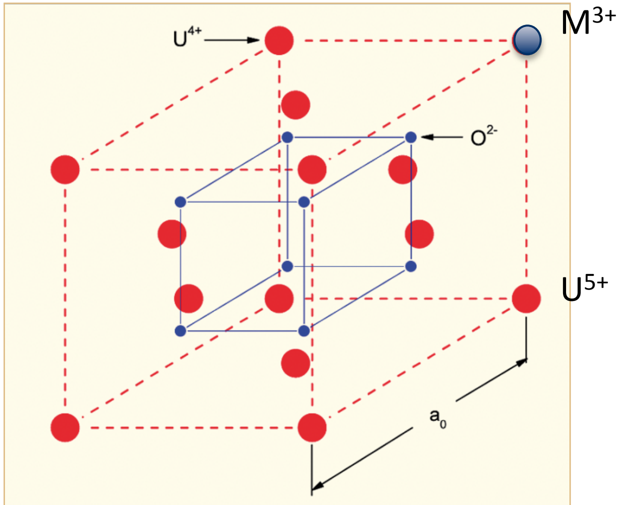


[Levin & McMurdie, 1975], [Olander, 1976], [Kim, 2000], [Guéneau et al, 2002], [Baichi et al, 2006], [Rudling et al, 2007]

- Fuel fabricated to be nearly stoichiometric; i.e., $UO_{2.00\pm}$ because:
  - It is the most stable
  - It has the highest melting temperature
- Will the O/M ratio go up or down during reactor operation?
  - It is complicated, because of the formation of fission products that also react with the oxygen

As fission products form, the valance state of the uranium can change

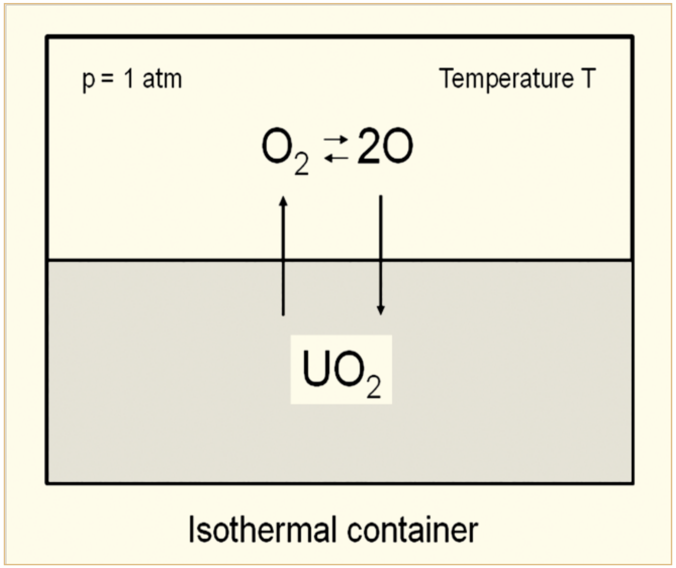
- Valance of soluble fission products is M^{3+} (typical)
- The uranium valance state changes to compensate
  - Oxygen liberated by fission
  - Fission products produced with M^{3+} valance state incorporated in fuel lattice
  - Uranium oxidizes from U^{4+} to U^{5+} or U^{6+} to maintain local electrical neutrality



b) Cation sublattice

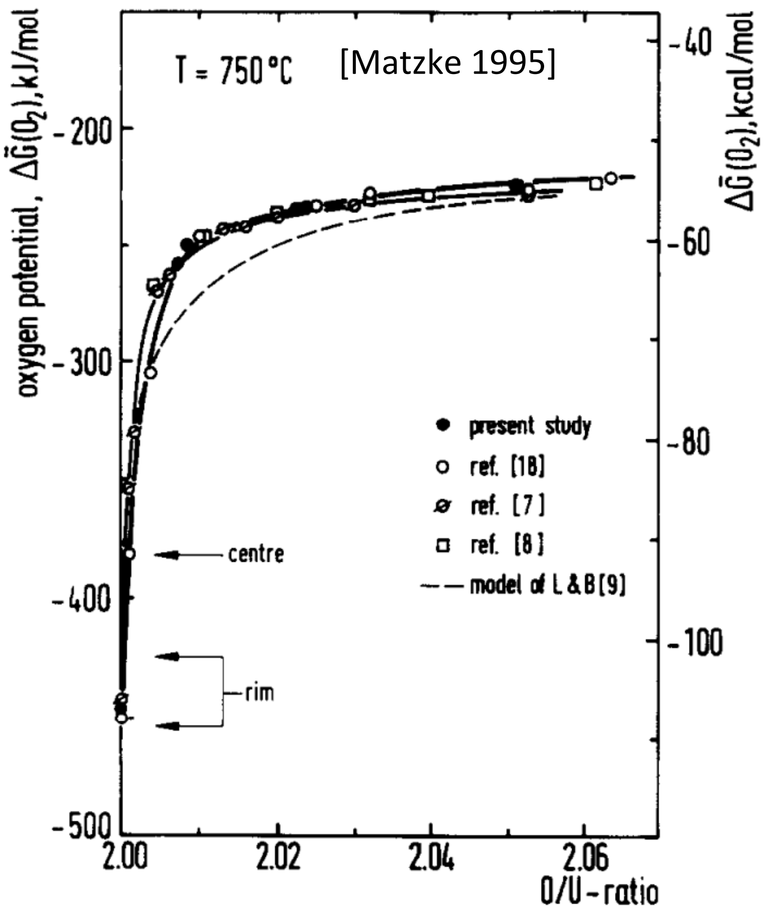
The oxygen potential is a measure of how free the oxygen is to escape/move around

- Oxygen potential is defined as $\Delta \bar{G}_{O_2} \equiv RT\ln\left(p_{O_2}\right)$ or, equivalently $\Delta \bar{G}_{O_2} = 2\mu_{O_{solution}} - G^{o}_{O_2}$
  - With $\mu_{Osolution}$ = Chemical potential of oxygen in solution
  - $G^{o}_{O_2}$ = Gibbs free energy of gaseous oxygen at temperature T and a standard pressure (1 atm)

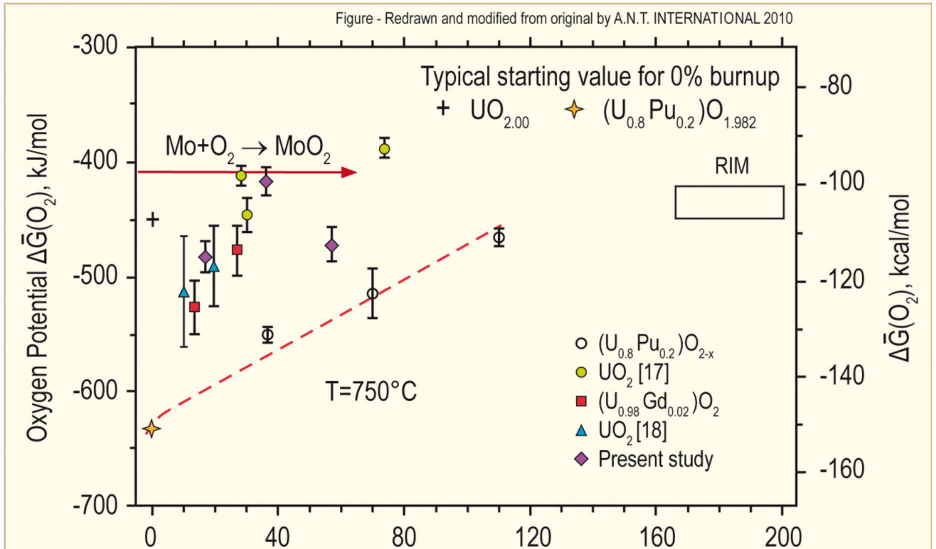


It is possible to determine the stoichiometry from the oxygen potential

- This is straight forward for unirradiated fuel but is complicated after fissioning has taken place



The oxygen potential changes during irradiation, indicating change in the O/M ratio



[Matzke, 1995]

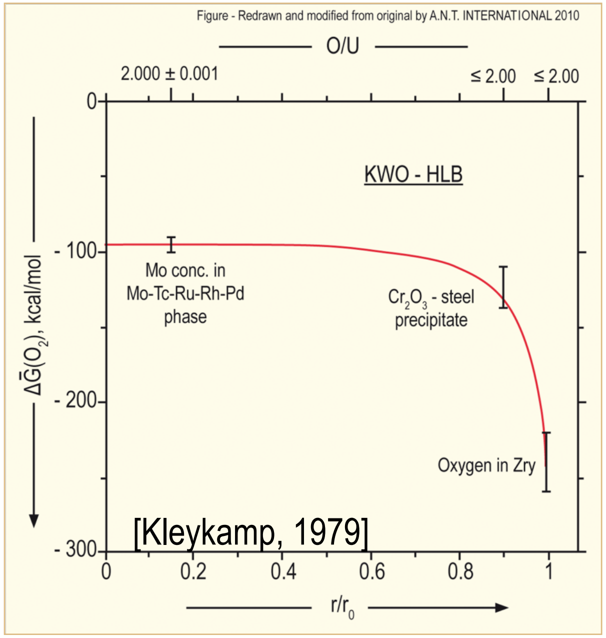
ΔO/M ~ 0.0013 per at.% burnup up to ~ 5 at.%

- Oxygen potential changes during irradiation due to
  - Liberation of oxygen by fission
  - Generation of fission products
  - Conversion of uranium to plutonium
  - Reaction of oxygen with U, Pu, fission products, and cladding

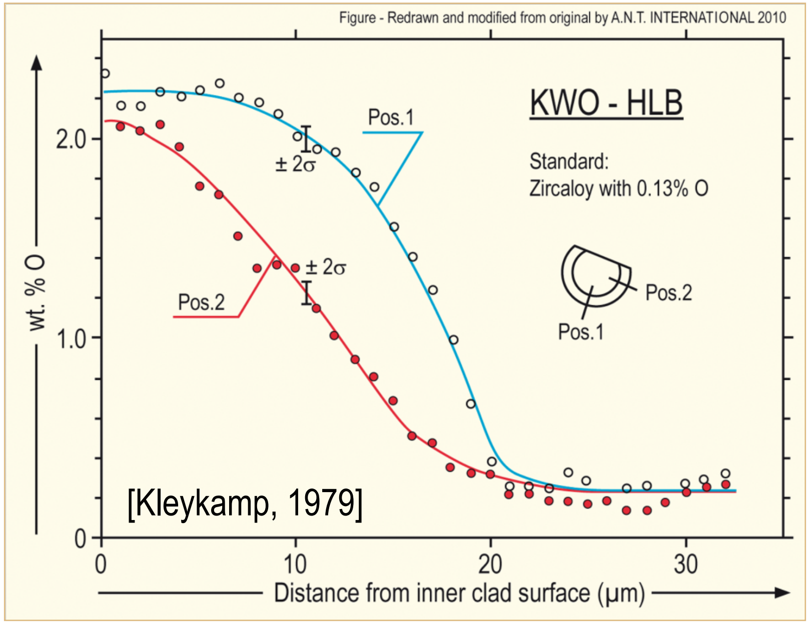
The oxygen potential stops changing due to the formation of Mo and its reaction with O

- Oxygen potential across pellet radius observed to be constant at the approximate value of Mo/MoO_2 reaction (from calculations)
- Oxygen potential is low near the cladding, because the oxygen enters the cladding

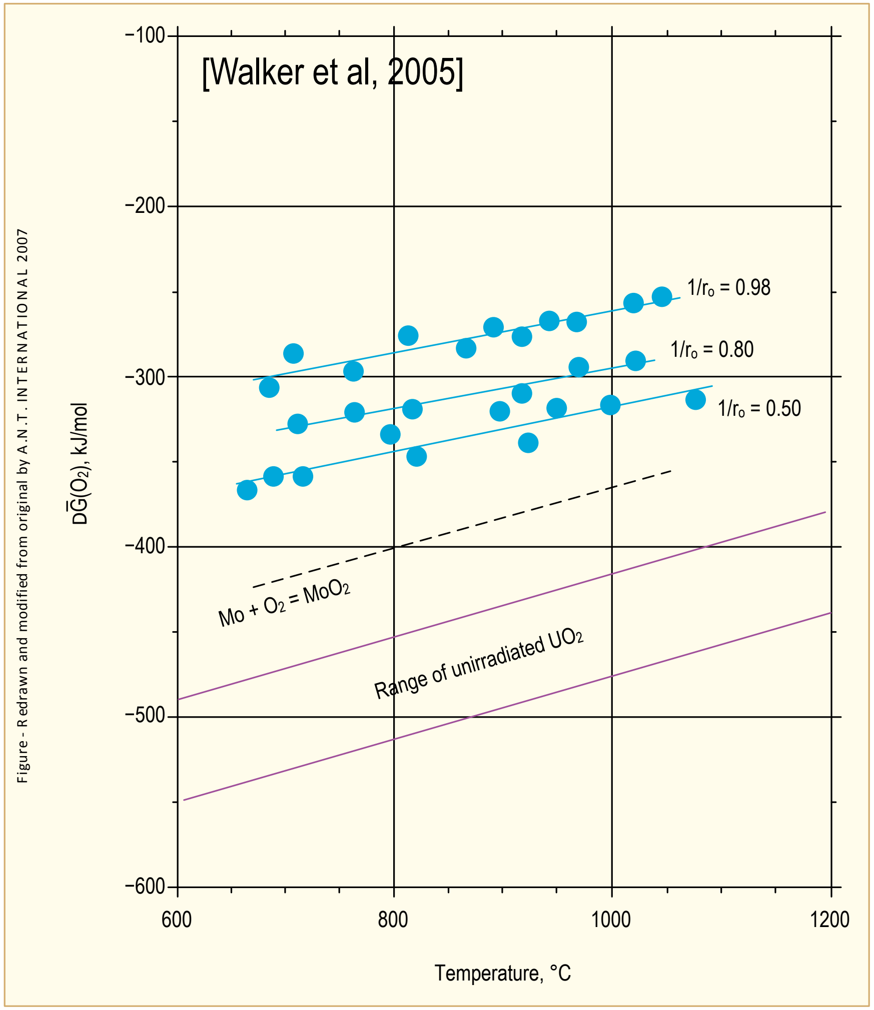
Oxygen potential in the fuel



Oxygen concentration in cladding



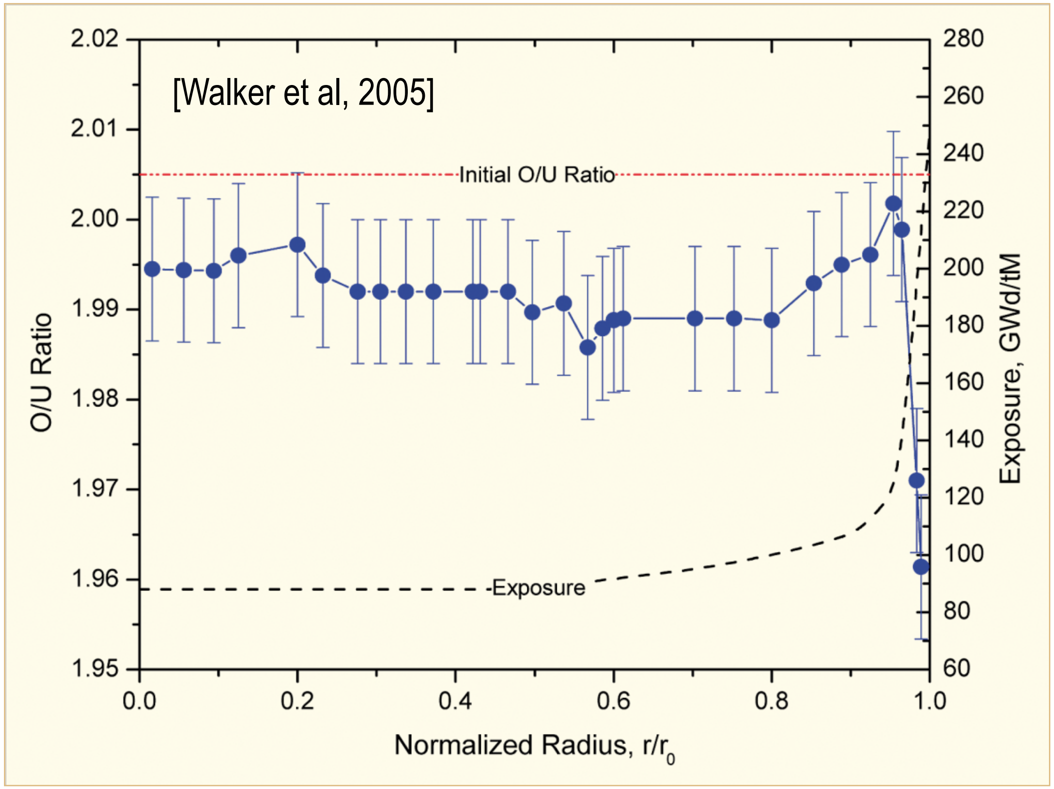
Other published results at high burnup show different behavior



- These data are taken from experimental measurements
- The fuel rod reached very high burnup, 100 MWd/kgHM
- The rod powers were low, causing the centerline temperature to be around 1200 K for most of the irradiation.

O/M ratio is below 2.0 in this high burnup fuel

- Changes due to M^{3+} fission products in fuel matrix

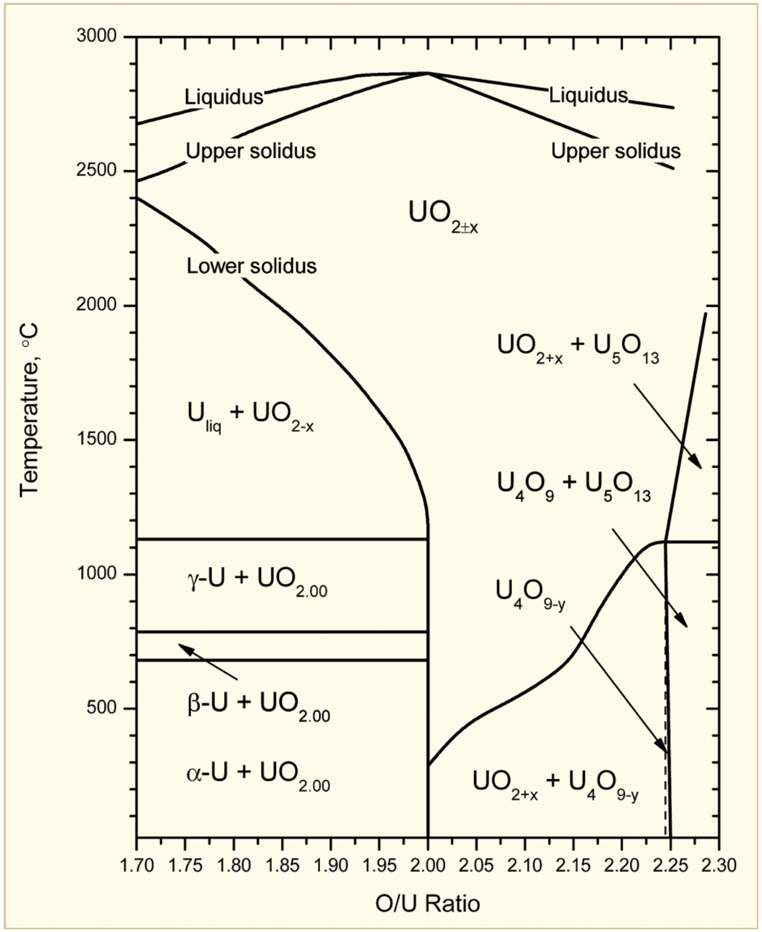


Here is a summary of what we have learned about fuel chemistry

- Some results indicate
  - Oxygen potential buffered by Mo/MoO_2 reaction and oxidation of cladding
  - O/U ratio remains near stoichiometric value; 1.995 – 2.001
- However, one result at low power and very high burnup found
  - Oxygen potential increases above value based on Mo/MoO_2 reaction
  - Limited pickup of oxygen by cladding (determined by looking at the thickness of the oxide layer on the inside of the cladding)

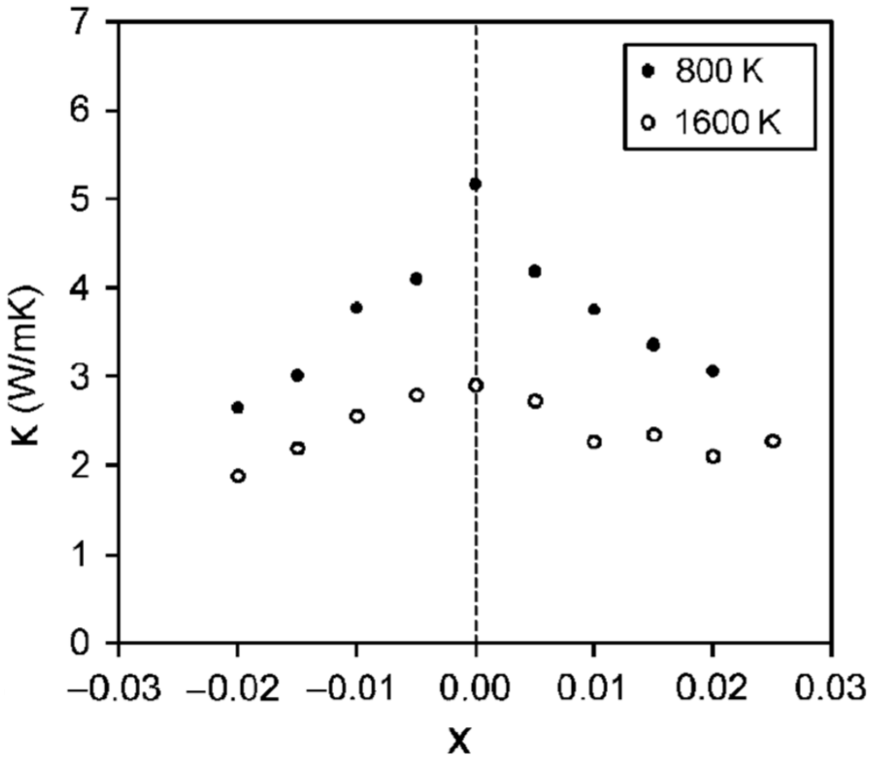
The stoichiometry of the fuel directly impacts the fuel performance

- Stoichiometry impacts
  - Melting temperature
  - Thermal conductivity
  - Processes dependent on diffusion
    - Grain growth
    - Fission gas release
    - Creep
  - Chemical state and behavior of fission products
  - Chemical reactions at inner cladding surface



The thermal conductivity is highest for stoichiometric UO_2

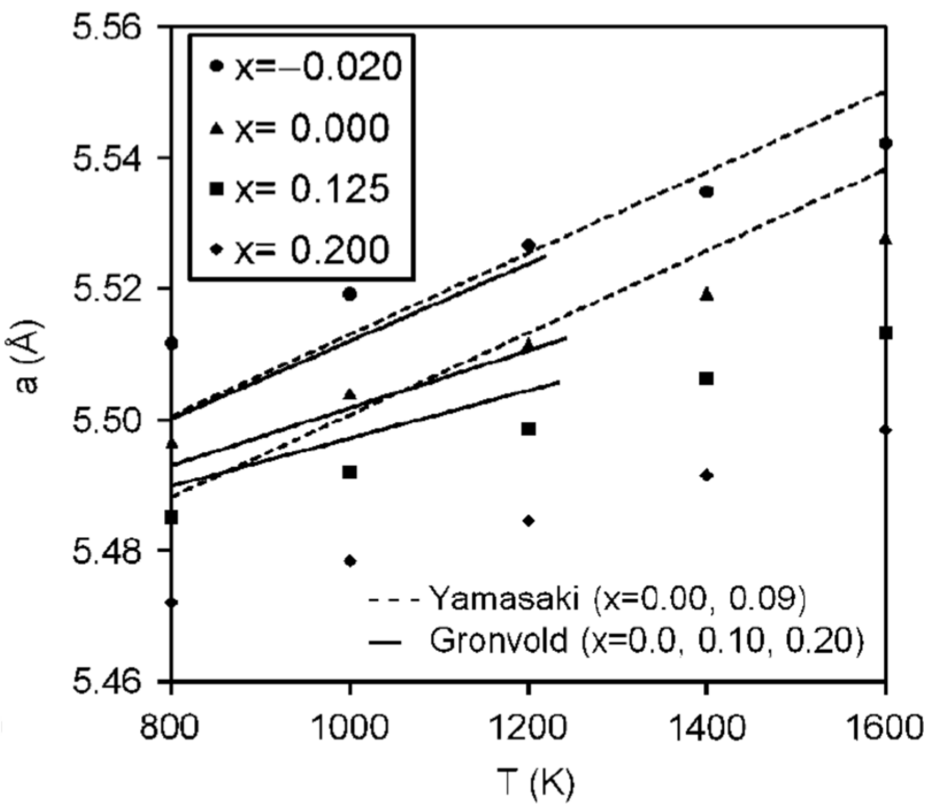
- These values are taken from atomistic simulation results



Watanabe et al., J. Am. Ceram. Soc., 92 [4] 850–856 (2009)

The size of the material decreases with increasing stoichiometry

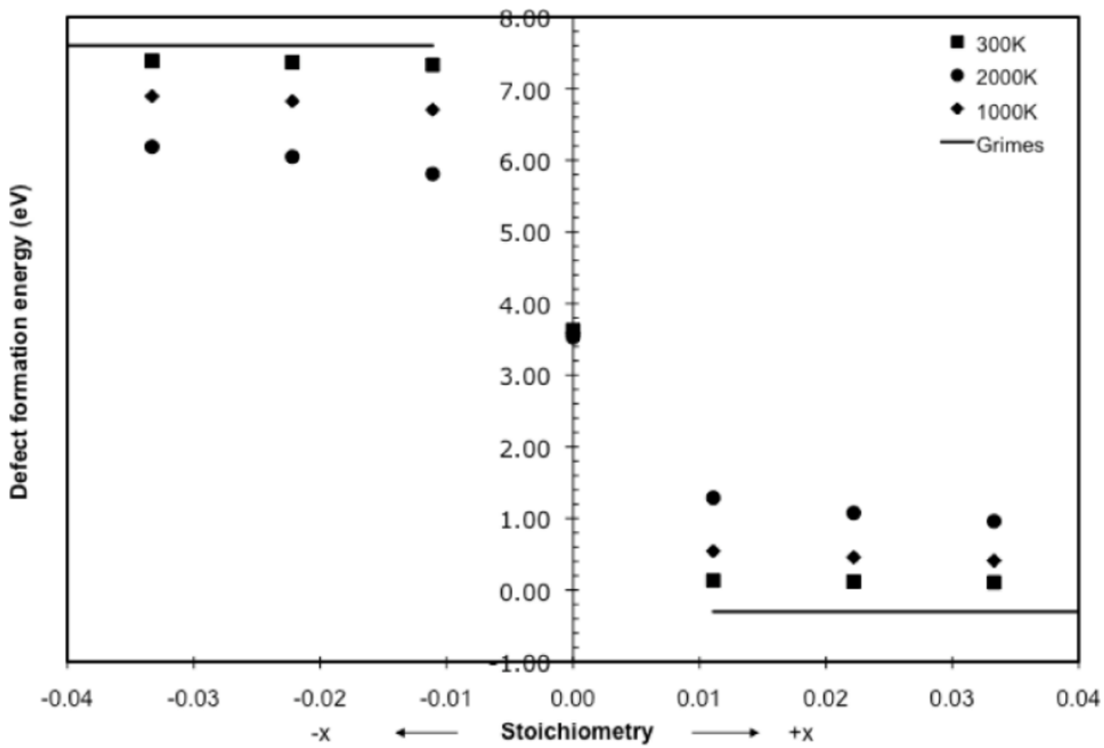
- These results show the lattice constant (size of the cubic structure) and are also from atomistic simulation



Watanabe et al., J. Am. Ceram. Soc., 92 [4] 850–856 (2009)

The energy it takes to form vacancies also changes with stoichiometry

- Results from atomistic simulations for the U lattice



P V Nerikar et al 2009 J. Phys.: Condens. Matter 21 435602 doi:10.1088/0953-8984/21/43/435602

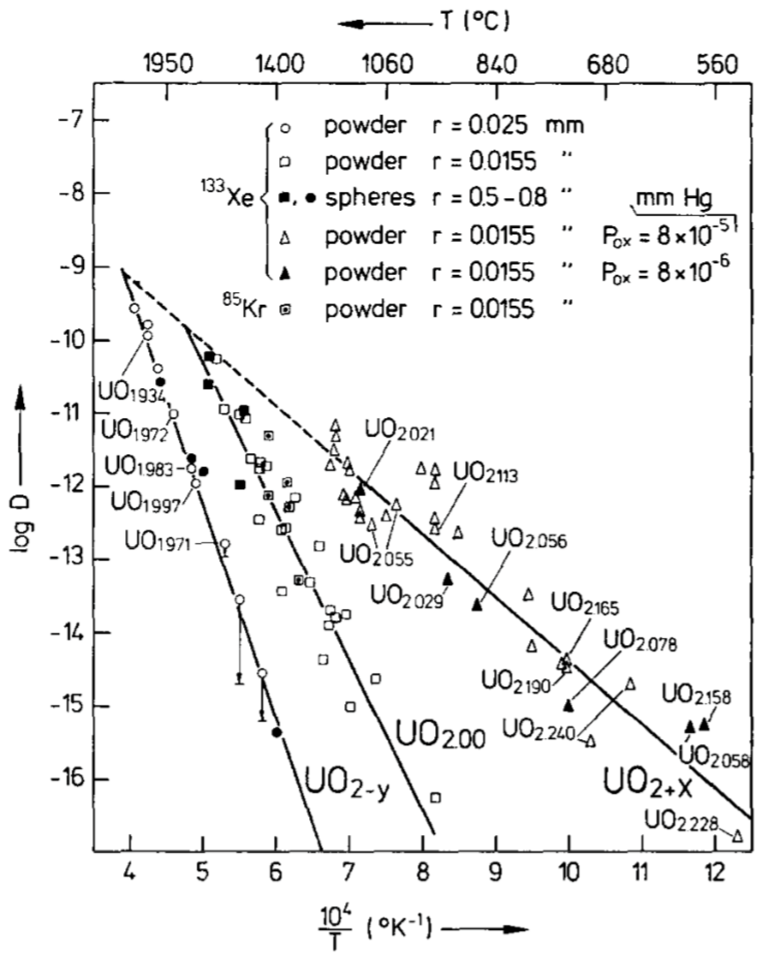
The solution energy of Xe, Cs, and Sr in UO_2 depends on stoichiometry as well

- This is the amount of energy required to put the fission product into the lattice (includes the cost of forming a defect to put it in)
- From DFT results (Nerikar et al., 2009)

Fission product	$UO_{1.97}$	UO_2	$UO_{2.03}$
Xe	3.88 eV	3.88 ev	2.61 eV
Cs	1.7 eV	-0.04 eV	-3.29 eV
Sr	-3.71 eV	-6.03 eV	-9.55 eV

The coefficient defining Xe diffusion also changes with stoichiometry

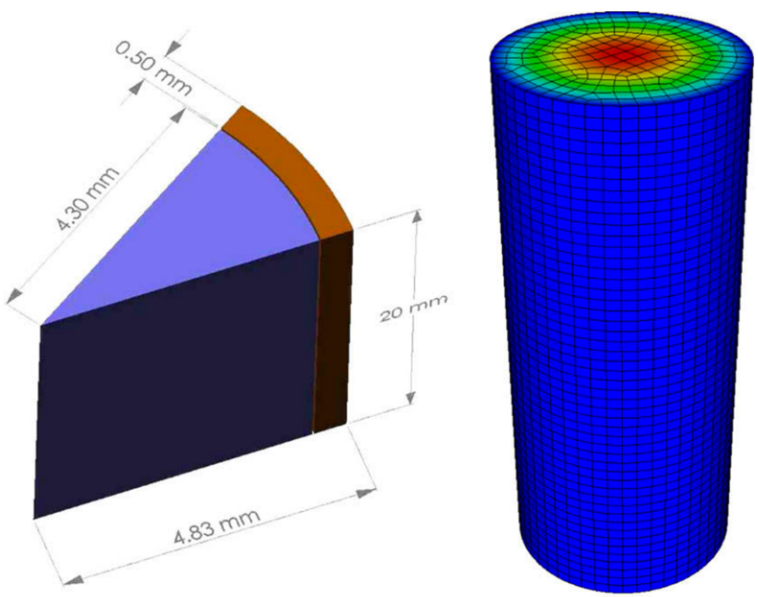
- These results are from experimental measurements

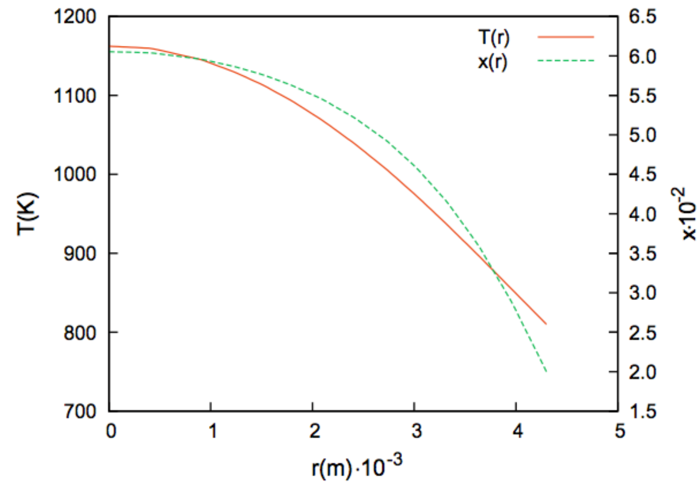


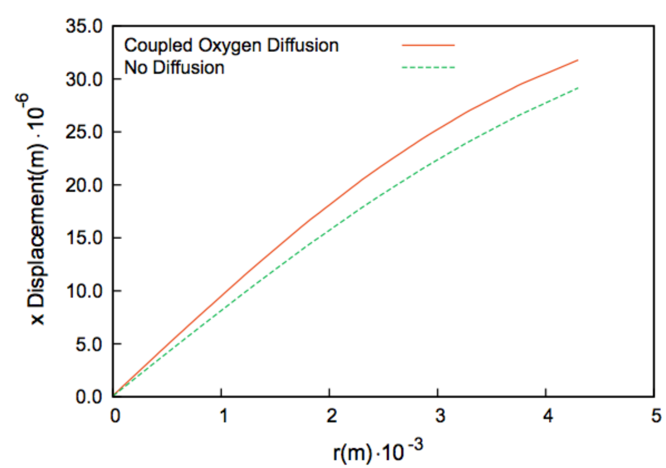
Miekeley, W., and F. W. Felix. "Effect of stoichiometry on diffusion of xenon in UO2." Journal of Nuclear Materials 42.3 (1972): 297-306.

Though stoichiometry matters, most fuel performance codes ignore it

- There are some preliminary results in BISON computing the stoichiometry, but this is still a work in progress







Newman, C., Hansen, G., & Gaston, D. (2009). Three dimensional coupled simulation of thermomechanics, heat, and oxygen diffusion in UO2 nuclear fuel rods. Journal of Nuclear Materials, 392(1), 6-15.

Summary

- UO_2 has a cubic flourite structure that is very stable
- The charges are balanced with a U^{4+} valance state
- However, the ratio of oxygen to uranium can change. We call this the stoichiometry and abreviate it as O/M ratio
- The O/M ratio changes during reactor operation, but it is complicated
- The O/M ratio impacts many properties of the fuel

How important is writing and oral communication for scientists and engineer?

- It is VERY important
- No matter how significant your work is, it is not impactful unless you can communicate it to others

As long as we can communicate with our peers, we should be fine, right?

- NO
- We have to be able to communicate with the general population if we want to impact the world
- To often people in other careers ignore scientific results because they say they aren't scientists
- We need to make our findings accessible to everyone, so that it can impact their decisions

Scientists and engineers are bad communicators and we need outside help for communication, right?

- NO!
- As long as we excuse ourselves by saying "scientists and engineers are bad communicators" we are giving ourselves an excuse
- It is your responsibility to make yourself a good communicator

Good communication skills will be one of the largest benefits you have in your career

- If you struggle with oral and/or written communication, work hard to improve.
- It will be worth it.
- I guarantee it.