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Ionic Diffusion Model of Uranium Oxidation

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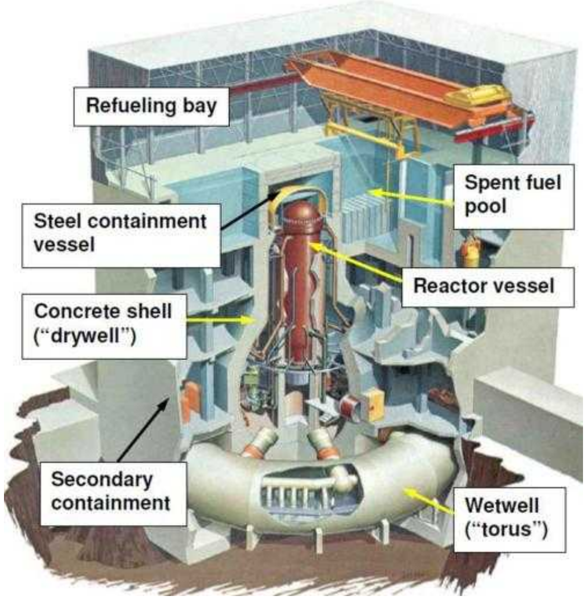
Outline

- **Motivation**
- **Review of Previous Work**
- **Ionic Diffusion Model**
- **Comparison with Oxidation Data**
- **Reaction Rate Constant Formulation**
- **Comparison with Empirical Formulas**

Motivation

- **Applications:**
  - **Nuclear Reactors**
  - **Nuclear Waste Storage**

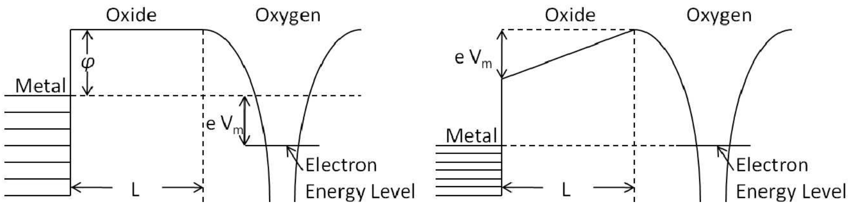
- **Uranium Oxidation Modeling**
  - **Current available models of uranium oxidation are empirical**
  - **Physics based model allows for greater understanding of the underlying causes of oxidation rates**



Review of Previous Work

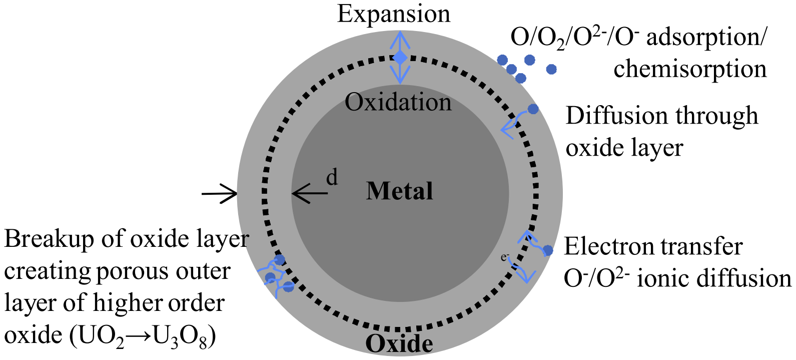
- **Uranium Oxidation:**
  - Empirical growth models (Evans, 1960)
    - Inverse logarithmic
    - Parabolic
    - Linear
    - Paralinear
  - Show trends, without need for understanding of physics
  - High variability in measurements due to differing material and environmental conditions yield large variations between models

- **Ionic Diffusion:** (Mott, 1947)
  - Increased diffusion of ions due to electric potential through oxide
  - Accounts for passivation as oxide thickness increases and inverse logarithmic growth trends
  - Shown to correctly prediction oxidation of common metals like copper and zinc.



(Cabrera, 1949)

Ionic Diffusion Model



Expansion

$O/O_2/O^{2-}/O^-$ adsorption/ chemisorption

Oxidation

Diffusion through oxide layer

d

Metal

Breakup of oxide layer creating porous outer layer of higher order oxide ($UO_2 \rightarrow U_3O_8$)

e^-

Electron transfer

O^-/O^{2-} ionic diffusion

Oxide

$$J_{ion} = \underbrace{4 a \nu \exp\left(\frac{-W}{k_b T}\right)}_{D/a} \sinh\left(\frac{ZE_0 a}{k_b T}\right) \left[\frac{C(L) - C(0)\exp\left(\frac{ZE_0 L}{k_b T}\right)}{1 - \exp\left(\frac{ZE_0 L}{k_b T}\right)}\right]$$

α = distance between U atoms

ν = oxygen atomic vibrational frequency in oxide

W = energy barrier

Z = ion charge

C = ion concentration

$E_0 = -V_m/L$

D = diffusion coefficient

Symbol	a	ν	W	$C(L)$	$C(0)$	Z
Value	3.87	19	1.24	1×10^{28}	Negl.	−2
Units	Å	THz	eV	$1/m^3$	$1/m^3$	—

- Uranium Oxidation modeled based on ionic diffusion of oxygen through oxide film (Fromhold, 1967)
- Model is applicable to oxidation before the oxide layer begins to crack due to stress of expansion from density change.
- Assumptions:
  - Electrons easily transfer from uranium to oxide outer surface
  - Oxygen ions adsorb to oxide surface up to a hyper-stoichiometry of 2.25
  - All ions that reach the uranium/oxide interface react with the uranium to form oxide

Submitted for publication: **P. E. Gharagozloo** and **M. P. Kanouff**, “Ionic Diffusion Model of Uranium Oxidation,” *Journal of Nuclear Materials*

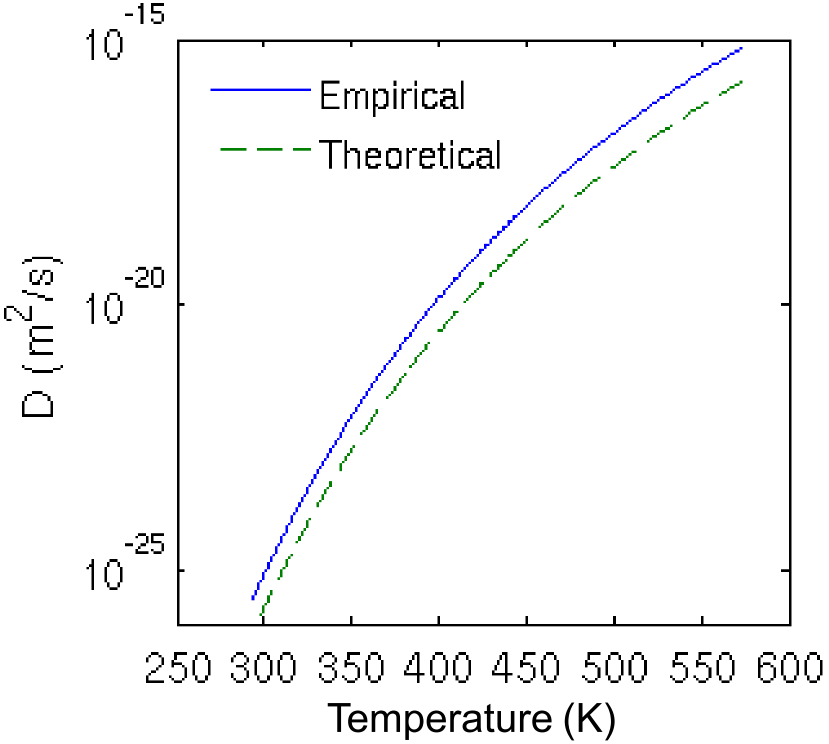
Chemical Diffusion Coefficient Comparison

$$D_{emp} = 5\times10^{-5}\left[\frac{m^2}{s}\right]\exp\left(-\frac{119244\,[J/mol]}{R_g T}\right)$$

(Lay, 1970)

$$D_{th} = 4a^2\nu\exp\left(-\frac{W}{k_b T}\right)$$

- Reported chemical diffusion activation energy consistent with reported anion migration energy for hyper-stoichiometric uranium dioxide of 1.3 eV (Catlow, 1977)
- Using reported activation energy, empirical and theoretical chemical diffusion coefficient are of same order of magnitude and differ by only a factor of 4



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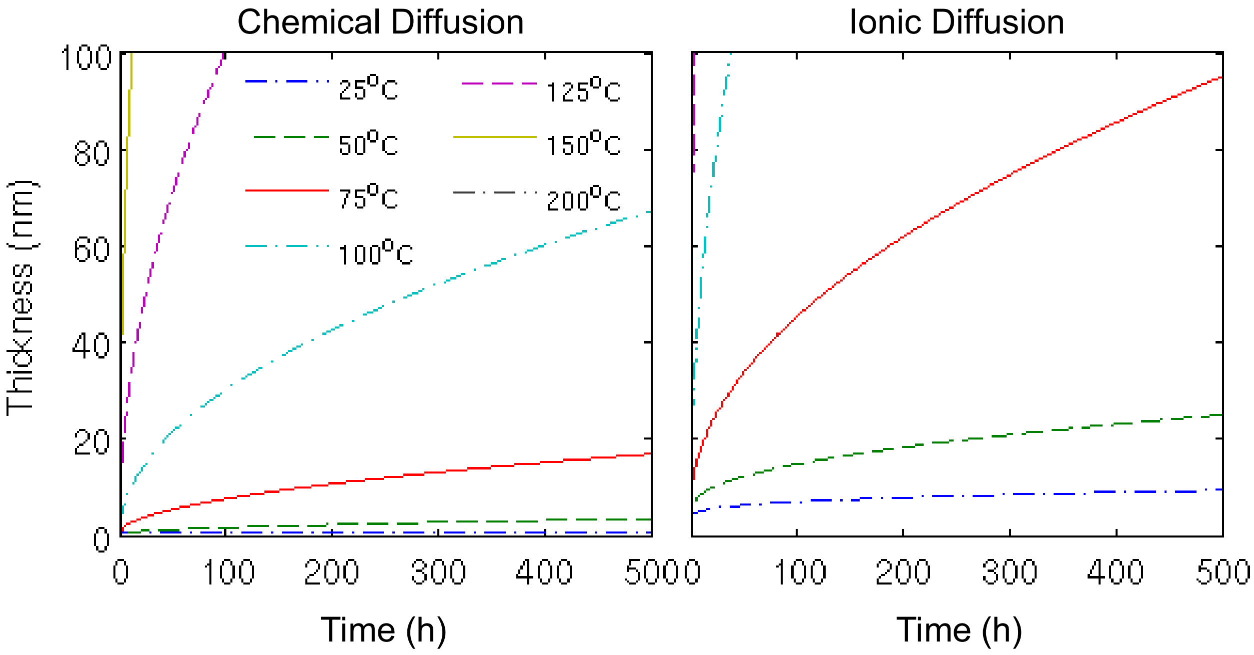
Chemical versus Ionic Diffusion



- Comparison of diffusion based oxidation for chemical diffusion using Fick's Law and ionic diffusion accounting for the added effect of the electric potential
- Electric potential greatly enhances oxide growth
- Ionic diffusion model shows inverse logarithmic growth behavior at low temperatures and transitions to parabolic behavior at higher temperatures

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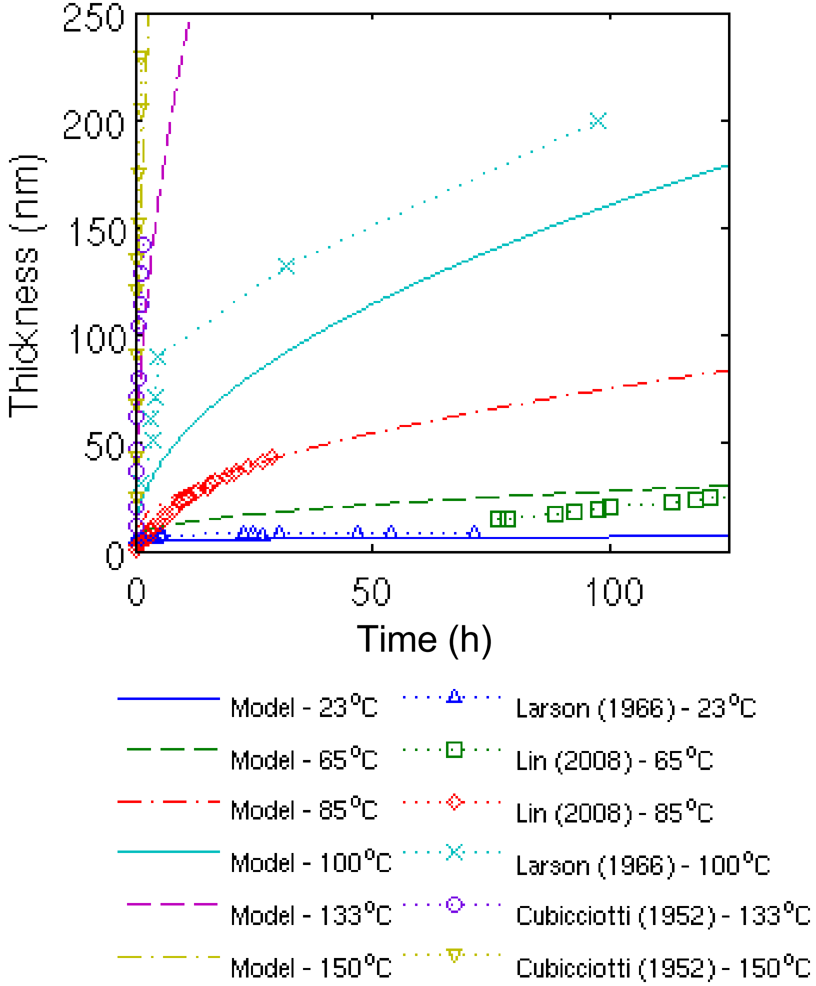
Comparison with Published Data



- **Results for modeled oxide thickness over time match previously reported experimental data well at small oxide thicknesses (< 300 nm)**
- **Agreement persists over multiple decades of data and varying measurement methods**
- **At larger thicknesses the cracking and spalling of oxide layer allows oxygen to penetrate surface**
- **At higher temperatures, the oxide thickness grows past 300 nm faster than measurements were conducted**

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Reaction Rate Constant Formulation

- Equate general empirical equation for thickening rate and ionic diffusion equation:

$$\frac{dL}{dt}=2K_1\exp\left(-\frac{W}{k_bT}\right)\sinh\left(\frac{K_2}{Lk_bT}\right)=V_{ion}J_{ion}\approx\underbrace{4V_{ion}a\nu C(L)}_{2K_1}\exp\left(-\frac{W}{k_bT}\right)\sinh\left(\frac{ZeV_ma}{Lk_bT}\right)\Big\}K_2$$

(Evans, 1960)

- Case of high temperature and moderate oxide thickness yields parabolic growth:

$$\frac{dL}{dt}\approx\frac{2K_1K_2}{Lk_bT}\exp\left(-\frac{W}{k_bT}\right)\Rightarrow\frac{1}{2}\left(L^2-L_0^2\right)=\left[\frac{2K_1K_2}{k_bT}\exp\left(-\frac{W}{k_bT}\right)\right](t-t_0)=k_p(t-t_0)$$

(Ritchie, 1984)

- Case of low temperature and small oxide thickness yields variation of inverse logarithmic:

$$\frac{d\left(\frac{K_2}{Lk_bT}\right)}{dt}=-\frac{K_1k_bT}{K_2}\left(\frac{K_2}{Lk_bT}\right)^2\sinh\left(\frac{K_2}{Lk_bT}\right)\exp\left(-\frac{W}{k_bT}\right)$$

$$\Rightarrow L_0^2\left[\ln\left(\frac{e^{K_2/L_0k_bT}-1}{e^{K_2/L_0k_bT}+1}\right)-\ln\left(\frac{e^{K_2/Lk_bT}-1}{e^{K_2/Lk_bT}+1}\right)\right]=\left[\frac{2K_1K_2}{k_bT}\exp\left(-\frac{W}{k_bT}\right)\right](t-t_0)=k_l(t-t_0)$$

(Ritchie, 1984)

- Both cases yield reaction rate constant:

$$k=\frac{a^5\nu C(L)ZeV_m}{k_bT}\exp\left(-\frac{W}{k_bT}\right)=\frac{0.641}{T}\left[\frac{m^2K}{s}\right]\exp\left(-\frac{14338[K]}{T}\right)$$

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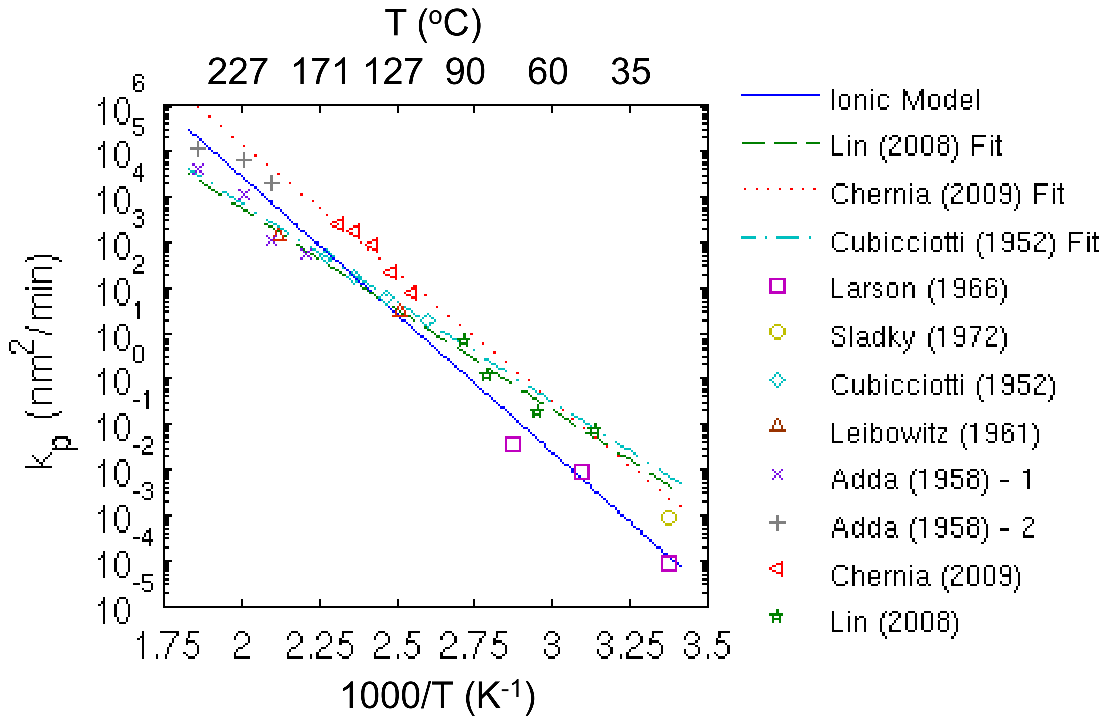
Reaction Rate Comparison



- Matches calculated values based on measurements well
- Fits data slightly better than empirical models
- Shows a slight non-linearity with temperature not discernable with empirical models

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Conclusions

- An ionic diffusion model was applied to the oxidation of uranium
- Ionic diffusion model predicts the transition between inverse logarithmic and parabolic growth trends
- The model agrees well with published data
- The theoretical reaction rate constant was derived
- Derived equation fits compiled data set as good as or better than empirically derived equations

Questions?