

# Thermodynamics and kinetics

- **Thermodynamic laws**
- **Half-cell reactions**
- **Kinetics**
- **Acid-Base**
- **Equilibrium calculations**
  - **Speciation calculation from complexation constants**
- **Provide review of concepts for applications to radiochemistry**

# Thermodynamic terms

- **Heat Capacity ( $C_p$ )**
    - Heat required to raise one gram of substance  $1\text{ }^\circ\text{C}$
    - Al;  $C_p = 0.895\text{ J/gK}$   
 $\rightarrow 1\text{ cal} = 4.184\text{ J}$
    - What is the heat needed to increase 40 g of Al by 10 K
    - $(0.895\text{ J/gK})(40\text{g})(10\text{K}) = 358\text{ J}$
  - **Exothermic**
    - Reaction produces heat (at  $25\text{ }^\circ\text{C}$ )
- $$\text{C(s)} + \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 393.76\text{ kJ}$$

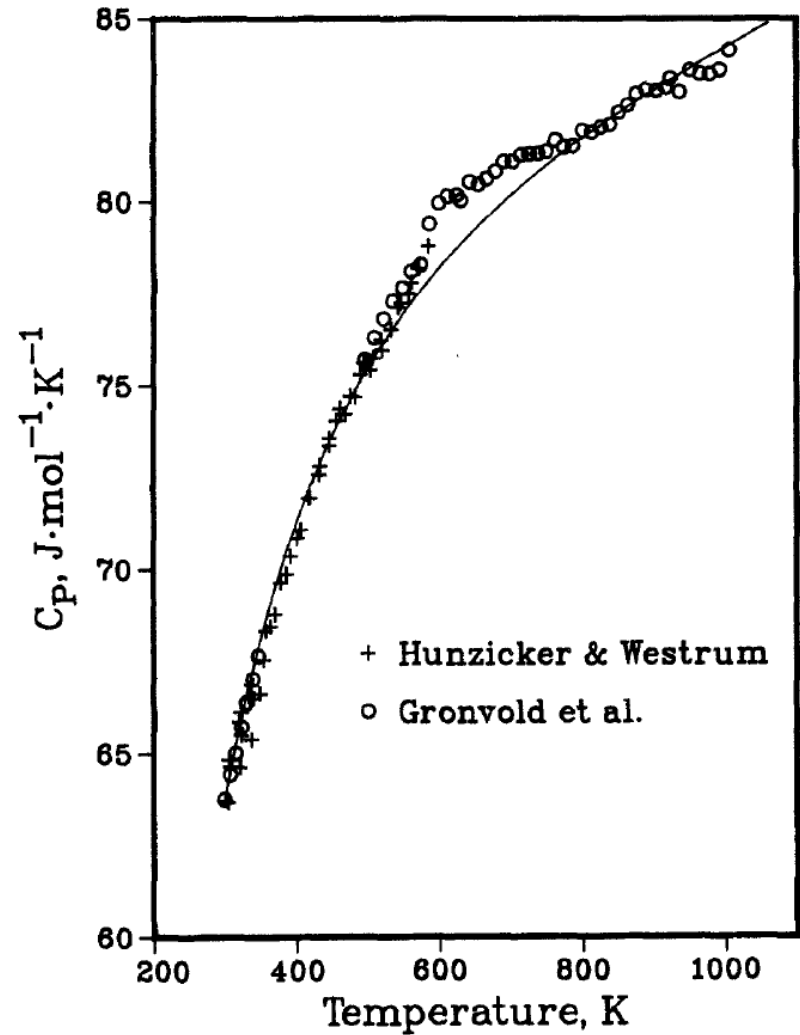


Fig. 2. Comparison of experimental and calculated heat capacity of  $\text{UO}_2$ .

# Thermodynamic terms

- **Endothermic**
  - **Reaction requires energy (at 25 °C)**  
$$2 \text{HgO} + 181.70 \text{ kJ} \rightleftharpoons 2 \text{Hg} + \text{O}_2$$
- **Enthalpy ( $\Delta H$ )**
- **Energy of a system (heat content)**
  - **Internal energy, volume, pressure**
  - **Accounts for energy transferred to environment by expansion or heating**
- $\Delta H = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$
- **Exothermic reactions, negative  $\Delta H$** 
  - **Negative  $\Delta H$  tend to be spontaneous**

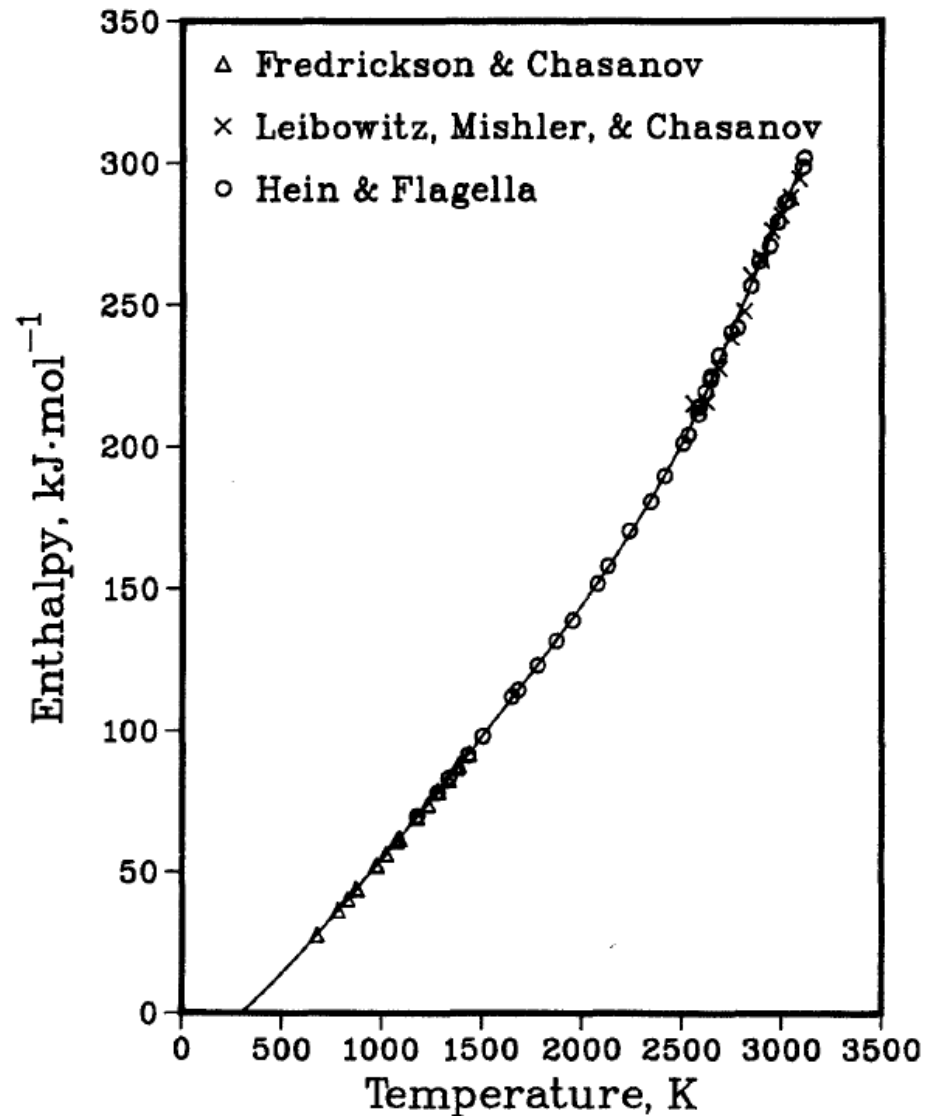
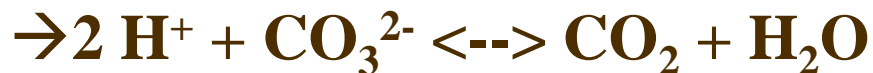


Fig. 1. Measured values of  $H_T^0 - H_{298.15}^0$  for  $\text{UO}_2$  and the equations to fit these data.

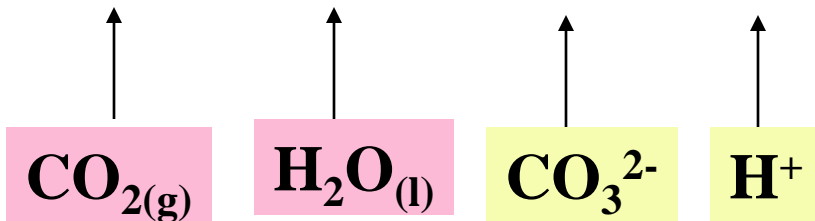
# Enthalpy ( $\Delta H$ )

- **Bond energies**
  - Can be used to estimate  $\Delta H$
  - $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$
  - $6(351.5) - 945.6 - 3(436.0) = -144.6 \text{ kJ/2 mole}$   
 $= -72.3 \text{ kJ/mole (actual -46.1 kJ/mol)}$
- **Aqueous Ions (use  $\Delta H$  values, databases available for different states)**

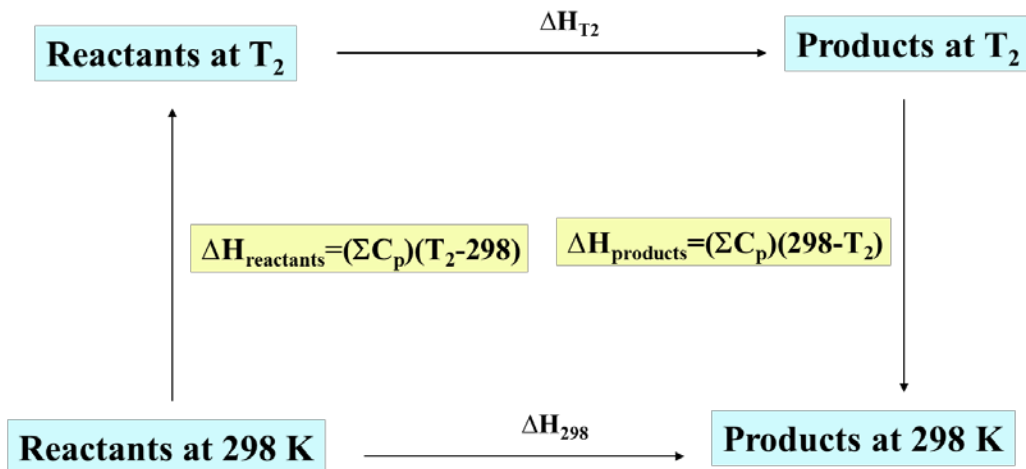
- $\Delta H_{\text{products}} - \Delta H_{\text{reactants}}$



$$\rightarrow -393.5 + (-285.8) - (-677.1 + 2(0)) = -2.2 \text{ kJ/mol}$$



# $\Delta H$ determination



$\Sigma C_p$  is the sum of the heat capacities

## Pure substance

CaC <sub>2</sub> O <sub>4</sub> (c)	-1360.6
CaF <sub>2</sub> (c)	-1219.6
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (c)	-4109.9
CaSO <sub>4</sub> (c,anhydrite)	-1434.1
Cd(g)	2623.54
Cd <sup>2+</sup> (g)	112.01
Cd(OH) <sub>2</sub> (c)	-560.7
CdS(c)	-161.9
Cl(g)	121.679
Cl-(g)	-233.13
ClO <sub>2</sub> (g)	102.5
Cu(g)	338.32
Cu <sub>2</sub> O(c,cuprite)	-168.6
CuO(c,tenorite)	-157.3
Cu(OH) <sub>2</sub> (c)	-449.8
Cu <sub>2</sub> S(c,chalcocite)	-79.5
CuS(c,covellite)	-53.1
F(g)	78.99
F-(g)	-255.39
Fe(g)	416.3

## Standard Solution

Ag+	105.579
AgCl <sub>2</sub> <sup>-</sup>	-245.2
Ag(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	-111.29
Ag(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	-1285.7
Al <sup>3+</sup>	-531
Br-	-121.55
BrO <sub>3</sub> <sup>-</sup>	-67.07
Ca <sup>2+</sup>	-542.83
Cd <sup>2+</sup>	-75.9
Cd(CN) <sub>4</sub> <sup>2-</sup>	428
Cd(NH <sub>3</sub> ) <sub>4</sub> <sup>2+</sup>	-450.2
Ce <sup>3+</sup>	-696.2
Ce <sup>4+</sup>	-537.2
CH <sub>3</sub> COO-	-486.01
CH <sub>3</sub> COOH	-485.76
CN-	150.6
CNS-	76.44
Cl-	-167.15
ClO <sub>4</sub> <sup>-</sup>	-129.33
CO <sub>2</sub>	-413.8
CO <sub>3</sub> <sup>2-</sup>	-677.14
H+	0
H <sub>2</sub> O <sub>2</sub>	-191.17
I-	-55.19
I <sub>3</sub> <sup>-</sup>	-51.5
IO <sub>3</sub> <sup>-</sup>	-221.3
K+	-252.38
NH <sub>3</sub>	-80.29
NH <sub>4</sub> <sup>+</sup>	-132.51
NO <sub>3</sub> <sup>-</sup>	-205
Na+	-240.12
OH-	-229.99
O <sub>2</sub>	-11.7
SO <sub>4</sub> <sup>2-</sup>	-909.27
Sn <sup>2+</sup>	-8.8
Sr <sup>2+</sup>	-545.8
Tl <sup>3+</sup>	196.6
U <sup>4+</sup>	-591.2
UO <sub>2</sub> <sup>2+</sup>	-1019.6

# Entropy ( $\Delta S$ ) and Gibbs Free Energy ( $\Delta G$ )

- Randomness of a system
  - increase in  $\Delta S$  tends to be spontaneous
- Enthalpy and Entropy can be used for evaluating the free energy of a system
- Gibbs Free Energy
  - $\Delta G = \Delta H - T\Delta S$
  - $\Delta G = -RT \ln K$ 
    - $K$  is equilibrium constant
    - Activity at unity

Compound	$\Delta G^\circ$ (kJ/mol) at 298.15 K
$H_2O$	-237.129
$OH^-_{(aq)}$	-157.244
$H^+_{(aq)}$	0



- What is the constant for the reaction?
  - Products-reactants
- At 298.15 K
  - $\Delta G(\text{rxn}) = 0 + -157.244 - (-273.129) = 79.9 \text{ kJ/mol}$
  - $\ln K = (79.9E3 / (-8.314 * 298.15)) = -32.2$ ;  $K = 1E-14$ ,  $K_w = [H^+][OH^-]$

# Thermodynamic Laws

- **1st law of thermodynamics**
  - **Energy is conserved in a system**
    - Can be changed or transferred
  - **Heat and work are energy transfer**
    - $\Delta E = q$  (heat absorbed) +  $w$  (work)
- **2nd law of thermodynamics**
  - **Reactions tend towards equilibrium**
    - Increase in entropy of a system
  - **Spontaneous reaction for  $-\Delta G$** 
    - $\Delta G = 0$ , system at equilibrium
- **3rd law of thermodynamics**
  - **Entropies of pure crystalline solids are zero at 0 K**
  - **Defines absolute zero**

# Redox Reactions: Faraday Laws

- In 1834 Faraday demonstrated quantities of chemicals which react at electrodes are directly proportional to charge passed through the cell
  - **96487 Coulomb (C) is the charge on 1 mole of electrons = 1F (faraday)**
- Cu(II) is electrolyzed by a current of 10 A (C/s) for 1 hr between Cu electrode
  - **How much Cu reacts**
- anode:  $\text{Cu} \leftrightarrow \text{Cu}^{2+} + 2\text{e}^-$
- cathode:  $\text{Cu}^{2+} + 2\text{e}^- \leftrightarrow \text{Cu}$ 
  - **Number of electrons**
    - 2 from redox reaction
    - \*  $(10\text{A})(3600 \text{ sec})/(96487 \text{ C/mol}) = 0.373 \text{ F}$
    - \*  $0.373 \text{ mole e}^- (1 \text{ mole Cu}/2 \text{ mole e}^-) = 0.186 \text{ mole Cu}$



# Half-cell potentials

- **Standard potential**
  - **Defined as  $\varepsilon^\circ=0.00$  V for**  
 $\rightarrow \text{H}_2(\text{atm}) \leftrightarrow 2 \text{H}^+ (1.000\text{M}) + 2\text{e}^-$
- **Other reactions compared to  $\text{H}_2$**
- **Cell reaction for**
  - **Zn and  $\text{Fe}^{3+/2+}$  at 1.0 M**
  - **Write as reduction potentials**  
 $\rightarrow \text{Fe}^{3+} + \text{e}^- \leftrightarrow \text{Fe}^{2+} \quad \varepsilon^\circ=0.77 \text{ V}$   
 $\rightarrow \text{Zn}^{2+} + 2\text{e}^- \leftrightarrow \text{Zn} \quad \varepsilon^\circ=-0.76 \text{ V}$
  - \* **Reduction potentials are available**  
<http://www.csudh.edu/oliver/chemdata/data-e.htm>
- **Reduction potential for  $\text{Fe}^{3+}$  is larger**
  - **$\text{Fe}^{3+}$  is reduced, Zn is oxidized in reaction**

# Half-Cell Potentials

- Overall balanced equation
  - $2\text{Fe}^{3+} + \text{Zn} \leftrightarrow 2\text{Fe}^{2+} + \text{Zn}^{2+}$   $\varepsilon^{\circ} = 0.77 + 0.76 = 1.53 \text{ V}$
- Use standard reduction potential
- Half cell potential values are not multiplied
  - $\varepsilon^{\circ}$  is for a mole of electrons

## Application of Gibbs Free Energy

- If work is done by a system
  - $\Delta G = -\varepsilon^{\circ}nF$  ( $n = e^{-}$ )
- Find  $\Delta G$  for Zn/Cu cell at 1.0 M
  - $\text{Cu}^{2+} + \text{Zn} \leftrightarrow \text{Cu} + \text{Zn}^{2+}$   $\varepsilon^{\circ} = 1.10 \text{ V}$
  - 2 moles of electrons ( $n=2$ )
    - $\Delta G = -2(96487\text{C/mole } e^{-})(1.10\text{V})$
    - $\Delta G = -212 \text{ kJ/mol}$

# Nernst Equation

- **Compensated for non unit activity (not 1 M)**
- **Relationship between cell potential and activities**
- **$aA + bB + ne^- \rightleftharpoons cC + dD$**

$$\varepsilon = \varepsilon^\circ - \frac{2.30RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- **At 298K  $2.3RT/F = 0.0592$**
- **What is potential of an electrode of Zn(s) and 0.01 M  $Zn^{2+}$**
- **$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad \varepsilon^\circ = -0.763 \text{ V}$**
- **activity of metal is 1**

$$\varepsilon = -0.763 - \frac{0.0592}{2} \log \frac{1}{0.01} = -0.822 \text{ V}$$

# Kinetics and Equilibrium

- Kinetics and equilibrium important concepts in examining and describing chemistry
  - Identify factors which determine rates of reactions
    - Temperature, pressure, reactants, mixing
  - Describe how to control reactions
  - Explain why reactions fail to go to completion
  - Identify conditions which prevail at equilibrium
- Rate of reaction
  - Can depend upon conditions
- Free energy does not dictate kinetics
  - Thermodynamics can be decoupled from kinetics
- Thermodynamics concerned with difference between initial and final state
- Kinetics account for reaction rates and describe the conditions and mechanisms of reactions
  - difficult to describe from first principles
- General factors effecting kinetics
  - Nature of reactants
  - Effective concentrations
  - Temperature
  - Presence of catalysts
  - Number of steps

# Nature of Reactants

- **Ions react rapidly**
  - **$\text{Ag}^+ + \text{Cl}^- \rightleftharpoons \text{AgCl(s)}$  Very fast**
- **Reactions which involve bond breaking are slower**
  - **$\text{NH}_4^+ + \text{OCN}^- \rightleftharpoons \text{OC(NH}_2)_2$**
- **Redox reactions in solutions are slow**
  - **Transfer of electrons are faster than those of atomic transfer**
- **Reactions between covalently bonded molecules are slow**
  - **$2 \text{HI(g)} \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$**
- **Structure**
  - **Phosphorus (white and red)**
- **Surface area**
  - **larger surface area increases reaction**
- **Mixing increases interaction**

# Rate Law

- Concentration of reactant or product per unit time
- Effect of initial concentration on rate can be examined
  - $\text{rate} = k[A]^x[B]^y$
  - $\text{rate order} = x + y$
  - knowledge of order can help control reaction
  - rate must be experimentally determined

Rate= $k[A]^n$ ; A=conc. at time t,  $A_0$ =initial conc., X=product conc.

**Order**   **rate equation**

**0**       $[A_0]-[A]=kt, [X]=kt$       **k**  
mole/L sec

**1**       $\ln[A_0]-\ln[A]=kt, \ln[A_0]-\ln([A_0]-[X])=kt$       **1/sec**

**2**       $\frac{1}{[A]} - \frac{1}{[A_0]} = kt$        $\frac{1}{[A_0]-[X]} - \frac{1}{[A_0]} = kt$       **L/mole sec**

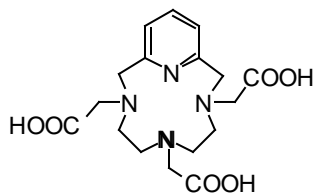
**3**       $\frac{1}{[A]^2} - \frac{1}{[A_0]^2} = \frac{kt}{2}$        $\frac{1}{([A_0]-[X])^2} - \frac{1}{[A_0]^2} = \frac{kt}{2}$       **L<sup>2</sup>/mole<sup>2</sup> sec**  
2-14

# Rate Law

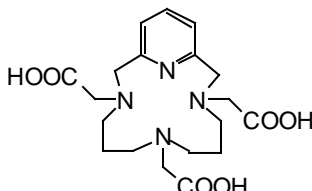
- **Temperature**
  - **Reactions tend to double for every 10 °C**
- **Catalysts**
  - **Accelerate reaction but are not used**
    - Pt surface
  - **Thermodynamically drive, catalysts drive kinetics**
  - **If not thermodynamically favored, catalysts will not drive reaction**
- **Autocatalytic reactions form products which act as catalysts**

# Complexation Kinetics

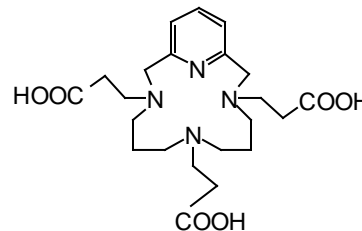
## Uranium and cobalt with pyridine based ligands



**111Py12**



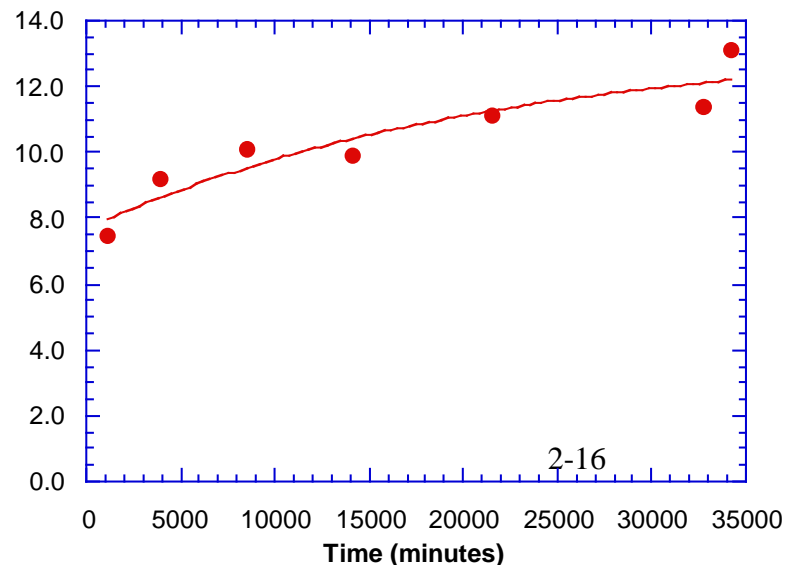
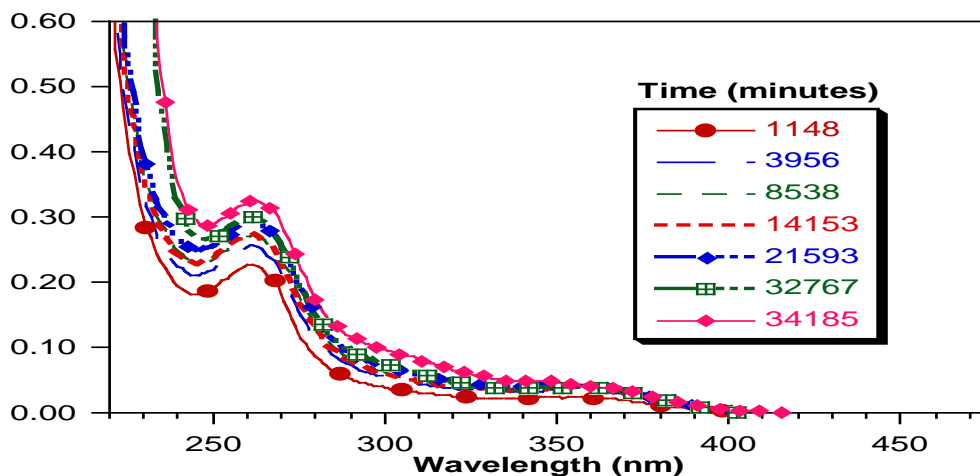
**111Py14**



**222Py14**

Examine complexation by UV-Visible spectroscopy

Absorbance sum from 250 nm to 325 nm for 111Py12 and uranium at pH 4





# Kinetic Data Evaluation

Evaluation of change in absorbance

$$\int_{\lambda_1}^{\lambda_2} \text{Abs}_t = \int_{\lambda_1}^{\lambda_2} \text{Abs}_o + \int_{\lambda_1}^{\lambda_2} \Delta \text{Abs}_{\text{eq}} (1 - e^{-kt})$$

Evaluation of absorbance and kinetic data for 111Py12 and 111Py14 with uranium at pH 4. The concentration of ligand and uranium is  $50 \times 10^{-6}$  mol/L.

Ligand	Abs <sub>o</sub>	$\Delta \text{Abs}_{\text{eq}}$	k (min <sup>-1</sup> )	95% Equilibrium Time (min)
111Py12	7.86±0.82	5.66±1.28	4.65±0.47×10 <sup>-5</sup>	6.44±0.65×10 <sup>4</sup>
111Py14	4.82±1.70	7.06±5.76	4.24±0.80×10 <sup>-5</sup>	7.07±1.33×10 <sup>4</sup>

# Acid-Base Equilibria

- **Brønsted Theory of Acids and Bases**

- **Acid**

→ Substance which donates a proton

- **Base**

→ Accepts proton from another substance



- Remainder of acid is base
- Complete reaction is proton exchange between sets
- Extent of exchange based on strength
- Water can act as solvent and reactant

	Conjugate Acid	Conjugate Base	
	$\text{HClO}_4$	$\text{ClO}_4^-$	
	$\text{H}_2\text{SO}_4$	$\text{SO}_4^{2-}$	
	$\text{HCl}$	$\text{Cl}^-$	
	$\text{H}_3\text{O}^+$	$\text{H}_2\text{O}$	
	$\text{H}_2\text{SO}_3$	$\text{HSO}_3^-$	
	$\text{HF}$	$\text{F}^-$	
	$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$	
	$\text{HSO}_3^-$	$\text{SO}_3^{2-}$	
	$\text{H}_2\text{S}$	$\text{HS}^-$	
	$\text{NH}_4^+$	$\text{NH}_3$	
	$\text{HCO}_3^-$	$\text{CO}_3^{2-}$	
	$\text{H}_2\text{O}$	$\text{OH}^-$	
	$\text{HS}^-$	$\text{S}^{2-}$	
	$\text{OH}^-$	$\text{O}^{2-}$	
	$\text{H}_2$	$\text{H}^-$	

# Dissociation Constants

- Equilibrium expression for the behavior of acid



Water concentration is constant

$$K = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}][\text{H}_2\text{O}]}$$

$$\text{p}K_a = -\log K_a$$

$$K_a = K[\text{H}_2\text{O}] = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

- Can also be measured for base

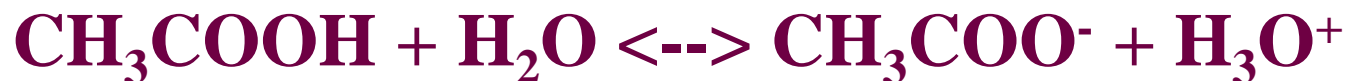
Constants are characteristic of the particular acid or base

Acid	Formula	$K_a$
Acetic	$\text{HC}_2\text{H}_3\text{O}_2$	$1.8\text{E-}5$
Carbonic	$\text{H}_2\text{CO}_3$	$3.5\text{E-}7$
	$\text{HCO}_3^-$	$5\text{E-}11$
Phosphoric	$\text{H}_3\text{PO}_4$	$7.5\text{E-}3$
	$\text{H}_2\text{PO}_4^-$	$6.2\text{E-}8$
	$\text{HPO}_4^{2-}$	$4.8\text{E-}13$
Oxalic	$\text{H}_2\text{C}_2\text{O}_4$	$5.9\text{E-}2$
	$\text{HC}_2\text{O}_4^-$	$6.4\text{E-}5$

# Calculations

- 1 L of 0.1 M acetic acid has pH = 2.87

What is the pK<sub>a</sub> for acetic acid



$$[\text{CH}_3\text{COO}^-] = [\text{H}_3\text{O}^+] = 10^{-2.87}$$

$$K_a = K[\text{H}_2\text{O}] = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

$$K_a = \frac{10^{-(2 \times 2.87)}}{0.1 - 10^{-2.87}} = 1.84 \times 10^{-5}$$

$$\text{p}K_a = 4.73$$

# Buffers: Weak acids and bases

- Weak acid or weak base with conjugate salt
- Acetate as example
  - Acetic acid,  $\text{CH}_3\text{COONa}$
  - $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$   
large quantity   huge quantity   large quantity   small quantity
  - **If acid is added**
    - hydronium reacts with acetate ion, forming undissociated acetic acid
  - **If base is added**
    - Hydroxide reacts with hydronium, acetic acid dissociates to replace reacted hydronium ion

# Buffer Solutions

- Buffers can be made over a large pH range
- Can be useful in controlling reactions and separations
  - **Buffer range**
    - Effective range of buffer
    - Determined by  $pK_a$  of acid or  $pK_b$  of base



$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

$$[\text{H}_3\text{O}^+] = \frac{K_a [\text{HA}]}{[\text{A}^-]}$$

Write as pH

$$\text{pH} = \text{p}K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

- The best buffer is when  $[\text{HA}] = [\text{A}^-]$ 
  - largest buffer range for the conditions
  - $\text{pH} = \text{p}K_a - \log 1$
- For a buffer the range is determined by  $[\text{HA}]/[\text{A}^-]$ 
  - $[\text{HA}]/[\text{A}^-]$  from 0.1 to 10
  - Buffer pH range =  $\text{p}K_a \pm 1$
  - Higher buffer concentration increase durability

# Hydrolysis Constants

- **Reaction of water with metal ion**
  - **Common reaction**
  - **Environmentally important**
  - **Strength dependent upon metal ion oxidation state**
- **$2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$** 
  - **Water concentration remains constant, so for water:**
  - **$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1\text{E-}14$  at  $25^\circ\text{C}$**
- **Metal ions can form hydroxide complexes with water**
- **$\text{M}^{z+} + \text{H}_2\text{O} \rightleftharpoons \text{MOH}^{z-1+} + \text{H}^+$**
- **Constants are listed for many metal ion with different hydroxide amounts**
  - **Database at:**  
**<http://www.escholarship.org/uc/item/9427347g>**

# Thermodynamics and kinetics

- **Thermodynamic laws**
- **Half-cell reactions**
- **Kinetics**
- **Acid-Base**
- **Equilibrium calculations**
  - **Speciation calculation from complexation constants**
- **Provide review of concepts for applications to radiochemistry**



# Equilibrium

- Reactions proceed in the forward and reverse direction simultaneously
  - $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$
  - Initially contains nitrogen and hydrogen
    - Forward rate decreases as concentration (pressure) decreases
    - Ammonia production increase reverse rate
    - Eventually, forward rate is equal to reverse rate
    - No net change in concentration
- Reaction still occurring at equilibrium
  - Forward and backward rates equal
- Some reactions have a negligible reverse rate
  - Proceeds in forward direction
  - Reaction is said to go to completion

# Equilibrium: Le Châtelier's Principle

- At equilibrium, no further change as long as external conditions are constant
- Change in external conditions can change equilibrium
  - A stressed system at equilibrium will shift to reduce stress
    - concentration, pressure, temperature
- $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3 + 22 \text{ kcal}$ 
  - What is the shift due to
    - Increased temperature?
    - Increased  $\text{N}_2$ ?
    - Reduction of reactor vessel volume?

# Equilibrium Constants

- For a reaction
  - $aA + bB \rightleftharpoons cC + dD$
- At equilibrium the ratio of the product to reactants is a constant
  - By convention, constants are expressed as products over reactants
  - Constant can change with conditions
    - Temperature, ionic strength
    - Conditions should explicitly provided

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- Strictly speaking, activities, not concentrations should be used

$$K = \frac{\gamma_C [C]^c \gamma_D [D]^d}{\gamma_A [A]^a \gamma_B [B]^b}$$

- At low concentration, activities are assumed to be 1
- constant can be evaluated at a number of ionic strengths and the overall activities fit to equations

# Activities

- Debye-Hückel (Physik Z., 24, 185 (1923))

$Z_A$  = charge of species A

$\mu$  = molal ionic strength

$R_A$  = hydrated ionic radius in Å (from 3 to 11)

$$-\log \gamma_A = \frac{0.5085 Z_a^2 \sqrt{\mu}}{1 + 0.3281 R_A \sqrt{\mu}}$$

First estimation of activity

- Debye-Hückel term can be written as:

$$D = \frac{0.5107 \sqrt{\mu}}{1 + 1.5 \sqrt{\mu}}$$

- Specific ion interaction theory

- Uses and extends Debye-Hückel

→ long range Debye-Hückel

→ Short range ion interaction term

$\epsilon_{ij}$  = specific ion interaction term

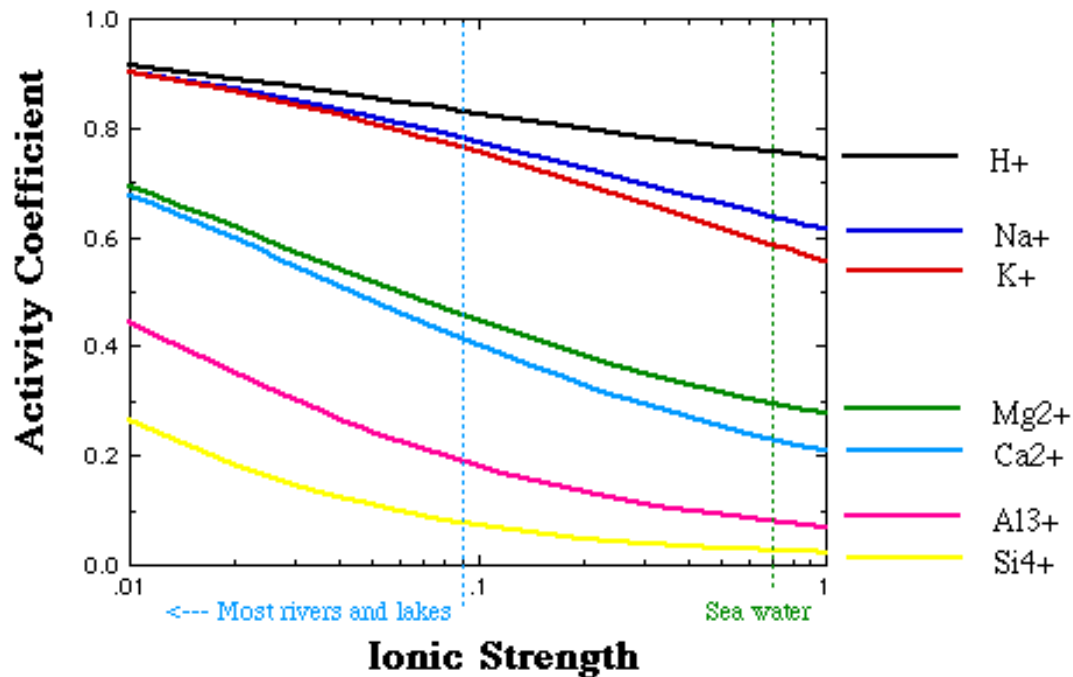
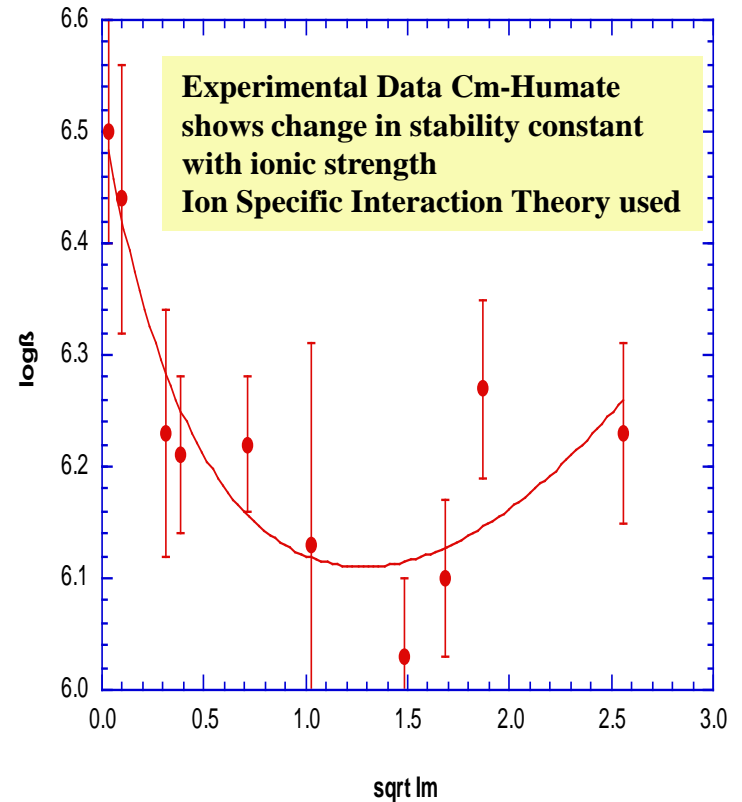
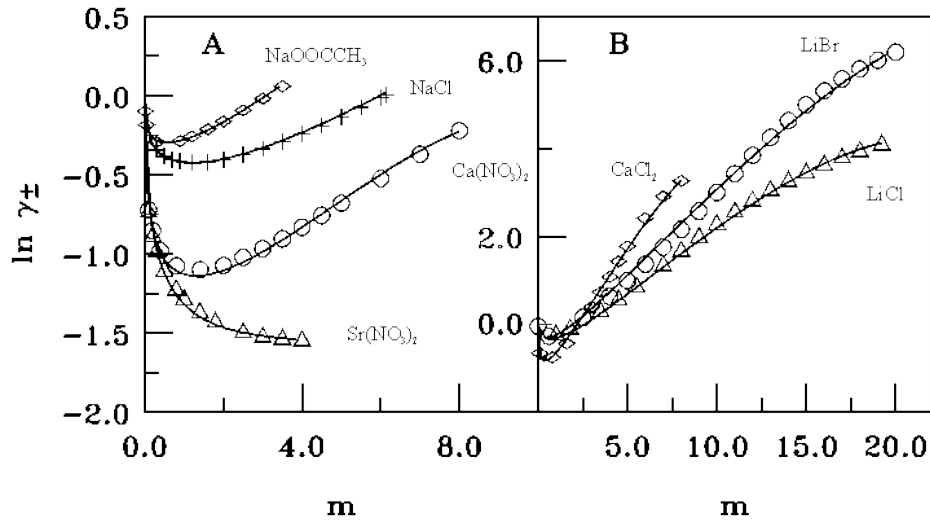
$$\log \gamma_i = -Z_i^2 D + \epsilon_{ij} \mu$$

- Pitzer

$$\log \beta(\mu) = \log \beta(0) + \Delta Z_i^2 D - \Delta \epsilon_{ij} \mu$$

- Binary (3) and Ternary (2) interaction parameters
  - [http://en.wikipedia.org/wiki/Pitzer\\_equations](http://en.wikipedia.org/wiki/Pitzer_equations)

# Activity data



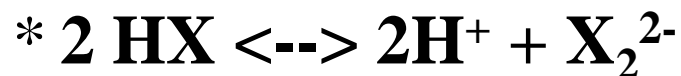
Debye Huckel estimates of activity for common clay ions in chloride solutions of various ionic strength at 15° C

# Constants

- Constants can be listed by different names

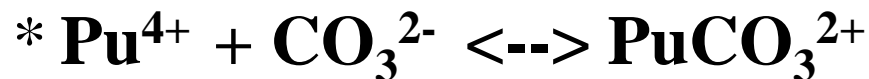
- **Equilibrium constants (K)**

- Reactions involving bond breaking



- **Stability constants ( $\beta$ ), Formation constants (K)**

- Metal-ligand complexation



- \* Ligand is written in deprotonated form

- **Conditional Constants**

- An experimental condition is written into equation



- ✂ Constant can vary with concentration, pH

- Must look at equation!

# Using Equilibrium Constants

- Constants and balanced equation can be used to evaluate concentrations at equilibrium

$$K = \frac{[H^+]^2[X_2^{2-}]}{[HX]^2}$$



- $K=4\text{E}-15$

- If you have one mole of HX initially, what are the concentration of all species at equilibrium?

- Try to write species in terms of one unknown

→ Start with species of lowest concentration

→  $[X_2^{2-}] = x$ ,  $[H^+] = 2x$ ,  $[HX] = 1 - 2x$ ,

- Since  $K$  is small,  $x$  must be small

→ Use the approximation  $1 - 2x \approx 1$

→ Substitute  $x$  and rearrange  $K$

$$K = \frac{[x][2x]^2}{[1-2x]^2} = \frac{[x][2x]^2}{1} = 4x^3$$

- Solve for  $x$

- $[X_2^{2-}] = 1\text{E}-5$ ,  $[H^+] = 2\text{E}-5$

$$4\text{E} - 15 = 4x^3$$

$$1\text{E} - 15 = x^3$$

$$x = 1\text{E} - 5$$

# Realistic Case

- Metal ion of interest may be in complicated environment
  - May different species to consider simultaneously
- Consider uranium in an aquifer
  - Example is still a simplified case
- Species to consider in this example include
  - free metal ion:  $\text{UO}_2^{2+}$
  - hydroxides:  $(\text{UO}_2)_x(\text{OH})_y$
  - carbonates:  $\text{UO}_2\text{CO}_3$
  - humates:  $\text{UO}_2\text{HA}(\text{II})$ ,  $\text{UO}_2\text{OHHA}(\text{I})$
- Need to get stability constants for all species
  - Example:  $\text{UO}_2^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{UO}_2\text{CO}_3$
- Know or find conditions
  - Total uranium, total carbonate, pH, total humic concentration



# Stability constants for selected uranium species at 0.1 M ionic strength

<u>Species</u>	<u>log<math>\beta</math></u>
UO <sub>2</sub> OH <sup>+</sup>	8.5
UO <sub>2</sub> (OH) <sub>2</sub>	17.3
UO <sub>2</sub> (OH) <sub>3</sub> <sup>-</sup>	22.6
UO <sub>2</sub> (OH) <sub>4</sub> <sup>2-</sup>	23.1
(UO <sub>2</sub> ) <sub>2</sub> OH <sup>3+</sup>	11.0
(UO <sub>2</sub> ) <sub>2</sub> (OH) <sup>2+</sup>	22.0
UO <sub>2</sub> CO <sub>3</sub>	8.87
UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup>	16.07
UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>4-</sup>	21.60
UO <sub>2</sub> HA(II)	6.16
UO <sub>2</sub> (OH)HA(I)	14.7±0.5

Other species may need to be considered. If total uranium concentration is low enough, binary or tertiary species can be excluded.

# Equations

- Write concentrations in terms of species
- Total uranium in solution,  $[U]_{\text{tot}}$ , is the sum of all solution phase uranium species
  - $[U]_{\text{tot}} = \text{UO}_2^{2+}{}_{\text{free}} + \text{U-carb} + \text{U-hydroxide} + \text{U-humate}$
  - $[\text{CO}_3^{2-}]_{\text{free}} = f(\text{pH})$ 
    - From Henry's constant for  $\text{CO}_2$  and  $K_1$  and  $K_2$  from  $\text{CO}_3\text{H}_2$
    - $\log[\text{CO}_3^{2-}]_{\text{free}} = \log K_{\text{H}} K_1 K_2 + \log(\text{pCO}_2) - 2\log[\text{H}^+]$ 
      - \* With  $-\log[\text{H}^+] = \text{pH}$
      - $\log[\text{CO}_3^{2-}]_{\text{free}} = \log K_{\text{H}} K_1 K_2 + \log(\text{pCO}_2) + 2\text{pH}$
  - $[\text{OH}^-] = f(\text{pH})$
  - $[\text{HA}]_{\text{tot}} = \text{UO}_2\text{HA} + \text{UO}_2\text{OHHA} + \text{HA}_{\text{free}}$

# Uranium speciation equations

- Write the species in terms of metal, ligands, and constants
  - Generalized equation, with free uranium, free ligand A and free ligand B

$$\beta_{xab} = \frac{[(UO_2)_x A_a B_b]}{[UO_2^{2+}]^x [A]^a [B]^b}$$

$$[(UO_2)_x A_a B_b] = \beta_{xab} [UO_2^{2+}]^x [A]^a [B]^b$$

- Provide free ligand and metal concentrations as pX value
    - $pX = -\log[X]_{\text{free}}$
    - $pUO_2^{2+} = -\log[UO_2^{2+}]$
- Rearrange equation with pX values
  - Include  $-\log\beta_{xab}$ , treat as pX term
  - $[(UO_2)_x A_a B_b] = 10^{-(xpUO_2 + apA + bpB - \log_{xab})}$
- Specific example for  $(UO_2)_2(OH)_2^{2+}$ 
  - $[(UO_2)_2(OH)_2^{2+}] = 10^{-(2pUO_2 + 2pOH - 22.0)}$
- Set up equations where total solution uranium concentration is sum of all species and solve for known terms

**Speciation calculations:**  
**Excel spreadsheets**  
**CHES Program**

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	A	B	C	D	E	F	G	H	I	J	K	L	
1			pka1co3	pka2co3	logksum		pKw	UO2HA	UO2OHHA	UO2OH	UO2(OH)2	UO2(OH)3	
2			6.30	10.25	-17.55		13.92	logB1100	logB11-10	logK10-10	logK10-20	logk10-30	
3								6.16	14.70	-5.40	-10.50	-19.20	
4													
5	pH	pH	pp CO2	[UO2]t M	[HA(II)]tot	p[CO3]f	pHA(II)f	pM	[UHA(II)]	[UOHHA(I)]	[UOH]	[U(OH)2]	[U(OH)3]
6	1.0	1.0	3.50E-04	2.00E-07	3.00E-04	19.01	4.00	7.00	1.45E-05	1.21E-09	3.98E-12	3.16E-16	6.31E-24
7	1.1	1.1	3.50E-04	2.00E-07	3.00E-04	18.81	4.00	7.00	1.45E-05	1.52E-09	5.01E-12	5.01E-16	1.26E-23
8	1.2	1.2	3.50E-04	2.00E-07	3.00E-04	18.61	4.00	7.00	1.45E-05	1.91E-09	6.31E-12	7.94E-16	2.51E-23
9	1.3	1.3	3.50E-04	2.00E-07	3.00E-04	18.41	4.00	7.00	1.45E-05	2.40E-09	7.94E-12	1.26E-15	5.01E-23
10	1.4	1.4	3.50E-04	2.00E-07	3.00E-04	18.21	4.00	7.00	1.45E-05	3.03E-09	1.00E-11	2.00E-15	1.00E-22
11	1.5	1.5	3.50E-04	2.00E-07	3.00E-04	18.01	4.00	7.00	1.45E-05	3.81E-09	1.26E-11	3.16E-15	2.00E-22
12	1.6	1.6	3.50E-04	2.00E-07	3.00E-04	17.81	4.00	7.00	1.45E-05	4.80E-09	1.58E-11	5.01E-15	3.98E-22
13	1.7	1.7	3.50E-04	2.00E-07	3.00E-04	17.61	4.00	7.00	1.45E-05	6.04E-09	2.00E-11	7.94E-15	7.94E-22
14	1.8	1.8	3.50E-04	2.00E-07	3.00E-04	17.41	4.00	7.00	1.45E-05	7.60E-09	2.51E-11	1.26E-14	1.58E-21
15	1.9	1.9	3.50E-04	2.00E-07	3.00E-04	17.21	4.00	7.00	1.45E-05	9.57E-09	3.16E-11	2.00E-14	3.16E-21
16	2.0	2.0	3.50E-04	2.00E-07	3.00E-04	17.01	4.00	7.00	1.45E-05	1.21E-08	3.98E-11	3.16E-14	6.31E-21
17	2.1	2.1	3.50E-04	2.00E-07	3.00E-04	16.81	4.00	7.00	1.45E-05	1.52E-08	5.01E-11	5.01E-14	1.26E-20
18	2.2	2.2	3.50E-04	2.00E-07	3.00E-04	16.61	4.00	7.00	1.45E-05	1.91E-08	6.31E-11	7.94E-14	2.51E-20
19	2.3	2.3	3.50E-04	2.00E-07	3.00E-04	16.41	4.00	7.00	1.45E-05	2.40E-08	7.94E-11	1.26E-13	5.01E-20

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	A	B	C	D	E	F	G	H	I	J	K	L	
1			pka1co3	pka2co3	logksum		pKw	UO2HA	UO2OHHA	UO2OH	UO2(OH)2	UO2(OH)3	
2			6.30	10.25	-17.55		13.92	logB1100	logB11-10	logK10-10	logK10-20	logk10-30	
3								6.16	14.70	-5.40	-10.50	-19.20	
4													
5	pH	pH	pp CO2	[UO2]t M	[HA(II)]tot	p[CO3]f	pHA(II)f	pM	[UHA(II)]	[UOHHA(I)]	[UOH]	[U(OH)2]	[U(OH)3]
6	1.0	1.0	3.50E-04	2.00E-07	3.00E-04	19.01	4.00	7.00	1.45E-05	1.21E-09	3.98E-12	3.16E-16	6.31E-24
7	1.1	1.1	3.50E-04	2.00E-07	3.00E-04	18.81	4.00	7.00	1.45E-05	1.52E-09	5.01E-12	5.01E-16	1.26E-23
8	1.2	1.2	3.50E-04	2.00E-07	3.00E-04	18.61	4.00	7.00	1.45E-05	1.91E-09	6.31E-12	7.94E-16	2.51E-23
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11	1.5	1.5	3.50E-04	2.00E-07	3.00E-04	18.01	4.00	7.00	1.45E-05	3.81E-09	1.26E-11	3.16E-15	2.00E-22
12	1.6	1.6	3.50E-04	2.00E-07	3.00E-04	17.81	4.00	7.00	1.45E-05	4.80E-09	1.58E-11	5.01E-15	3.98E-22
13	1.7	1.7	3.50E-04	2.00E-07	3.00E-04	17.61	4.00	7.00	1.45E-05	6.04E-09	2.00E-11	7.94E-15	7.94E-22
14	1.8	1.8	3.50E-04	2.00E-07	3.00E-04	17.41	4.00	7.00	1.45E-05	7.60E-09	2.51E-11	1.26E-14	1.58E-21
15	1.9	1.9	3.50E-04	2.00E-07	3.00E-04	17.21	4.00	7.00	1.45E-05	9.57E-09	3.16E-11	2.00E-14	3.16E-21
16	2.0	2.0	3.50E-04	2.00E-07	3.00E-04	17.01	4.00	7.00	1.45E-05	1.21E-08	3.98E-11	3.16E-14	6.31E-21
17	2.1	2.1	3.50E-04	2.00E-07	3.00E-04	16.81	4.00	7.00	1.45E-05	1.52E-08	5.01E-11	5.01E-14	1.26E-20
18	2.2	2.2	3.50E-04	2.00E-07	3.00E-04	16.61	4.00	7.00	1.45E-05	1.91E-08	6.31E-11	7.94E-14	2.51E-20
19	2.3	2.3	3.50E-04	2.00E-07	3.00E-04	16.41	4.00	7.00	1.45E-05	2.40E-08	7.94E-11	1.26E-13	5.01E-20

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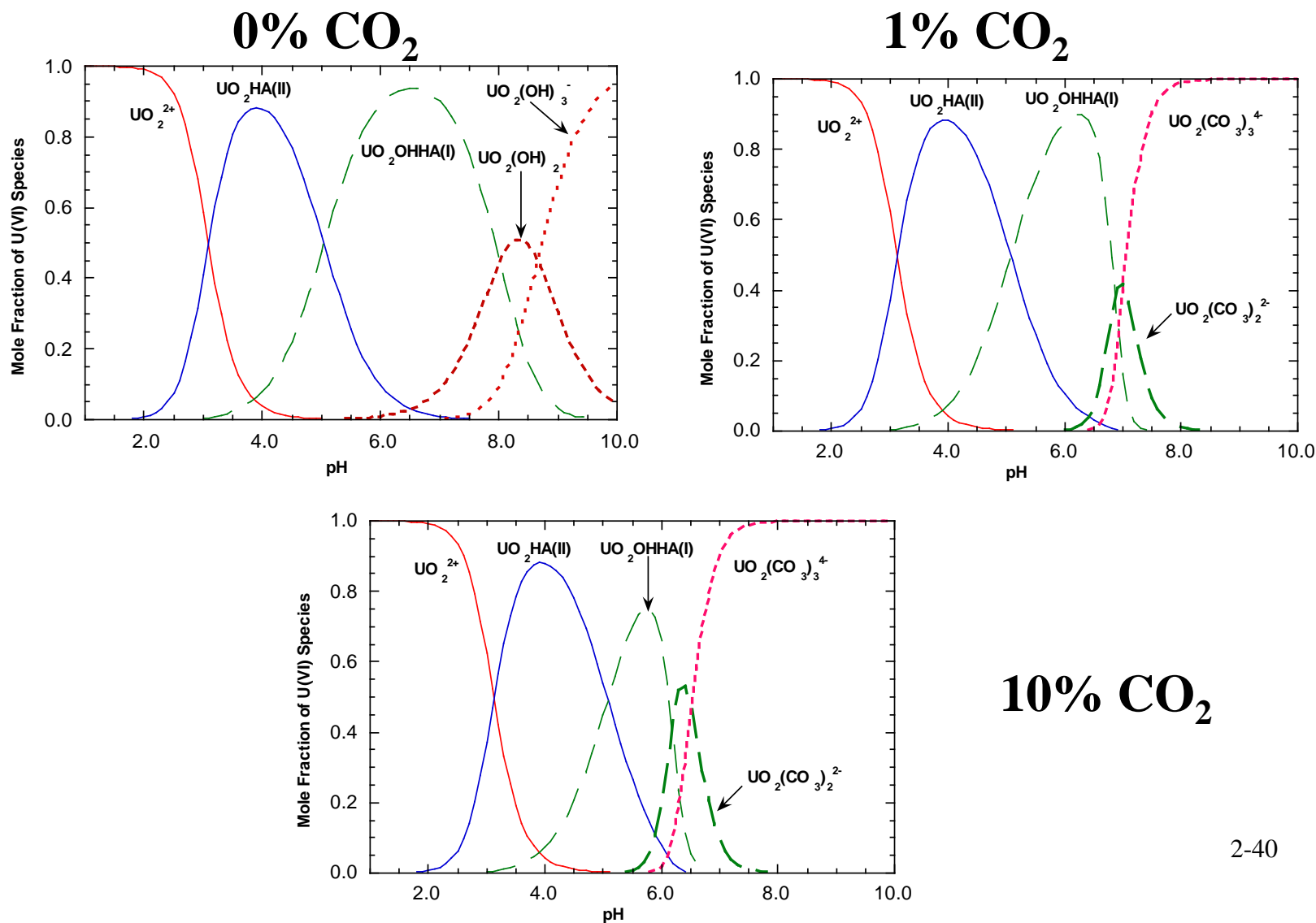
	A	B	C	D	E	F	G	H	I	J	K	L	M
9	nH	[Fe]	[Oxalate]	pM	pL	FeL	FeOH	Fe(OH)2	Fe(OH)3	Fe(OH)4	Fe2(OH)2	Fe3(OH)4	LH2
1													
2	K						-2.19	-5.67	-12	-21.6	-2.95	-6.3	
3	β	pkw				7.65	11.73	22.17	29.76	34.08	24.89	49.38	4.8
4	Fe	13.92				1	1	1	1	1	2	3	0
5	Oxalate					1	0	0	0	0	0	0	1
6	H					0	0	0	0	0	0	0	2
7	OH					0	1	2	3	4	2	4	0
8													
9	pH	[Fe]	[Oxalate]	pM	pL	FeL	FeOH	Fe(OH)2	Fe(OH)3	Fe(OH)4	Fe2(OH)2	Fe3(OH)4	LH2
10	1	3.00E-05	4.50E-05	4.89	7.56	1.61E-05	8.40E-07	2.78E-09	1.30E-14	3.27E-23	1.90E-11	1.10E-17	1.75E-05
11	1.1	3.00E-05	4.50E-05	4.96	7.43	1.82E-05	8.90E-07	3.71E-09	2.18E-14	6.91E-23	2.13E-11	1.65E-17	1.48E-05
12	1.2	3.00E-05	4.50E-05	5.04	7.31	2.00E-05	9.31E-07	4.88E-09	3.62E-14	1.44E-22	2.33E-11	2.38E-17	1.23E-05
13	1.3	3.00E-05	4.50E-05	5.13	7.19	2.15E-05	9.64E-07	6.37E-09	5.94E-14	2.98E-22	2.50E-11	3.33E-17	1.02E-05
14	1.4	3.00E-05	4.50E-05	5.21	7.08	2.29E-05	9.90E-07	8.23E-09	9.67E-14	6.10E-22	2.64E-11	4.54E-17	8.40E-06
15	1.5	3.00E-05	4.50E-05	5.31	6.96	2.40E-05	1.01E-06	1.06E-08	1.57E-13	1.24E-21	2.75E-11	6.08E-17	6.86E-06
16	1.6	3.00E-05	4.50E-05	5.40	6.85	2.50E-05	1.03E-06	1.35E-08	2.52E-13	2.52E-21	2.84E-11	8.02E-17	5.57E-06
17	1.7	3.00E-05	4.50E-05	5.49	6.75	2.57E-05	1.04E-06	1.72E-08	4.04E-13	5.09E-21	2.91E-11	1.05E-16	4.51E-06
18	1.8	3.00E-05	4.50E-05	5.59	6.64	2.64E-05	1.05E-06	2.19E-08	6.47E-13	1.03E-20	2.96E-11	1.36E-16	3.63E-06

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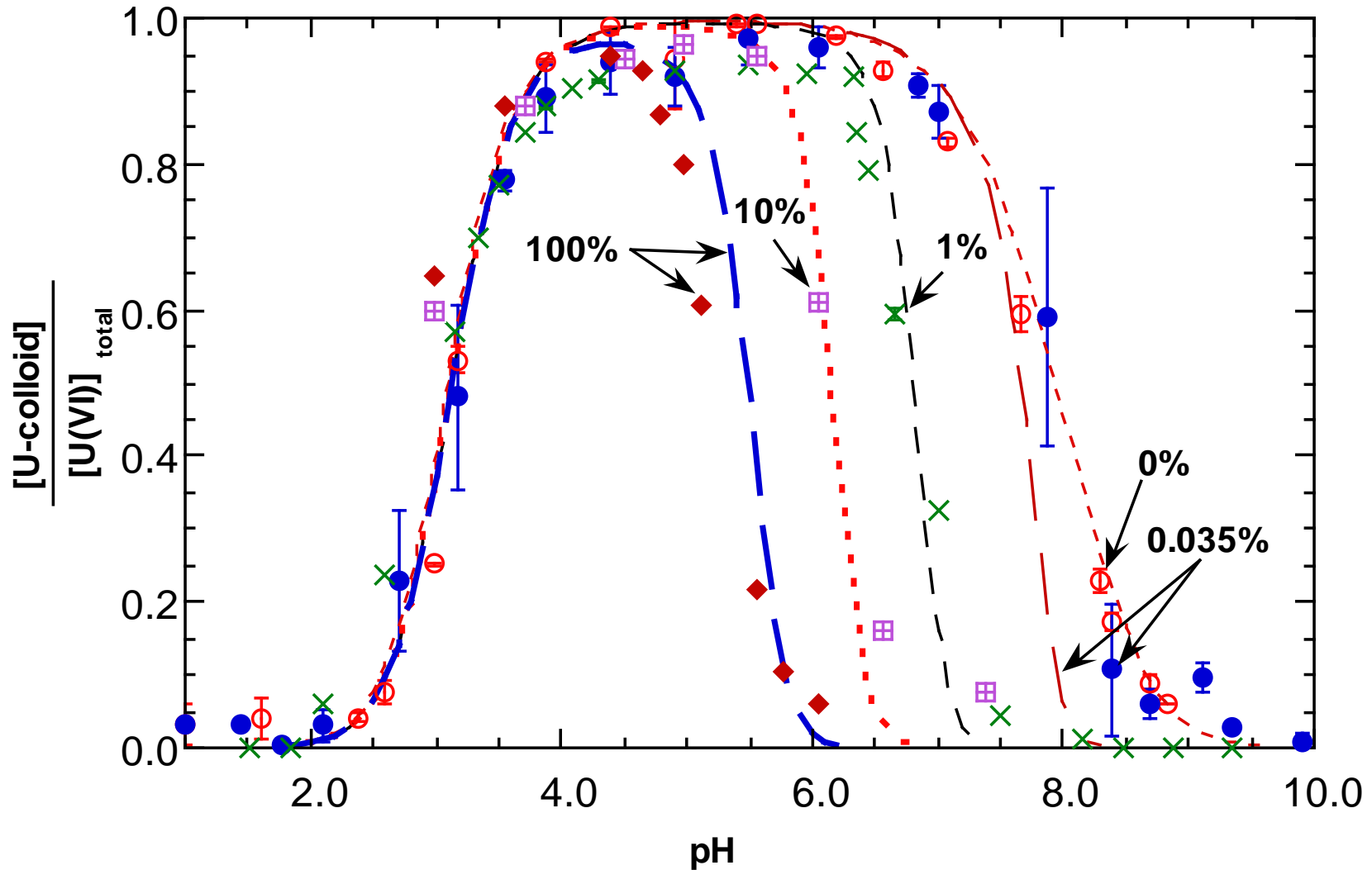
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# U speciation with different CO<sub>2</sub> partial pressure





# Comparison of measured and calculated uranyl organic colloid





Main solution Solids Reactions Sorption Database Output Piper JPlot

quantity	species	value	unit

Temperature: 25 C

Volume: 1.0 l

Time: sec

Density:  fix  free  
1000.0 g/l

Balance on: disabled

add... edit... remove import...

Redox state

enabled

disabled

set by

all

Np[3+], NpO2[+] ▼

Activity-correction models

Solvent: none ▼

Species: truncated-davies ▼

# Energy terms

- Constants can be used to evaluate energetic of reaction

- From Nernst equation

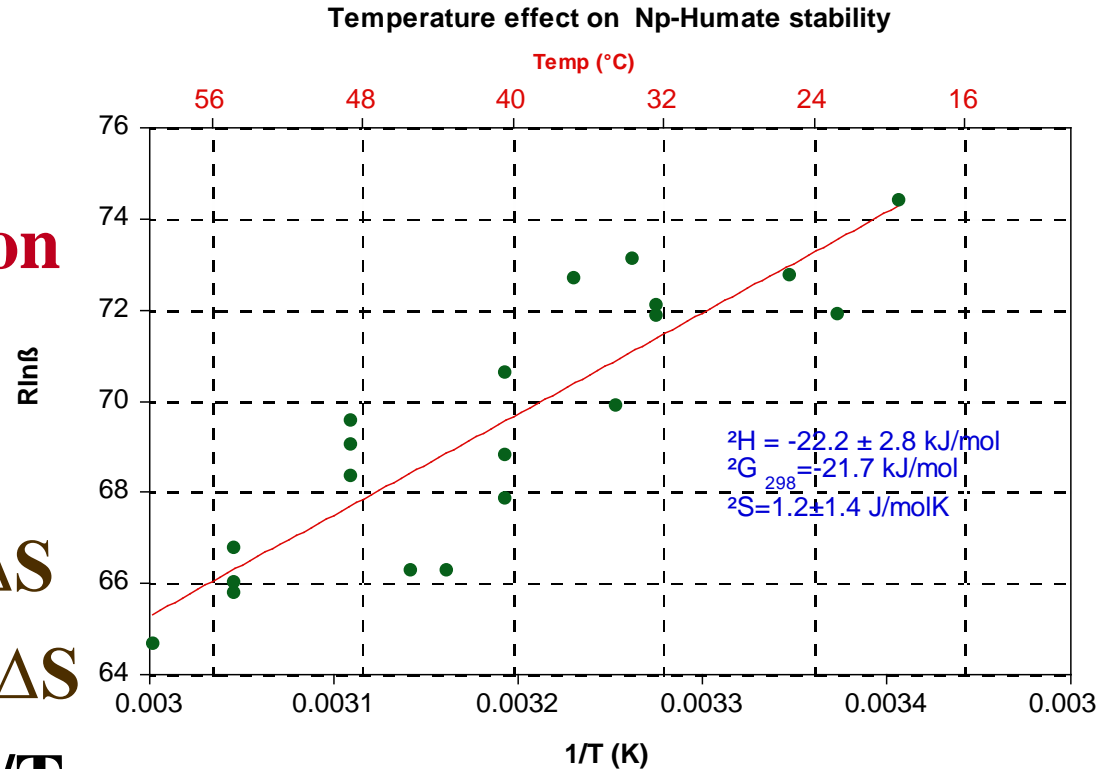
$$\rightarrow \Delta G = -RT \ln K$$

- $\Delta G = \Delta H - T\Delta S$

$$\rightarrow -RT \ln K = \Delta H - T\Delta S$$

$$\rightarrow R \ln K = -\Delta H/T + \Delta S$$

\* Plot  $R \ln K$  vs  $1/T$



# Solubility Products

- **Equilibrium involving a solid phase**



$$K = \frac{[\text{Cl}^-][\text{Ag}^+]}{[\text{AgCl}]}$$

- **AgCl concentration is constant**

- Solid activity and concentration is treated as constant

- By convention, reaction goes from solid to ionic phase in solution

- **Can use  $K_{sp}$  for calculating concentrations in solution**

$$K_{sp} = K[\text{AgCl}] = [\text{Cl}^-][\text{Ag}^+]$$

# Solubility calculations

- **AgCl(s) at equilibrium with water at 25°C gives 1E-5 M silver ion in solution. What is the  $K_{sp}$ ??**
  - **AgCl(s)  $\leftrightarrow$  Ag<sup>+</sup> + Cl<sup>-</sup>: [Ag<sup>+</sup>] = [Cl<sup>-</sup>]**
  - **$K_{sp} = 1E-5^2 = 1E-10$**
- **What is the [Mg<sup>2+</sup>] from Mg(OH)<sub>2</sub> at pH 10?**
  - **$K_{sp} = 1.2E-11 = [Mg^{2+}][OH]^2$**
  - **[OH] = 10<sup>-(14-10)</sup>**

$$[Mg^{2+}] = \frac{1.2E-11}{1E-8} = 1.2E-3$$

# Solubility calculations

- $K_{sp}$  of  $UO_2 = 10^{-52}$ . What is the expected  $U^{4+}$  concentration at pH 6. Generalize equation for any pH

- **Solubility reaction:**



- $K_{sp} = [U^{4+}][OH^-]^4$

- $[U^{4+}] = K_{sp} / [OH^-]^4$

- $pOH + pH = 14$

- At pH 6,  $pOH = 8$ ,  $[OH^-] = 10^{-8}$

- $[U^{4+}] = 10^{-52} / [10^{-8}]^4 = 10^{-52} / 10^{-32} = 10^{-20} M$

- **For any pH**

- $[U^{4+}] = 10^{-52} / [10^{-(14-pH)*4}]$

- $\text{Log } [U^{4+}] = -52 + ((14-pH)*4)$

# Limitations of $K_{sp}$

- Solid phase formation limited by concentration
  - below  $\approx 1E-5$ /mL no visible precipitate forms  
→ colloids
- formation of supersaturated solutions
  - slow kinetics
- Competitive reactions may lower free ion concentration
- Large excess of ligand may form soluble species
  - $AgCl(s) + Cl^- \rightleftharpoons AgCl_2^-(aq)$

$K_{sp}$  really best for slightly soluble salts

# Overview

- **Understand heats of reactions**
  - **Enthalpy, entropy, Gibbs free energy**
  - **Reaction data from constituents**
- **Understand half-cell reactions**
  - **Nernst Equation**
- **Kinetics**
  - **Influence of reaction conditions**
- **Equilibrium and constants**
  - **Use to develop a speciation spreadsheet**



# Questions

- **What is the difference between 1<sup>st</sup> and 2<sup>nd</sup> order kinetics?**
- **What can impact reaction rates?**
- **How can a compound act as a base and acid? Provide an example.**
- **What does the dissociation constant of an acid provide?**
- **Provide the speciation of acetic acid at pH 3.5, 4.5, and 5.5.**
- **What are the species from carbonic acid at pH 4.0, 6.0, and 8.0?**
- **Set up the equations to describe the speciation of uranyl, the uranyl monocarbonate, and the uranyl dicarbonate.**

# Questions

- **Comment in blog**
- **Respond to PDF questions**