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Environmental Management Science Program

FY2003 EMSP Principal Investigator Workshop

Project 81883

Mechanisms and Kinetics of Organic Aging and Characterization of Intermediates in High-Level Waste

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Project Description

- This project studies reactions leading to the degradation of organic model compounds in high-level waste (HLW) simulants.
- The work is closely coordinated with an EMSP project at the Notre Dame Radiation Laboratory:

  NOx System in Homogeneous and Heterogeneous Nuclear Waste (55229), PI: Dan Meisel
- Objective is to develop quantitative and predictive understanding of HLW chemistry and computational capabilities to model that chemistry.
- Effort is meant to assist in establishing technical baseline knowledge required to make decisions on issues as they arise.

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Mechanisms and Kinetics of Organic Aging and Characterization of Intermediates in High Level Waste

ENVIRONMENTAL REMEDIATION

- Waste Issues:
  - Safe Storage
  - Treatment
  - Tank Closure
- Impacted by chemical reactions driven by radiolysis and heat

REACTION MODELS

- Predictions

  Degradation of organics, flammable and toxic gas generation, etc.
- Input:

  Rxns/rate constants

  Energies (ΔH and ΔG)

  Redox potentials ($E°$)

  Acidities (K_a)

DATA

Experiment

Comp. Chem.

Experiment and Computation

- **Experimental Studies**
  - Product and rate studies of oxidation of complexants by NO_2
  - Tests of mechanism for aluminum(III)-catalyzed organic aging
  - Application of Photoacoustic Calorimetry (PAC) for measuring reaction rate constants and thermochemistry of radicals in aqueous solutions.
- **Modeling Studies**
  - Development and use of dielectric continuum models for predicting solution properties of HLW intermediates

Primary Radicals from Radiolysis in HLW Convert to NO_2 and NO

- ***Hydroxyl Radicals:***

  $OH + NO_2^- \rightarrow NO_2 + OH^-$ $\quad k = 1.0\times10^{10}\ M^{-1}s^{-1}$

  and their basic form, O^-:

  $O^- + NO_2^- (+ H_2O) \rightarrow NO_2 + 2OH^-$ $\quad k = 3.1\times10^{8}\ M^{-1}s^{-1}$

- ***Hydrated Electrons:***

  $e^-_{aq} + NO_3^- \rightarrow NO_3^{2-}$ $\quad k = 9.7\times10^{9}\ M^{-1}s^{-1}$

  $\tau \leq 20\ \mu s$: $NO_3^{2-} (+ H_2O) \rightarrow NO_2 + 2OH^-$

- ***Hydrogen Atoms:***

  $H + NO_2^- \rightarrow HNO_2^-$ $\quad k = 1.6\times10^{9}\ M^{-1}s^{-1}$

  $\tau \leq 200\ \mu s$: $HNO_2^- (+ H_2O) \rightarrow NO_2^{2-} \rightarrow NO + 2OH^-$

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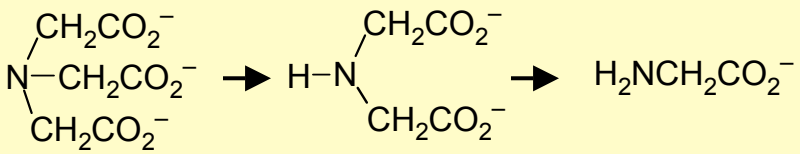
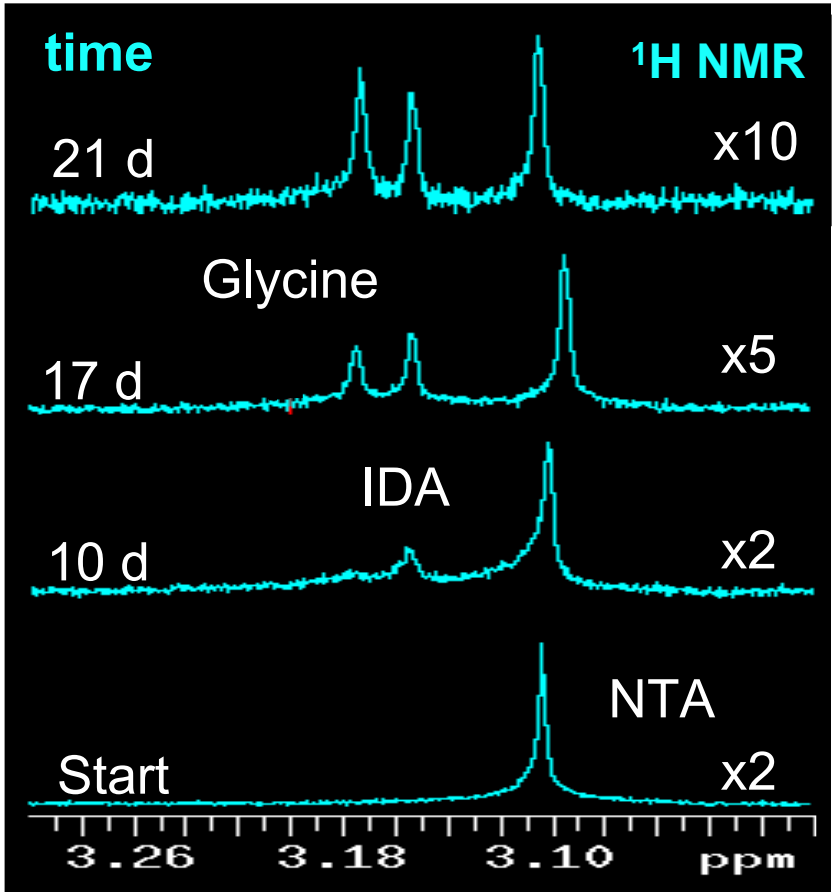
NO_2 Oxidizes Organic Complexants in 1 M NaOH



NTA IDA Glycine

- **Reactivity:**
  - NTA~IDA>Glycine
  - Glycine/Glycolate ~ 4
  - Glycolate/Formate ~ 20
- **Other products include**
  - Formate, Oxalate, Carbonate
  - Adducts



Summary: NO_2 Oxidation of Organic Complexants

- **Oxidations generally proceed towards simpler, more oxidized organic species; eventually formate, oxalate and carbonate.**
- **However, condensation of glycine with glyoxal to 2-amino-3-hydroxysuccinate is favored when [NO_2^-] < 1 M.**
  - ***shows that conditions may occur in which fuel-rich organic complexants do not age completely to less energetic and innocuous products, nor to compounds less capable of complexing metal ions***
- **Future work (in collaboration with NDRL):**
  - **extend rate determinations to other complexants and remnant organics; elucidate mechanisms of NO_2 attack: electron transfer v. hydrogen abstraction; develop capabilities to predict rates and products**

Mechanism for Al-Catalyzed Organic Aging

- Aluminate ion catalyzes thermal aging of glycolate and HEDTA ions.
- Ashby et al. (WHC-EP-0823) proposed:

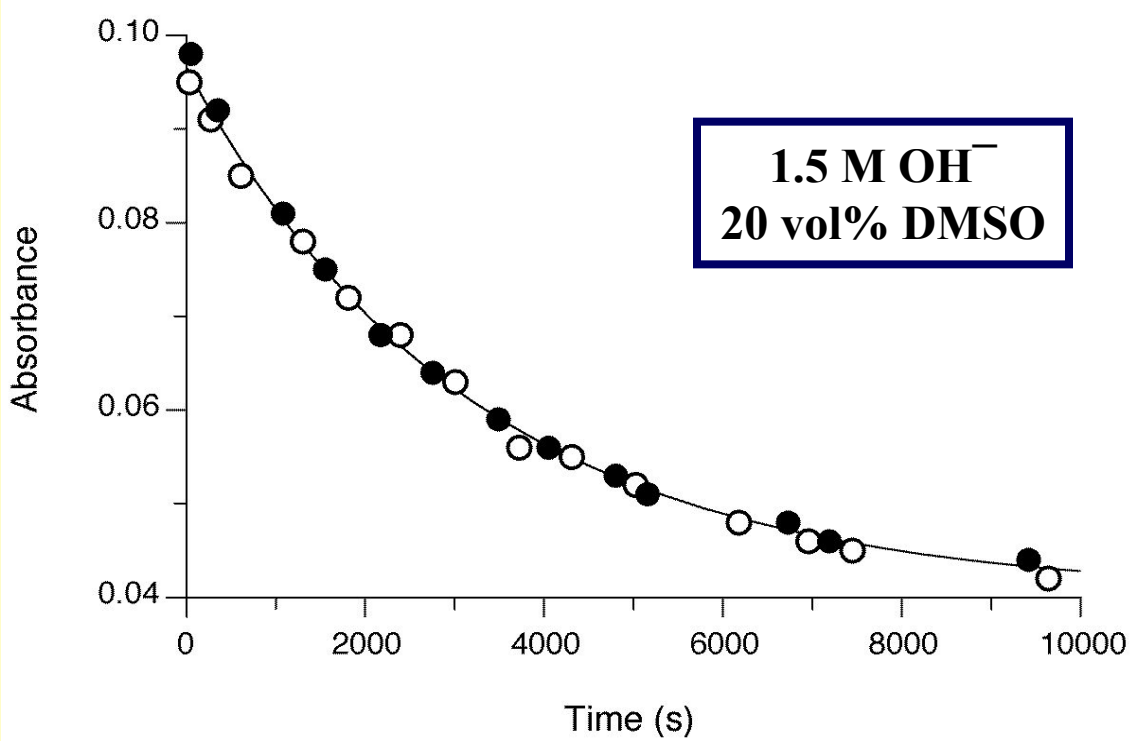
$$\equiv AlOH^- + NO_2^- \rightleftharpoons \equiv AlONO^- + OH^-$$

$$\equiv AlONO^- + ROH \xrightarrow{slow} \equiv AlOH^- + RONO \xrightarrow{fast} Products$$

- Our studies of the hydrolysis of nitritoacetate ($ONOCH_2CO_2^-$) contradict this mechanism.

$$RONO + OH^- \xrightarrow{faster} ROH + NO_2^-$$

Decrease of Absorbance at 355 nm of Ethyl Nitrite in Aqueous Hydroxide Solution



(●) 0.375 M sodium aluminate (○) without sodium aluminate

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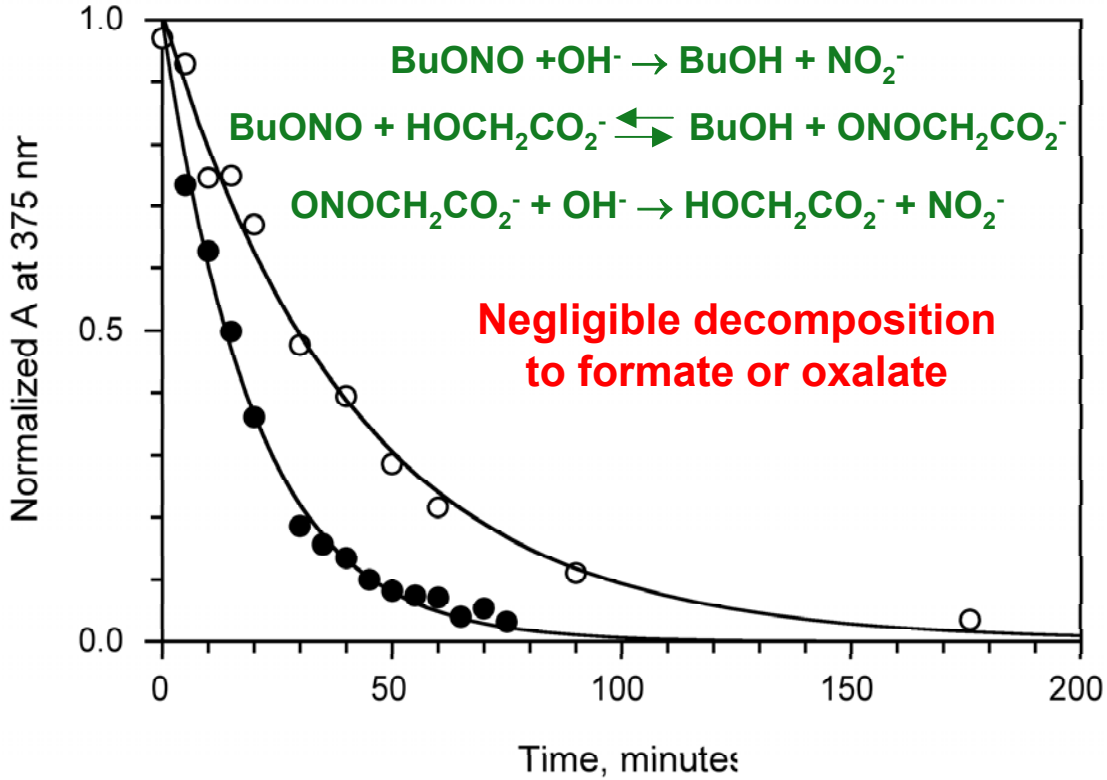
Hydrolysis of Nitrite Esters of *tert.*-Butanol and Glycolate ion



Hydrolysis of *t*-BuONO in 1M OH^- (○) with 0.5 M glycolate anion (●) at 60 °C.

The rate increase with glycolate present shows nitritoacetate hydrolyzes faster than *t*-BuONO.

Alternate Mechanism: Al-Catalyzed Organic Aging

- Aluminum may bind glycolate anion; then the complex reacts with nitrite ion

$$\geqslant AlOH^- + {}^-OCH_2CO_2^- \rightleftarrows \geqslant AlOCH_2CO_2^-$$

$$\geqslant AlOCH_2CO_2^- + NO_2^- \rightarrow [{}^-ONO\overset{|}{\underset{|}{A}}lOCH_2CO_2^-] \rightarrow \text{Products}$$

- Aluminum screens coulombic repulsion and serves as a bridge for electron transfer.

- Future work to validate mechanism through experiment and computational models.

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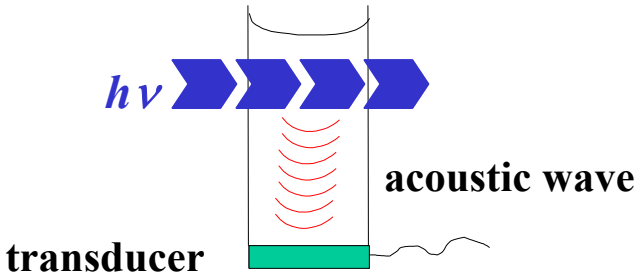
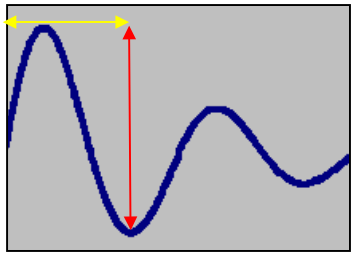
Novel Direct Measurements of Radical Thermochemistry in Aqueous Media

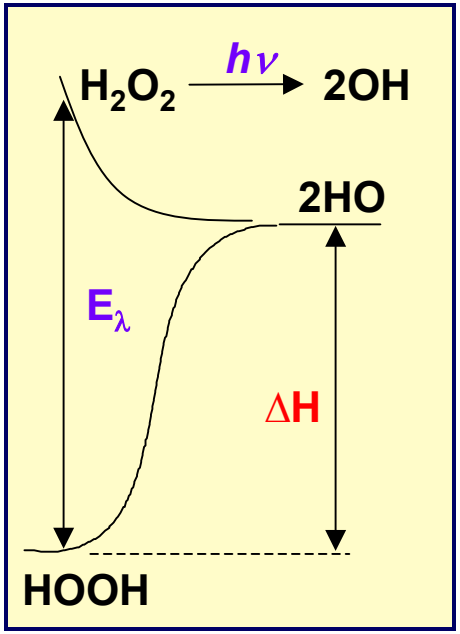




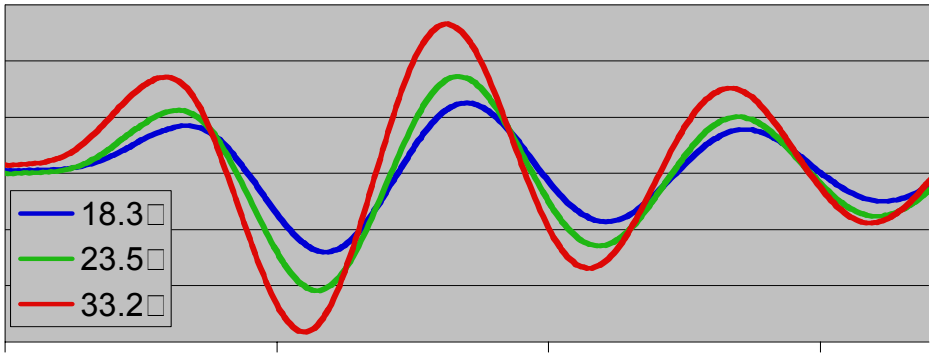
- **Pulsed Photoacoustic Calorimetry (PAC)**
- **Signal depends on reaction energetics, volumes and kinetics: ΔH_r, ΔV_r, k**
- **Solution properties of radicals**
  - **Activation parameters**
  - **Solvation energies (ΔH_s, ΔG_s)**
  - **Energies of formation (ΔH_f, ΔG_f)**

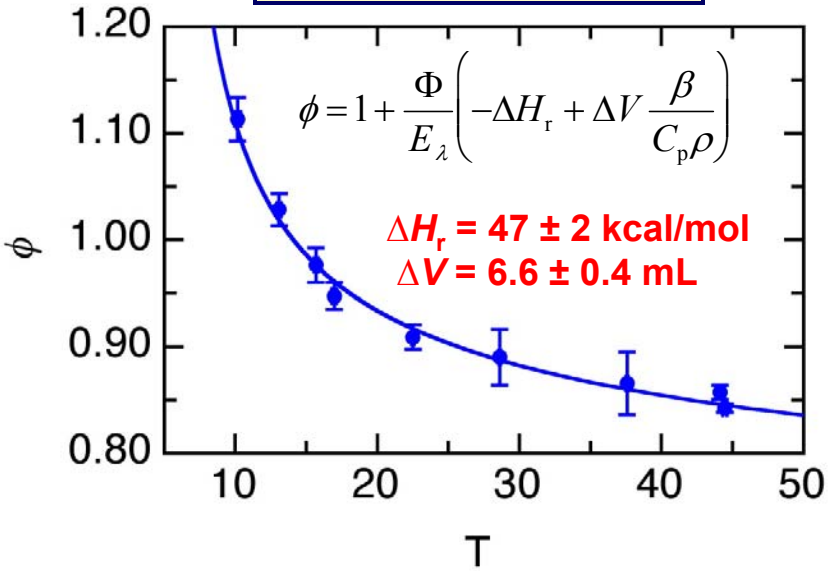
} **Inputs & *benchmarks for predictive models***

Thermochemistry of Hydroxyl Radical by PAC



PAC Signal from H_2O_2 at Different Temperatures





Thermochemical Data (kcal/mol)

	This work	Lit.
$H_2O_2 \rightarrow 2\ OH$		
$\Delta H°$	46.7 ± 1.4	45.5
$\Delta G°$	46. ± 2	44.3
$OH(g) \rightarrow OH(aq)$		
$\Delta H°$	-9	-10.
$\Delta G°$	-1	-2.
OH (aq):		
$\Delta H_f°$	0. ± 1.4	-0.8
$\Delta G_f°$	7.4 ± 1.4	6.2

Photoacoustic Calorimetry … Conclusions

- The PAC-H_2O_2 system provides a unique, novel tool for determining reaction energies and kinetics of intermediates in solution.
- Opens the way to obtaining the thermochemical properties ($\Delta H_f°$, $\Delta G_f°$) of most radicals that can be formed by reaction of OH with aqueous substrates.

  •OH + RH → HOH + R•, $\Delta H_r°$, $\Delta G_r°$
- Future work will provide thermochemistry of radicals derived from glycolate, its complexes with aluminum ions, and related systems.
- The data will provide benchmarks for predictive models under development and insight to the mechanism of aluminate-catalyzed organic aging.

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Computation of Solution Properties, e.g., Electrode potentials ($E°$)

Near chemical accuracy (~ 1 kcal/mol)

$$Ox^{+m}(g) + n\,e^- \underset{}{\overset{\Delta G_r°}{\rightleftharpoons}} Red^{-n+m}(g)$$

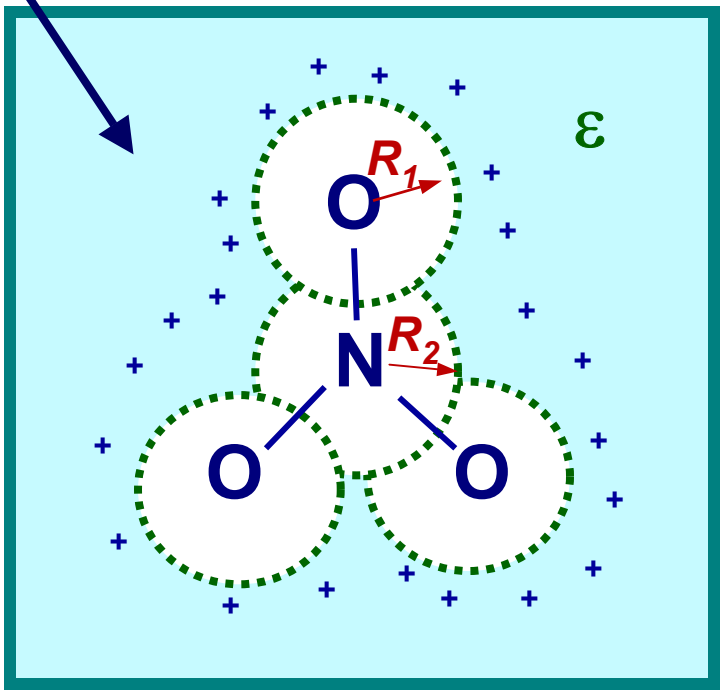
$\Delta G_s°(Ox)$ ⇅ $\Delta G_s°(Red)$

$$Ox^{+m}(aq) + n\,e^- \underset{}{\overset{E°}{\rightleftharpoons}} Red^{-n+m}(aq)$$

Larger errors for ions !

Dielectric Continuum Models of Solvation

- Polarizable continuum model of solvent
- Cavity as interlocked spheres
- Radii parameterized to reproduce expt.



Mean Errors

COSMO/UA/HF/6-31+G*

~0.4 kcal/mol for 43 neutrals

~3.2 kcal/mol for 27 ions

SM5/HF/6-31+G*

~0.0 kcal/mol for 275 neutrals/91 solvents

~3.7 kcal/mol for 49 ions

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New Parameterization …

Free Energy of Solvation for Oxoanions and Related Neutral Compounds

Training Set:

Anions:

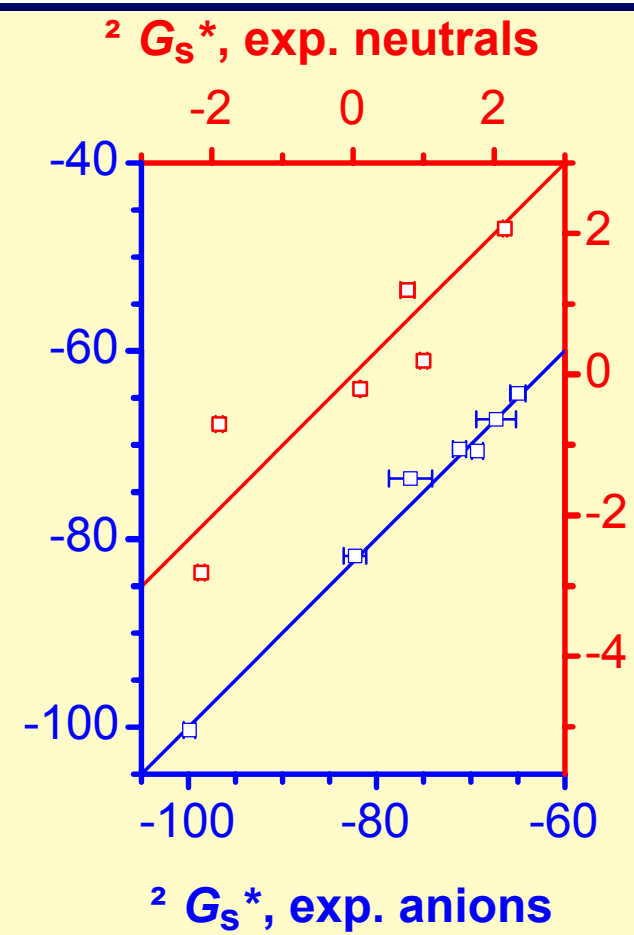
O^-, O_2^-, HCO_2^-, O_3^-, NO_2^-, ClO_2^-, NO_3^-

Neutrals:

SO_2, ClO_2, O_3, CO_2, NO_2, O_2

***Mean unsigned errors*: ≤ 1 kcal/mol**

Camaioni, Dupuis, Bentley, *J. Phys. Chem. A*, in press



New Parameterization … Progress and Future Work

- Reaching predictive capabilities for reduction half-reactions (±0.05 V error) for oxoanions and neutral compounds related to HLW.

  O^-, O_2^-, CO_2^-, HCO_2^-, CO_3^-, NO_2, NO_2^-, NO_3^-, transition metal oxo anions

- Future work:
  - Extension to dianions and other classes of ions

    glycolates, aminocarboxylates, and radical ions
    Transition metal complexes
  - Extension to high ionic strength (Dan Chipman)

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- **Dr. Harry Babab (Richland)**
- **Prof. Leon Stock (Portland)**