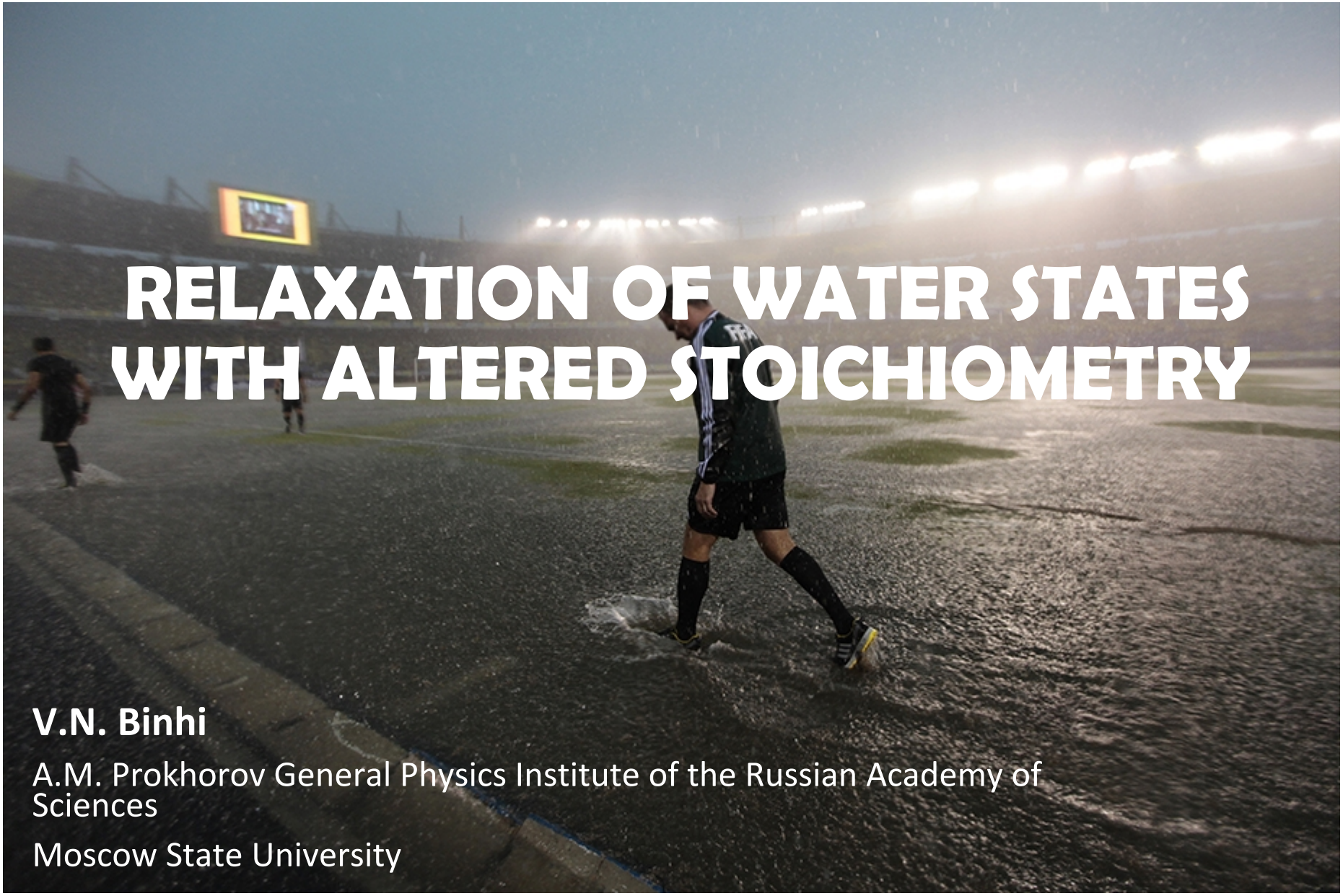

RELAXATION OF WATER STATES WITH ALTERED STOICHIOMETRY

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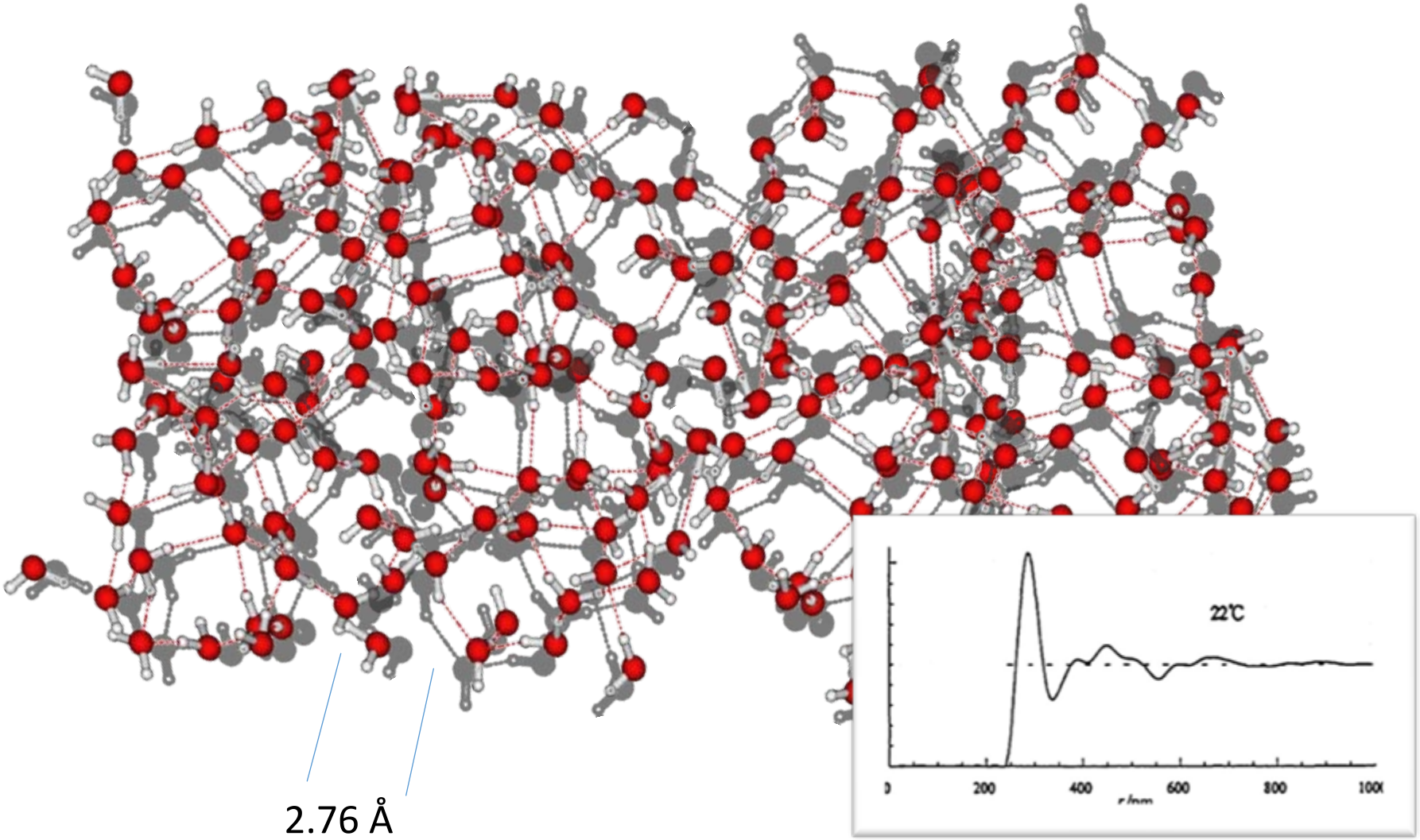
Water in magnetobiology

- A possible intermediate for EMF signal transfer from the physical to the biological variables
- Stoichiometry of the element composition, hydrogen-oxygen compounds, chemical kinetics, relaxation
- An association with magnetic effects

Hydrogen Bond Net

The continuous network of hydrogen bonds with the dynamic heterogeneity

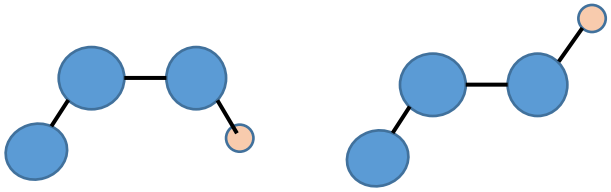
Malenkov G. J. Struct. Chem. 47(S):5, 2006

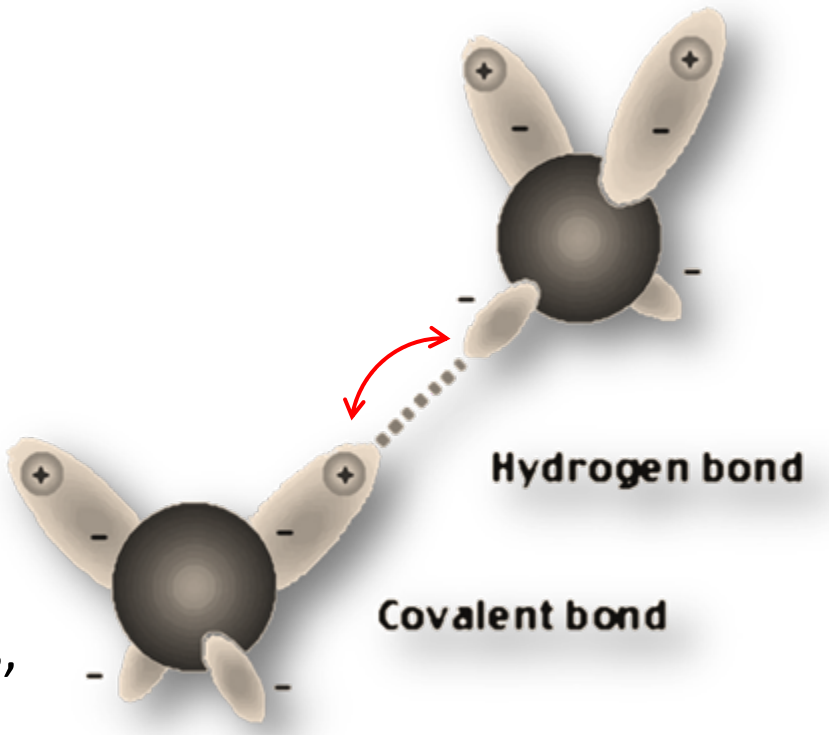


What is missing in the computer models of water?

- **Chemical conversions**
  - Quantum effects
  - Proton transport
    - Kinetic phenomena
  - Spin subsystem
- Non-binary interactions
  - Long-range interactions strongly modify H-bonds
  - HO_3 – *cis* in a few particle-models, *trans* in many-particle models

[Chalmet S. et al. J. Chem. Phys. 124, 194502, 2006]





Stoichiometry: Greek στοιχείο = element

- The proportions in which elements are combined in compounds

- The proportions between reactants and products in chemical reactions

FeO – ideal stoichiometry

$\mathrm{Fe}_{1-x}\mathrm{O}$ – a deviation $x = 0 \div 0.2$ due to $3\mathrm{Fe}^{2+} \leftrightarrow 2\mathrm{Fe}^{3}$

- For convenience:
  two types of stoichiometry – element and kinetic

Solutions → Pure water

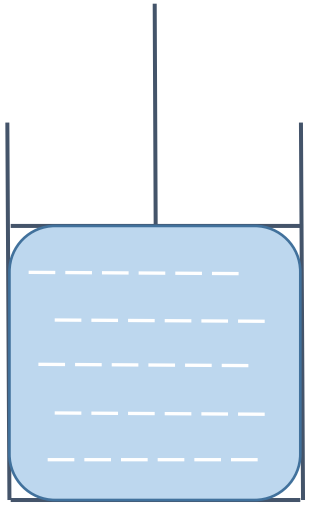
Equilibrium state:

n1 H_2O + n2 OH^- + n3 OH_3^+ + n4 H_2O_2 + n5 O_2 + …

n1 : n2 : n3 : n4 : … --- also a stoichiometry

$\sum H : \sum O$ --- element stoichiometry

Which Water Is Under Study?



- **Closed system**: no matter exchange, $T, P = Const$
- **Oxygen and hydrogen**^{1H} **elements** only
- **Homogeneous system**, $V \approx Const$
- **Chemical conversions** are allowed
- i-type compound - $\mathrm{H}_{\alpha_i}\mathrm{O}_{\beta_i}\mathrm{e}_{\gamma_i}$:
  γ – electric charge (electrons that exceed $\alpha + 8\beta$)
- Constraints (n_i is the number of i-type molecules)
  - **Substance conservation**: $\sum_i n_i\alpha_i = Const$, $\sum_i n_i\beta_i = Const$ (Amounts of elements do not change)
  - **Electric neutrality**: $\sum_i n_i\gamma_i = 0$

? What is $H_{2+x}O$

- $H_\alpha O_\beta$ – molecule

  α and β are small numbers

- $H_A O_B$ – sample of liquid water

  A and B are great numbers, $A \approx 2B$, or $A = (2 + x)B$

- $H_{(2+x)B} O_B \Rrightarrow B \otimes H_{2+x}O$

- $A, B \Rrightarrow \boldsymbol{x \equiv \frac{A}{B} - 2}$ (stoichiometric index of water)

A few reactions in water (of about 40) involving oxygen-hydrogen compounds

$$O_3 \rightleftarrows O + O_2$$

$$O + H_2O \rightarrow 2OH$$

$$O_3 + OH^- \rightarrow HO_2^- + O_2$$

$$H_2O_2 \rightleftarrows HO_2^- + H^+$$

$$O_3 + H_2O_2 \rightarrow OH + HO_2 + O_2$$

$$O_3 + HO_2^- \rightarrow O_3^- + HO_2$$

$$HO_2 \rightleftarrows O_2^- + H^+$$

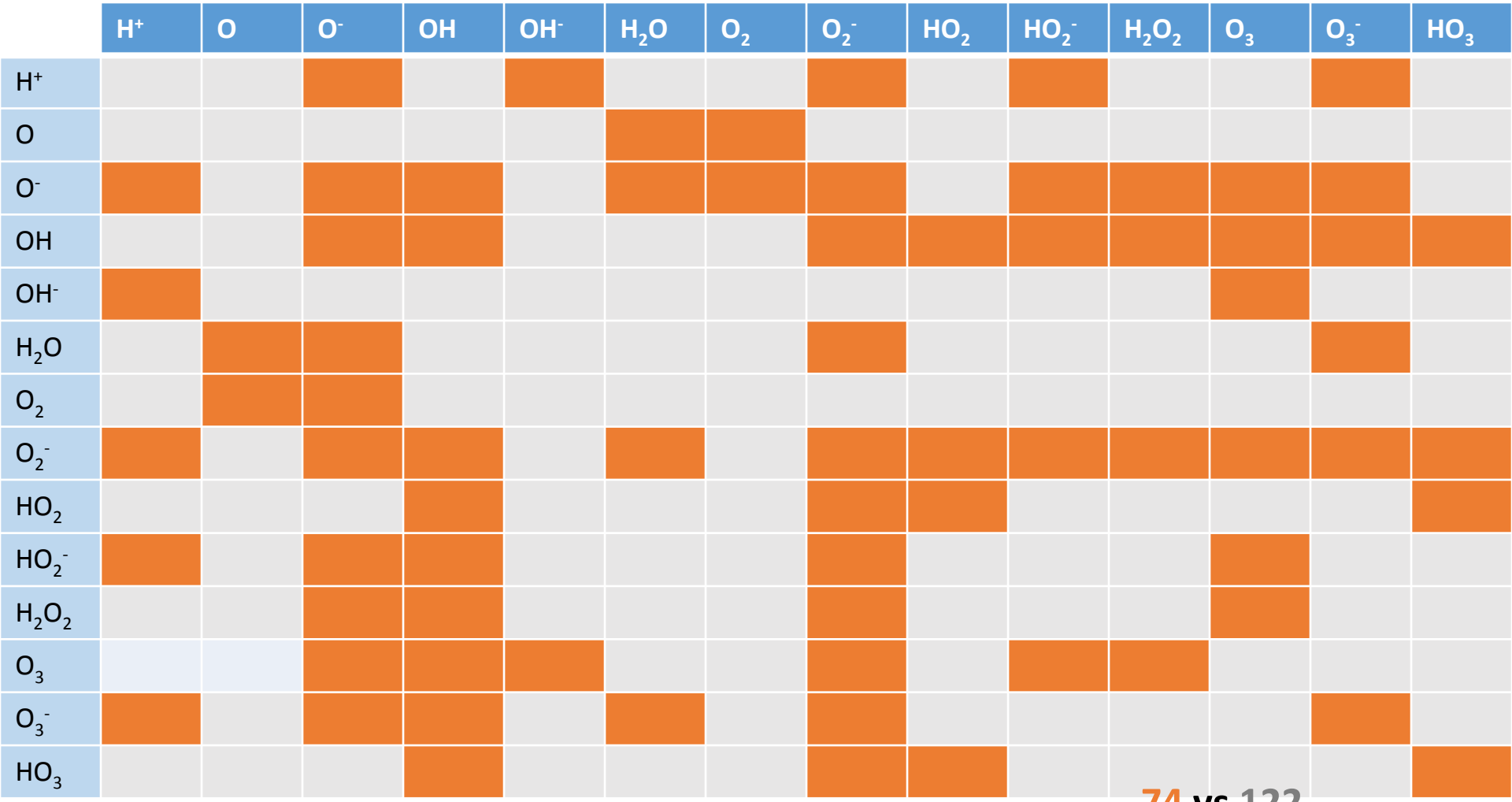
$$O_3^- + H^+ \rightleftarrows HO_3$$

$$O_2^- + HO_2^- \rightarrow O^- + OH^- + O_2$$

14 types of $H_\alpha O_\beta$ molecules

Interactions between $H_\alpha O_\beta$ compounds

$$H_{\alpha'}O_{\beta'} + H_{\alpha''}O_{\beta''} \longrightarrow \ldots$$



74 vs 122

Chemical kinetics formalism
terminology

- Kinetic scheme: N components enter in S reactions

$$\sum_{n=1}^{N} x_{sn}\,\mathrm{X}_n = 0\,, \qquad s = 1, 2, \ldots, S$$

X_n is a chemical compound (component)

s is a reaction number

x_{sn} is a "stoichiometry matrix" of S rows, N columns

Costraints:

charge and mass balance

- Example of element composition: $\mathrm{H_2O} \Longrightarrow \{2_{\mathrm{H}}, 1_{\mathrm{O}}\}$
- In case of J elements:

$$\{a_{\mathrm{A}1}, a_{\mathrm{A}2}, \dots, a_{\mathrm{A}J}\} \text{ or } \{a_1, a_2, \dots, a_J\}$$

- Mass balance in s-th reaction:

$$\sum_{n=1}^{N} a_{nj}\, x_{sn} = 0\,, \qquad s = 1, 2, \dots, S;\;\; j = 0, 1, \dots J$$

a_{nj} is a "molecular matrix" of N rows, J columns

Notation for reaction rates

- s-th reaction:

$$\mathrm{X}_1 + \mathrm{X}_2 + \cdots \underset{k_{s-}}{\overset{k_s}{\rightleftarrows}} \mathrm{X}_i + \mathrm{X}_{i+1} + \cdots$$

- Let the set of $k_s, s = 1, \ldots, S$ be $\boldsymbol{k}_s$
- And the set of $X_n,\ n = 1, \ldots N$ be $\boldsymbol{X}_n$
- Rate of the s-th reaction:

$$v_s = v_s^+ - v_s^- = v_s(\boldsymbol{k}_s, \boldsymbol{X}_n)$$

- Overall rate of n-th component:

$$v^{(n)} = \sum_{s=1}^{S} x_{sn}\, v_s = \sum_{s=1}^{S} x_{sn}\, v_s(\boldsymbol{k}_s, \boldsymbol{X}_n)$$

Equations

$$\frac{dX_n}{dt} \equiv v^{(n)} = \sum_{s=1}^{S} x_{sn}\, v_s(\boldsymbol{k}_s, \boldsymbol{X}_n) \qquad N' - J'$$

$$0 = \sum_{n=1}^{N} a_{nj}\,(X_n - X_{n0}) \qquad J'$$

$$N' = \mathrm{rank}(x_{sn}), \qquad J' = \mathrm{rank}(a_{nj})$$

Stationary conditions $(t \to \infty)$

$$0 = \sum_{s=1}^{S} x_{sn}\, v_s(\boldsymbol{k}_s, \boldsymbol{X}_n)$$

$$\sum_{n=1}^{N} a_{nj}\, X_n = \sum_{n=1}^{N} a_{nj}\, X_{n0} \qquad J'$$

$$\boldsymbol{I} \equiv \sum_{n=1}^{N} a_{nj}\, X_{n0} \quad , \qquad \text{a column of } J' \text{ rows}$$

Varying initial conditions:

?Whether $\boldsymbol{\delta}$ exist that satisfies the equation?

$$\boldsymbol{I(\delta)} \equiv \sum_{n=1}^{N} a_{nj}(X_{n0} + \delta_n)$$

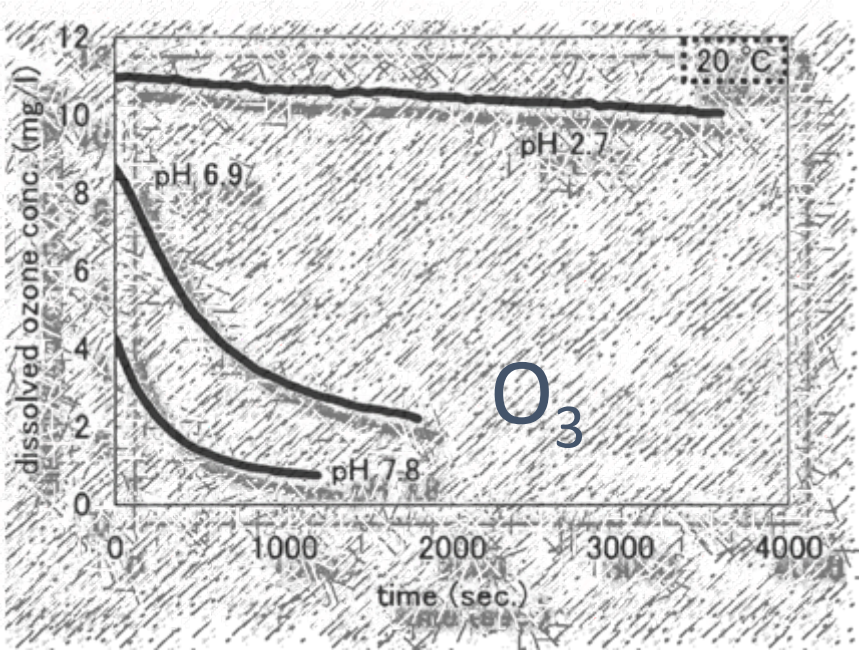
$$\boldsymbol{I(\delta) = I(0)}$$

$$\sum_{n=1}^{N} a_{nj}\,\delta_n = 0 \ , \qquad J' \text{ equations for } N' \text{ variables}$$

$$\boldsymbol{\delta = \delta}(C_1, C_2, \ldots, C_{N'-J'})$$

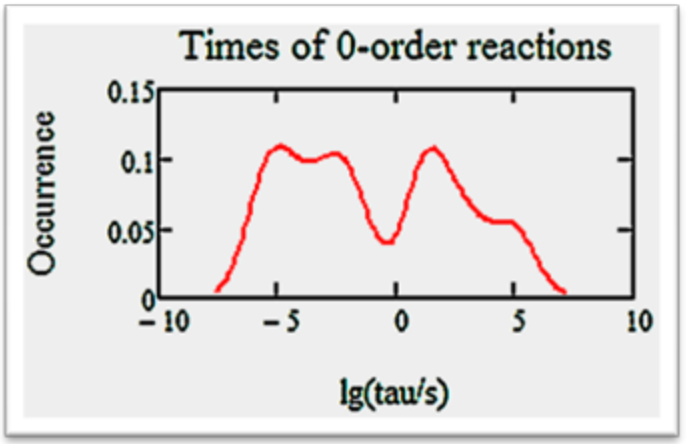
Water:
N'~N~15
S~40
J'=J=2

Slow relaxation in water
(closed system)

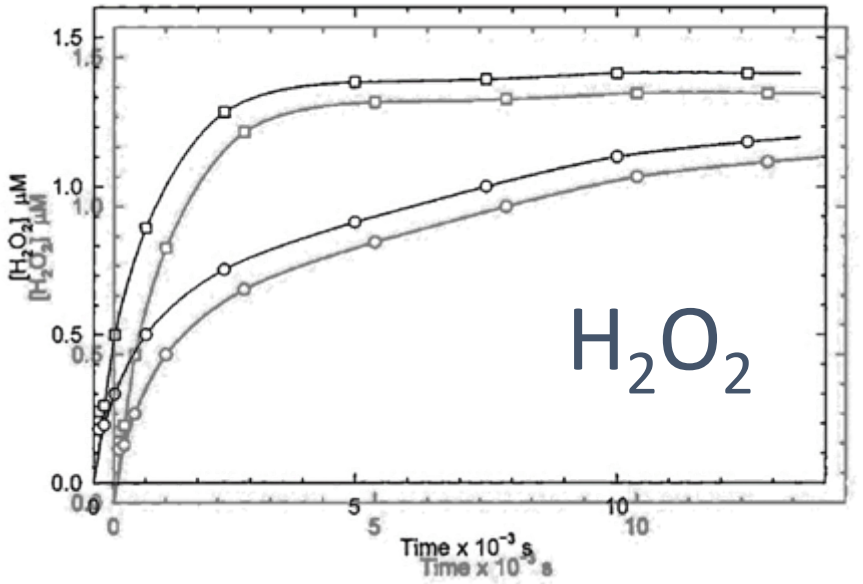


Mizuno T. et al. Ozone: Sci. Eng., 29:55, 2007

10 mg O2 /L ~ 2.10^{-4} M



Sehested K. et al. J. Phys. Chem. A, 102:2667,1998



Equilibrium vs metastable states

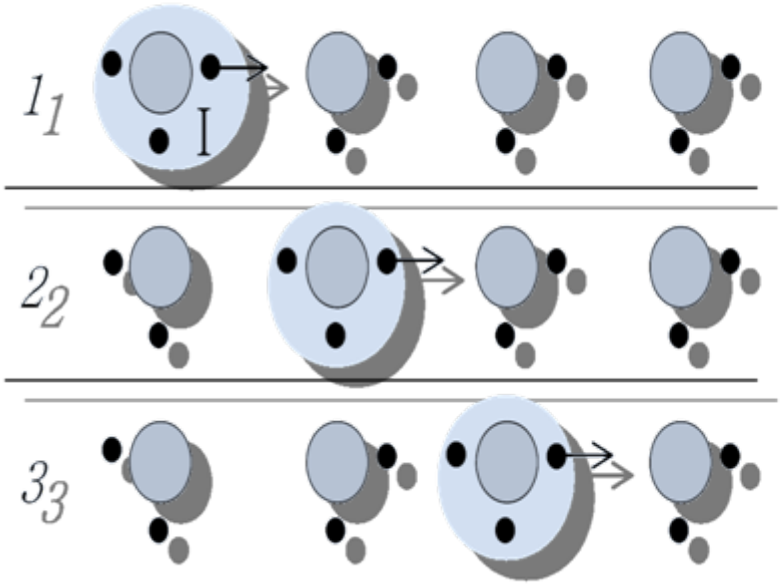
Compound	Concentration, mol/L		
	Equilibrium	Metastable1 (closed system, O_3 added)	Metastable2 (open system)
O_2	10^{-4} $(x = 4 \cdot 10^{-4})$	10^{-4}	10^{-3}
OH^-, H^+	10^{-7}	-	pH = ~ 7 ± 1 (4-9)
H_2O_2	10^{-7}	$1.1\ 10^{-7}$	$2\ 10^{-5}$
OH	10^{-10}	$1.7\ 10^{-9}$	$3\ 10^{-4}$
HO_2^-, O_3^-	10^{-12}	$4.5\ 10^{-7}$	
O_2^-, HO_3	10^{-13}	$4\ 10^{-12}$	
HO_2	10^{-14}	10^{-12}	
O^-	10^{-15}	$3\ 10^{-9}$	
H and H_2			???

How to get $H_{2+x}O$ with $x \neq 0$?

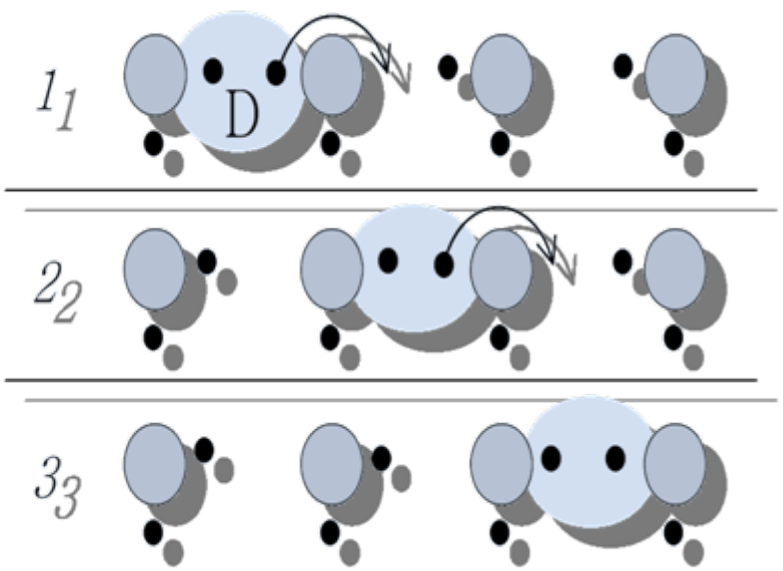
- Sorption at
  - Ion flow (adsorption)
  - Shaking (absorption)
- Electrolysis -->
- other

Proton transport mechanism
(Grotthuss mechanism)

Hydroxonium

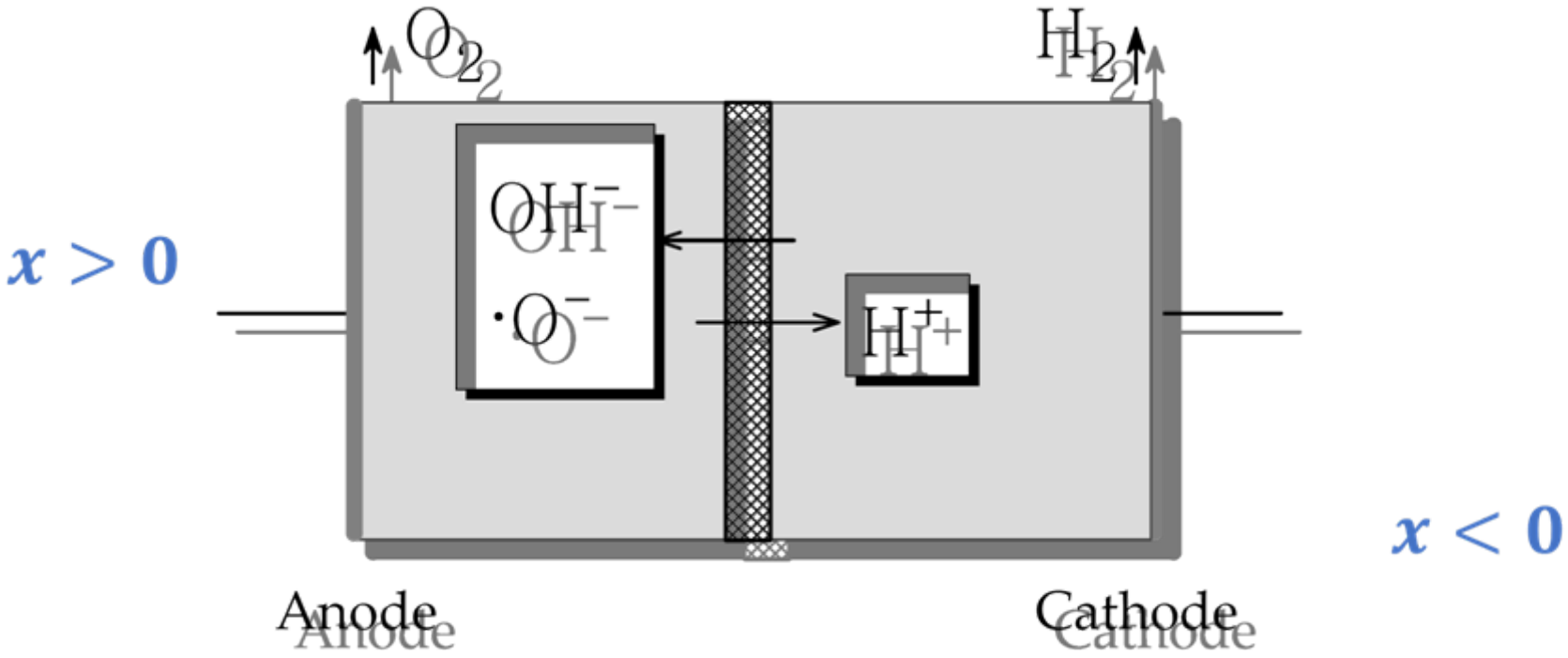


Bjerrum D-defect



Formation of water states $H_{2+x}O$

with $x \neq 0$ in a membrane electrolyzer

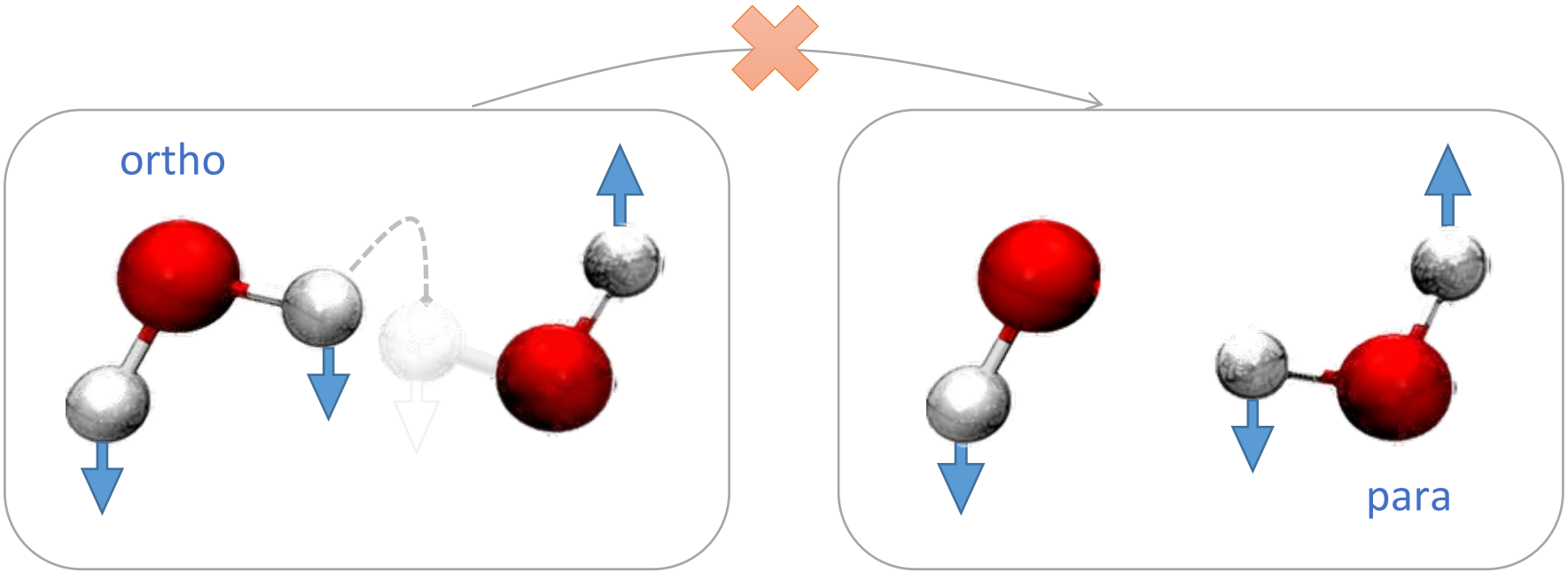


growth for $[OH_3^+]$ (pH drops)

Le Chatelier's principle: to restore the equilibrium

growth for $[OH^-]$, $[H_2O_2]$, $[O_2]$

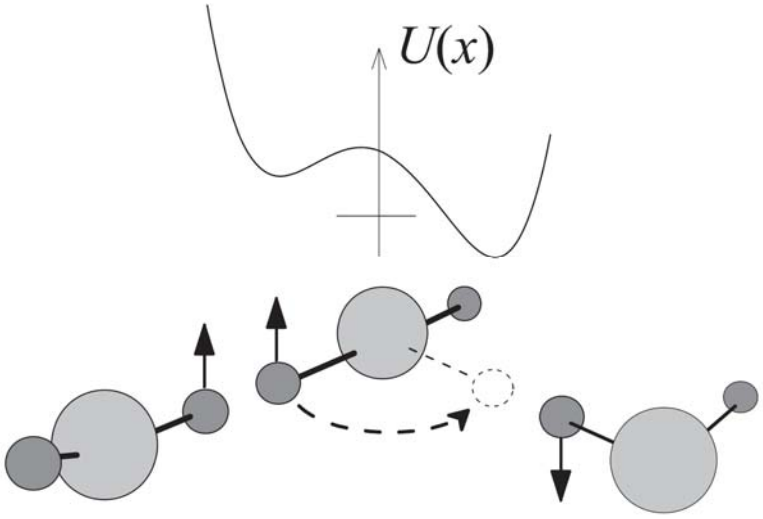
Water and magnetic fields?



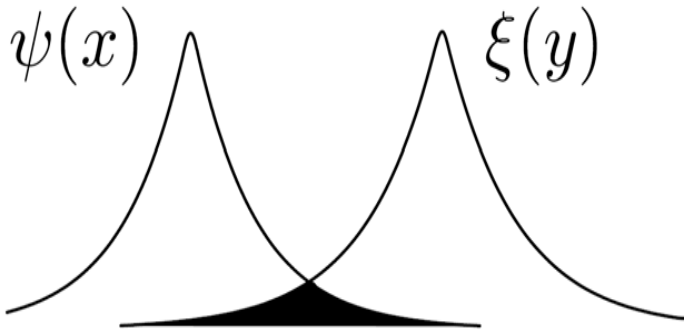
- There is a fast proton exchange: $H_2O + HO^- \rightarrow HO^- + H_2O$
- Protons (vs electrons) have localized wave functions
- Experiment: ortho-to-para ratio is conserved
- Consequence: only proton transfer is allowed that retains two-spin states

Proton exchange interaction

Bjerrum D-defect motion



Proton's wave functions
(λ_B~2Å)



$\frac{J_{\text{exch}}}{J_{\text{Coulomb}}} \sim 1$ where p-binding energy < than a tenth of the H-bond energy

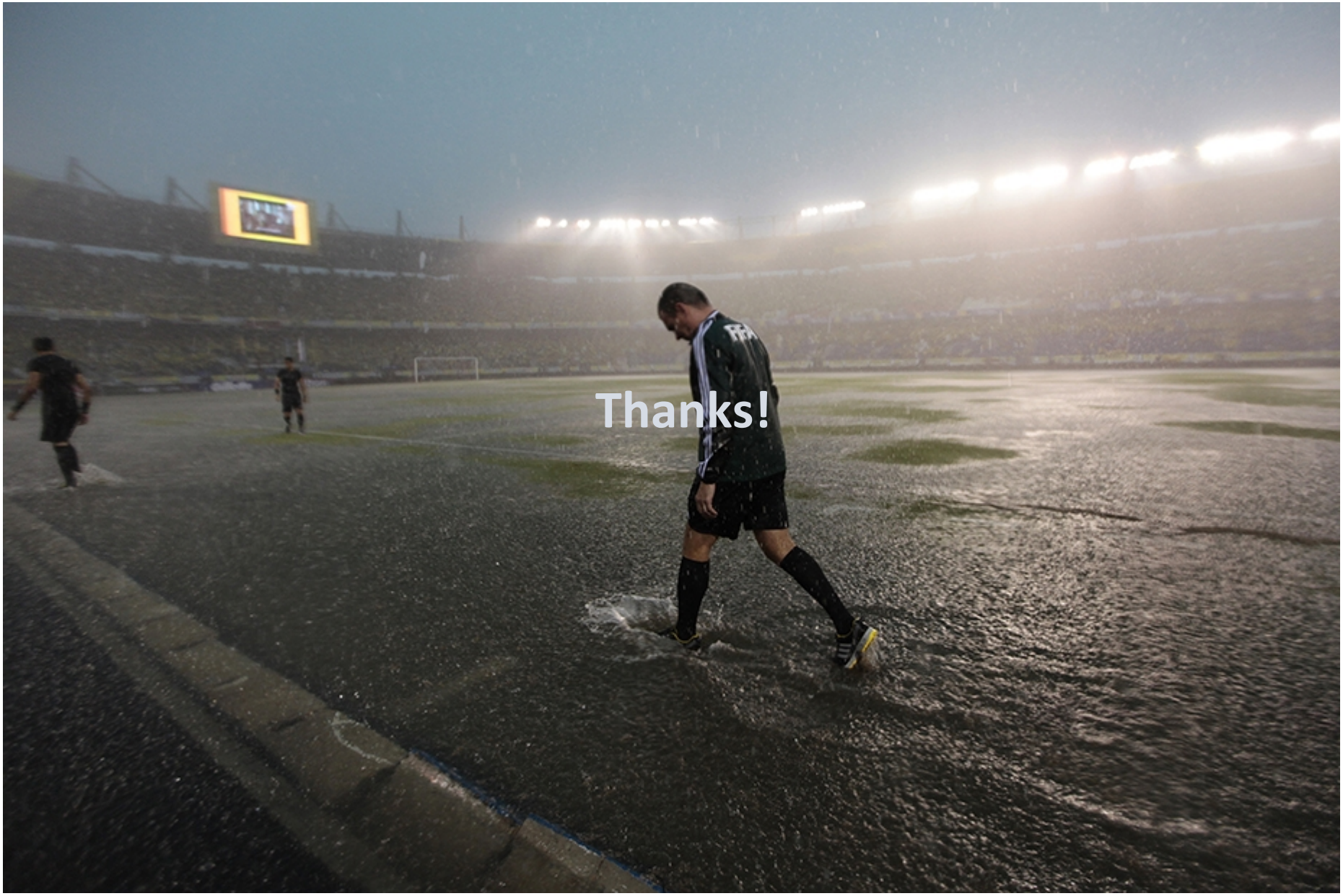
Conclusion

- Deviation x in water stoichiometry is an independent factor that determines the equilibrium state
- x is measurable through the density (refraction) of water
- $x > 0$ and ^{17}O might facilitate proton exchange and observation of magnetic effects in water

Water states and QM limitations

- Is there a complete set of chemical reactions in pure water?
- Are there precise values of the rate constants?
- Can we measure a few properties simultaneously?

- Is the sample of water a holistic object?


Thanks!