Charge and mass transfer across the metal-solution interface

E. Gileadi

School of Chemistry

Tel-Aviv University, ISRAEL

gileadi@post.tau.ac.il

Time-Resolved Kinetics

- The idea of different time scales for electron transfer and solvent reorganization is inherent in the Marcus theory

- The characteristic time for different processes is:

  Electron transfer ≈ 1 fs

  Solvent reorganization ≈ 1 ps $(10^3$ fs)

  Diffusion across the interface ≈ 0.1 ns $(10^5$ fs)

The Marcus Theory of Charge Transfer

- Symmetrical electron transfer

$$\left[Fe\left(H_2O\right)_n\right]^{3+} + e^- \rightarrow \left[Fe\left(H_2O\right)_m\right]^{2+}$$
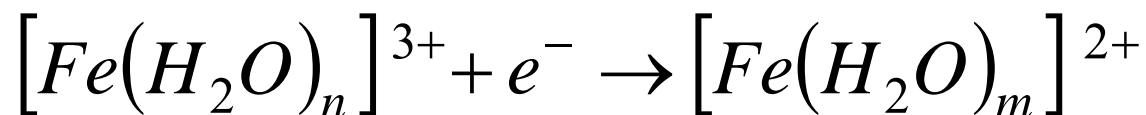
- The energy of the system as a whole does not change **BUT:** immediately following electron transfer, both ions find themselves in an unstable position, hence the total energy of the system will increase:

$$\left[Fe\left(H_2O\right)_n\right]^{2+} \text{ and } \left[Fe\left(H_2O\right)_m\right]^{3+}$$

Fe^{2+} with a solvation shell of Fe^{3+} and vice versa

3

Time-Resolved Kinetics

- Common wisdom: An unstable intermediate can be stabilized by adsorption

- Example: $Fe^{2+} + e \rightarrow Fe^+_{ads}$

- Problem: There are two processes taking place

  - $Fe^{2+} + e \rightarrow Fe^+_{soln}$ $\approx$ 1 fs
  - $Fe^+_{soln} \rightarrow Fe^+_{ads}$ $\approx$ 10^5 fs

- Problem: Although Fe^+ may be stabilized by adsorption, it must first be formed in solution, where it is highly unstable

Formation of Adsorbed Intermediate

$$Fe_{soln}^{2+} + e_{crys} \xrightarrow{\text{1 fs}} Fe_{soln}^{+}$$

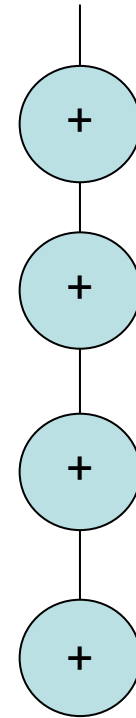$$Fe_{soln}^{+} \xrightarrow{10^5 \text{ fs}} Fe_{ads}^{+}$$
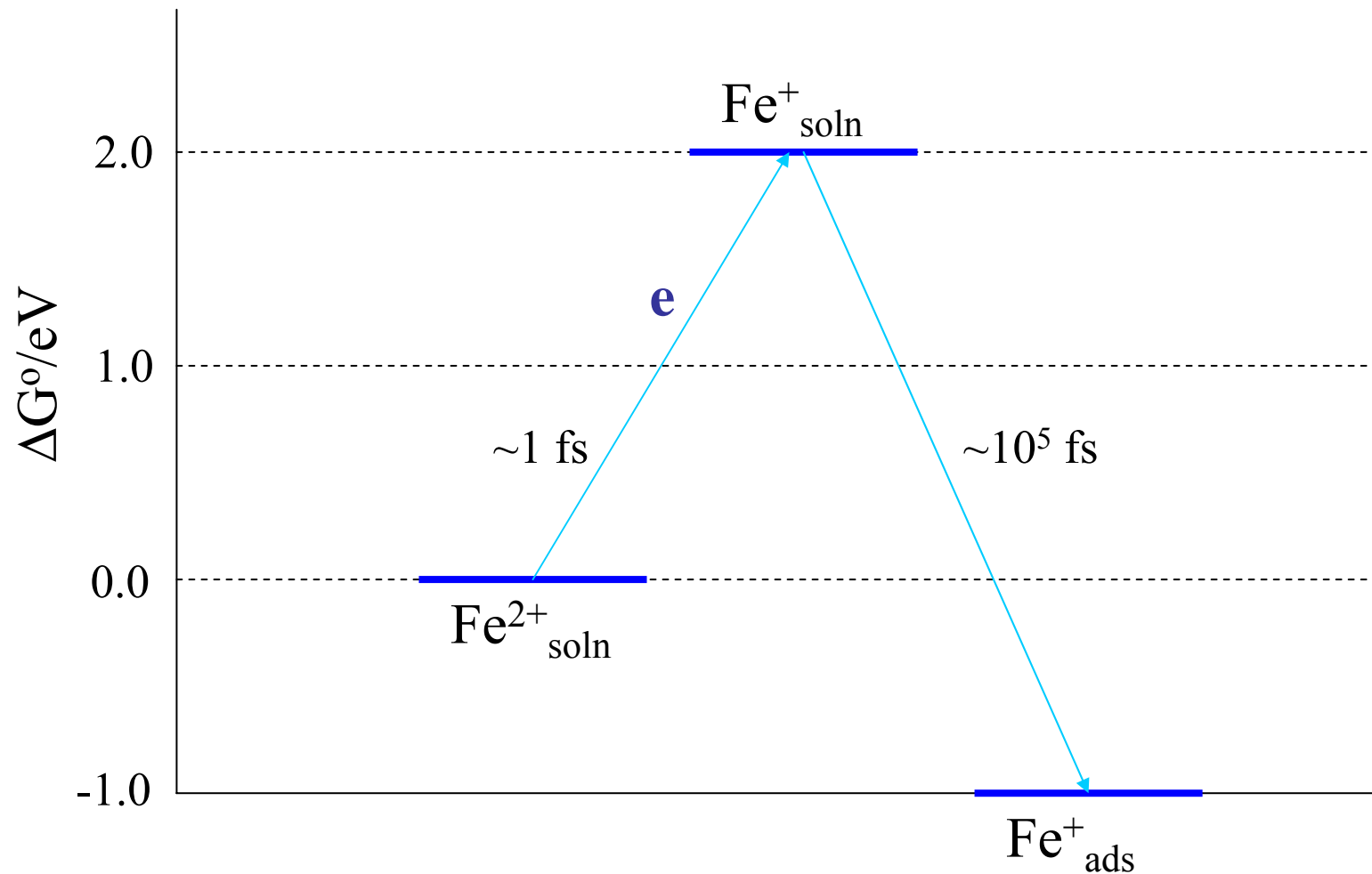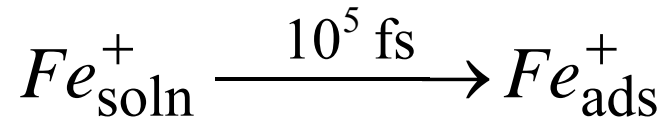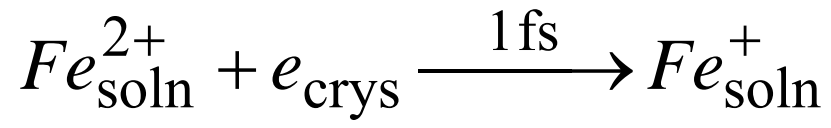
Metal surface
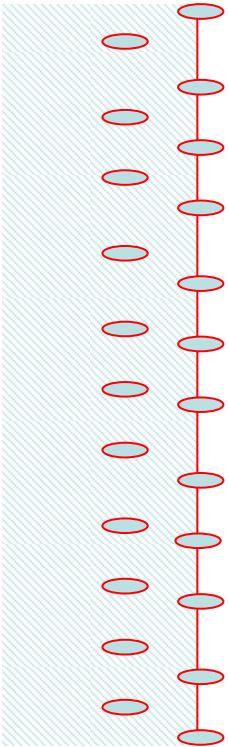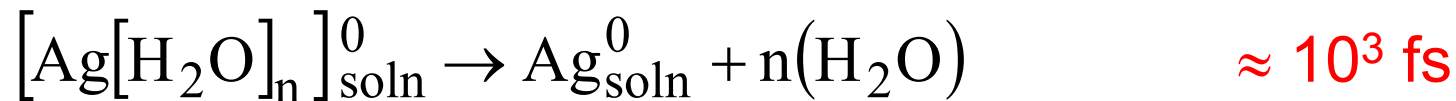
OHP

Charge Transfer in Metal Deposition-Dissolution

- **The common wisdom**: Charge is carried across the interface by electrons

- **Two problems**:

  – Highly unstable neutral atoms would be formed on the solution side of the interface

  – There is no driving force for neutral atoms to cross the interface

- **Conclusion**:   **Charge is carried across the interface by ions**

Proof for ion transfer mechanism

Reductio Ad Absurdum

Assume that electron transfer does occur:

$$[Ag(H_2O)_n]^+_{soln} + e_{crys} \rightarrow [Ag(H_2O)_n]^0_{soln} \qquad \approx 1 \ \text{fs}$$

$$[Ag[H_2O]_n]^0_{soln} \rightarrow Ag^0_{soln} + n(H_2O) \qquad \approx 10^3 \ \text{fs}$$

$$Ag^0_{soln} \rightarrow Ag^0_{crys} \qquad \approx 10^5 \ \text{fs}$$
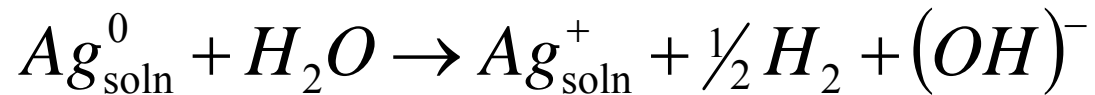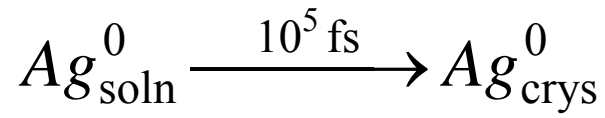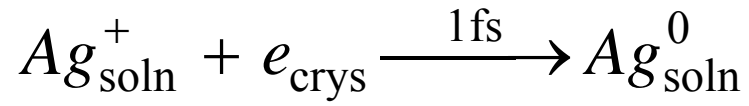
8

The Fate of the Neutral Species Formed by Electron Transfer

The neutral atoms could:

1. Be incorporated in the metal

2. Diffuse away into the solution

3. Interact with the solvent to form H_2

The last two processes would decrease the

Faradaic efficiency

$$Ag^0_{soln} + H_2O \rightarrow Ag^+_{soln} + \frac{1}{2}H_2 + \left(OH\right)^-$$

$$Ag^+_{\text{soln}} + e_{\text{crys}} \xrightarrow{\text{1 fs}} Ag^0_{\text{soln}}$$

$$Ag^0_{\text{soln}} \xrightarrow{10^5 \text{ fs}} Ag^0_{\text{crys}}$$

Metal surface
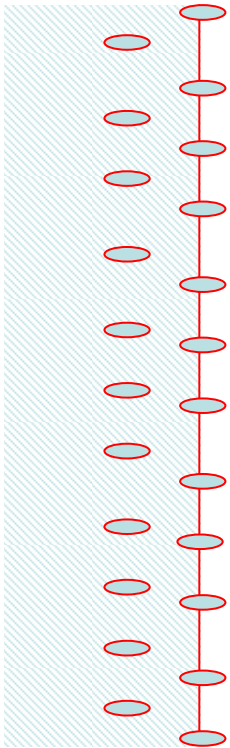
OHP
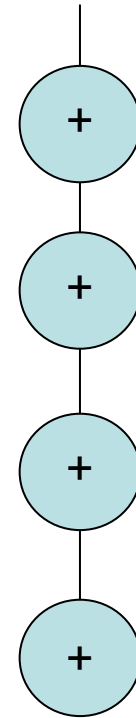
The Energy of a Neutral Atom in Solution

$$(Ag_{soln}^{+} + e_{crys}) \xleftrightarrow{\Delta G=0} Ag_{crys}^{0}$$

$$\downarrow \Delta G \approx \Delta G_{subl} \qquad\qquad\qquad \downarrow \Delta G_{subl}$$

$$Ag_{soln}^{0} \xleftarrow{\Delta G \approx 0} - - - - - Ag_{gas}^{0}$$
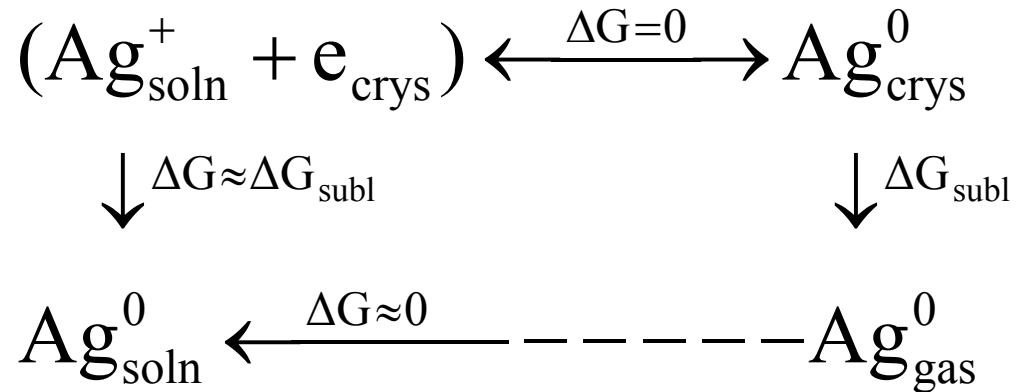
The difference between the Gibbs energies of a neutral atom and a hydrated ion in solution is roughly equal to the energy of sublimation.

Silver as an Example

For silver one finds ΔG_{subl} = 2.55 eV.

For the reaction:

$$Ag^+_{soln} + e_{crys} \rightarrow Ag^0_{soln}$$

E^0 = - 2.55 V *vs*. Ag^+/Ag = - 1.75 V *vs*. SHE

This reaction could not occur at or near the Ag^+/Ag reversible potential.

A sobering thought

- "In metal deposition charge is carried across the interface by ions, not by electrons".
- D.C. Graham   1955
- K. Vetter   1967
- V.V Losev   1972
- N. Sato   2002

- Non of these scientist took the next obvious step of realizing that the mechanism of ion transfer can be radically different from that of electron transfer.

The Marcus theory of electron transfer (ii)
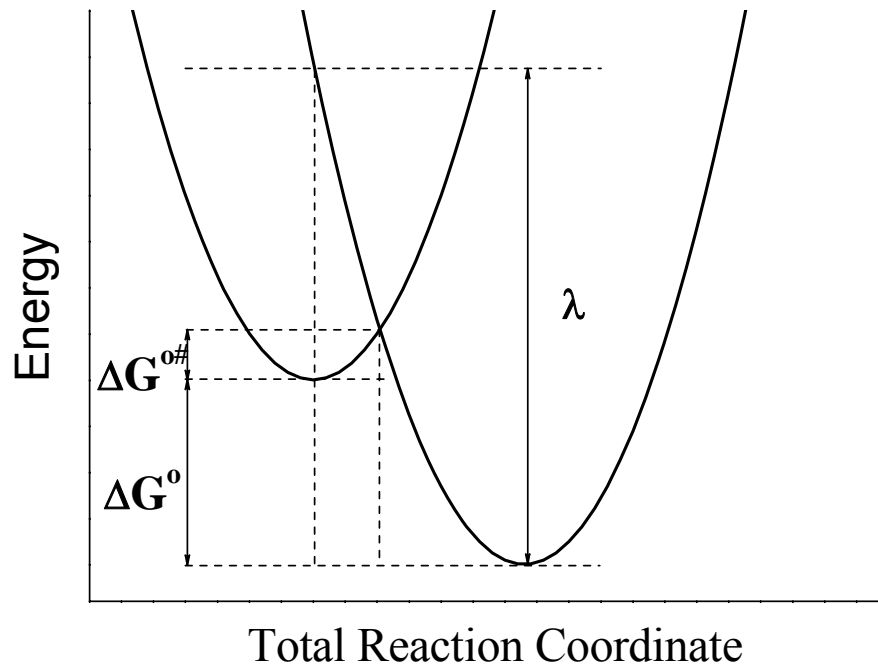
The Gibbs energy of activation is given by

$$\Delta G^{0\#} = \frac{\left(\lambda + \Delta G^0\right)^2}{4\lambda}$$

Replacing the Gibbs energy by the electrochemical Gibbs energy yields

$$\Delta \overline{G}^{0\#} = \Delta G^{0\#} - \beta F |\eta| = \frac{\left(\lambda + \Delta G^0 - F|\eta|\right)^2}{4\lambda}$$

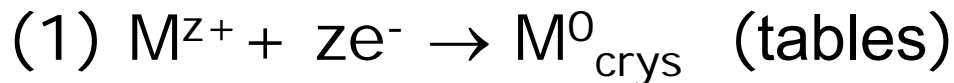$$\beta = 0.5 + \frac{\Delta G^0}{2\lambda} - \frac{F}{4\lambda}|\eta|$$

The quantities involved in determining the energy of activation

Vertical electron transfer leads to an increase of the total energy of the system

Energy

$\Delta G^{o\#}$

ΔG^o

λ

Total Reaction Coordinate

Calculated reversible potentials

- <u>METAL: Fe   Ni   Cu   Zn   Sn   Ag</u>
- $\Delta G/n$ -1.92   -1.99   -1.55   -0.50   -1.39   -2.55   eV
- $E^0(1)$ -0.41   -0.23   +0.34   -0.76   -0.14   +0.80 V/SHE
- $E^0(2)$ -2.33   -2.22   -1.21   -1.26   -1.53   -1.75   V/SHE

$$(1) \quad M^{z+} + ze^- \rightarrow M^0_{crys} \quad \text{(tables)}$$

$$(2) \quad M^{z+} + ze^- \rightarrow M^0_{soln} \quad \text{(hypothetical)}$$

Metal deposition is too fast!

- The rate constants for metal deposition are comparable to those for outer-sphere charge transfer.

- They should not be!

- For a divalent metal $\triangle G^0 \approx 20$ eV and for outer-sphere charge transfer $\lambda = 1\text{-}2$ eV.

Comparison between rates of outer sphere charge transfer and metal deposition on Hg

Pb^{2+}/Pb	2.0	0.38
$[Cr(CN)_6]^{-3/-4}$	0.9	0.18
Tl^+/Tl	1.8	0.34
$[Fe(CN)_6]^{-3/-4}$	0.09	0.018
Cd^{2+}/Cd	1.0	0.19
Fe^{3+}/Fe^{2+}	5×10^{-3}	1.0×10^{-3}
Bi^{3+}/Bi	3×10^{-4}	6×10^{-5}
V^{+4}/V^{+3}	1×10^{-3}	2×10^{-4}

What is the mechanism of charge transfer for metal deposition?

- It cannot be electron transfer because

- (a) It would form an unstable intermediate

- (b) Some of the neutral atom would diffuse into the solution, never reaching the electrode

- (c) It is too fast

- Conclusion:

- Charge must be transferred by the cations

Field-induced ion transfer

- It is proposed that the high electrostatic field in the double layer is the driving force. Example:

$$\vec{E} = \eta / \delta = 0.3\,\mathrm{V} / 0.6\,\mathrm{nm} = 5\mathrm{x}10^{8}\,\mathrm{V}/\mathrm{cm}$$

But what about the field at $\eta = 0$?

$$\Delta\bar{\mu} = \Delta\mu + zF\Delta\phi$$

But when an overpotential is applied, the chemical potential is not changed, hence

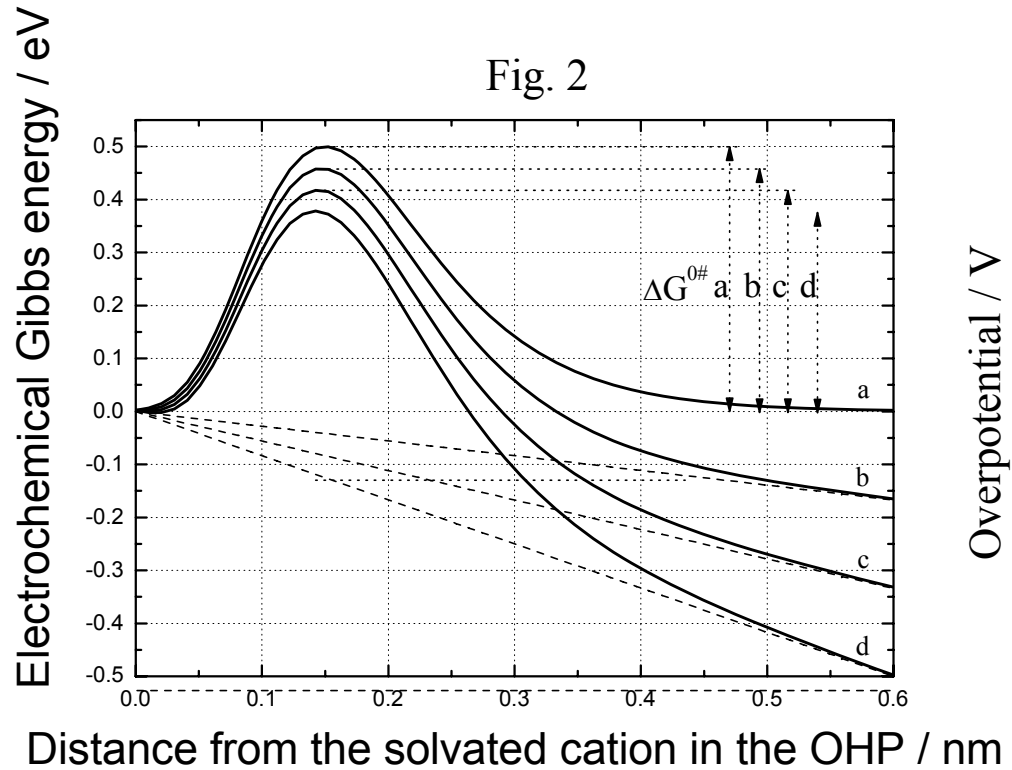$$\Delta\bar{\mu} = nF\eta, \quad \frac{\partial\left(\Delta\bar{\mu}\right)}{\partial x} = nF\frac{\partial\eta}{\partial x}$$

21

Variation of the electrochemical potential with the reaction coordinate

Fig. 1
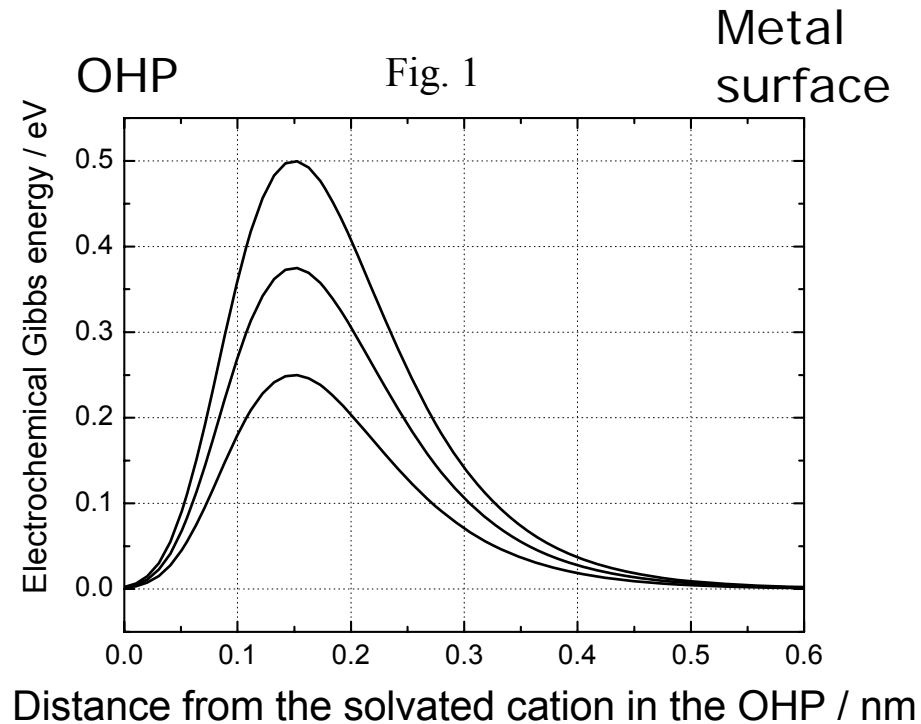
Influence of the overpotential

The barrier is lowered by the gradient of η

Fig. 2

Comparison with experiment

- For the deposition of a divalent metal, one often finds
  $b_c = 0.12V$; $b_a = 0.04V$,   ($\alpha_c = 0.5$; $\alpha_a = 1.5$)
- For ion transfer, the rate equation is

$$j = j_0 \exp\left(-\beta nF\eta/RT\right)$$

In Fig.2, $\beta_c = 0.25$, hence $\alpha_c = 0.5$

•

Also, $\beta_a = 0.75$, hence $\alpha_a = 1.5$

How can we explain the high rate constants?

- The solvation shell is removed in many small steps, each requiring a very small solvent rearrangement energy.

- The effective charge also changes in small increments. Transfer of a full electron is not assumed along the reaction coordinate.

- There is a break-before-make mechanism. Interaction with the surface starts well before there is physical contact

Conclusions

- In metal deposition charge is carried across the interface by the positive ions, not the electrons

- In outer-sphere charge transfer, charge is carried across by electrons

- The above two processes are physically different and cannot be treated by the same formalism

- A mechanism of ion transfer assisted by the electrostatic field is proposed

- A full theory of ion transfer is yet to be developed.

References

- E. Gileadi, J. Electroanal. Chem, **532** (2002) 181
- E. Gileadi, Chem. Phys Lett, **392** (2004) 421
- E. Gileadi, Proc. Symp. Electrochem. Processing in ULSI and MEMS, H. Deligianni et-al, Eds.   Vol. **17**, (2004) 3
- E. Gileadi and E. Kirowa-Eisner, Corr. Sci. **47** (2005) 3068
- E. Gileadi, Electrochem. Soc. Trans: 5th Symposium on Proton-Exchange Membrane Fuel Cells. T. Fuller et-al Eds. **1 (6)** (2005) 3
- E. Gileadi, Isr. J. Chem, (2008) in press

Final Conclusion

IN ORDER TO CREATE
ONE MUST FIRST
QUESTION THAT WHICH EXISTS

The New Challenge: are all interpretations of Electrode Kinetics Wrong?

- There are some types of electrode kinetic where the notion of adsorbed intermediates seems to fit the experimental results:

1. The hydrogen evolution reaction
2. Oxygen evolution
3. Oxidation of large anions
4. Organic oxidation or reduction (e.g. Kolbe)

Application to Hydrogen Evolution

- Common wisdom: Formation of H_{ads} as an intermediate is assumed.

$$H_3O^+ + e \rightarrow H_{ads} + H_2O$$
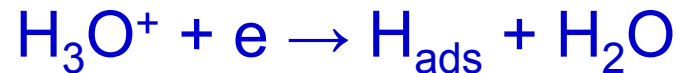
- This may be correct, since:

  - The surface is solvated.

  - The ion is solvated (as $[H_3O(H_2O)_n]^+$)

  - There are initially hydrogen atoms in contact with the surface

  - Electron transfer may lead to formation of H_{ads} by redistribution of charges, without significant movement of atoms

Details of formation of H_{ads}

$$H_2O_{ads} + e^- \rightarrow H_{ads} + OH^-$$

$$OH^- + H_3O^+ \rightarrow 2H_2O$$
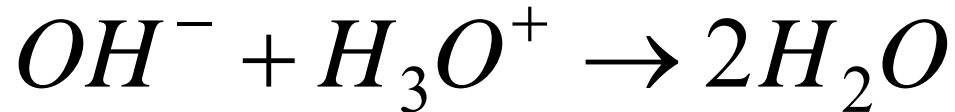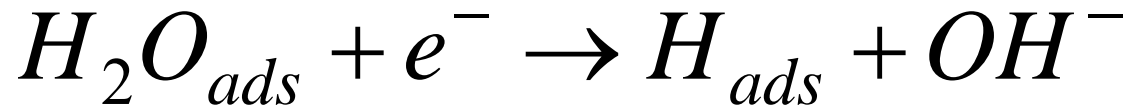
An electron is added to an adsorbed species,
not one in the OHP

Application to Oxygen Evolution

- Common wisdom: Formation of OH_{ads} as

  intermediate is assumed

$$OH^- \rightarrow OH_{ads} + e_{crys}$$

- This may be correct, for the same reasons as for H_{ads}

Details of formation of OH$_{ads}$

$$H_2O_{ads} \rightarrow H_2O_{ads}^+ + e^-$$

$$H_2O_{ads}^+ + OH^- \rightarrow HO_{ads} + H_2O$$
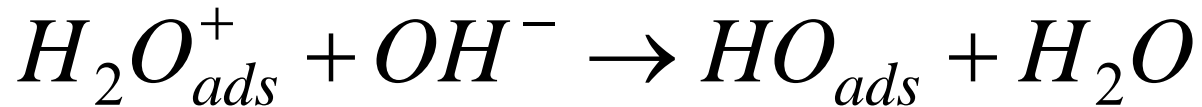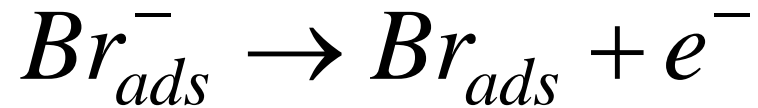
An electron is removed from an adsorbed species, not one in the OHP

Discharge of Large Anions

Consider the reaction $Br^- \longrightarrow Br_{ads} + e$

- ## This is an intermediate case

  - If the anion is "contact adsorbed" (having replaced water from the surface), the above equation is correct

  - If there is a layer of water on the surface, it may be necessary to write the above equation in two steps, since the Br^- ion will have to move after electron transfer

Details of formation of Br$_{ads}$

$$Br_{ads}^- \rightarrow Br_{ads} + e^-$$

$$Br_{ads} + Br_{ads}^- \rightarrow Br_2 + e^-$$

An electron is removed from an adsorbed species, not one in the OHP

Oxidation of Anions

H$_2$O

Br$^-$

Ag$^+$

IHP   OHP
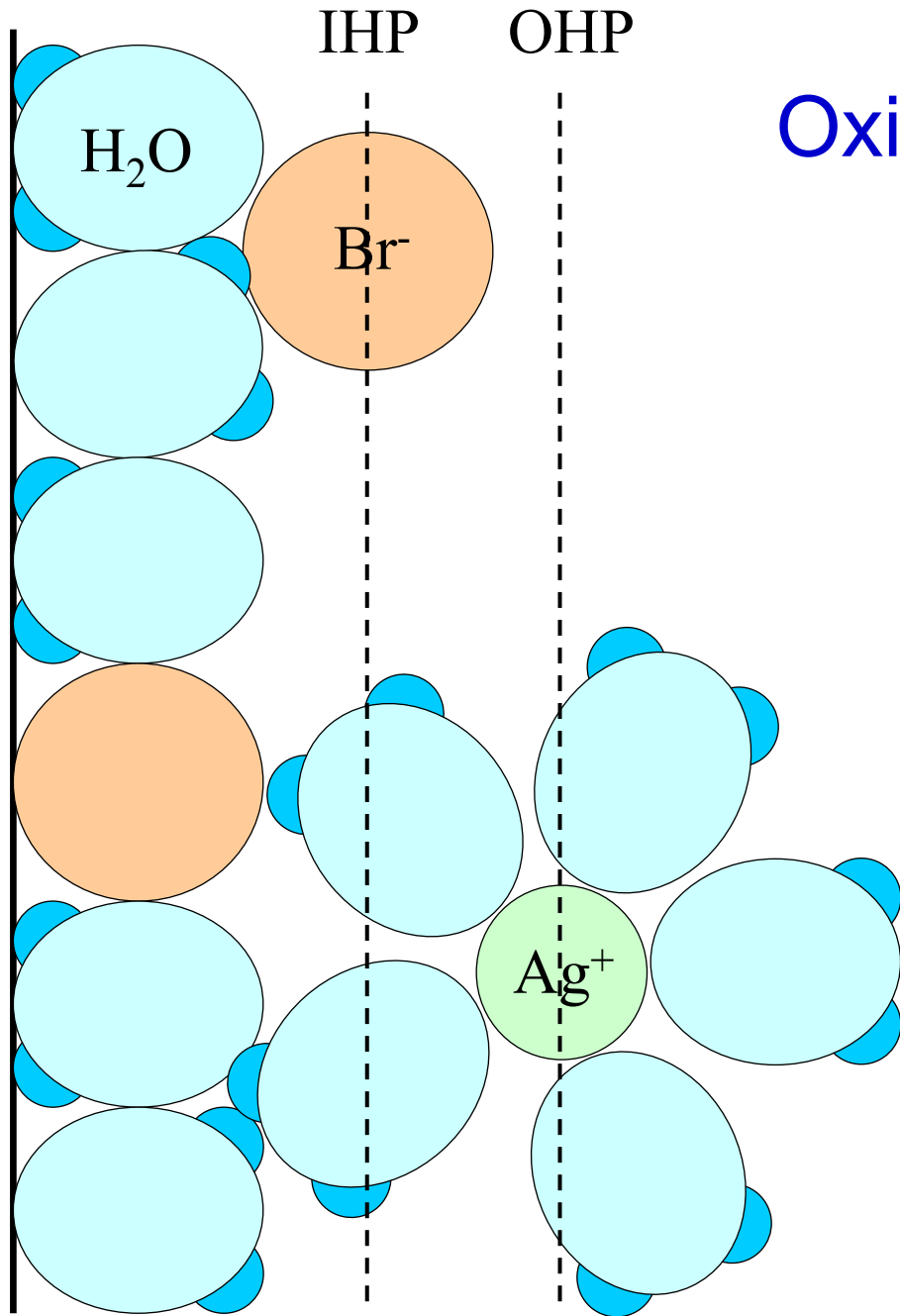
Conclusions (1)

- Metal deposition and dissolution occur by ion transfer, not by electron transfer

- A reaction in which both electrons and ions are transferred across the interface cannot be considered as a single step

- The formation of unstable intermediate following electron transfer cannot be justified by adsorption.

- Exceptions may be where the species is already adsorbed, before electron transfer has occurred

Conclusions (2)

- Steps in electrode kinetics may involve
  - Electron transfer
  - Proton transfer
  - Heavy ion transfer
- Such steps occur on widely different time scales
- Changes in the Gibbs energy must be regarded for each step individually
- New ways of analyzing electrode kinetics must be found.