



University of Pretoria



**Inaugural Lecture and Address
at University of Pretoria, 28 July 2005**

Virtual Thermodynamic Potential

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Outline of the presentation

Introduction

A bit of history

Dynamic physical chemistry (kinetics)

Equilibrium physical chemistry (thermodynamic)

Solution chemistry - work done in South Africa

Potentiometric (equilibrium) data by non-equilibrium equation

Dynamic (non-equilibrium) data by potentiometric equation

Virtual thermodynamics in action - examples

Conclusions

Department of Chemistry at UP – my vision

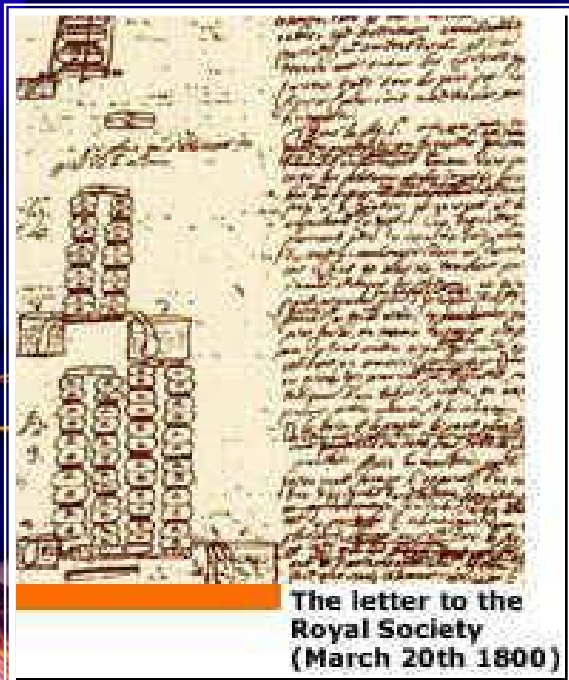
Acknowledgements



Alessandro Giuseppe Antonio Anastasio



VOLTA (1745 – 1827)



On 20 March 1800, Volta, Italian physicist, informs the President of the Royal Society, Sir Joseph Banks, of the invention of the pile.

Pile device was **the first in history "electric battery"** a source of continuous current

New source of energy





Volta demonstrating the
Voltaic Pile to Napoleon
Bonaparte



In June 1800, Napoleon reconfirms
Volta as Professor of Experimental
Physics

at the University of Pavia.

Till today presidents of some European countries confirm
scientists as Full Professor at Universities





Michael Faraday (1791-1867)

English physicist and chemist



Faraday at work in his bottle-lined laboratory in the basement of the Royal Institution in London.





**Michael
Faraday**

Theory of electrochemistry

Faraday's two laws of electrochemistry:

- (1) The amount of a substance deposited on each electrode of an electrolytic cell is directly proportional to the quantity of electricity passed through the cell.**
- (2) The quantities of different elements deposited by a given amount of electricity are in the ratio of their chemical equivalent weights**





Here, members of the Royal Institution attend a lecture on

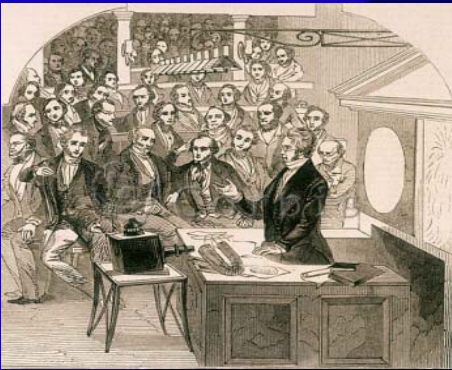
Magnetism and Light

by Professor Faraday

(London 1846)

Many years later, as **Maxwell** later freely admitted, the basic **ideas** for his mathematical theory of electrical and magnetic fields **came from Faraday**.





Faraday introduced to science
paramagnetics and diamagnetics

Tyndall said:

"Michael Faraday was the greatest experimental philosopher the world has ever seen; ... the mighty investigator"

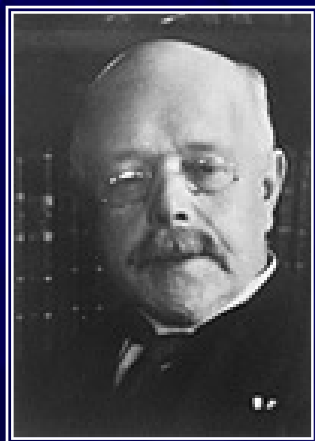
Every year on Christmas Day, he presented at the Royal Institution his **Faraday Lectures for Children**

Christmas lectures for children continue to this day.

Two electrical units (for capacitance and inductance) are named after Michael Faraday to honour his accomplishments.



The discoveries by Galvani, Volta, Faraday and others indicated a promising future for dynamic electrochemistry.



Walther Hermann Nernst (1864 - 1941)
German physicist and chemist

The Nobel Prize in Chemistry 1920

Nobel Lecture, December 12, 1921

Studies in Chemical Thermodynamics





The Nernst Equation and the Third Law of Thermodynamics

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$\ln K = E^\circ \frac{nF}{RT}$$

$$\Delta_r G^\circ = -RT \ln K$$
$$\Delta_r G^\circ = -nFE^\circ$$

Overthermodynamical approach prevents
development of charge transfer at interfaces.

The direct conversion of chemical to electrical energy
was stopped for some 50 years.

Dynamic Electrochemistry becomes recognised



Max Volmer (1885 – 1965)

German professor of physical chemistry and electrochemistry

Max Volmer's work formed the basis of phenomenological kinetic electrochemistry

Butler-Volmer equation

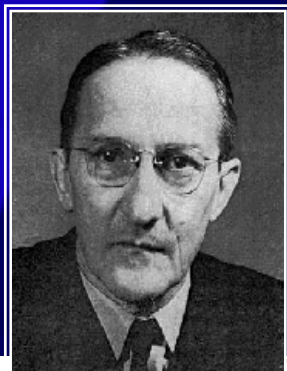
$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$i = i_0 \left[\exp\left(\frac{\alpha_A n F}{RT} \eta\right) - \exp\left(-\frac{\alpha_C n F}{RT} \eta\right) \right]$$

Max Volmer became a director of the Institute of Physical Chemistry and Electrochemistry.



Dynamic Electrochemistry – highest Honours



J. Heyrovský

(1890 - 1967)

Charles University,
Prague



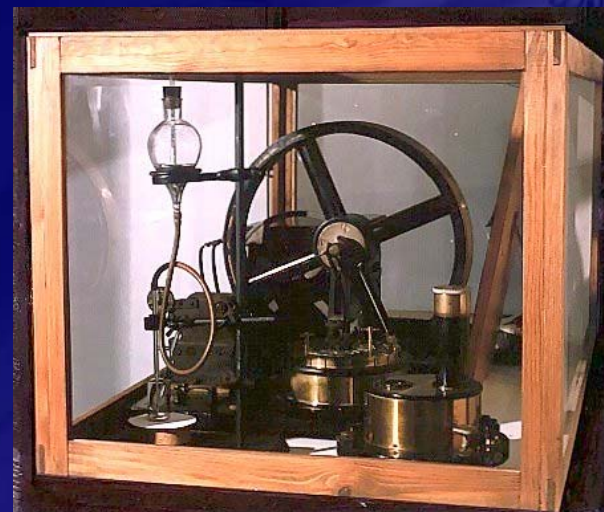
1959

Jaroslav Heyrovský, father of electroanalytical chemistry, recipient of the Nobel Prize.

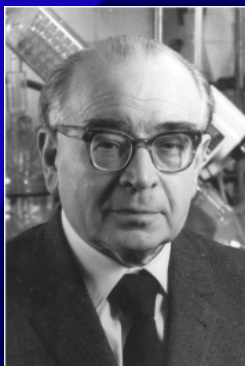
All voltammetric methods used now in electroanalytical chemistry originate from polarography developed by him.



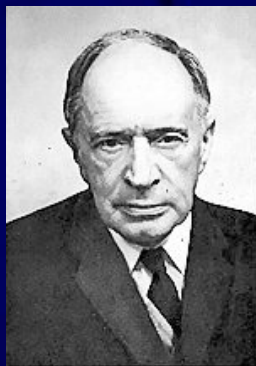
Jaroslav Heyrovský and his son Michael



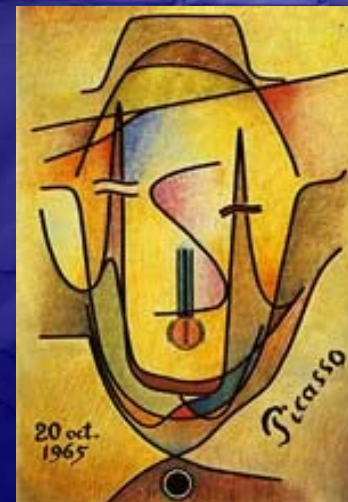
Dynamic Electrochemistry - well established science



Wiktor Kemula



Alexander Naumovich Frumkin
"father" of Russian
electrochemistry.



The portrait of Frumkin
painted in the Picasso's
manner



*A.N. Frumkin and J. O'M.
Bockris (U.S.A. 1960)*

According to Bockris:

*"The Great Nernstian Hiatus"
was ended by Frumkin*



**EQUILIBRIUM
E-CHEMISTRY**



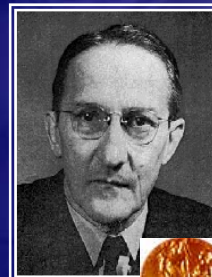
Walther Hermann Nernst

**Physical Chemistry textbook
by Atkins**

**Physical Chemistry textbook
by Levine**

**Analytical Chemistry
textbooks**

**DYNAMIC E-CHEMISTRY
(KINETICS)**



M. Volmer J. Heyrovský A.N. Frumkin

**Physical Chemistry textbook
by Atkins**

**Analytical Chemistry
textbooks**

Metal-Ligand interactions ($M_pL_qH_r$)

Model of a Metal-Ligand system & thermodynamic stability constants

EQUILIBRIUM E-CHEMISTRY

Glass electrode potentiometry

Nernst equation

Thermodynamic potential

DYNAMIC E- CHEMISTRY

Voltammetric techniques

Many simplified equation

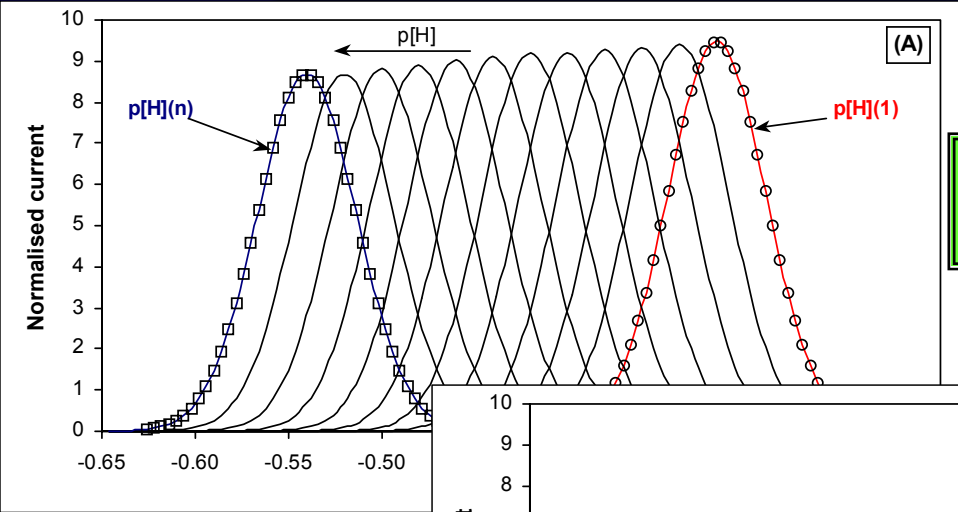
Thermodynamics

Kinetics (electron transfer)

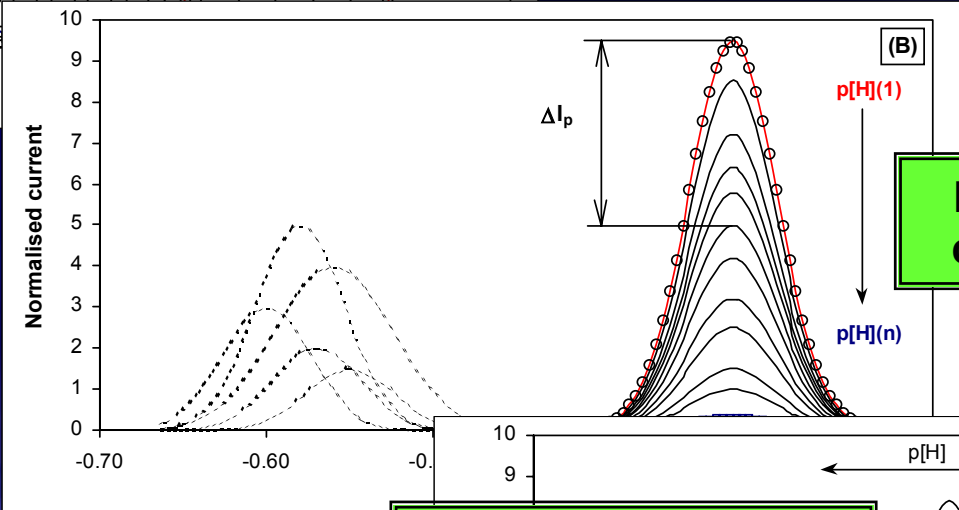
Transport (to & from interface)

Two different WORLDS that did not talk to each other at all.

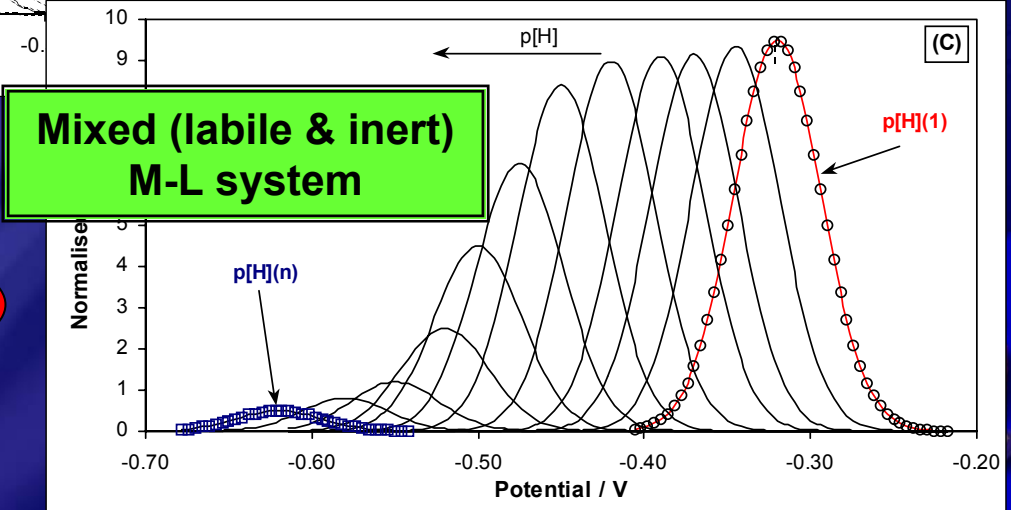




Dynamic and labile M-L system



Inert metal complexes



Mixed (labile & inert) M-L system

Homogeneous Equilibria

Interfacial kinetics?

Reversible

Quasi-Reversible

Irreversible

1) Main experimental variable – ΔE

$$\Delta E_{1/2} - \frac{RT}{nF} \ln \frac{I(c)}{I(s)} = \frac{RT}{nF} \ln \beta_{ML_j} [L_T]^j$$

Skoog, ...Fundamentals of Anal. Chem 6th ed. 1992
Lingane
1941

$$\Delta E_{1/2} - \frac{RT}{nF} \ln \frac{I(c)}{I(s)} = \frac{RT}{nF} \ln \sum_0^N \beta_{ML_j} [L_T]^j$$

DeFord-Hume
1951

Still regarded as the method in the field

$$F_0[X] = \sum_0^N \beta_{MX_j} [X_T]^j$$

Leden–DeFord–Hume
1951

$$F_{00}[X, Y] = \sum_0^N \beta_{MX_j Y_i} [X_T]^j [Y_T]^i$$

Leden–Schaap–Mc Master
1961

Dynamic and labile M-L system

No rigorous refinement of stability constants

Mass-balance equations not involved

Limited applications with quite uncertain results



2) Experimental variable – ΔI

$$\bar{D} = \frac{D_M + D_{ML}K_{ML}[L]}{1 + K_{ML}[L]}$$

Kačena and Matoušek

1953

Inert complex ML (at fixed pH)

$$K_{ML} = K_{NL} \times \frac{(I_N - I_{N(M)})(c_M I_N - c_N I_{N(M)})}{(I_{N(M)})^2}$$

Schwarzenbach

1952

No rigorous data evaluation

Is there any room for
further development?



A paradigm shift
(1996)

Any kind of complex $M_xL(1)_yL(2)_z$ (at any experimental conditions)

Corrected shift in potential (ΔE_p or $\Delta E_{1/2}$) or change in potential (ISE)

$$(E(s) - E(c))_{x(i)} - \frac{RT}{nF} \ln \left(\frac{I(c)}{I(s)} \right)_{x(i)} = \frac{RT}{nF} \ln \left(\frac{[M_T]}{[M]} \right)_{x(i)}$$

[M] from mass-balance equations; modelling-refinement: ECFC & CCFC

I. Cukrowski, *Anal. Chim. Acta* 336 (1996) 23-36

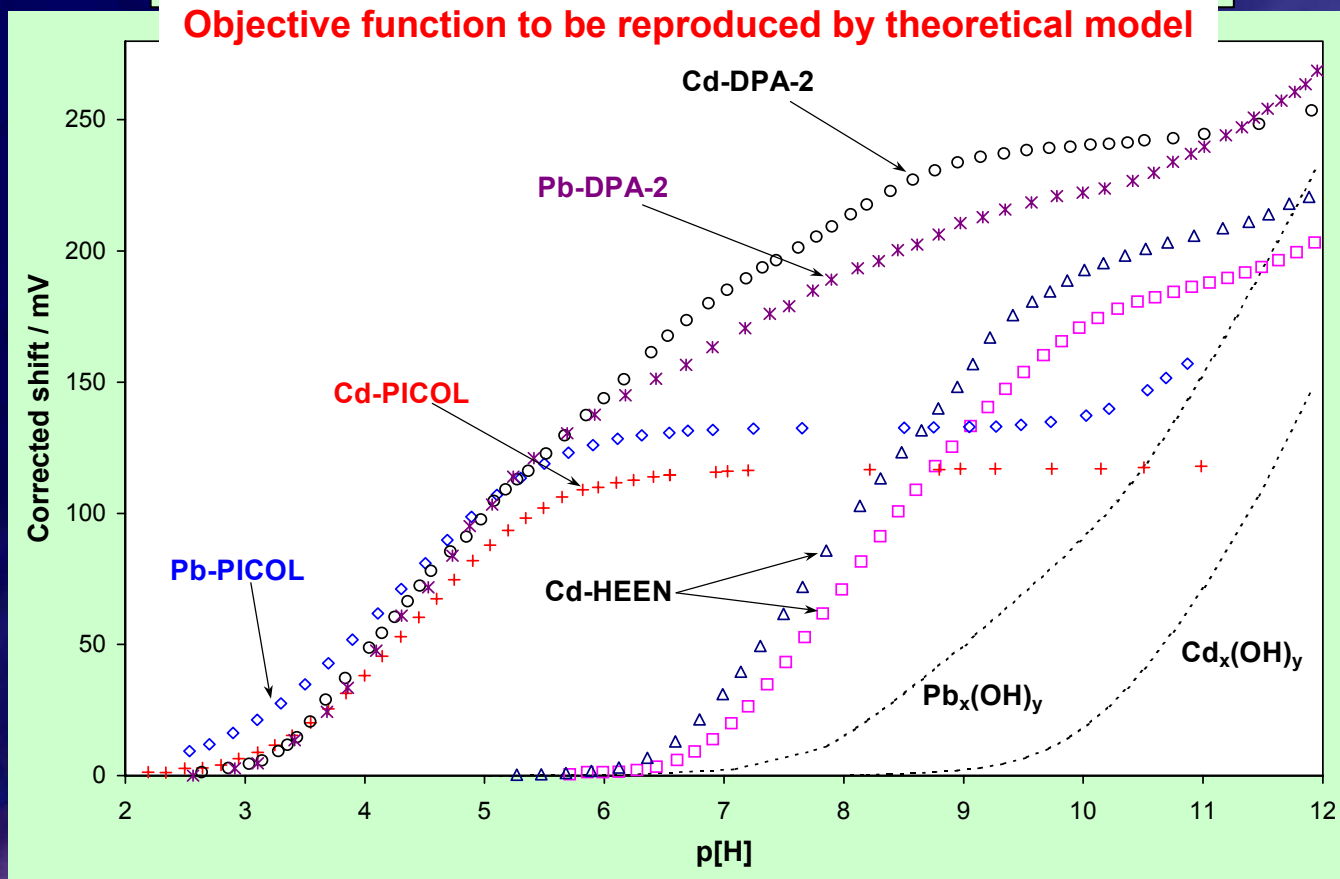
I. Cukrowski, M. Adsetts, *J. Electroanal. Chem.* 429 (1997) 129-137



Corrected shift & Experimental Complex Formation

$$CS_{x(i)} = (E(s) - E(c))_{x(i)} - \frac{RT}{nF} \ln \left(\frac{I(c)}{I(s)} \right)_{x(i)}$$

Objective function to be reproduced by theoretical model

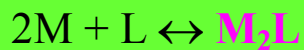




$$\beta_{M(H_4L)} = [MH_4L] / [M][H]^4[L]$$



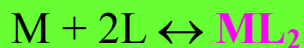
$$\beta_{M(H_2L)} = [MH_2L] / [M][H]^2[L]$$



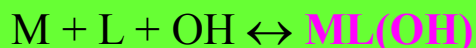
$$\beta_{M_2L} = [M_2L] / [M]^2[L]$$



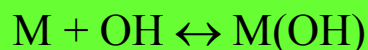
$$\beta_{ML} = [ML] / [M][L]$$



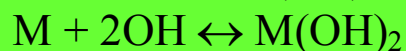
$$\beta_{ML_2} = [ML_2] / [M][L]^2$$



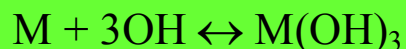
$$\beta_{ML(OH)} = [ML(OH)] / [M][L][OH]$$



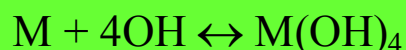
$$\beta_{M(OH)} = [M(OH)] / [M][OH]$$



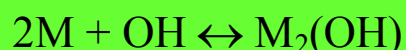
$$\beta_{M(OH)_2} = [M(OH)_2] / [M][OH]^2$$



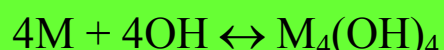
$$\beta_{M(OH)_3} = [M(OH)_3] / [M][OH]^3$$



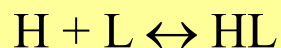
$$\beta_{M(OH)_4} = [M(OH)_4] / [M][OH]^4$$



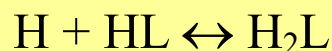
$$\beta_{M_2(OH)} = [M_2(OH)] / [M]^2[OH]$$



$$\beta_{M_4(OH)_4} = [M_4(OH)_4] / [M]^4[OH]^4$$



$$K_1^H = [HL] / [H][L]$$



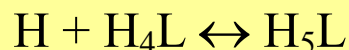
$$K_2^H = [H_2L] / [H][HL]$$



$$K_3^H = [H_3L] / [H][H_2L]$$



$$K_4^H = [H_4L] / [H][H_3L]$$



$$K_5^H = [H_5L] / [H][H_4L]$$



$$K_6^H = [H_6L] / [H][H_5L]$$

Complexes:

Protonated

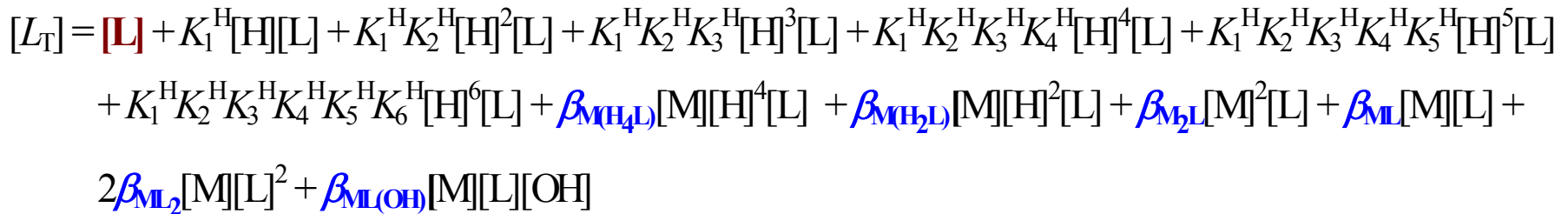
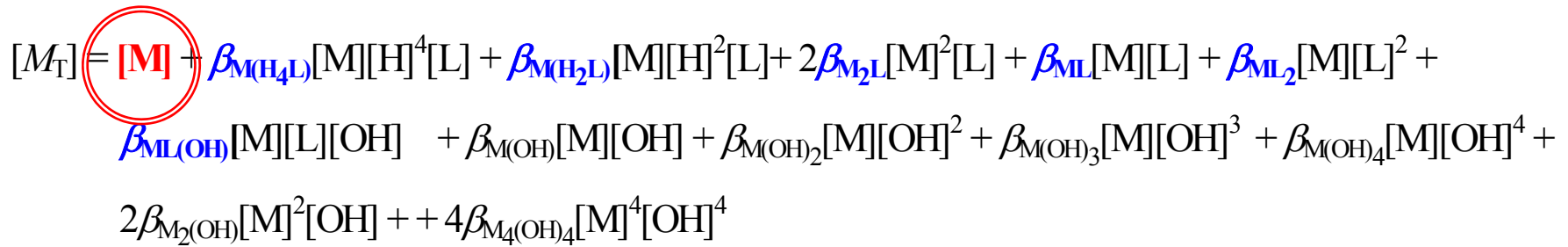
Polynuclear

Labile

Inert

hydroxo





$$\{q(RT/nF)\}/p$$

$$\frac{RT}{nF} \ln \left(\frac{[M_T]}{[M]} \right)_{x(i)}$$

Computed
Complex
Formation Curve

Theoretical
model

New definition of Nernstian slope
(modelling of M-L systems)

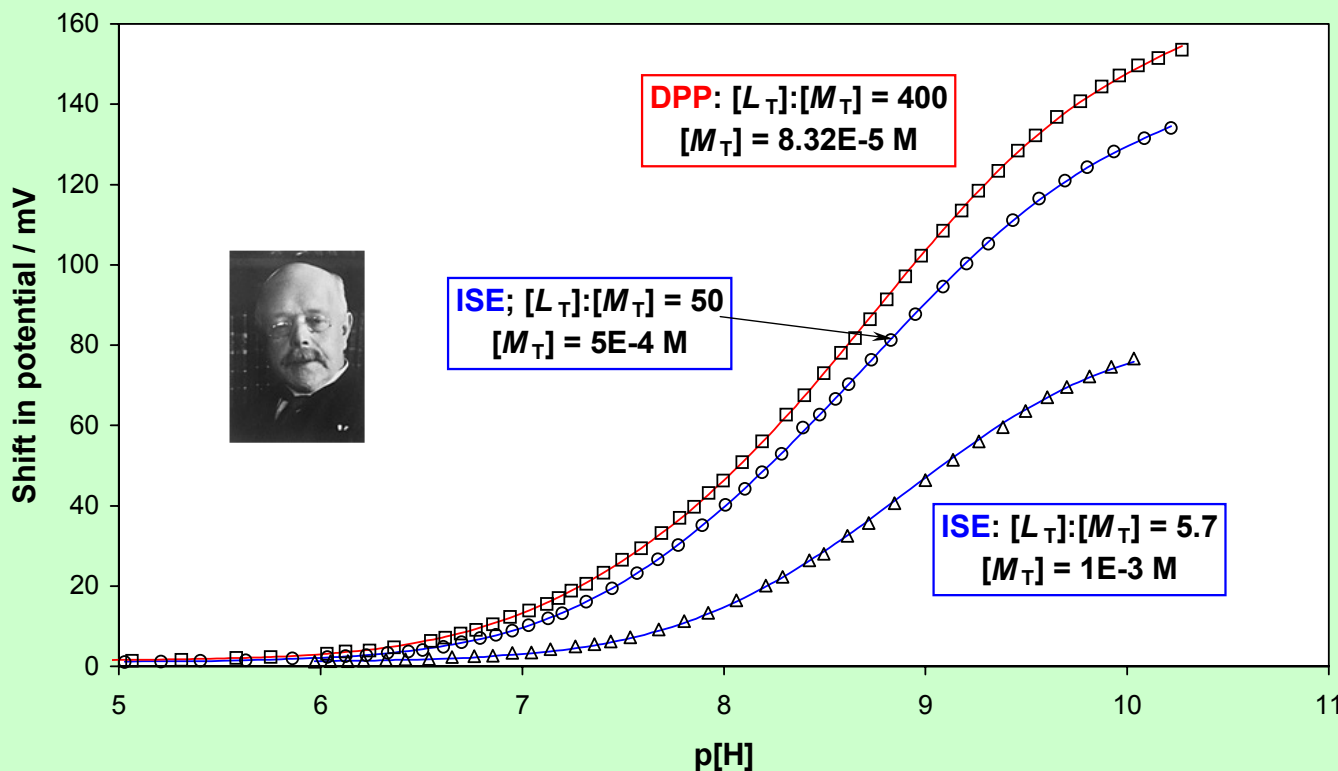


Nernstian data by DYNAMIC ELECTROCHEMISTRY equation

$$(E(s) - E(c))_{x(i)}$$

$$= \frac{RT}{nF} \ln \left(\frac{[M_T]}{[M]} \right)_{x(i)}$$

ECFC and CCFC for Cd(II)-Glycine system studied by DPP and ISE



Metal-Ligand interactions ($M_pL_qH_r$)

Model of a Metal-Ligand system & thermodynamic stability constants

EQUILIBRIUM E-CHEMISTRY

Potentiometric data changed to
Virtual dynamic data

DYNAMIC E-CHEMISTRY

$$(E(s) - E(c))_{x(i)} = \frac{RT}{nF} \ln \left(\frac{[M_T]}{[M]} \right)_{x(i)}$$

The same equation is valid for fully dynamic
and reversible M-L system studied by voltammetry



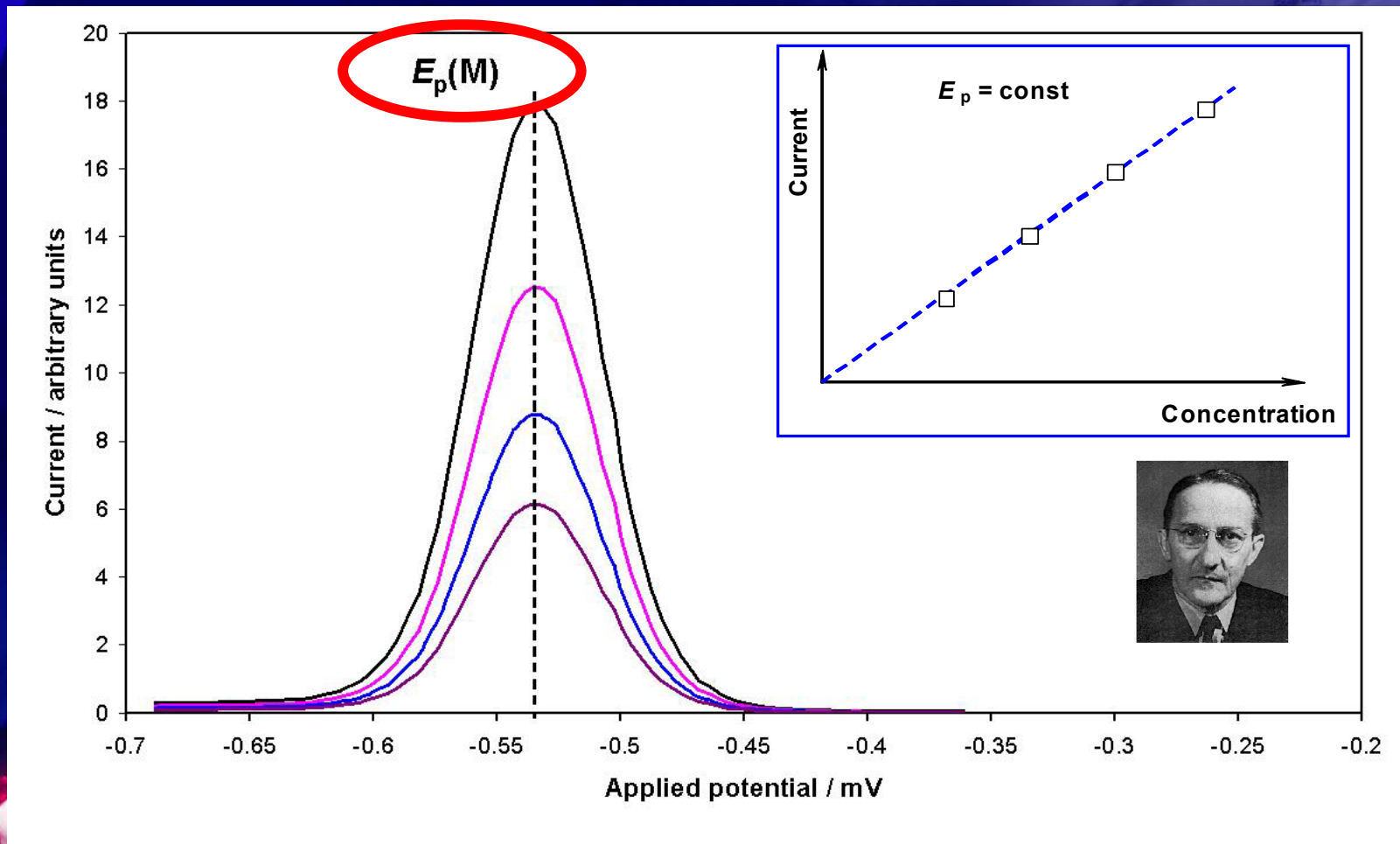
Nernst domain by equation for the dynamic data treatment
at any experimental conditions

I. Cukrowski, G. Ngigi, *Electroanalysis* 13 No. 15 (2001) 1242-1252

I. Cukrowski, N. Maseko, *Electroanalysis* 15 No. 17 (2003) 1377-1388

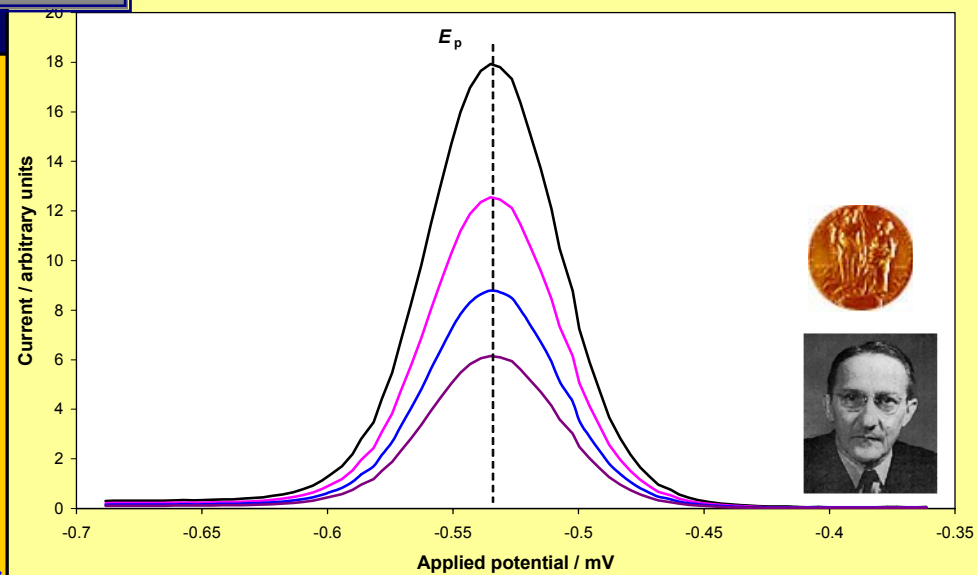
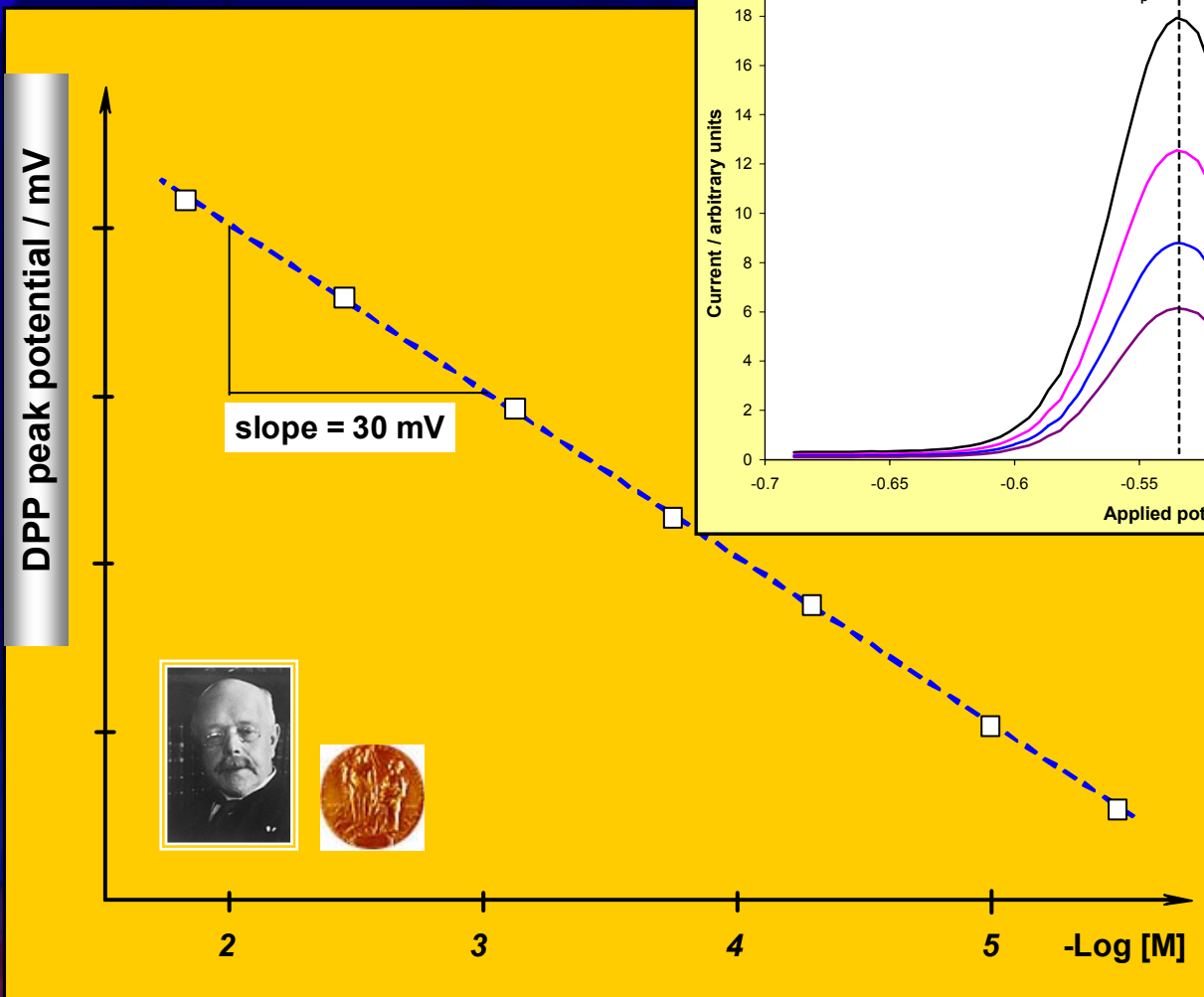


Quantitative voltammetric analysis of a metal ion

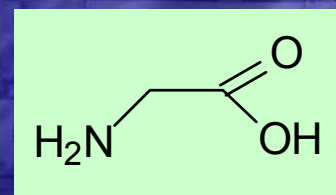


'Virtual ISE' from polarographic results

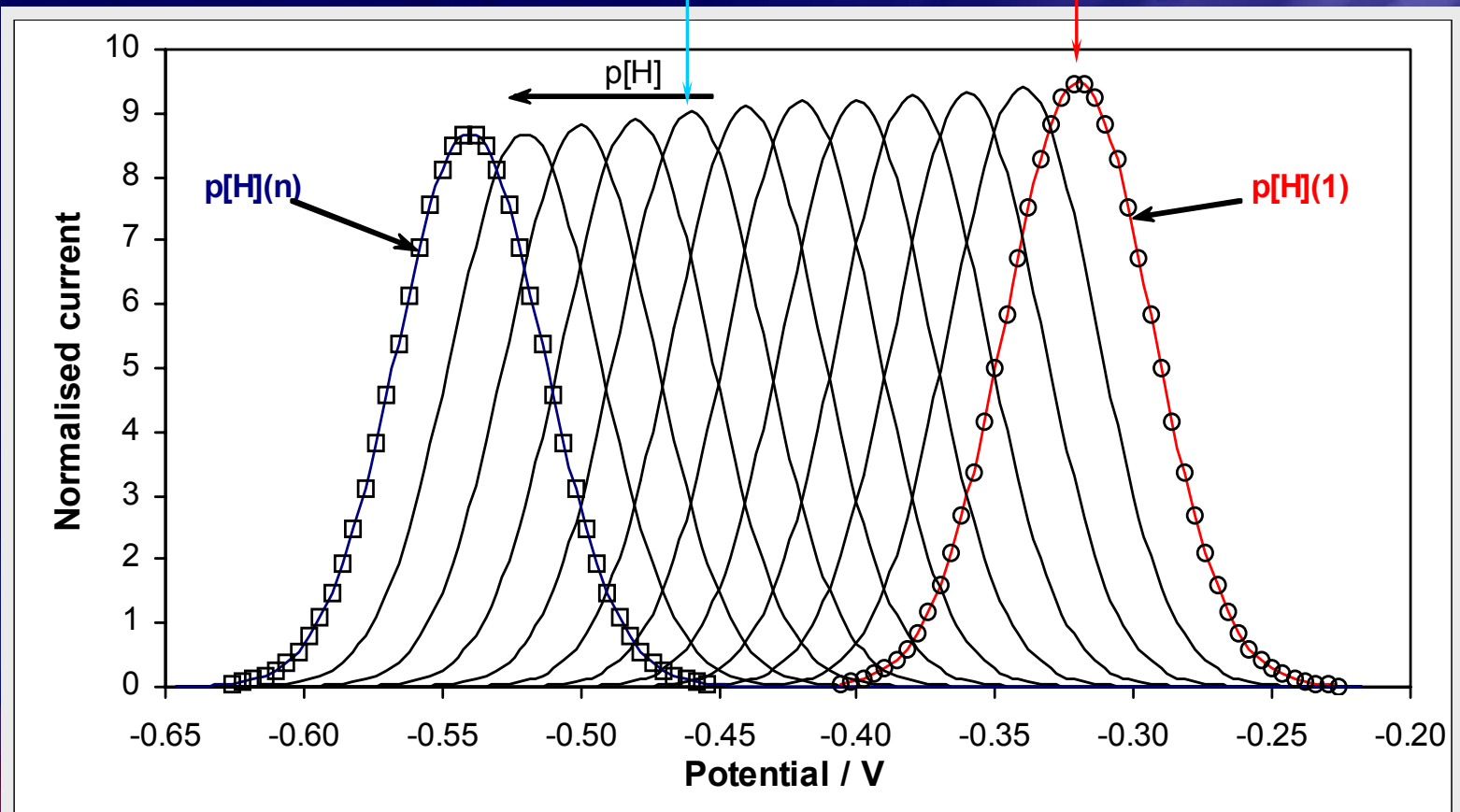
Virtual thermodynamic data



DPP of a labile (or dynamic) M-L system



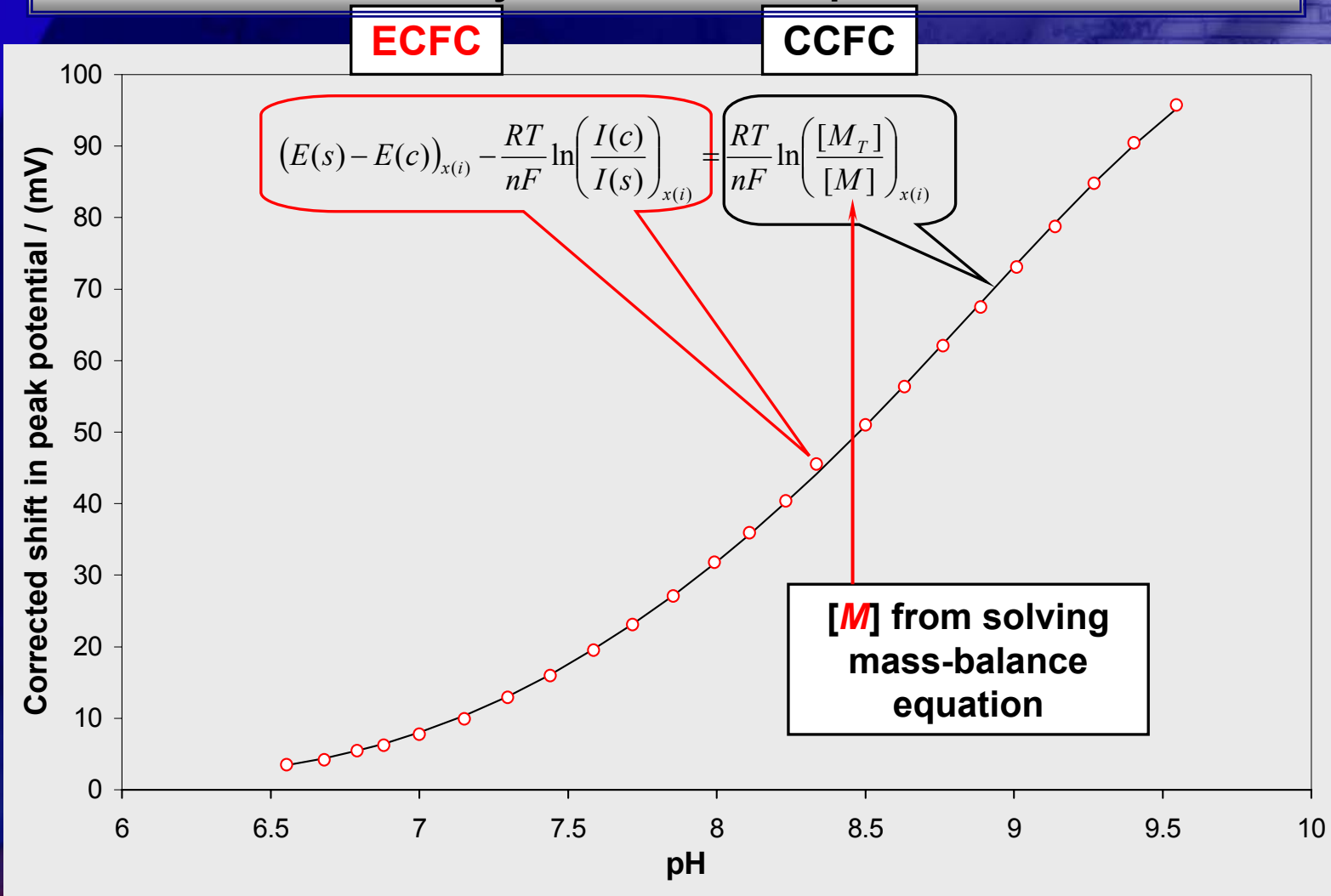
Glycine



Cd-Glycine-OH system



Refinement of stability constants: complex formation curves



I. Cukrowski, *Anal. Chim. Acta* 319 (1996) 39 – 48.

I. Cukrowski, M. Adsetts, *J. Electroanal. Chem.* 429 (1997) 129 - 137

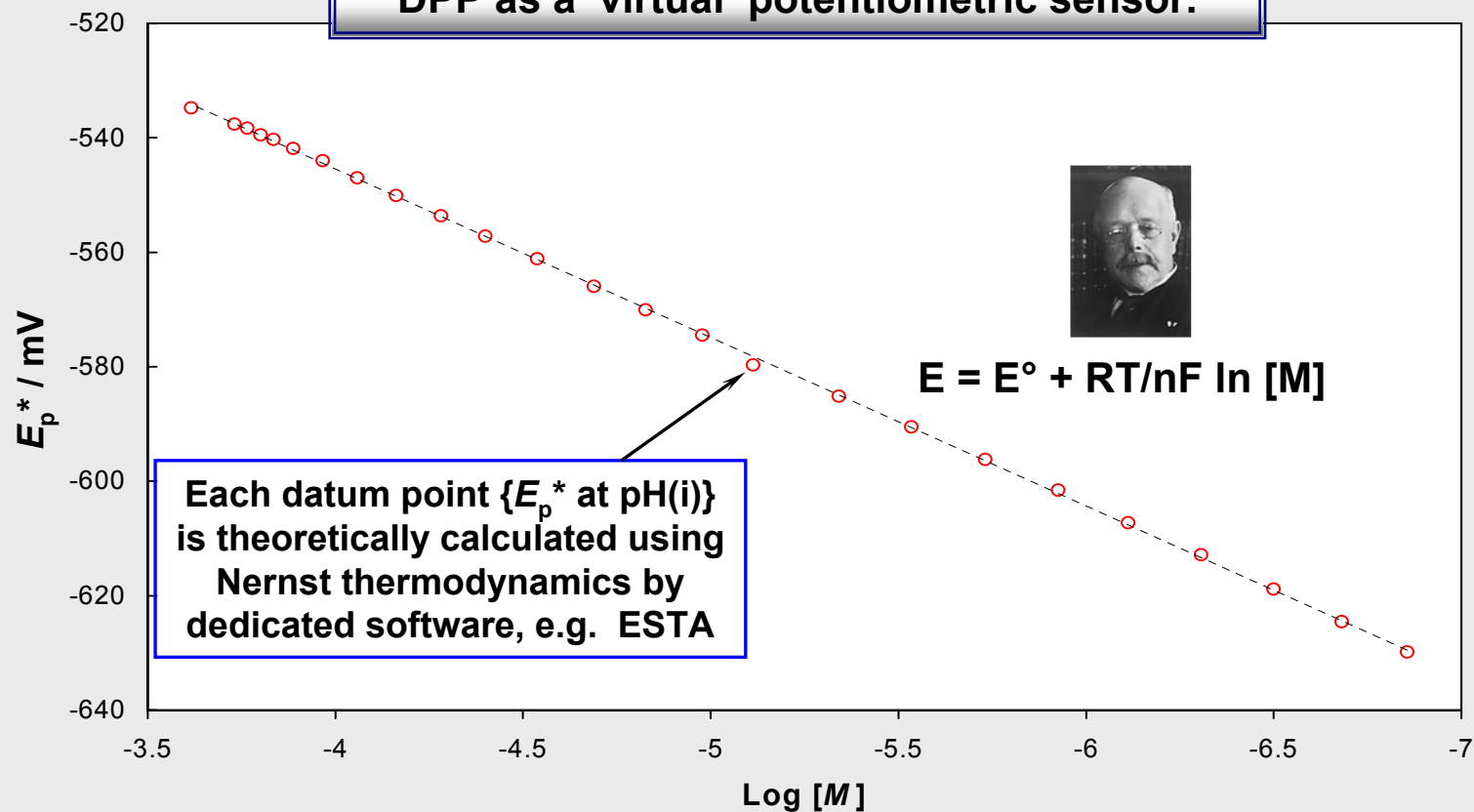
Cd-Glycine-OH system



$$E_p(c)_{x(i)} + \frac{RT}{nF} \ln \left(\frac{I(c)}{I(s)} \right)_{x(i)} = (E_p^*)_{x(i)}$$

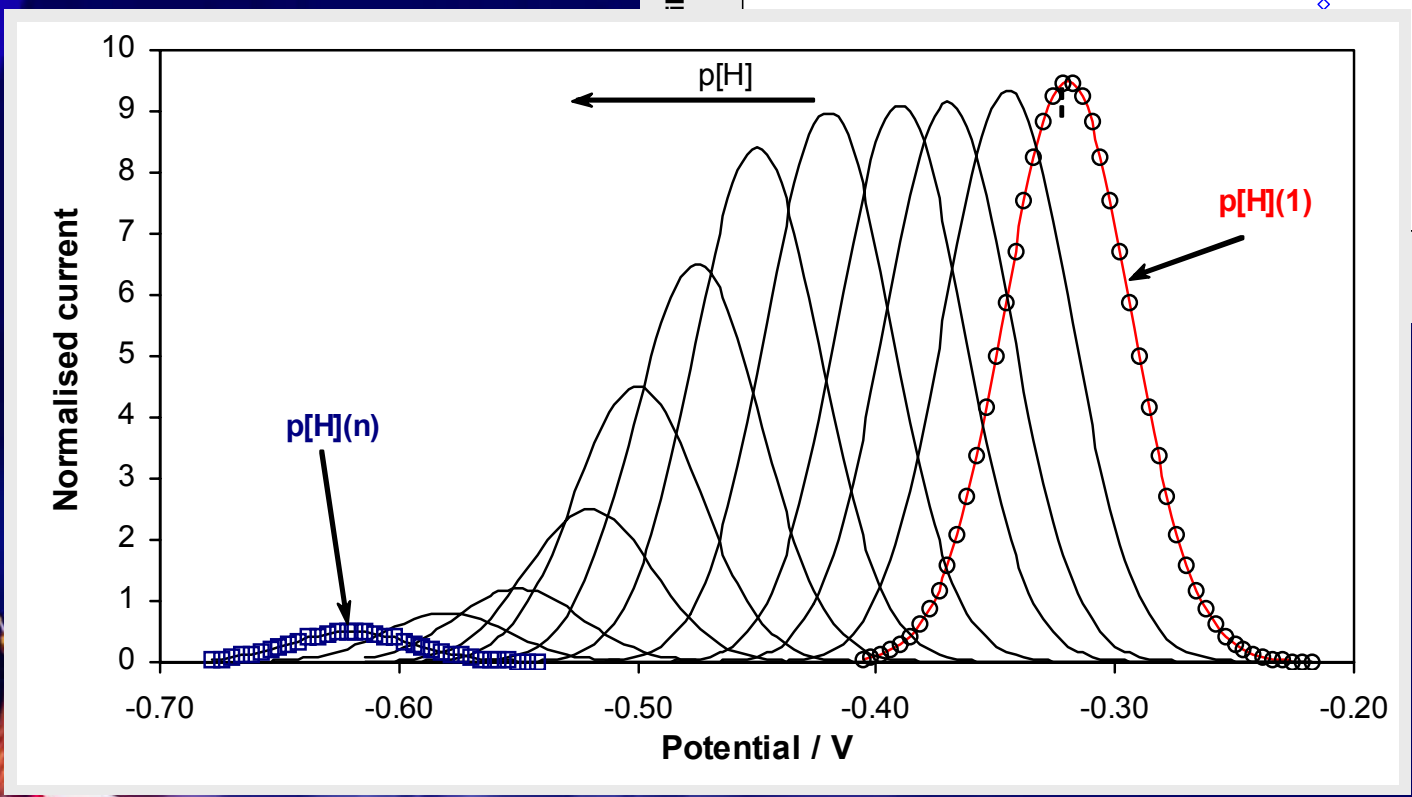
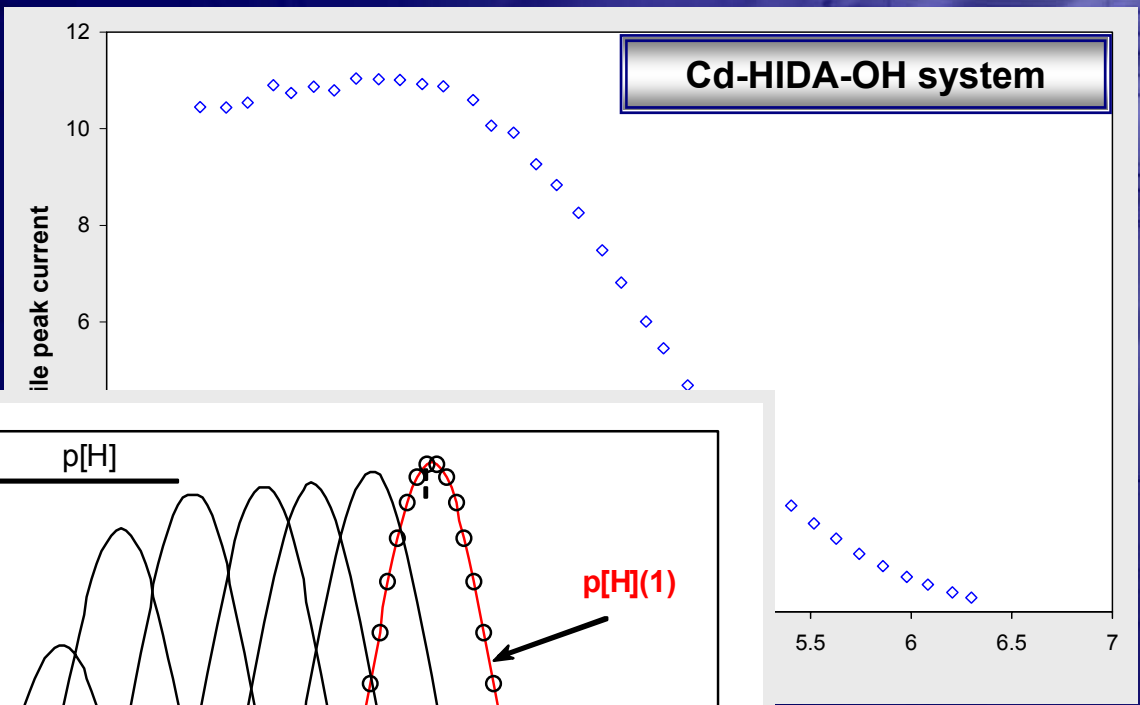
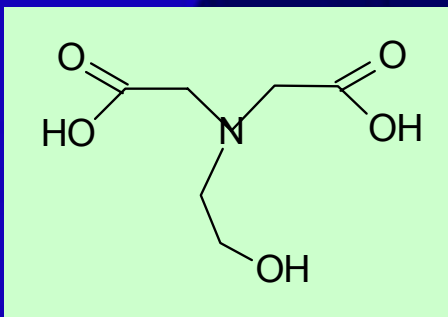
$$E_p^* < E_p(c) \quad \text{if} \quad I(c) < I(s)$$

DPP as a 'virtual' potentiometric sensor.

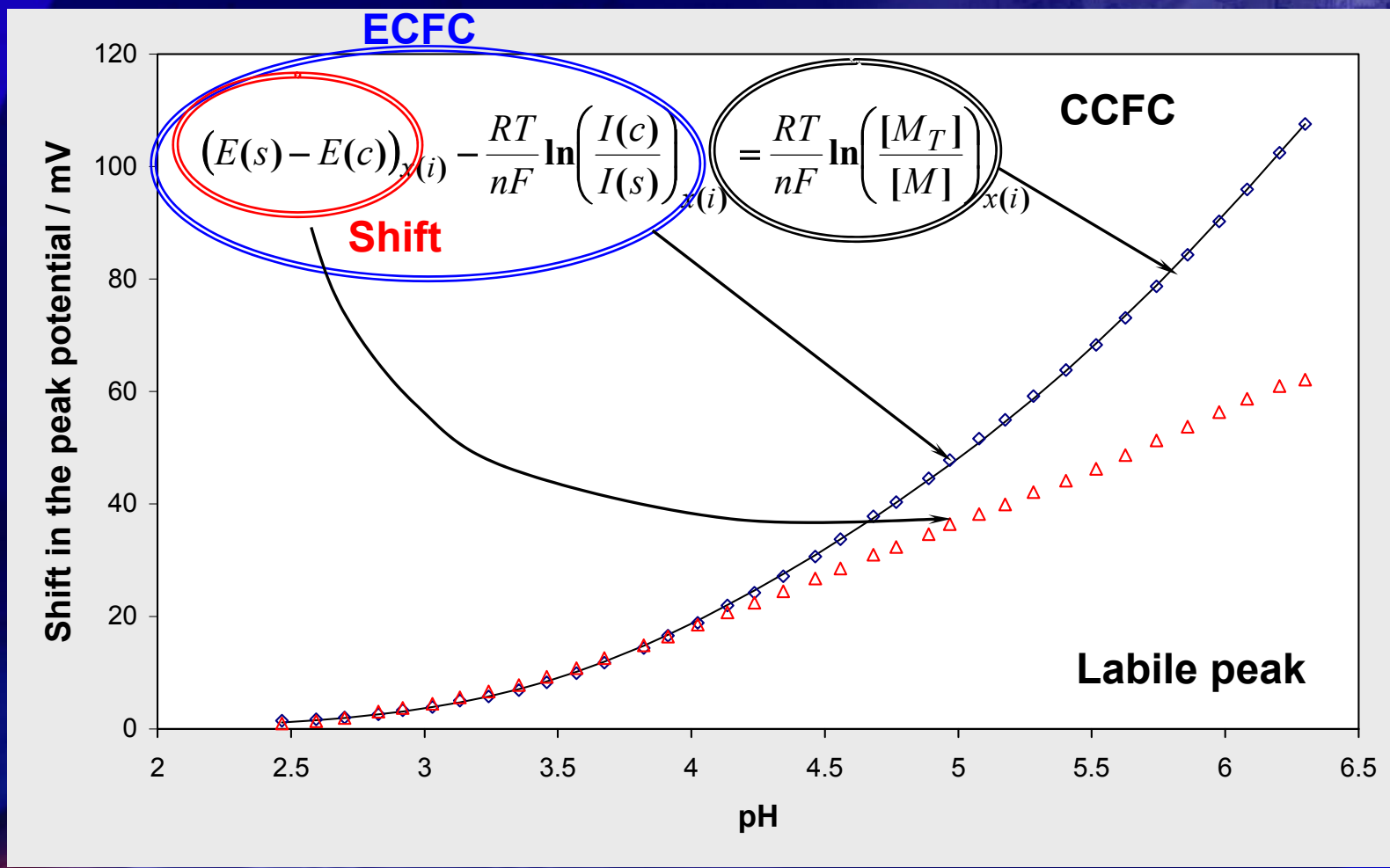


Cd-Glycine-OH system





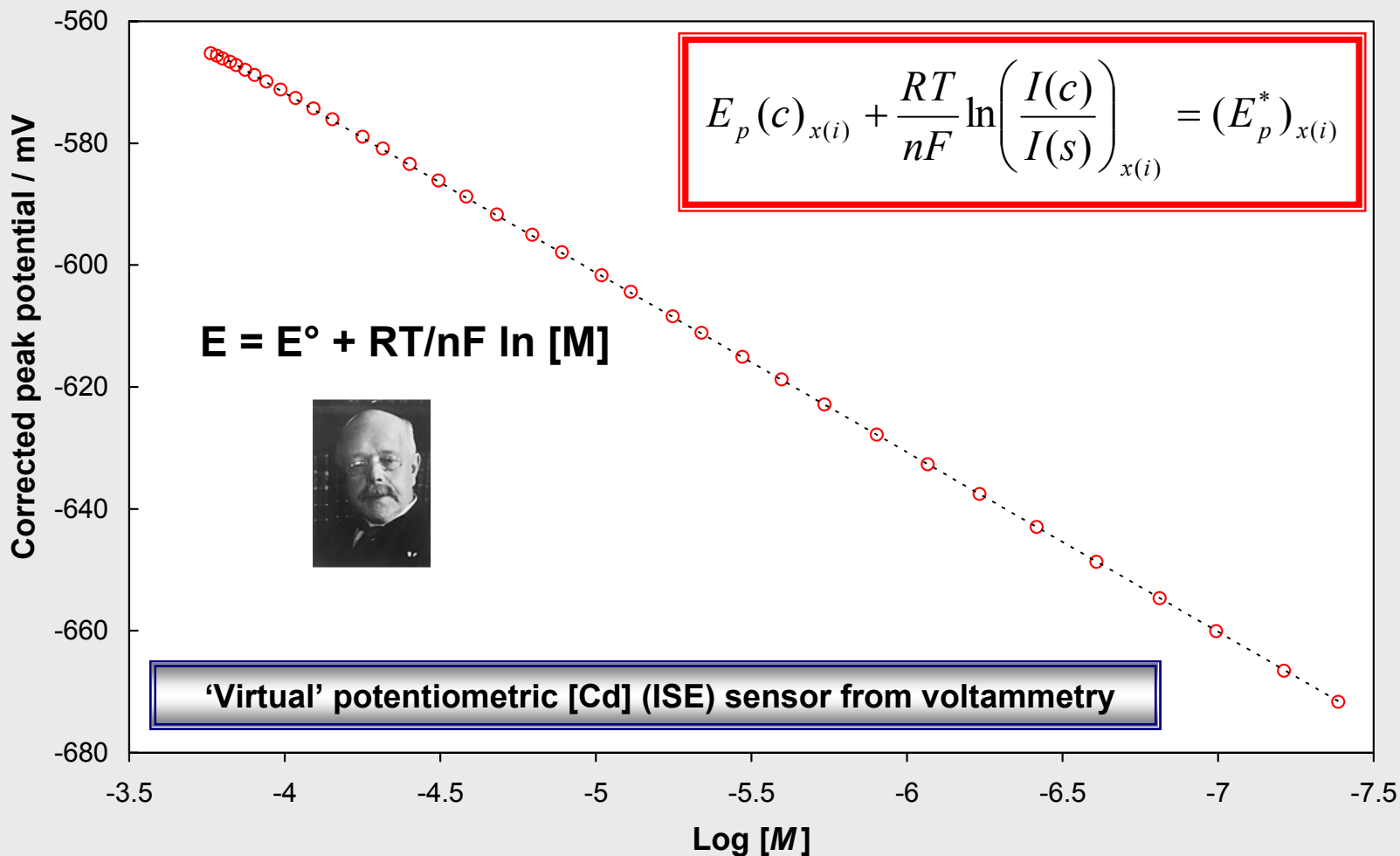
Experimental and Computed Complex Formation Curves



Cd-HIDA-OH system



Virtual thermodynamic data

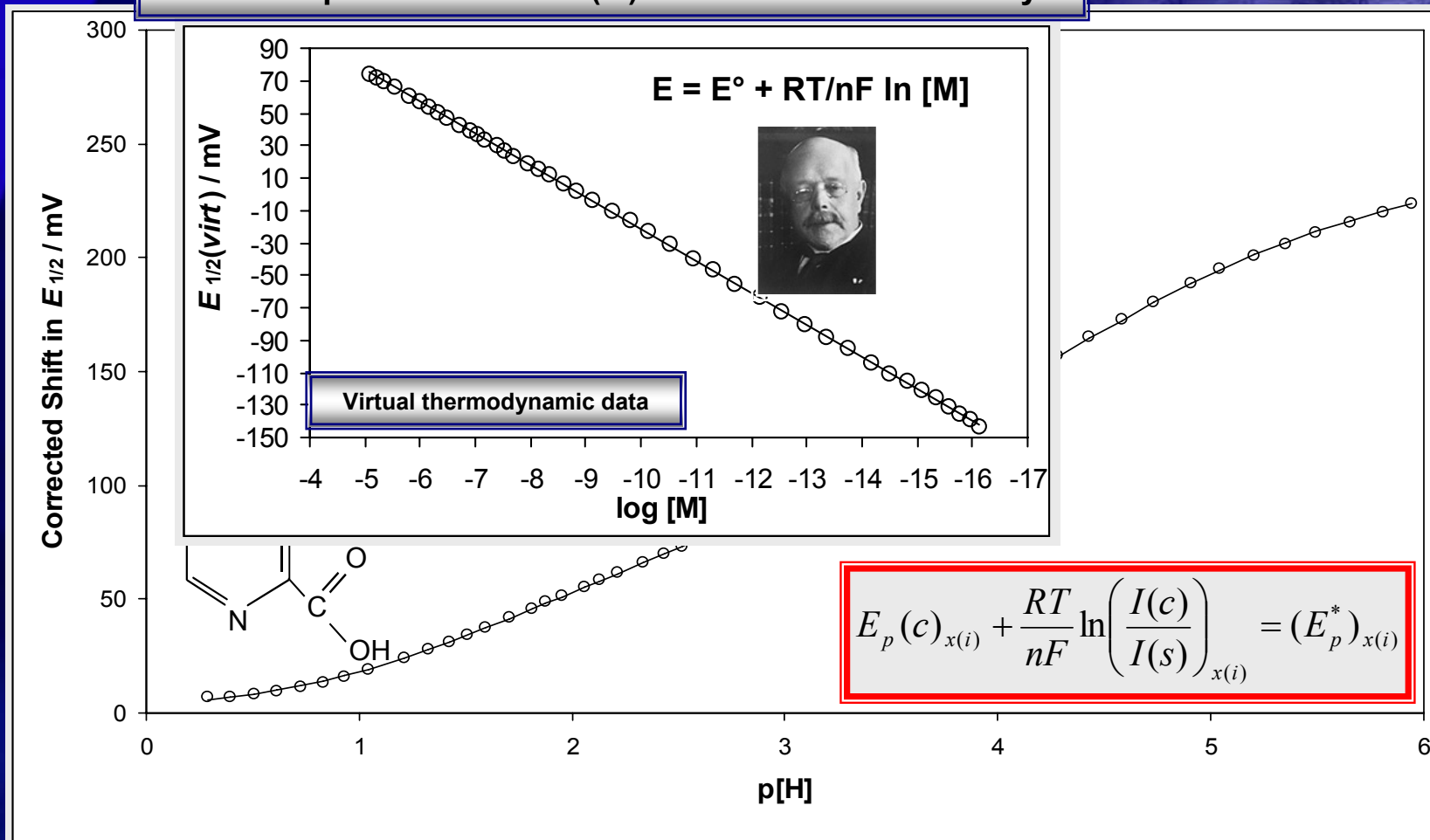


I. Cukrowski, J.M. Zhang, unpublished results

Cd-HIDA-OH system



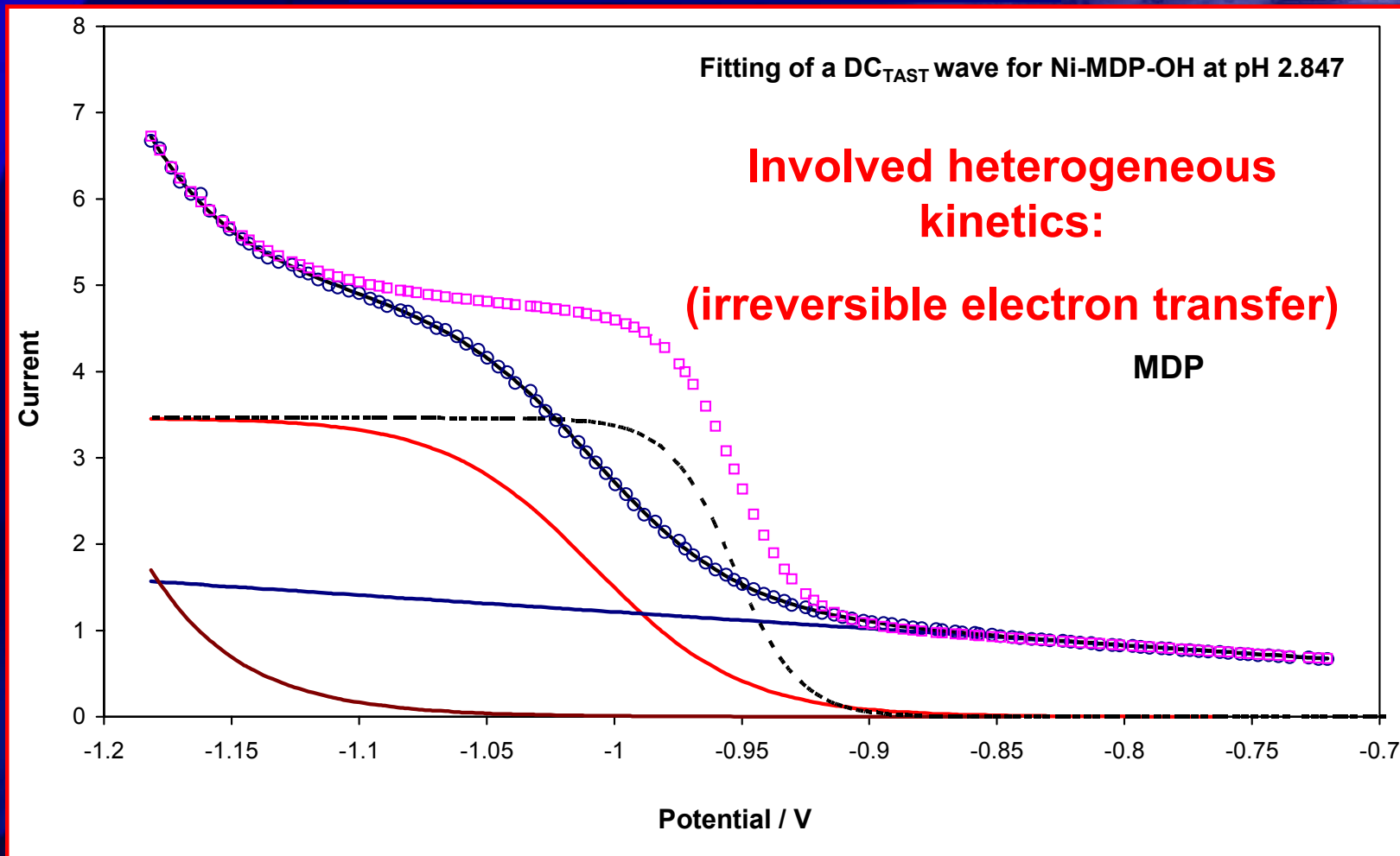
'Virtual' potentiometric Bi(III) sensor from voltammetry



Bi(III)-(Picolinic Acid)-OH system



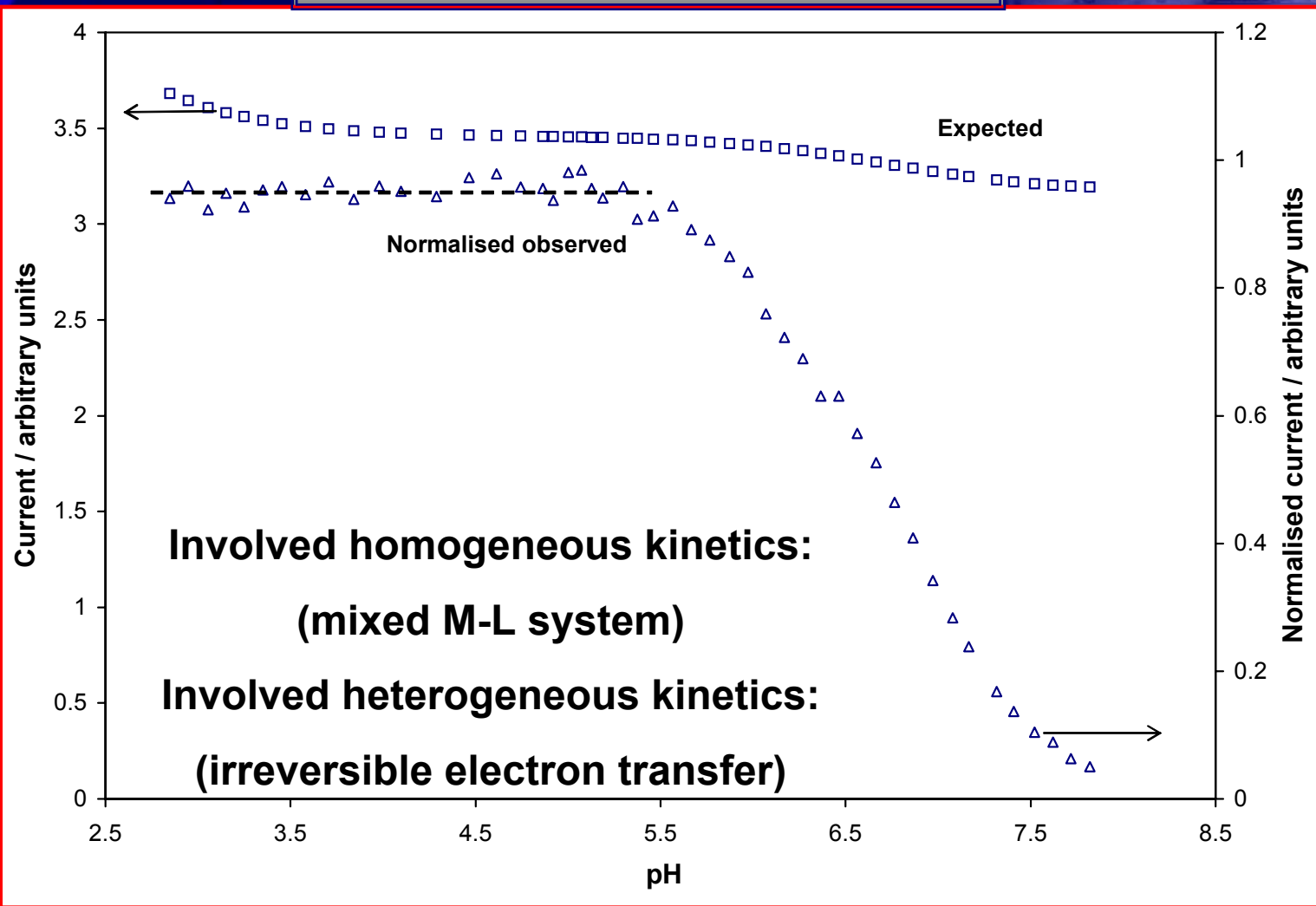
Irreversible and mixed M-L-OH system



Ni-MDP-OH system



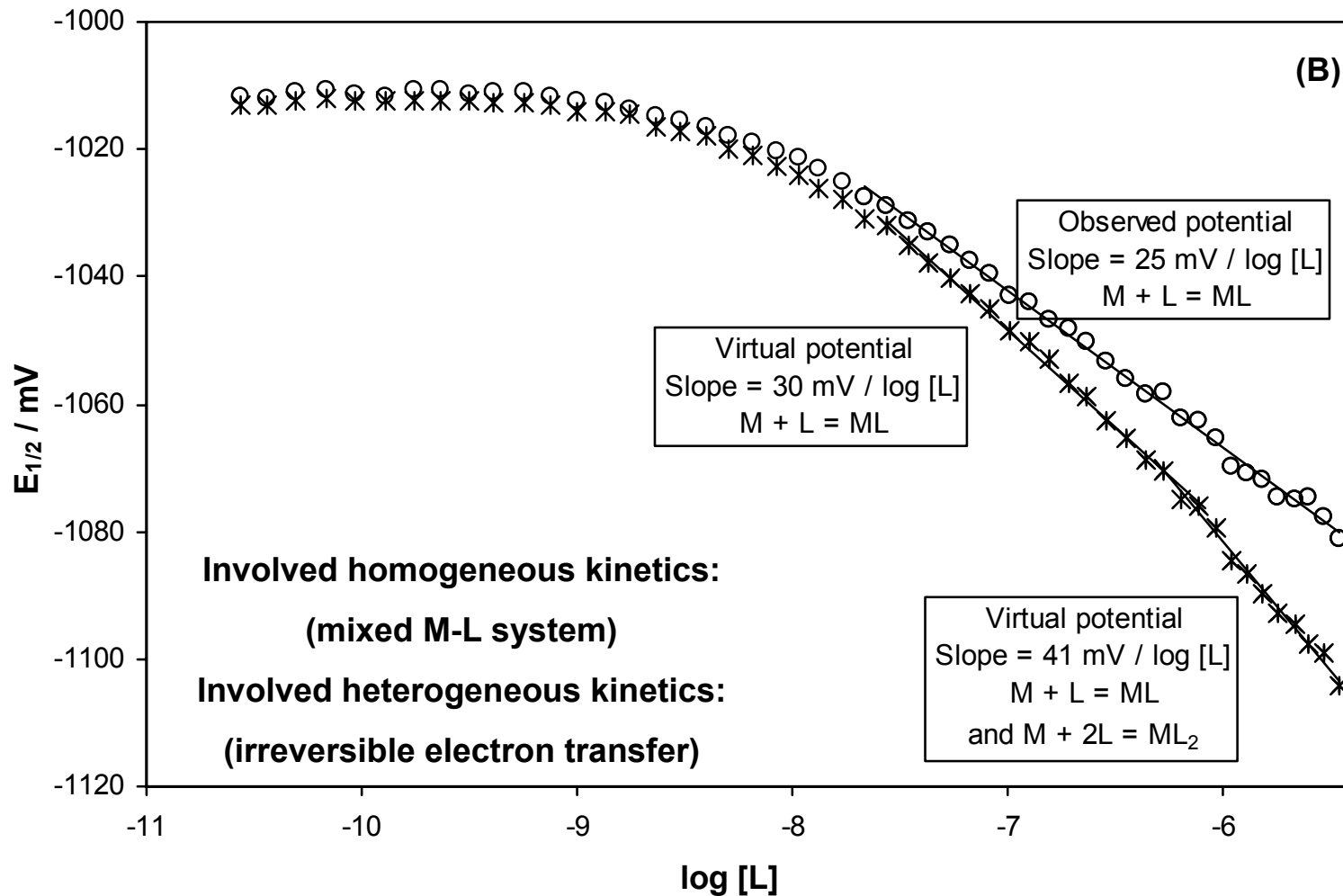
Kinetics of the M-L-OH system



Ni-MDP-OH system



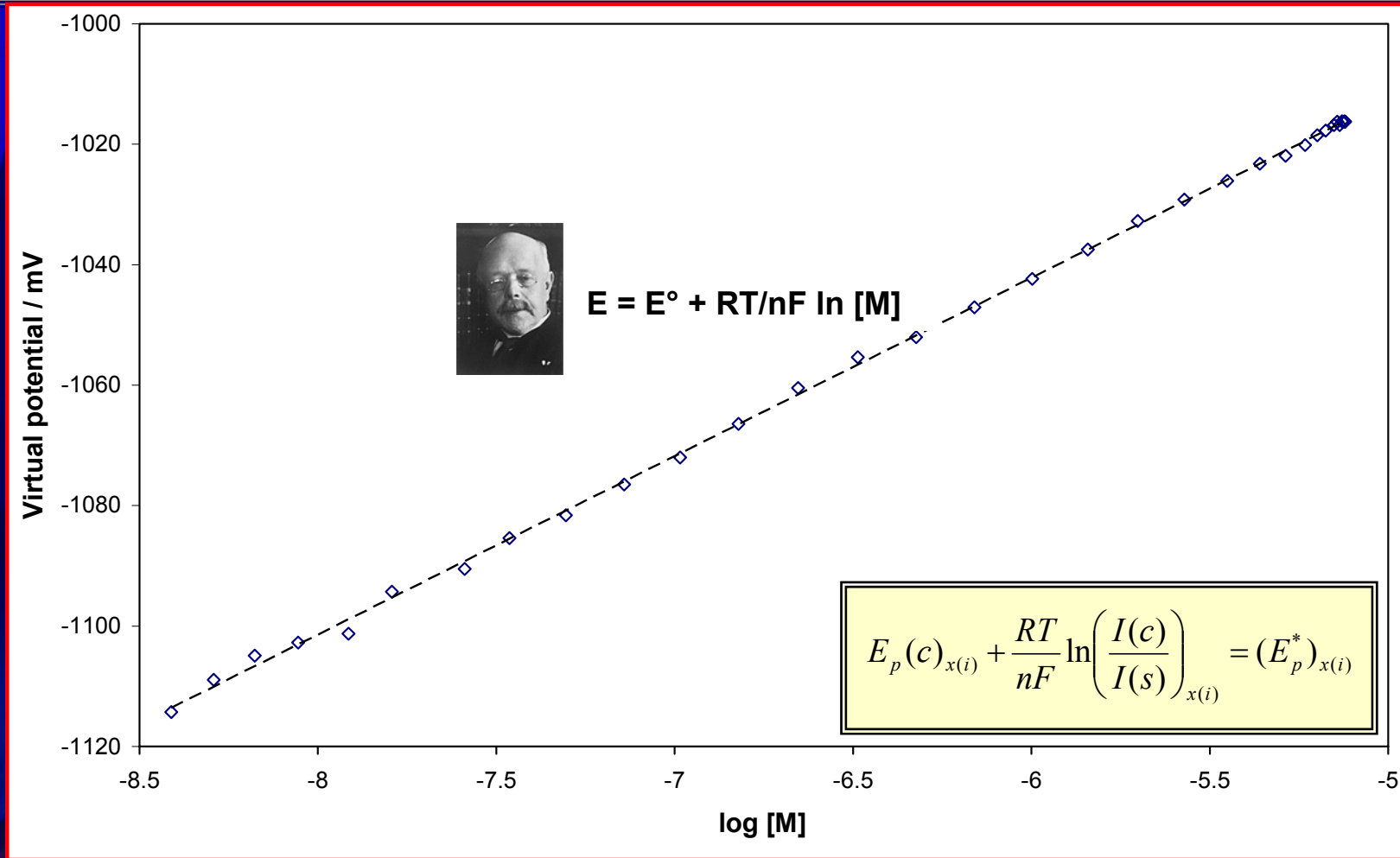
Virtual potential in modelling of the M-L-OH system



Ni-MDP-OH system



Virtual potential ($E_{1/2}^*$) vs. [Ni]. DCP as a 'virtual' potentiometric sensor.

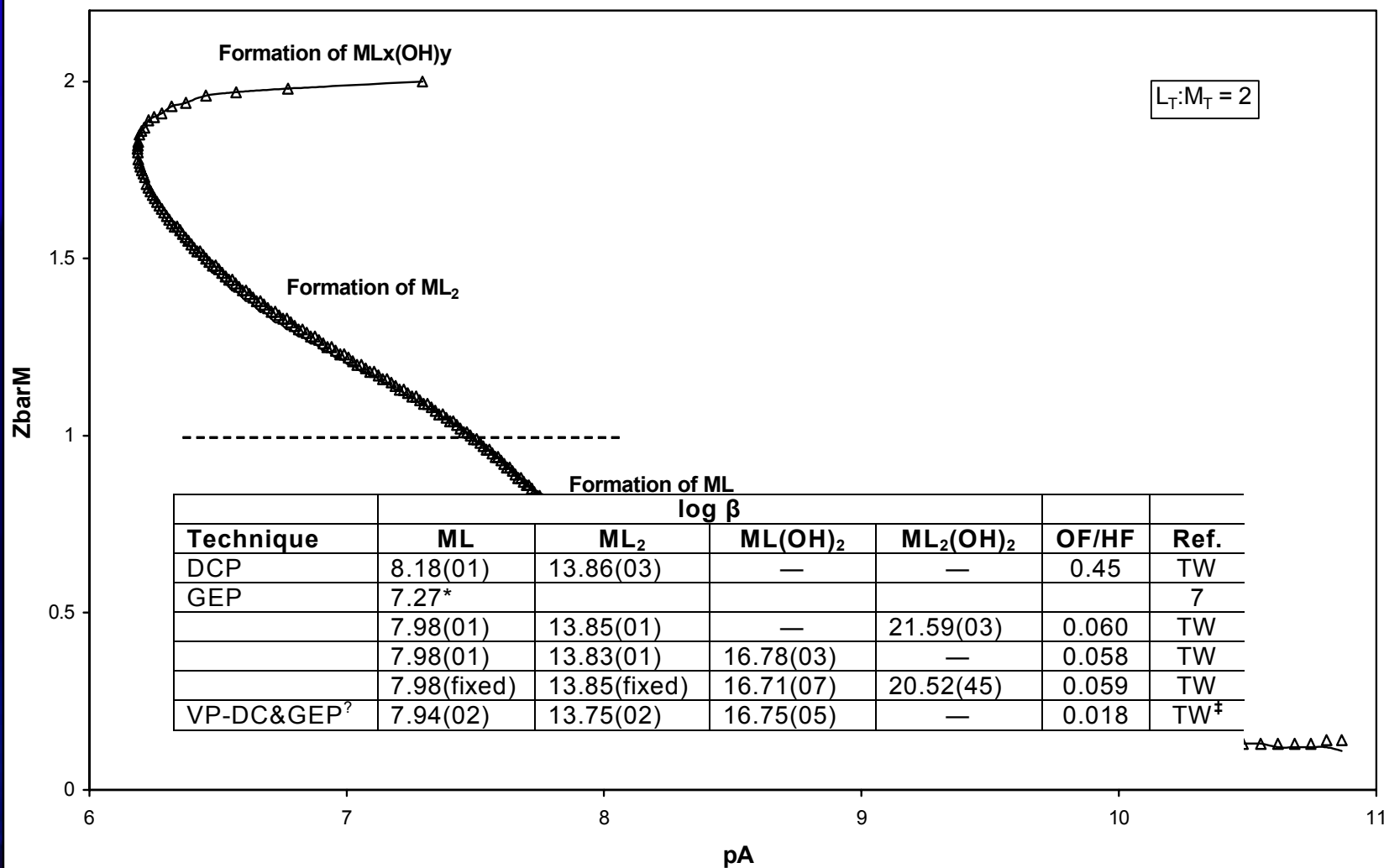


Ni-MDP-OH system

I. Cukrowski, D.M. Mogano and J.R. Zeevaert, sent to *J. Inorg. Biochem.*



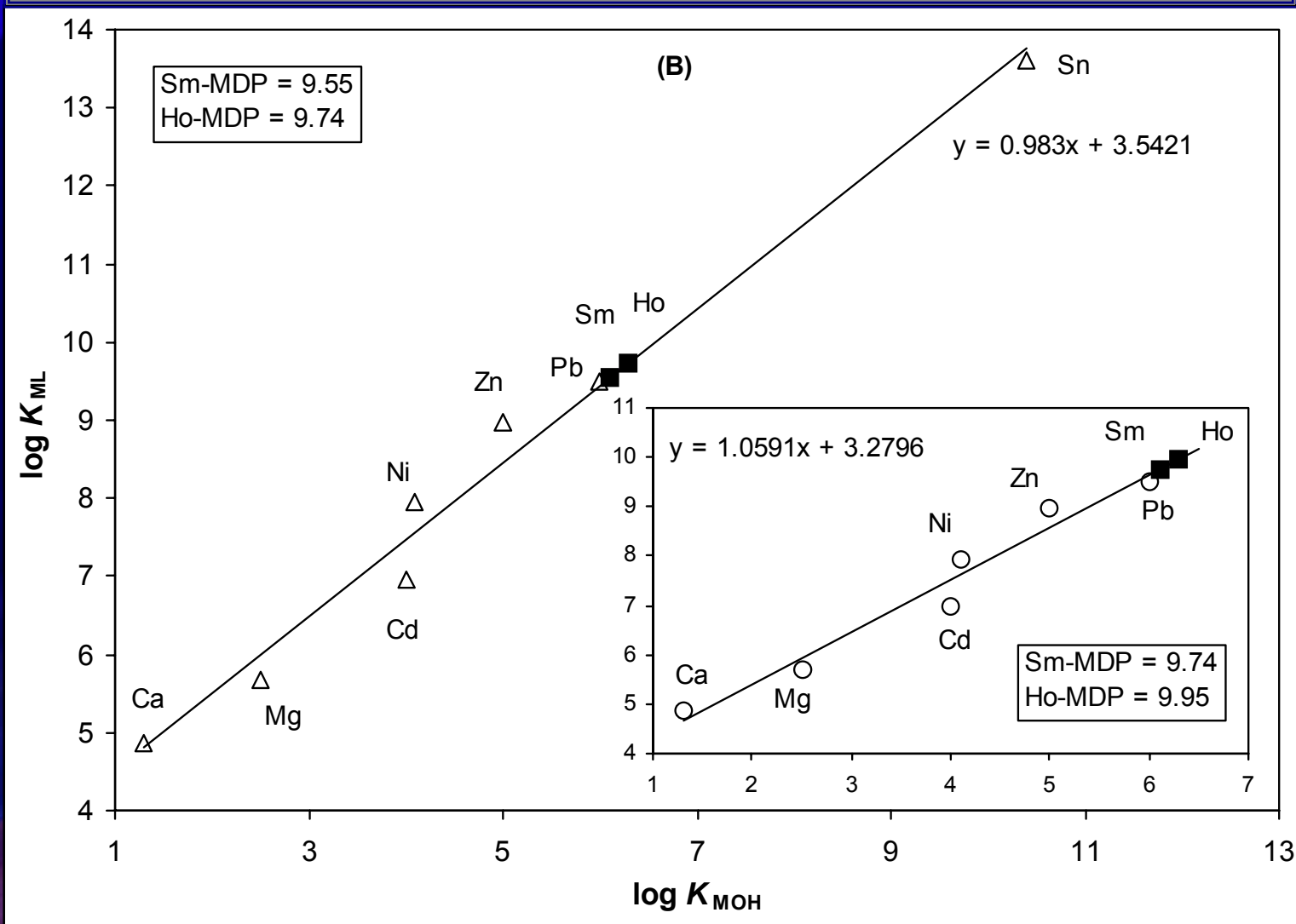
Kinetic and equilibrium data working together in refinement operations



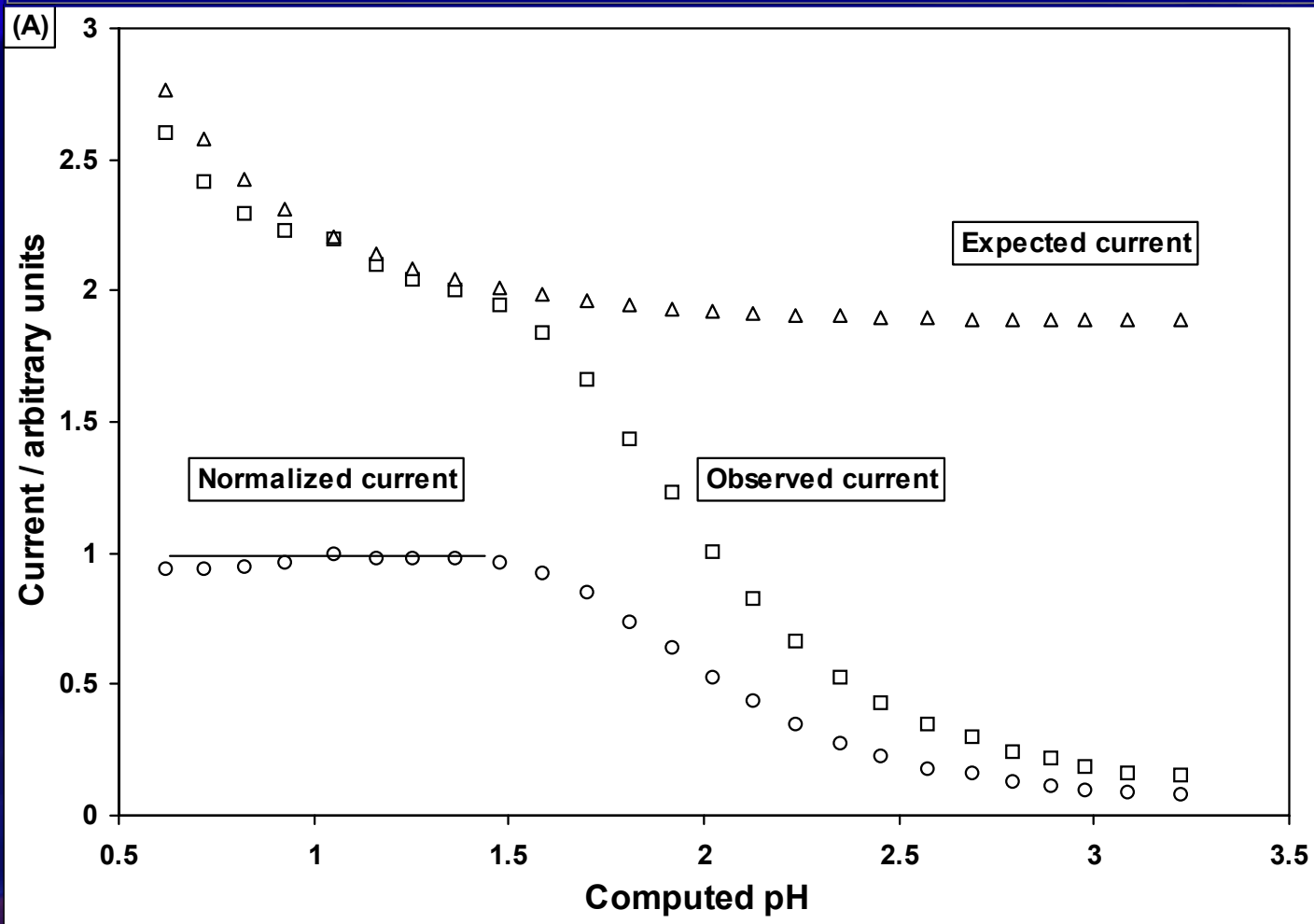
Ni-MDP-OH system



Linear Free Energy Relationships in prediction of $\log K_1$



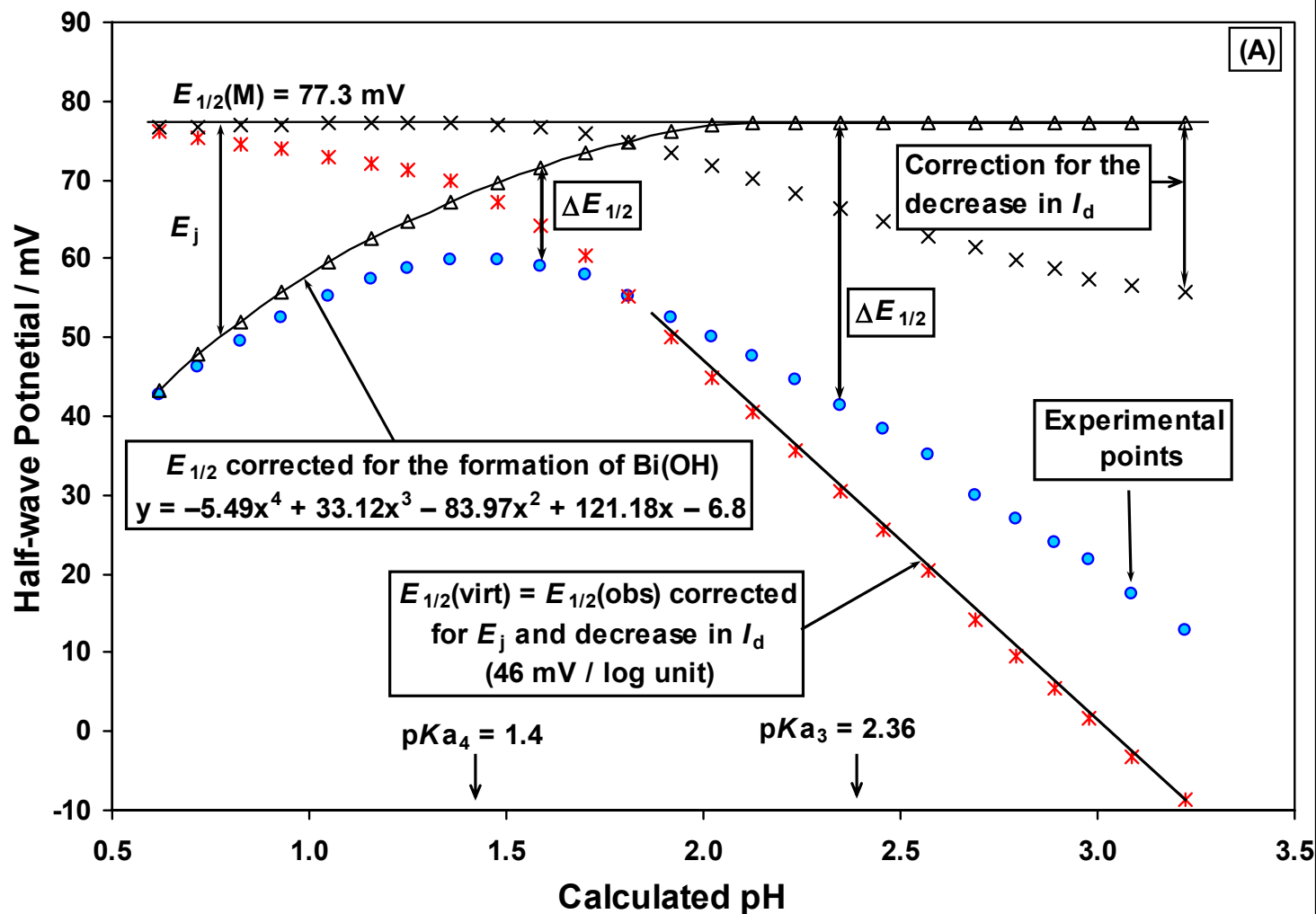
A study of Bi(III) by 2 voltammetric techniques



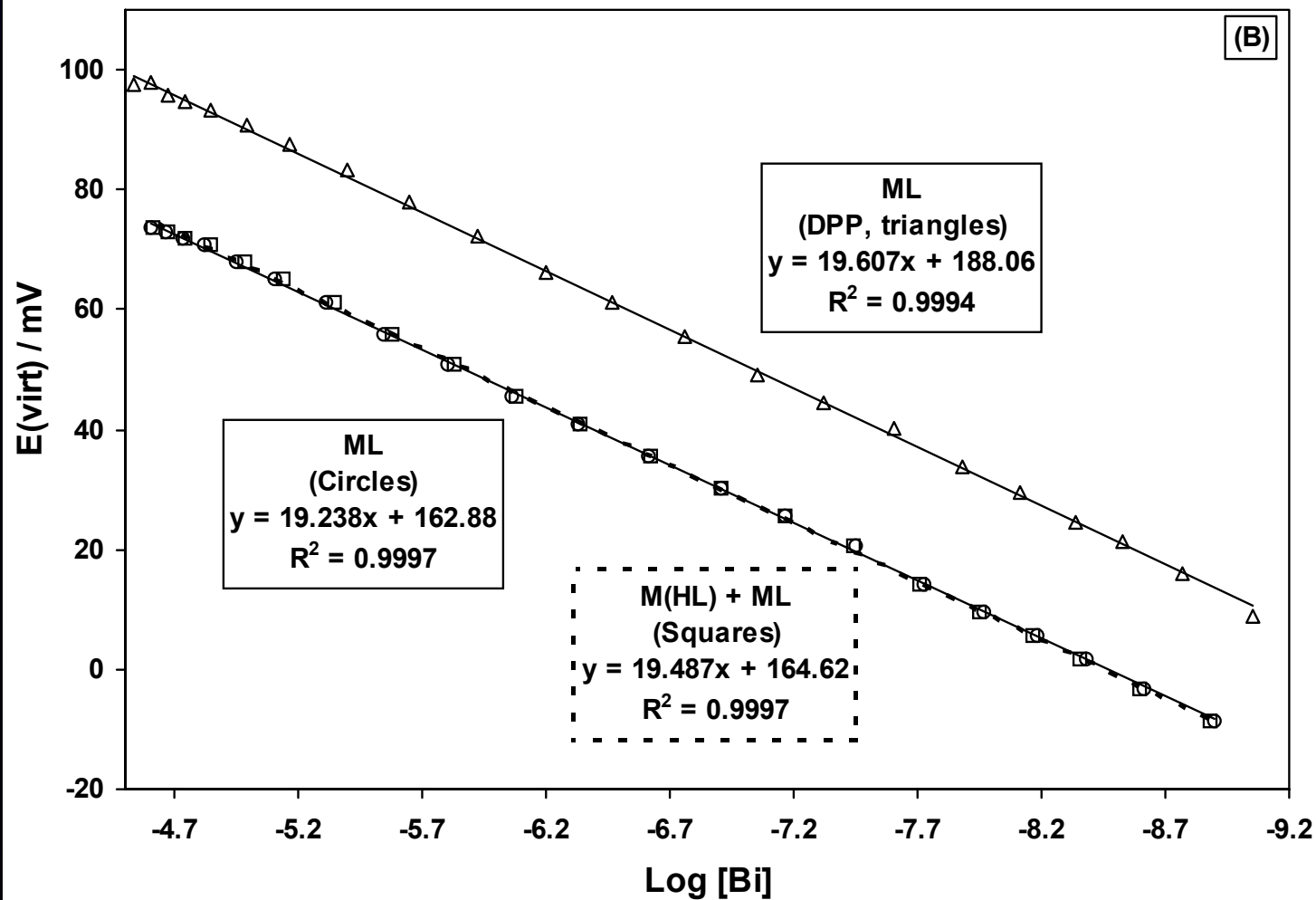
Bi(III)-EDDA-OH system
 M(HL) – labile; ML & ML₂ - inert



A study of Bi(III) by 2 voltammetric techniques

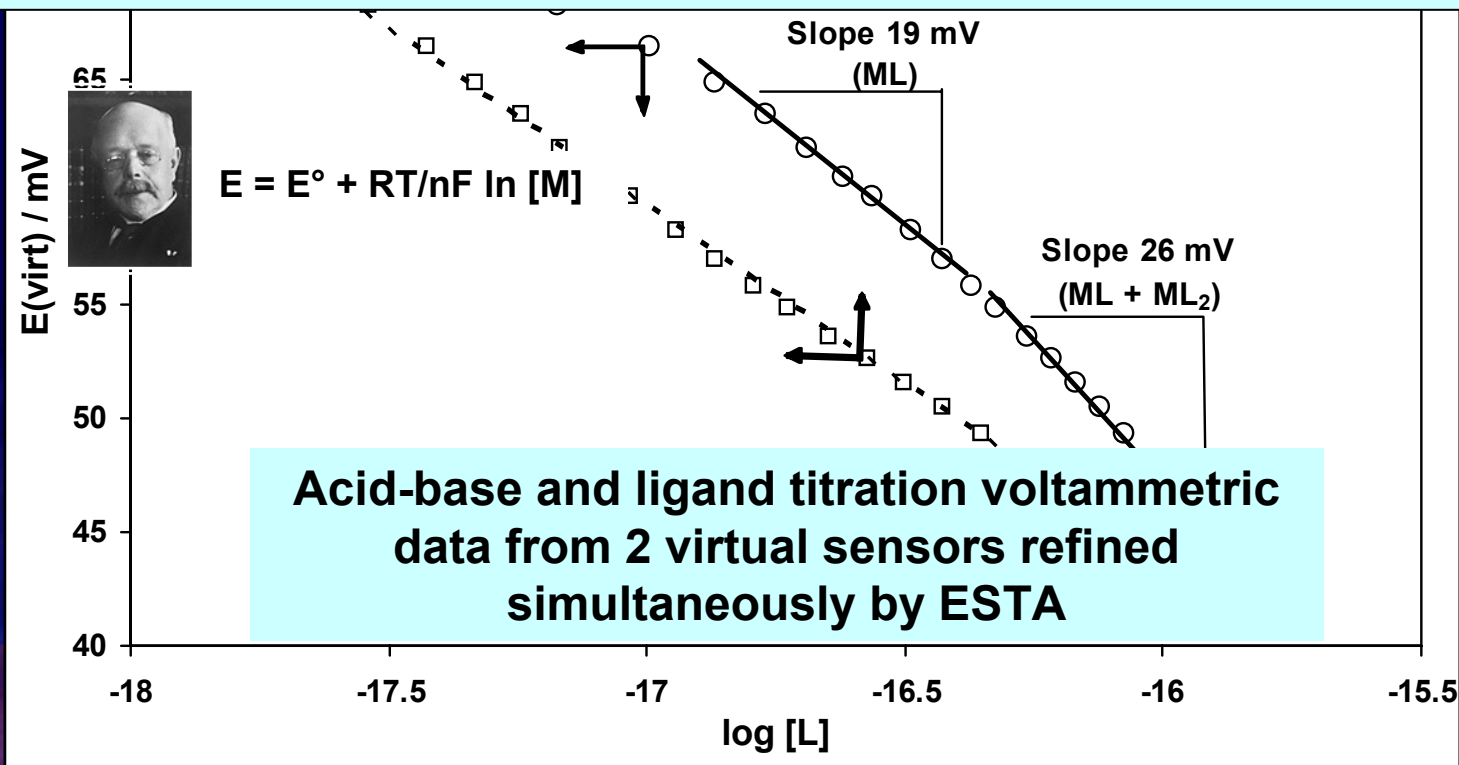


2 voltammetric techniques as virtual ISE in the study of Bi



Double function of virtual potential (modelling & refinement)

		M(HL) labile	ML labile	ML ₂ inert	
pH 1.7 and A-B	VP-DP & VP-DC	18.85 ± 0.07	17.07 ± 0.08	31.70 ± 0.04	0.039



Metal-Ligand interactions ($M_pL_qH_r$)

Model of a Metal-Ligand system & thermodynamic stability constants

EQUILIBRIUM E-CHEMISTRY

Change in thermodynamic potential (ISE)

Virtual dynamic data



$$E = E^\circ - \frac{RT}{nF} \ln Q$$

DYNAMIC E-CHEMISTRY

$$(E(s) - E(c))_{x(i)} = \frac{RT}{nF} \ln \left(\frac{[M_T]}{[M]} \right)_{x(i)}$$

Dynamic data in the form of a virtual thermodynamic potential

$$E_p(c)_{x(i)} + \frac{RT}{nF} \ln \left(\frac{I(c)}{I(s)} \right)_{x(i)} = (E_p^*)_{x(i)}$$

Now two different WORLDS are talking to each other

Virtual THERMODYNAMICS is working



Conclusions (Solution Chemistry)

1. Polarography-based virtual potentiometric sensor:
 - a) does not have linearity range limits (its response is of the widest-known linearity, by far better than reigning for many years glass electrode)
 - b) is ion non-specific (opposite to ISE)
 - c) in principle, several metal ions might be monitored (opposite to ISE)
 - d) should be possible to monitor pH (if the M-L system is known)
2. Simultaneous refinement of data from several polarographic experiments (e.g. DPP and DCP).
3. Simultaneous refinement of glass electrode potentiometric (low $[L_T]:[M_T]$) and polarographic (high $[L_T]:[M_T]$) from several titrations.
4. Simultaneous refinement of glass electrode, and ISE or metallic potentiometric and polarographic data from several titrations.
5. Prediction of species formed (modelling of solution composition) must be based on the analysis of virtual potential
6. Significantly improved reliability of models and refined stability constants.



Quo Vadis?

Nobel Prize in Literature 1905

Henryk Sienkiewicz

simply

The Best



For any University in the world the challenge is to:

- 1. Accept public support and broaden its social contribution without compromising its traditional independence**
- 2. Strike a satisfactory balance between teaching and research**
- 3. Find an ideal blend of required and elected courses**
- 4. Satisfy students continuous demands for better instruction and satisfy promotion criteria based mainly on faculty member's scholarly work**



Each university's basic traditional function is to:

- 1. Enable students to learn from their cultural heritage**
- 2. Help students to realize their intellectual and creative abilities**
- 3. Encourage students to become humane and responsible people**
- 4. Expend knowledge across the entire spectrum of disciplines**
- 5. Add to the understanding and enjoyment of life**
- 6. Provide imaginative solutions to the problems of society**



University of Pretoria:

1. In many respects, is as any other University in the World
2. Has the same social functions to perform
3. Has the same aims and goals to achieve
4. Is, to some extent, a unique establishment, as any other University is

We, as the University, are not that different

But as Department of Chemistry, we are very much different

simply

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What is University known and internationally recognized for?

- Number of students, or number of faculty staff?
- Rector, Dean, HOD (administrative leaders)?
- Wonderful or excellent (or unbearable) administration?
- Best (or worst) teaching facilities (lecture theatres or laboratories)?

No, not at all

- ✓ Famous scientists (discoveries made)?
- ✓ Nobel prize winners – where they were educated?
- ✓ Nobel prize winners – where they have made their contributions?
- ✓ Published excellent research work

Yes, very much so



simply

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Inaugural Lecture at UP 28 July 2005

To become a strong Research Department requires

Existing Research

Build on existing strengths

Develop potential strengths

Outstanding Research

Unique Expertise
in the Department

Centre of Excellence

Strong
research activities

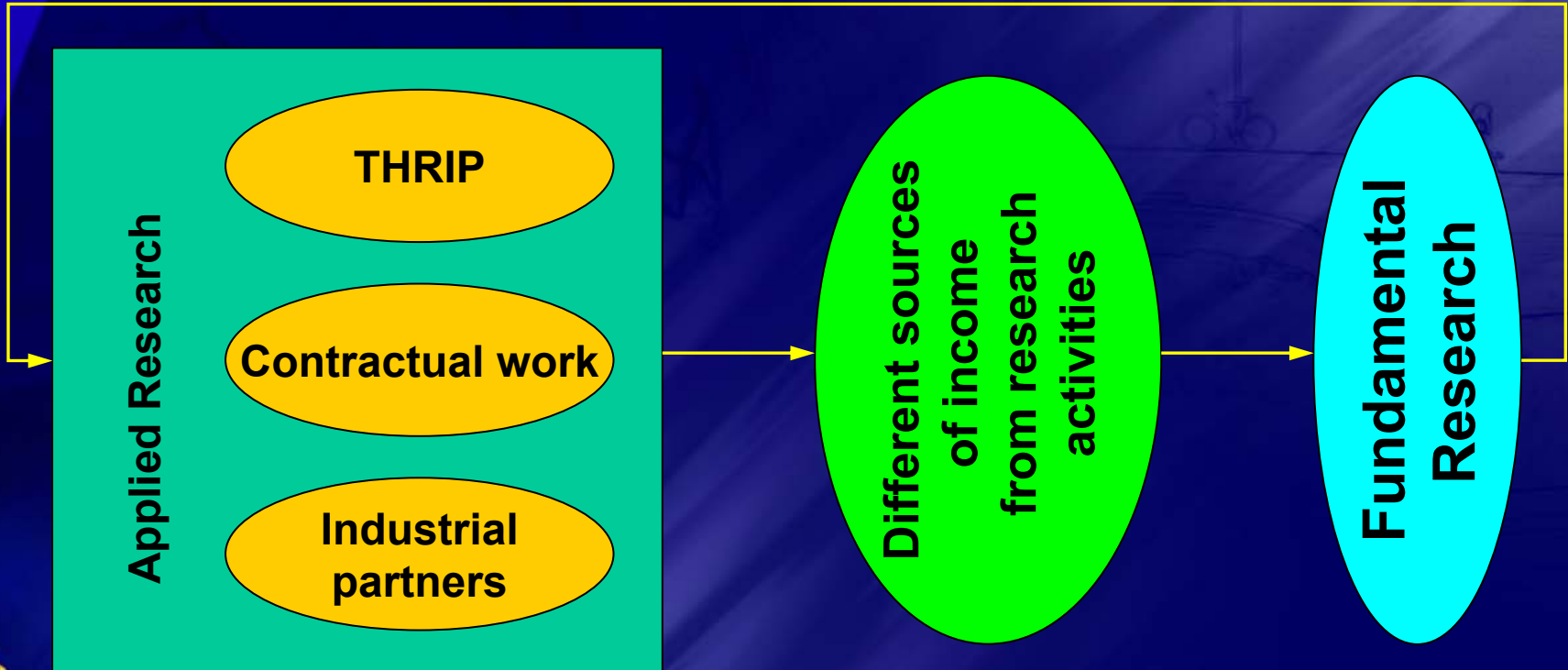


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Promote fundamental
and applied research



simply

The Best

**Dedication to
highest quality teaching**

- 1. Excellence in teaching of 1st year chemistry**
- 2. Establish and support a team of staff members dedicated to education**
- 3. Research in education to be tested on our own chemistry students (continuous refinement of operation in improving educational goals)**
- 4. Well-designed teaching program throughout the whole chemistry course, from 1st to 4th year level**
- 5. Promote and support students with outstanding performance in chemistry**



Operational Structure of the Department

Departmental Committees

1. **Educational Research Activities (ERA) - Marietjie Potgieter**
2. **Departmental Teaching Coordination Committee - Wentzel Schoeman**
3. **Research Coordination Committee (RCC) - Simon Lotz**
4. **Maintenance and Safety Committee (MSC) - Robert Vleggaar**
5. **Communication (liaison, publicity) Committee (CC) – Wentzel Schoeman**
6. **Aesthetics Committee (AC) – Christien Strydom**
7. **Support and Technical Staff Committee (STSC) – Robin Muir**
8. **Fixed Facilities Committee (FFC) – Peet van Rooyen**
9. **Centre for Interfacial Chemistry Committee (CICC) – Ignacy Cukrowski**
10. **IT (PhD students and Staff Facilities) Committee (ITC) – Peet van Rooyen**
11. **Finance Committee (FC) – Robert Vleggaar**



Recent students involved in solution chemistry

Inaugural Lecture at UP 28 July 2005

Acknowledgments



Anton



Preeti



Valentine



Christian



Tumaini



Jian



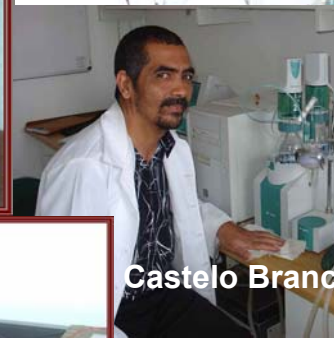
Caren



Janine



Carina



Castelo Branco

University of Pretoria

Wits University

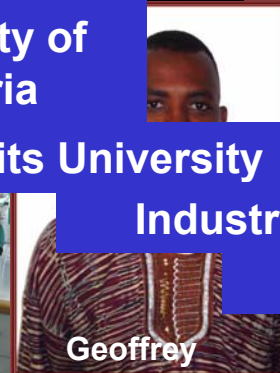
Industry (SASOL, Anglo-Platinum, NECSA, CISA, PBMR)
Metrohm (Switzerland) and Swiss Lab (SA)

NRF

Co-workers (local and abroad)



Winny



Geoffrey



Philemon



**Thank you for attending my
Inaugural Address at UP**

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