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

Virtual Thermodynamic Potential

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Inaugural Lecture at UP   28 July 2005

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
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 charge) were 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

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

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

Max Volmer became a director of the Institute of Physical Chemistry and Electrochemistry.
Dynamic Electrochemistry – highest Honours

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.

(1890 - 1967)

Charles University, Prague

1959

Jaroslav Heyrovský and his son Michael
Dynamic Electrochemistry - well established science

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
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.
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Dynamic and labile M-L system

Inert metal complexes

Mixed (labile & inert) M-L system

Homogeneous Equilibria

Reversible

Interfacial kinetics?

Quasi-Reversible

Irreversible
1) **Main experimental variable – \( \Delta E \)**

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

Still regarded as the method in the field

\[
F_0[X] = \sum_{0}^{N} \beta_{MXj} [X_T]^j
\]

\[
F_{00}[X,Y] = \sum_{0}^{N} \beta_{MXjY_i} [X_T]^j [Y_T]^i
\]

- **Dynamic and labile M-L system**
- **No rigorous refinement of stability constants**
- **Mass-balance equations not involved**
- **Limited applications with quite uncertain results**

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**Skoog, ...Fundamentals of Anal. Chem 6th ed. 1992**

**Lingane**

1941

**DeFord-Hume**

1951

**Leden–DeFord–Hume**

1951

**Leden–Schaap–Mc Master**

1961
2) Experimental variable – $\Delta I$

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

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

Is there any room for further development?

No rigorous data evaluation
A paradigm shift (1996)

Any kind of complex $M_xL_1L_2L_3$ (at any experimental conditions)

Corrected shift in potential ($\Delta E_p$ 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


Corrected shift & Experimental Complex Formation Curves

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

Objective function to be reproduced by theoretical model

Complexes:
Protonated
Polynuclear
Labile
Inert
hydroxo

$\begin{align*}
M + 4H + L & \leftrightarrow M(H_4L)  & \beta_{M(H_4L)} = [MH_4L] / [M][H]^4[L] \\
M + 2H + L & \leftrightarrow M(H_2L)  & \beta_{M(H_2L)} = [MH_2L] / [M][H]^2[L] \\
2M + L & \leftrightarrow M_2L  & \beta_{M_2L} = [M_2L] / [M]^2[L] \\
M + L & \leftrightarrow ML  & \beta_{ML} = [ML] / [M][L] \\
M + 2L & \leftrightarrow ML_2  & \beta_{ML_2} = [ML_2] / [M][L]^2 \\
M + L + OH & \leftrightarrow ML(OH)  & \beta_{ML(OH)} = [ML(OH)] / [M][L][OH] \\
M + OH & \leftrightarrow M(OH)  & \beta_{M(OH)} = [M(OH)] / [M][OH] \\
M + 2OH & \leftrightarrow M(OH)_2  & \beta_{M(OH)_2} = [M(OH)_2] / [M][OH]^2 \\
M + 3OH & \leftrightarrow M(OH)_3  & \beta_{M(OH)_3} = [M(OH)_3] / [M][OH]^3 \\
M + 4OH & \leftrightarrow M(OH)_4  & \beta_{M(OH)_4} = [M(OH)_4] / [M][OH]^4 \\
2M + OH & \leftrightarrow M_2(OH)  & \beta_{M_2(OH)} = [M_2(OH)] / [M]^2[OH] \\
4M + 4OH & \leftrightarrow M_4(OH)_4  & \beta_{M_4(OH)_4} = [M_4(OH)_4] / [M]^4[OH]^4 \\
H + L & \leftrightarrow HL  & K_1^H = [HL] / [H][L] \\
H + HL & \leftrightarrow H_2L  & K_2^H = [H_2L] / [H][HL] \\
H + H_2L & \leftrightarrow H_3L  & K_3^H = [H_3L] / [H][H_2L] \\
H + H_3L & \leftrightarrow H_4L  & K_4^H = [H_4L] / [H][H_3L] \\
H + H_4L & \leftrightarrow H_5L  & K_5^H = [H_5L] / [H][H_4L] \\
H + H_5L & \leftrightarrow H_6L  & K_6^H = [H_6L] / [H][H_5L] \\
\end{align*}$

\[
[M_T] = [M] + \beta_{M(H_4L)}[M][H]^4[L] + \beta_{M(H_2L)}[M][H]^2[L] + 2\beta_{M_2L}[M]^2[L] + \beta_{ML}[M][L] + \beta_{ML_2}[M][L]^2 + \\
\beta_{ML(OH)}[M][L][OH] + \beta_{M(OH)}[M][OH] + \beta_{M(OH)_2}[M][OH]^2 + \beta_{M(OH)_3}[M][OH]^3 + \beta_{M(OH)_4}[M][OH]^4 + \\
2\beta_{M_2(OH)}[M]^2[OH] + 4\beta_{M_4(OH)_4}[M]^4[OH]^4
\]

\[
K_1^H K_2^H K_3^H K_4^H K_5^H K_6^H[H]^6[L] + \beta_{M(H_4L)}[M][H]^4[L] + \beta_{M(H_2L)}[M][H]^2[L] + \beta_{M_2L}[M]^2[L] + \beta_{ML}[M][L] + \\
2\beta_{ML_2}[M][L]^2 + \beta_{ML(OH)}[M][L][OH]
\]

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

Computed Complex Formation Curve

Theoretical model

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

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

DPP: \( [L_T]:[M_T] = 400 \)
\( [M_T] = 8.32 \times 10^{-5} \) M

ISE: \( [L_T]:[M_T] = 50 \)
\( [M_T] = 5 \times 10^{-4} \) M

ISE: \( [L_T]:[M_T] = 5.7 \)
\( [M_T] = 1 \times 10^{-3} \) M

Metal-Ligand interactions \((M_pL_qH_r)\)

Model of a Metal-Ligand system & thermodynamic stability constants

EQUILIBRIUM E-CHEMISTRY

DYNAMIC E-CHEMISTRY

Potentiometric data changed to Virtual dynamic data

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

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

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


Quantitative voltammetric analysis of a metal ion

$E_p(M)$

$E_p = \text{const}$
'Virtual ISE' from polarographic results
Virtual thermodynamic data

DPP peak potential / mV
slope = 30 mV

Applied potential / mV
Current / arbitrary units

E_p

E_p

-0.7 -0.65 -0.6 -0.55 -0.5 -0.45 -0.4 -0.35

2 3 4 5
-Log [M]
DPP of a labile (or dynamic) M-L system

Peak representing all metal species

Peak of a free metal ion

Shift in $E_p$

$\{E_p(s) - E_p(c)\}$

Potential / V

Normalized current

$[H](1)$

$[H](n)$

$\text{Cd-Glycine-OH system}$

Glycine
Refinement of stability constants: complex formation curves

\[ \frac{RT}{nF} \ln \left( \frac{I(c)}{I(s)} \right)_{x(i)} = \frac{RT}{nF} \ln \left( \frac{[M^+]}{[M]} \right)_{x(i)} \]

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

[\( M \)] from solving mass-balance equation

Cd-Glycine-OH system

Virtual thermodynamic data

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

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

DPP as a ‘virtual’ potentiometric sensor.

Each datum point \{\(E^*_p\) at pH\(i\)}
is theoretically calculated using Nernst thermodynamics by dedicated software, e.g. ESTA

\[ E = E^° + \frac{RT}{nF} \ln [M] \]

Cd-Glycine-OH system

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I. Cukrowski, N. Maseko, Electroanalysis 15 No. 17 (2003) 1377-1388
Experimental and Computed Complex Formation Curves

\[
\text{ECFC: } (E(s) - E(c))_{(i)} - \frac{RT}{nF} \ln \left( \frac{I(c)}{I(s)} \right)_{(i)}
\]

\[
\text{CCFC: } \frac{RT}{nF} \ln \left( \frac{[M_T]}{[M]} \right)_{(i)}
\]

Shift in the peak potential / mV vs pH

Labile peak

Cd-HIDA-OH system

Virtual thermodynamic data

E = E° + RT/nF \ln [M]

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

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

Cd-HIDA-OH system
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‘Virtual’ potentiometric Bi(III) sensor from voltammetry

$E = E^\circ + \frac{RT}{nF} \ln [M]$ 

Virtual thermodynamic data

$E_{p(c)}(i) + \frac{RT}{nF} \ln \left( \frac{I(c)}{I(s)} \right)_{x(i)} = \left( E^+_p \right)_{x(i)}$

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

Fitting of a DC_{TAST} wave for Ni-MDP-OH at pH 2.847

**Involved heterogeneous kinetics:**
(irreversible electron transfer)
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Kinetics of the M-L-OH system

Involved homogeneous kinetics:
(mixed M-L system)

Involved heterogeneous kinetics:
(irreversible electron transfer)

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

- **Virtual potential**
  - \( \text{Slope} = 30 \text{ mV/ log } [L] \)
  - \( M + L = ML \)

- **Observed potential**
  - \( \text{Slope} = 25 \text{ mV/ log } [L] \)
  - \( M + L = ML \)

- **Involved homogeneous kinetics:**
  - (mixed M-L system)

- **Involved heterogeneous kinetics:**
  - (irreversible electron transfer)
  - \( M + 2L = ML_2 \)

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

$$E = E^0 + \frac{RT}{nF} \ln [M]$$

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

Kinetic and equilibrium data working together in refinement operations

### Ni-MDP-OH system


<table>
<thead>
<tr>
<th>Technique</th>
<th>ML</th>
<th>ML₂</th>
<th>ML(OH)₂</th>
<th>ML₂(OH)₂</th>
<th>OF/HF</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCP</td>
<td>8.18(01)</td>
<td>13.86(03)</td>
<td>—</td>
<td>—</td>
<td>0.45</td>
<td>TW</td>
</tr>
<tr>
<td>GEP</td>
<td>7.27*</td>
<td>13.85(01)</td>
<td>—</td>
<td>21.59(03)</td>
<td>0.060</td>
<td>TW</td>
</tr>
<tr>
<td></td>
<td>7.98(01)</td>
<td>13.83(01)</td>
<td>16.78(03)</td>
<td>—</td>
<td>0.058</td>
<td>TW</td>
</tr>
<tr>
<td></td>
<td>7.98(fixed)</td>
<td>13.85(fixed)</td>
<td>16.71(07)</td>
<td>20.52(45)</td>
<td>0.059</td>
<td>TW</td>
</tr>
<tr>
<td>VP-DC&amp;GEP</td>
<td>7.94(02)</td>
<td>13.75(02)</td>
<td>16.75(05)</td>
<td>—</td>
<td>0.018</td>
<td>TW ²</td>
</tr>
</tbody>
</table>

*Note: The ratio of $L_1:M_1$ is 2.*

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**Figure Description:**
- The graph illustrates the formation of different species, with the concentration of $ML$, $ML_2$, $ML(OH)_2$, and $ML_2(OH)_2$ plotted against $pA$.
- The x-axis represents $pA$, and the y-axis represents the concentration of species.
- The data table provides equilibrium constants ($\log \beta$) for various techniques and their corresponding species.
- Techniques include DCP, GEP, VP-DC&GEP, and 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

Experimental points

$E_{1/2}^{\text{(M)}} = 77.3 \text{ mV}$

$E_{1/2}$ corrected for the formation of Bi(OH)

$y = -5.49x^4 + 33.12x^3 - 83.97x^2 + 121.18x - 6.8$

$E_{1/2}^{\text{(virt)}} = E_{1/2}^{\text{(obs)}}$ corrected for $E_j$ and decrease in $I_d$

(46 mV / log unit)

$pK_a^4 = 1.4$

$pK_a^3 = 2.36$

Correction for the decrease in $I_d$

$\Delta E_{1/2}$

2 voltammetric techniques as virtual ISE in the study of Bi

Double function of virtual potential (modelling & refinement)

<table>
<thead>
<tr>
<th>pH 1.7 and A-B</th>
<th>VP-DP &amp; VP-DC</th>
<th>M(HL) labile</th>
<th>ML labile</th>
<th>ML₂ inert</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.85 ± 0.07</td>
<td>17.07 ± 0.08</td>
<td>31.70 ± 0.04</td>
<td>0.039</td>
<td></td>
</tr>
</tbody>
</table>

\[ E = E^\circ + \frac{RT}{nF} \ln [M] \]

Acid-base and ligand titration voltammetric data from 2 virtual sensors refined simultaneously by ESTA

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**

- Dynamic data in the form of a virtual thermodynamic potential
  - \( (E_s - E_c)_{x(i)} = \frac{RT}{nF} \ln \left( \frac{[M_T]}{[M]} \right)_{x(i)} \)
  - \( E_p(c)_{x(i)} + \frac{RT}{nF} \ln \left( \frac{I(c)}{I(s)} \right)_{x(i)} = (E^*_p)_{x(i)} \)

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 so 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 data (large \([L_T]:[M_T]\)) from several titrations.

4. Simultaneous refinement of glass electrode, and ISE or metallic potentiometric as well as polarographic data from several titrations.

5. Prediction of species formed (modelling of solution composition) must be based on the analysis of virtual potential

Quo Vadis?

Nobel Prize in Literature 1905

Henryk Sieńkiewicz

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 extend, 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

The Best
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**
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simply

The Best

To become the best implies

TEAM WORK

Outstanding research

Exceptional teaching

National and international standing and recognition
To become a strong Research Department requires

Existing Research

Build on existing strengths

Outstanding Research

Unique Expertise in the Department

Centre of Excellence

Strong research activities

Develop potential strengths
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Promote fundamental and applied research

- THRIP
- Contractual work
- Industrial partners

Different sources of income from research activities

Fundamental Research

simply

The Best
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
Simply

The Best

Operational Structure of the Department

TEAM WORK
Operational Structure of the Department

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
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Recent students involved in solution chemistry

University of Pretoria
Wits University

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

Co-workers (local and abroad)

Acknowledgments
Thank you for attending my Inaugural Address at UP