The Nernst Equation in Equilibrium Electrochemistry:

Content and Didactic Methodology
(Pedagogical Content Knowledge)

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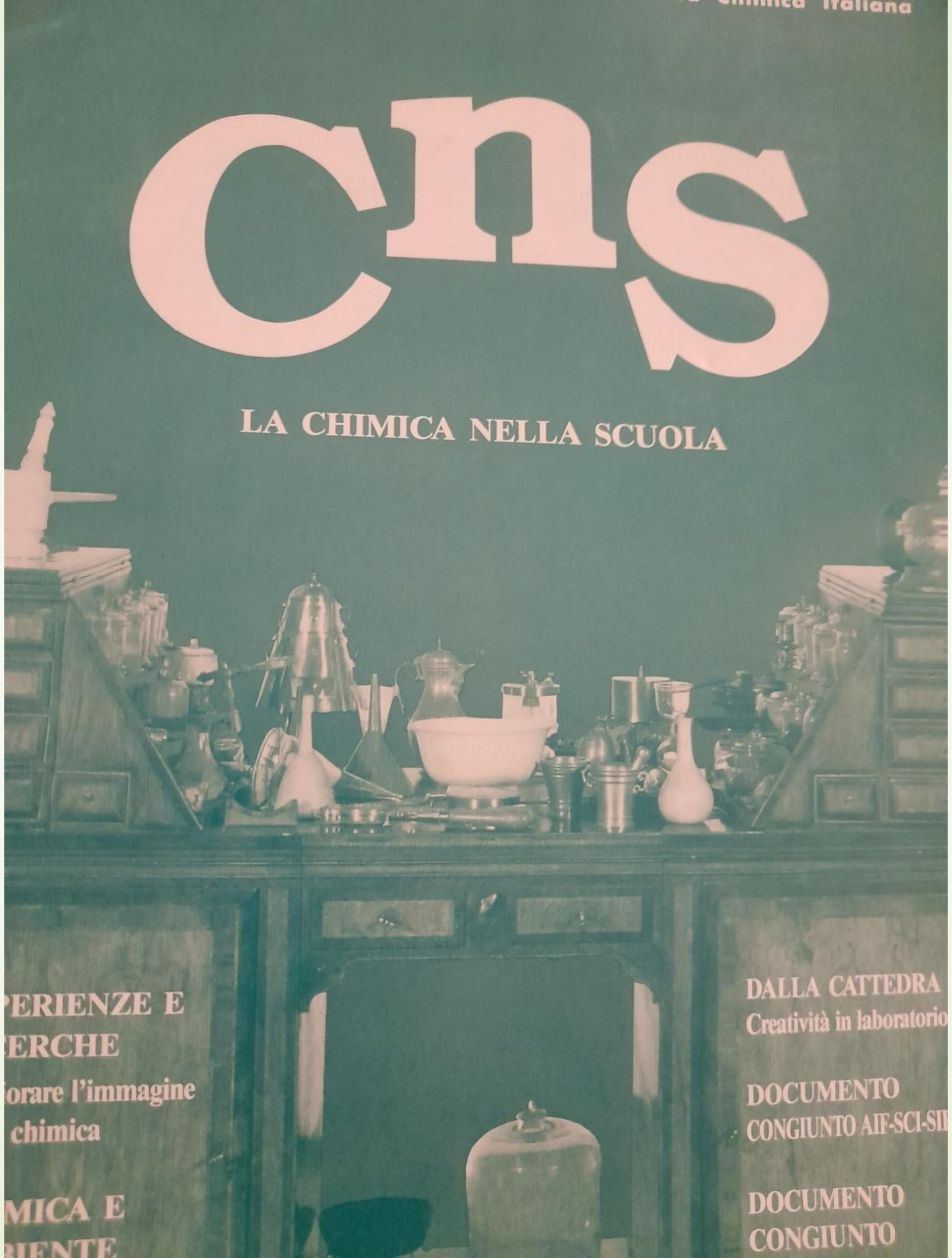

Chimica Italiana

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LA CHIMICA NELLA SCUOLA

PERIENZE E
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MICA E
BIENTE

DALLA CATTEDRA
Creatività in laboratorio

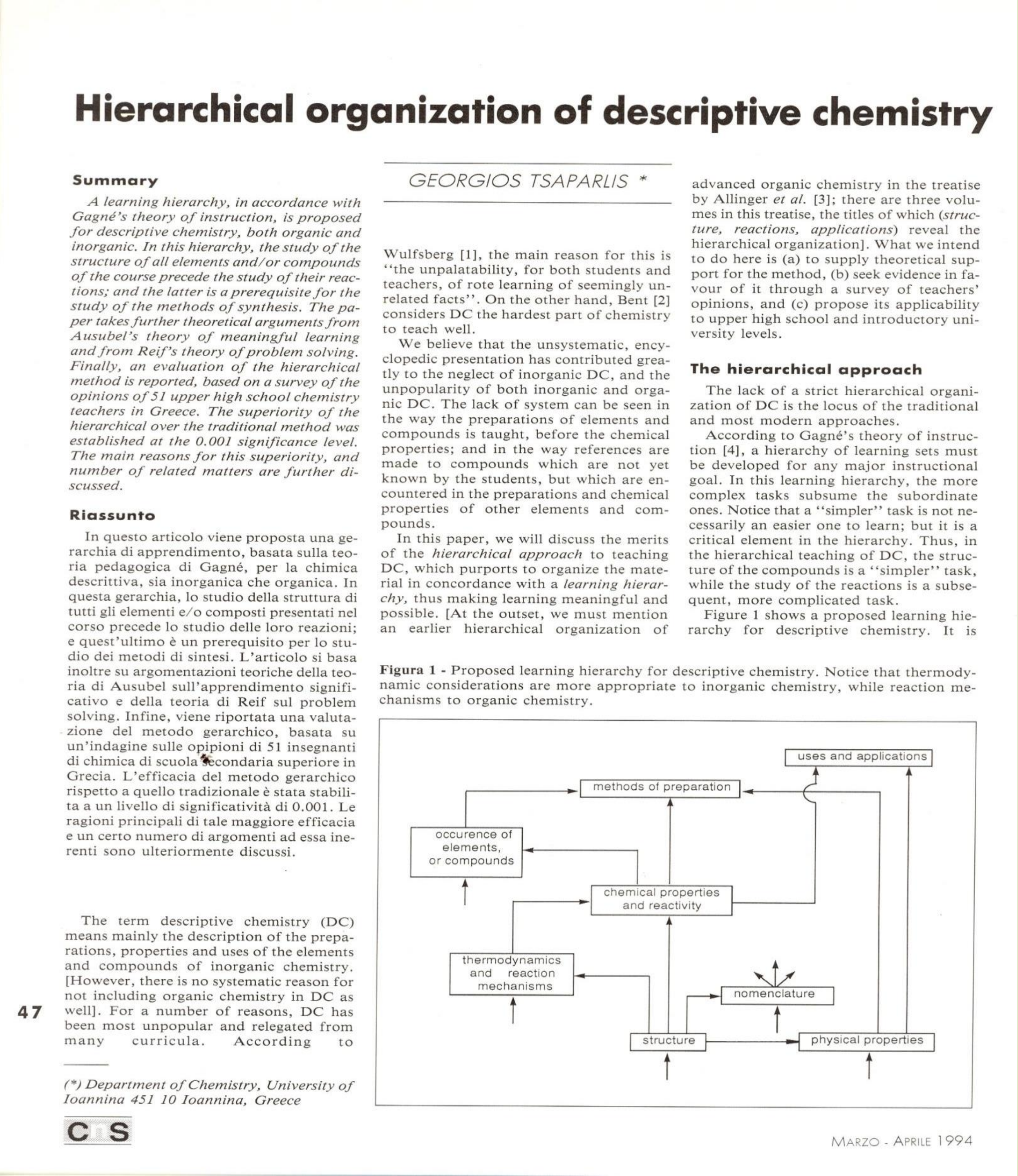
DOCUMENTO
CONGIUNTO AIF-SCI-SI

DOCUMENTO
CONGIUNTO

G. Tsaparlis

Hierarchical organization of descriptive chemistry

La Chimica nella Scuola
1994, N.2, 47-49.



Hierarchical organization of descriptive chemistry

GEORGIOS TSAPARLIS *

Summary

A learning hierarchy, in accordance with Gagné's theory of instruction, is proposed for descriptive chemistry, both organic and inorganic. In this hierarchy, the study of the structure of all elements and/or compounds of the course precede the study of their reactions; and the latter is a prerequisite for the study of the methods of synthesis. The paper takes further theoretical arguments from Ausubel's theory of meaningful learning and from Reif's theory of problem solving. Finally, an evaluation of the hierarchical method is reported, based on a survey of the opinions of 51 upper high school chemistry teachers in Greece. The superiority of the hierarchical over the traditional method was established at the 0.001 significance level. The main reasons for this superiority, and number of related matters are further discussed.

Riassunto

In questo articolo viene proposta una gerarchia di apprendimento, basata sulla teoria pedagogica di Gagné, per la chimica descrittiva, sia inorganica che organica. In questa gerarchia, lo studio della struttura di tutti gli elementi e/o composti presentati nel corso precede lo studio delle loro reazioni; e quest'ultimo è un prerequisito per lo studio dei metodi di sintesi. L'articolo si basa inoltre su argomentazioni teoriche della teoria di Ausubel sull'apprendimento significativo e della teoria di Reif sul problem solving. Infine, viene riportata una valutazione del metodo gerarchico, basata su un'indagine sulle opinioni di 51 insegnanti di chimica di scuola secondaria superiore in Grecia. L'efficacia del metodo gerarchico rispetto a quello tradizionale è stata stabilita a un livello di significatività di 0.001. Le ragioni principali di tale maggiore efficacia e un certo numero di argomenti ad essa inerenti sono ulteriormente discussi.

The term descriptive chemistry (DC) means mainly the description of the preparations, properties and uses of the elements and compounds of inorganic chemistry. [However, there is no systematic reason for not including organic chemistry in DC as well]. For a number of reasons, DC has been most unpopular and relegated from many curricula. According to Wulfsberg [1], the main reason for this is "the unpalatability, for both students and teachers, of rote learning of seemingly unrelated facts". On the other hand, Bent [2] considers DC the hardest part of chemistry to teach well.

We believe that the unsystematic, encyclopedic presentation has contributed greatly to the neglect of inorganic DC, and the unpopularity of both inorganic and organic DC. The lack of system can be seen in the way the preparations of elements and compounds is taught, before the chemical properties; and in the way references are made to compounds which are not yet known by the students, but which are encountered in the preparations and chemical properties of other elements and compounds.

In this paper, we will discuss the merits of the *hierarchical approach* to teaching DC, which purports to organize the material in concordance with a *learning hierarchy*, thus making learning meaningful and possible. [At the outset, we must mention an earlier hierarchical organization of advanced organic chemistry in the treatise by Allinger *et al.* [3]; there are three volumes in this treatise, the titles of which (*structure, reactions, applications*) reveal the hierarchical organization]. What we intend to do here is (a) to supply theoretical support for the method, (b) seek evidence in favour of it through a survey of teachers' opinions, and (c) propose its applicability to upper high school and introductory university levels.

The hierarchical approach

The lack of a strict hierarchical organization of DC is the locus of the traditional and most modern approaches.

According to Gagné's theory of instruction [4], a hierarchy of learning sets must be developed for any major instructional goal. In this learning hierarchy, the more complex tasks subsume the subordinate ones. Notice that a "simpler" task is not necessarily an easier one to learn; but it is a critical element in the hierarchy. Thus, in the hierarchical teaching of DC, the structure of the compounds is a "simpler" task, while the study of the reactions is a subsequent, more complicated task.

Figure 1 shows a proposed learning hierarchy for descriptive chemistry. It is

Figura 1 - Proposed learning hierarchy for descriptive chemistry. Notice that thermodynamic considerations are more appropriate to inorganic chemistry, while reaction mechanisms to organic chemistry.

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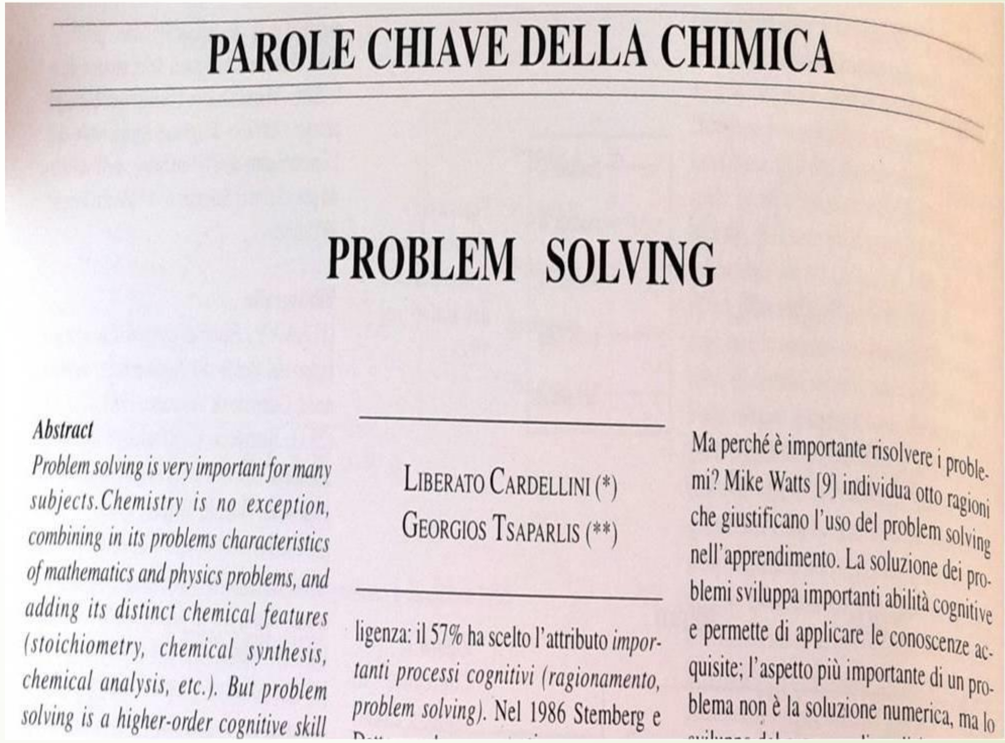
L. Cardellini & G. Tsaparlis
Problem Solving

La Chimica nella Scuola,
1998, N.3, 86-93.



PAROLE CHIAVE DELLA CHIMICA

PROBLEM SOLVING

LIBERATO CARDELLINI (*)
GEORGIOS TSAPARLIS (**)

Abstract

Problem solving is very important for many subjects.Chemistry is no exception, combining in its problems characteristics of mathematics and physics problems, and adding its distinct chemical features (stoichiometry, chemical synthesis, chemical analysis, etc.). But problem solving is a higher-order cognitive skill

ligenza: il 57% ha scelto l'attributo *importanti processi cognitivi (ragionamento, problem solving)*. Nel 1986 Stemberg e

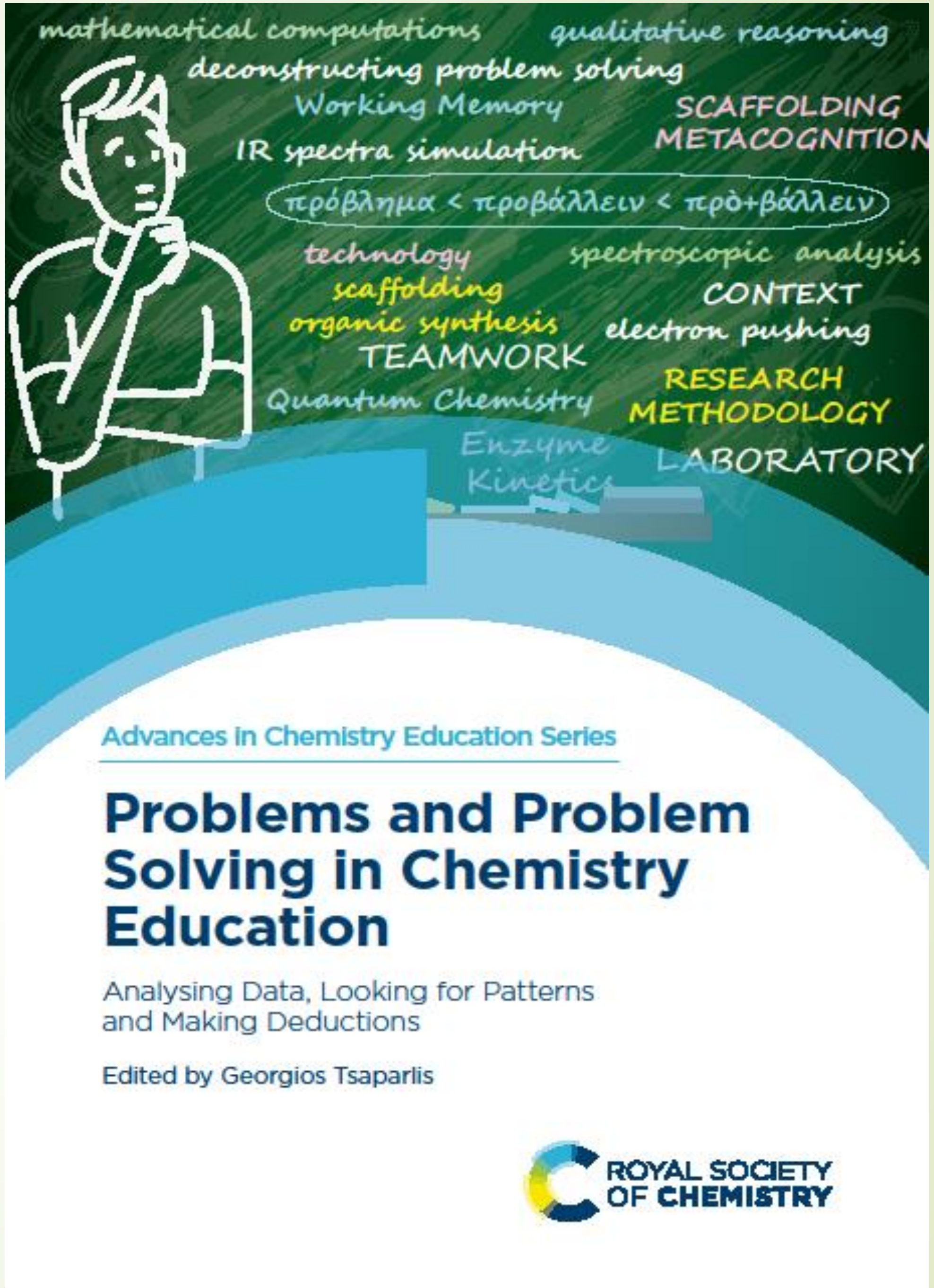
Ma perché è importante risolvere i problemi? Mike Watts [9] individua otto ragioni che giustificano l'uso del problem solving nell'apprendimento. La soluzione dei problemi sviluppa importanti abilità cognitive e permette di applicare le conoscenze acquisite; l'aspetto più importante di un problema non è la soluzione numerica, ma lo

G. Tsaparlis, Editor

Problems and Problem Solving in Chemistry Education

Royal Society of Chemistry
2021

(*Advances in Chemistry Education Series*)



Advances in Chemistry Education Series

Problems and Problem Solving in Chemistry Education

Analysing Data, Looking for Patterns
and Making Deductions

Edited by Georgios Tsaparlis

ROYAL SOCIETY
OF CHEMISTRY

Electrochemical energy transfer

- Studied by a very important branch of science and technology: **electrochemistry**.

- Electrochemistry constitutes a traditional part of **physical chemistry** and one or more electrochemistry chapters feature in most physical chemistry textbooks.
- It is also introduced in high-school and **general chemistry** and **analytical chemistry** courses.

Electrochemistry in secondary education

Fundamental concepts of electrochemistry

- electrolytes
- ions
- electrolytic conduction
- oxidation-reduction (redox) reactions, and often even
- electrochemical cells

Tsaparlis G. (2012)

Electrolysis, electrolytes, and galvanic cells

In K. S. Taber (Ed.), *Teaching secondary chemistry, new 2nd edn.*, Ch. 8. London: Association for Science Education / Hodder Education. London, pp. 253–278.

Electrochemistry

- Electricity: the most useful and widespread form of energy transfer.
- It is mainly produced by power generators, using energy transferred during the combustion of various combustible materials and substances.

Electrochemistry

- This mode of energy production has two major drawbacks:

(i) the laws of thermodynamics dictate that the efficiency of thermal engines (e. g. motor cars) is well below 100%, and

(ii) combustion reactions produce gaseous products that pollute the atmosphere and the environment.

Electrochemistry

- Electrochemical energy conversion is based on the direct transfer of electrical energy, with a very high efficiency (90% and more) during a spontaneous chemical reaction that occurs in an electrochemical/galvanic cell,
- e. g. by the "cool combustion" of hydrogen in a fuel cell:

$$2H_2 + O_2 \rightarrow H_2O$$

Ionic electrochemistry and Electrode electrochemistry

Ionic electrochemistry – studies the electrolyte systems:

- ionic compound melts and electrolyte solutions (acids, bases and salts)
- ion-solvent interactions
- ion-ion interactions
- ionic conduction, etc.

Electrode electrochemistry

It studies electrochemical cells:

- galvanic cells and
- electrolytic cells.

Akiro Yoshino:*

"Battery technologies are electrochemistry, a complex and difficult interdisciplinary field".

*Professor Akira Yoshino, of Meijo University, Japan, received the 2018 Japan Prize and is considered as the father of the lithium ion batteries:

M.-K. Looi, *Chemistry World*, **2018**, *15* (8) 58.

Sodium comes to the battery world.
Sodium-ion technology is ready, cheap, and safe, but can it oust lithium ion?

Alex Scott, *Chemical & Engineering News*, **2022**, Volume 100, Issue 19, May 24

https://cen.acs.org/business/inorganic-chemicals/Sodium-comes-battery-world/100/i19?utm_source=NonMember&utm_medium=Newsletter&utm_campaign=CEN

(i) Equilibrium electrochemistry and (ii) Dynamic electrochemistry or Electrochemical kinetics

- **Equilibrium electrochemistry**: thermodynamics of ionic equilibria and of electrochemical cells,
- **Dynamic electrochemistry**: time dimension in the study of electrochemical phenomena.

- So far, very little education research appears to have dealt with topics such as mass transport or the kinetics of electrode processes

This presentation:

- Emphasis on basic concepts of electrochemistry and on the thermodynamics of electrochemical cells, with emphasis on problem solving involving the Nernst equation

Teaching and Learning Electrochemistry

Georgios Tsaparlis
Israel Journal of Chemistry: **2019**, *59*, 478 –492

DOI: 10.1002/ijch.201800071

Israel Journal of Chemistry

IJC

The Israel Chemical Society

החברה הישראלית לכימיה

- The paper reviews relevant studies and considers strategies and approaches for the effective teaching of electrochemistry.

- Then, the review focuses on problem solving in equilibrium electrochemistry, especially problems involving the Nernst equation.

Numerous conceptual difficulties and misconceptions

have been reported in the science and chemistry education literature about electrochemistry concepts, such as electrolytes, redox equations, and about electrochemical cells.

Other studies have considered teaching for overcoming misconceptions.

- Several studies have been at the general chemistry/freshman level, though many studies have also addressed electrochemical concepts and topics at high/secondary school.
- Relatively few studies have taken place within university physical chemistry courses.

This presentation focuses on:

- Pedagogical content aspects of problem solving in equilibrium electrochemistry, especially problems involving the Nernst equation.

Findings from three studies with Greek university chemistry students, dealing with:

(i) Algorithmic problem-solving ability;
(ii) Practice on problem solving; and
(iii) The effect of the format of a problem (***composite problem*** versus ***step-by-step problem***).

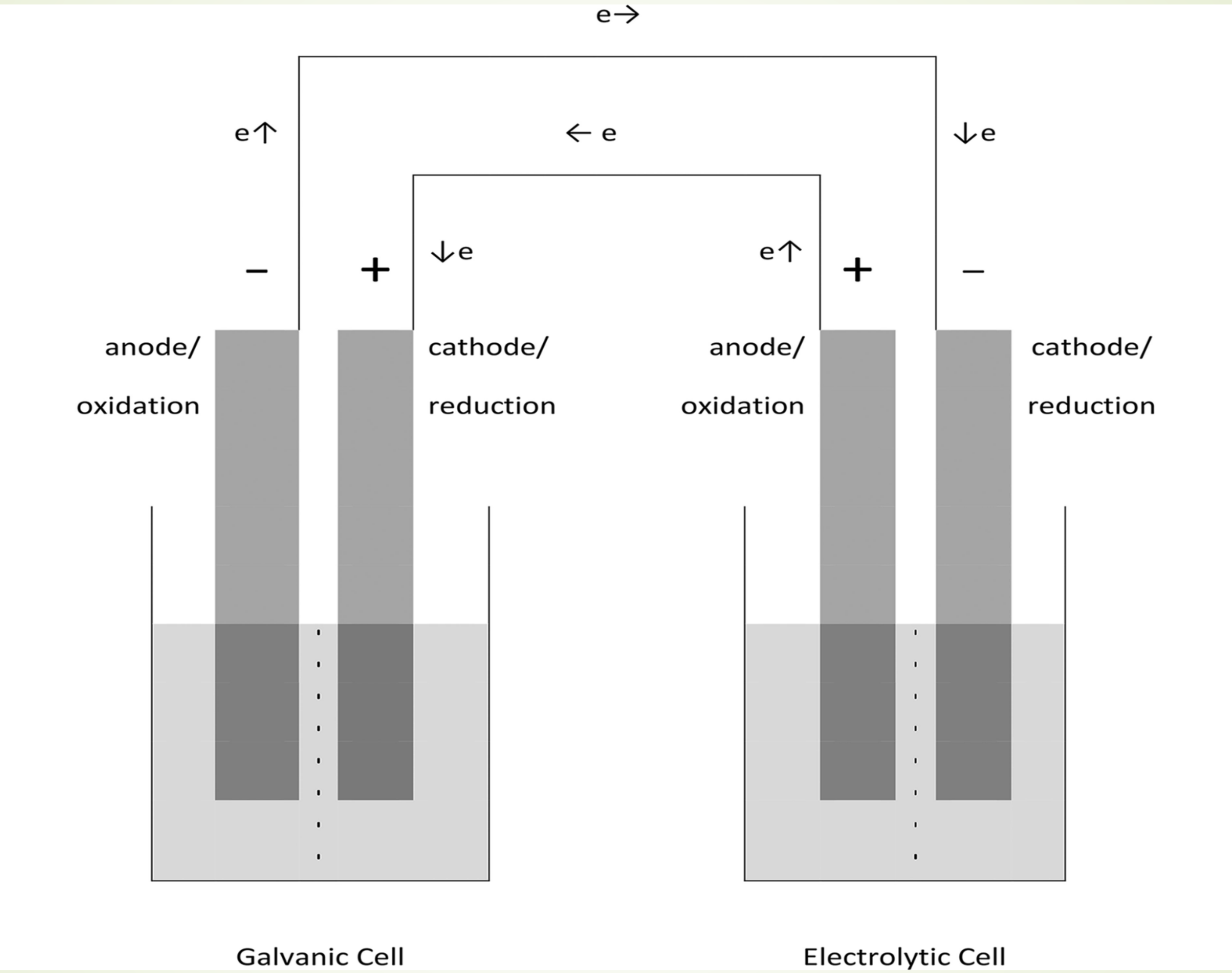
Pedagogical Content Knowledge (PCK)

Good science teaching and good student understanding require on the part of the teachers:

(a) *pedagogical knowledge* and

(b) *subject matter knowledge*.

- ***Pedagogical Content Knowledge (PCK):*** *pedagogical* aspects related to *subject matter content*.

e→
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−
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+
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anode/
oxidation
cathode/
reduction
anode/
oxidation
cathode/
reduction
Galvanic Cell
Electrolytic Cell

- We used data from final-semester examinations of the “Physical Chemistry II” compulsory course (which includes electrochemistry), taught to second-year/ fourth-semester chemistry students.

The instructional method was basically didactic (traditional lecture), but the instructor used his knowledge of student-centered, active-learning instruction, and often employed student questioning and direct involvement in the construction of new knowledge. For this course, the author distributed notes in Greek to the students.

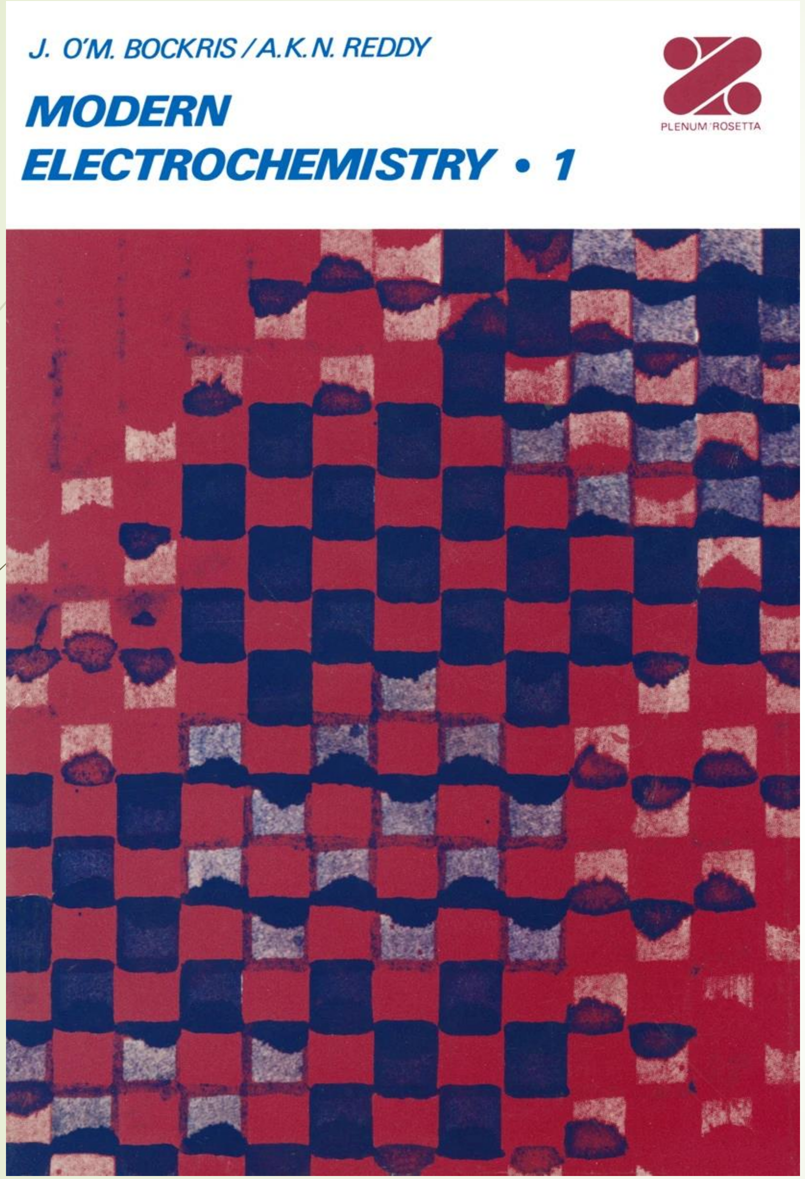
J. O'M. Bockris, A. K. N. Reddy:

Modern Electrochemistry

1st edition

Vol. 1, Ionics
Vol. 2, Electrodics

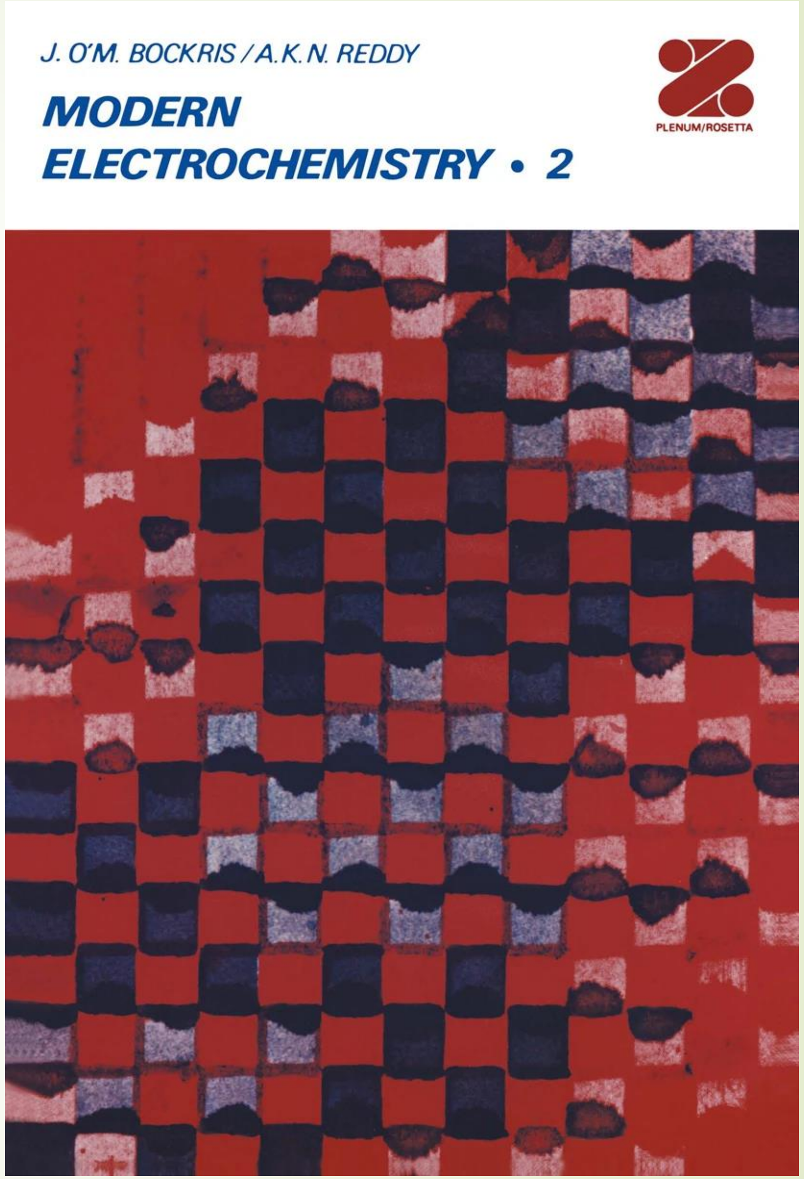
Plenum Press, New York, 1970



J. O'M. BOCKRIS / A.K.N. REDDY

MODERN
ELECTROCHEMISTRY • 1

PLENUM/ROSETTA



J. O'M. BOCKRIS / A.K.N. REDDY

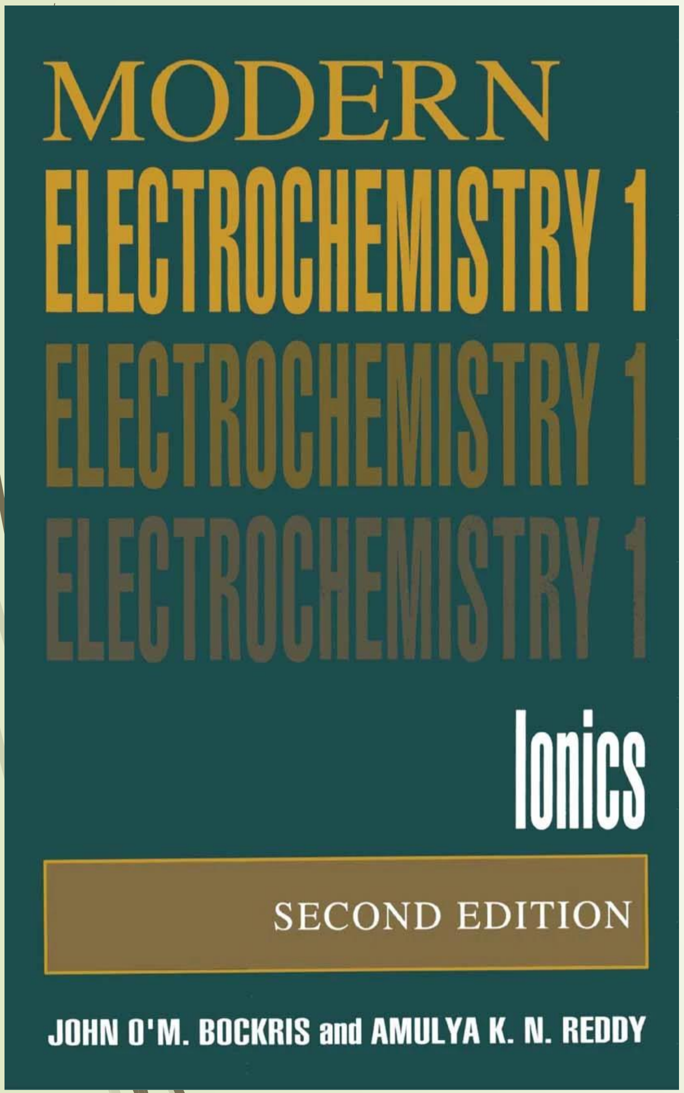
MODERN
ELECTROCHEMISTRY • 2

PLENUM/ROSETTA

J. O'M. Bockris, A. K. N. Reddy:

Modern Electrochemistry

2^{nd} edition (3 volumes), 1998

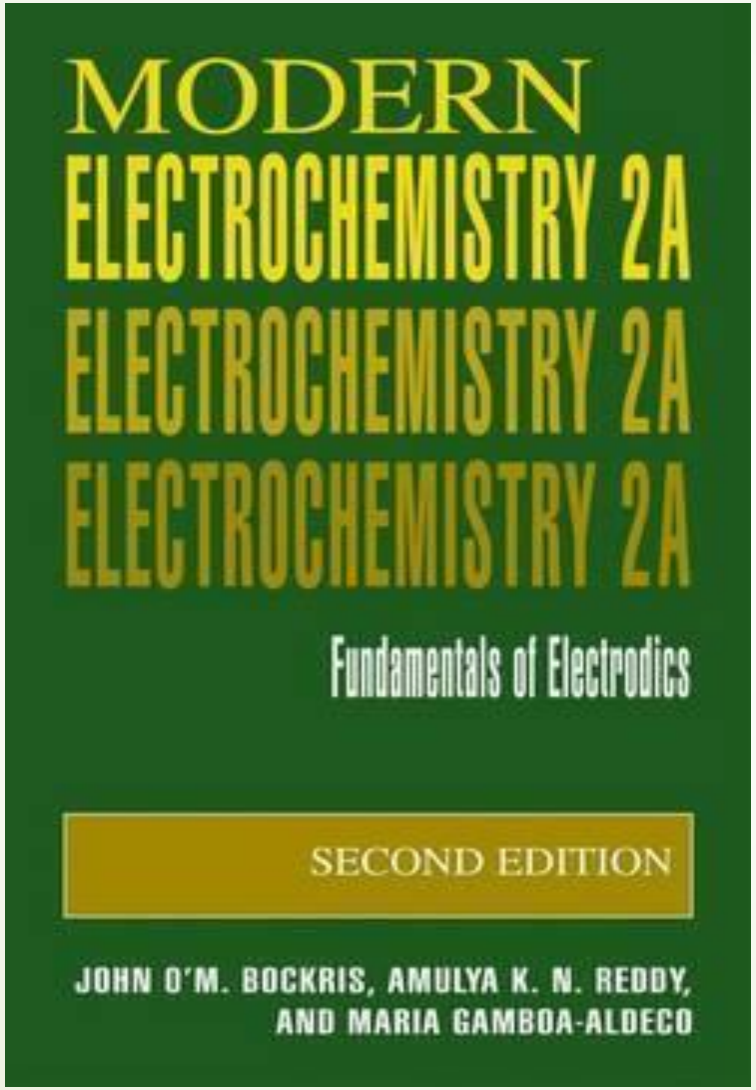


MODERN
ELECTROCHEMISTRY 1
ELECTROCHEMISTRY 1
ELECTROCHEMISTRY 1

Ionics

SECOND EDITION

JOHN O'M. BOCKRIS and AMULYA K. N. REDDY

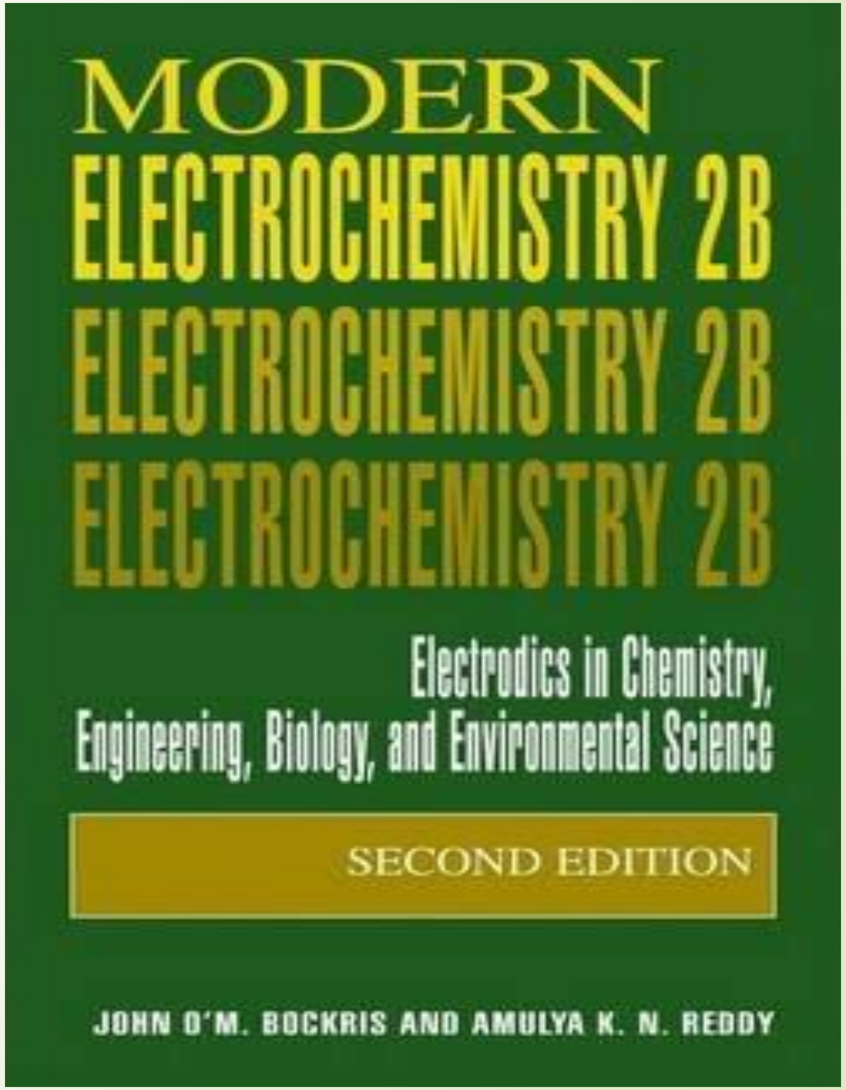


MODERN
ELECTROCHEMISTRY 2A
ELECTROCHEMISTRY 2A
ELECTROCHEMISTRY 2A

Fundamentals of Electrodics

SECOND EDITION

JOHN O'M. BOCKRIS, AMULYA K. N. REDDY,
AND MARIA GAMBOA-ALDECO



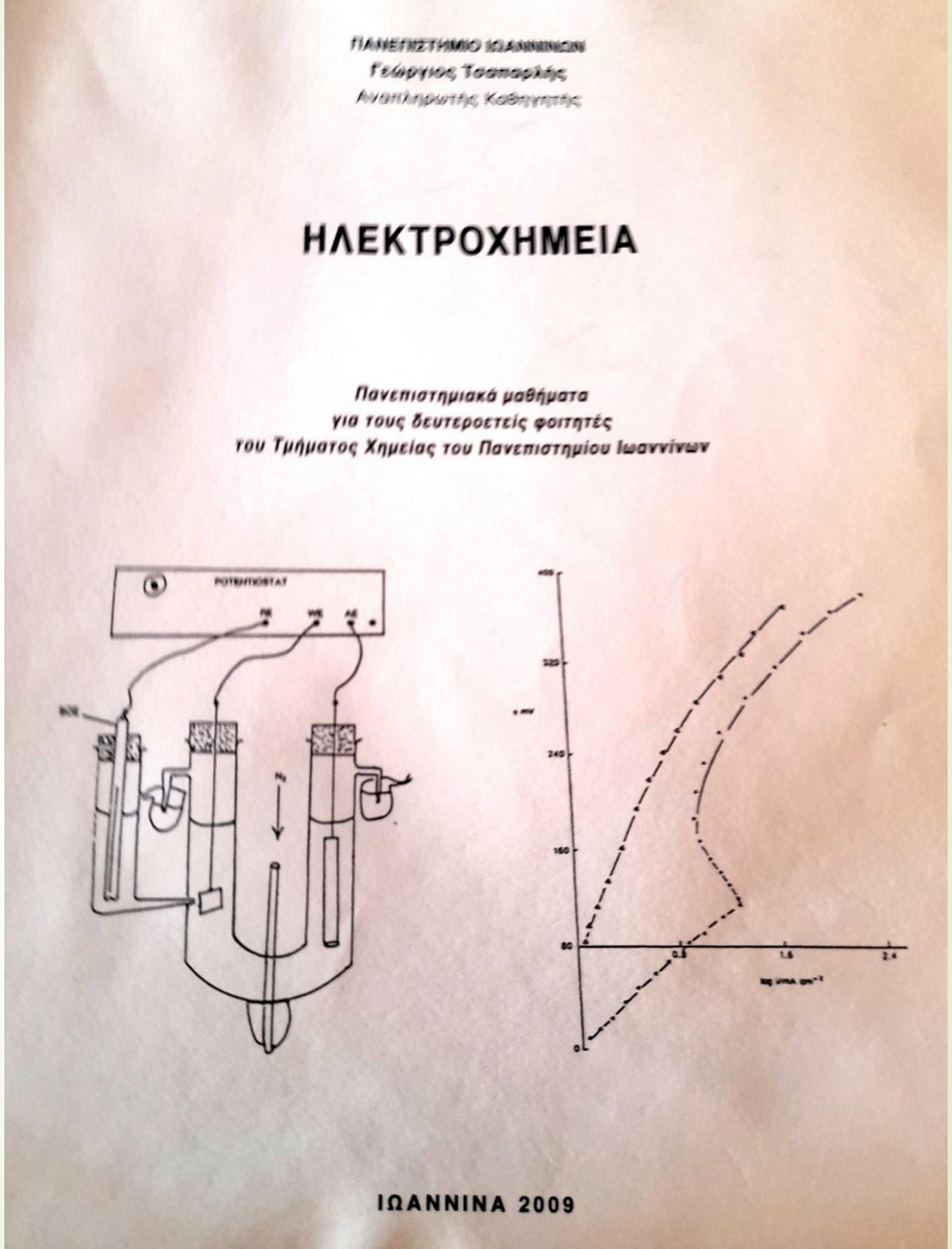
MODERN
ELECTROCHEMISTRY 2B
ELECTROCHEMISTRY 2B
ELECTROCHEMISTRY 2B

Electrodics in Chemistry,
Engineering, Biology, and Environmental Science

SECOND EDITION

JOHN O'M. BOCKRIS AND AMULYA K. N. REDDY

- 1st edition: 1986-1987
- 2nd edition: 1987-1988
- 3rd edition: 2001-2002
- Last edition: 2013-2014 (144+20=164 pages)



ΠΑΝΕΠΙΣΤΗΜΙΟ ΙΩΑΝΝΙΝΩΝ
Γεώργιος Τσαπαρλής
Αναπληρωτής Καθηγητής

ΗΛΕΚΤΡΟΧΗΜΕΙΑ

Πανεπιστημιακά μαθήματα
για τους δευτεροετείς φοιτητές
του Τμήματος Χημείας του Πανεπιστημίου Ιωαννίνων

ΙΩΑΝΝΙΝΑ 2009

- The course included ionic and electrode electrochemistry. Ionic electrochemistry involved the study of ion-solvent interactions and of ion-ion interactions, while electrode electrochemistry contained both equilibrium and dynamic electrochemistry.

- A great emphasis was placed on dealing with equilibrium electrochemistry problems, and notably with the application of the Nernst equation.

Study I: Students' Performance and Conceptual Difficulties when Dealing with Algorithmic Problems in Equilibrium Electrochemistry

- Data from seven examination papers, involving the solution of four problems (1, 2, 3, and 4) that were divided into eight sub-problems, were used. In each of the four problems, we distinguished two parts.
- The first part (1A, 2A, 3A, 4A) referred to the two half-reactions which entered in the galvanic cell, the overall spontaneous cell reaction, and the calculation of the corresponding $\Delta E°$ value.
- The second part (1B, 2B, 3B, 4B) referred to the application of the Nernst equation for the calculation of the equilibrium constant (1B,2B) or the calculation of the solubility product constant (3B, 4B).

Problem 2B

You are given the following galvanic cell at 298 K:

(-)Pt |$Fe^{2+}_{(aq)}$ (a=0.90), $Fe^{3+}_{(aq)}$(a=0.10) | |$Mn^{2+}_{(aq)}$ (a=0.10) |$MnO_{2(s)}$ |Pt (+)

(2A): Write the spontaneous reaction that takes place in this cell. Also calculate the standard cell potential difference ΔE° for the cell, and

(2B): Calculate the chemical equilibrium constant for the overall cell reaction at 298K.

- Data: $Fe^{3+}_{(aq)}/Fe^{2+}_{(aq)}$, E°=+0.77V; $MnO_{2(s)}/Mn^{2+}_{(aq)}$, E°=+1.23V

Subproblem	# scripts	# succcesful students in subproblem	% succes rate in subproblem	% succes rate in the overall electrochemistry exam
1A	16	1	6.3	87.5
2A	103	47	45.6	68.0
3A	140	71	50.7	66.4
4A	55	15	27.3	49.1
Overall A	314	134	42.7	65.0
1B	16	12	75.0	87.5
2B	103	35	34.0	68.0
3B	140	47	33.6	66.4
4B	55	12	21.8	49.1
Overall B	314	106	33.8	65.0

- In all subproblems, the success rates were much lower that in the corresponding overall electrochemistry exam, and this is reasonable if we take into account that the overall exam also included simple recall questions.
- The very low success rate (6.3%) in 1A can be attributed to the difficulty of the $Hg_2Cl_2(s)/Hg(l)$ redox couple:

$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^- (aq)$$

[Many students used the following half-reaction instead:

$2Hg^{2+} + 2e^- \rightarrow 2Hg(l)$ or $Hg_2^{2+} + 2e^- \rightarrow 2Hg(l)$]

- 4A and 4B had a low success rate, but this was not suprising, because they both were set as a composite problem (see study III).

Critical details

- Difficulties were encountered in completing the more complex half reactions, predicting the spontaneous reaction, and calculating $\Delta E°$.
- Several students did not take into account that at equilibrium the following equation applies: $\Delta E = 0$.
- Significant confusion was noted between the application of the European Convention and the application of the American Convention for the sign of $E°$

European Convention: Invariant sign

$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)\ E_1° = -0.762\ V$ (1)

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-\ E_1° = -0.762\ V$ (1a)

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)\ E_2° = +0.337 V$ (2)

$\Delta E° = E_2° - E_1° = +0.337 - (-0.762) = +1.099\ V$

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

European Convention: Invariant sign

$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$ $E_1° = -0.762$ V (1)
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ $E_2° = +0.337$V (2)

$\Delta E° = E_2° - E_1° = +0.337 - (-0.762) = +1.099$ V

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

American Convention: Changing sign

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E_1° = +0.762$ V (3)
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $E_2° = -0.337$V (4)

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

$\Delta E° = E_3° + E_2° = (+0.762) + (+0.337) = +1.099$V

Critical details - Instructional propositions

- We must pay attention to the relevant concepts and the relevant conceptual details.
- Taking into account the confusion between the European and the American Convention, it might be preferable to stick strictly and consistently to the use of the European convention.
- In addition, it is considered desirable to introduce small group tutorials (up to 15 students in each group) for theoretical university courses, where the teaching will be carried out using modern methodology, such as active learning, teacher-student interaction, and collaborative learning.
- Emphasis should be placed on encouraging and insisting that students carry out numerical calculations - in the present situation a significant proportion of students did not deal with numerical calculations at all, and from those who did very few got the right result.

Study II: A Study on Greek Students' Lecture Attendance, In–Course Practice on Problem Solving, and Success in Final Examinations in Equilibrium Electrochemistry

- It monitored students' attendance at lectures and provided in-course practice on problem solving on the topic of equilibrium electrochemistry.
- Students' attendance on the course and their engagement with the problems/exercises were studied, and a comparison was made between the performances in the final examinations of the students who participated in the exercises with those who did not.

Crippen and Brooks mode of **Interactive Compensatory Model of Learning (ICML):**

- Placing importance on motivation, practice, and feedback in instruction.

- It is assumed that three entities facilitate learning:

prior knowledge

ability

motivation

Crippen and Brooks mode of **Interactive Compensatory Model of Learning (ICML):**

Crippen and Brooks:

"At the core of quality instruction is a model of learning that considers the vital role that motivation plays for building "well-integrated cognitive structures".

"Instruction that requires students to learn from and interact with structured worked examples of closed-ended problems is consistent with contemporary models of human learning and produces efficient and effective results"

Research questions:

- (1) To find if providing students individualized help and feedback when dealing with electrochemistry problems during the course contributed to better achievement in the final exams.
- (2) To examine the effect of student attendance on the course and their engagement with the exercises on their achievement.

Findings

(1) Participation in the exercises was varied, with 51.2% of the students participating in only one exercise.

(2) A large majority (90.7%) of students who participated in the exercises (independent of the number of exercises) took the examination.

(3) Of the students who had participated in the exercises, about 2/3 (65.1%) succeeded in the exam.

(4) Over half of the students (54.5%) with high participation in the exercises (3 or more exercises) were successful in the final examination, while in the case of the low participation group (1–2 exercises) the pass figure was lower (40.0 %).

The overall performances of the students in the exams was low, reflecting a poor knowledge of electrochemistry.

- Our conclusion is that there is need for an overall change of the organization and operation of teaching in Greek universities.
- Students' attendance at the lessons must be regular if not compulsory, projects and exercises should be assigned by all instructors, followed by constructive feedback to the students.
- The introduction of tutorials and exploitation of the internet could certainly contribute to motivating and engaging students.

Study III: The Importance of the Formatting of the Problem: Student Performance in the Composite and the Step-by-Step Electrochemistry Problems

Study III: The Importance of the Formatting of the Problem: Student Performance in the Composite and the Step-by-Step Electrochemistry Problems

- In several of the final exams of the Greek "Physical Chemistry II" course, students were invited to attempt to solve a more demanding open-book question, at the start of the exam and separately from the standard closed-book part of the exam. To solve this problem, students had to think for themselves and devise their own steps to find a solution to the problem.

- We refer to this as the Composite Problem. Students were allowed to use their textbooks and course notes.

- No specific data were provided, so students had to consult general data tables (redox potentials and values of various constants).

- In order to allow students to deal with solving this composite problem in a more relaxed way, no time limit was set in advance. In general, an interval of 30–40 minutes proved sufficient, and students were eventually asked to complete their work. An additional short period (5–10 minutes) was then allowed before the student answers were collected.

- Although the composite problem was answered separately from the standard closed-book exam, it did carry some extra bonus marks, which were made known to the students in advance.

Composite problem

- A chemist in Mexico City, where the atmospheric pressure is 7.81×10^4Pa (that is $p/p° = 7.81\times10^4/10^5 = 0.781$bar), determined the *pH* of a solution at 25.0°C by making it the solution in a hydrogen electrode and measuring the potential of the electrode relative to some reference electrode (a calomel electrode).
- In calculating the *pH* of the solution from the potential measurement, (s)he assumed, erroneously, that the (hydrogen) gas bubbling out of the hydrogen electrode was at a pressure of 1 bar.
- If he found the *pH* to be 5.00, what was the correct value?

Ritchie, I. M., Thislethwaite, P. J. & Craig, R. A. (1975)

Problems in physical chemistry

(Sydney: Jon Wiley & Sons, Australasia)

Step-by-step problem

- **Subquestion 1**: Write down both the half reaction that takes place at the electrode (the half cell) involved in this problem, and the Nernst equation for this half reaction.
- **Subquestion 2**: Identify the gas that was bubbling out of the hydrogen electrode.
- **Subquestion 3**: Calculate the potential of the above half cell at 25.0°C.
- **Subquestion 4**: Calculate the correct *pH* value.

Exam	Composite problem	Stepwise problem
June 2005	(*n*=70) 38.1 (31.3)	(*n*=70) 61.5 (35.0)
June 2009 (students with practice in problem solving)	(*n*= 39) 37.2 (34.4)	(*n*=27)[b] 56.1 (33.7)
June 2009 (students without practice in problem solving)	(*n*= 96) 27.5 (35.2)	(*n*=50)[b] 46.2 (34.2)

[b] Not all students attempted the stepwise problem in these cases

Conclusions and Recommendations

- The procedure involved in solving a demanding equilibrium electrochemistry problem, requiring the application of the Nernst equation to a galvanic cell, is complex and accounts for students' difficulties when dealing with such problems.
- Although the nature of the solutions is such, that the problems can be turned into algorithmic exercises through extensive practice, the fact that most students find these problems hard and commit numerous errors can be explained by their lack of conceptual understanding.

Critical details

Even students with acceptable performance in the examination had difficulties dealing with topics such as:

- writing the two half reactions and the overall cell reaction,
- the equilibrium condition in a galvanic cell,
- the replacement of numerical values in the Nernst equation, and the calculation of the final numerical result.

Critical details

Both instructors and students should bear in mind that

- it is the two half reactions that actually take place in an electrochemical (galvanic or electrolytic) cell, with the overall cell reaction being the logistic result of combining the two half-reactions.
- The overall reaction is usually a redox reaction, but it need not be so.

Critical details

- Students should be given good practice in writing redox half reactions (both in acid and basic solutions) and
- deciding between the two half-reactions in a galvanic cell, which will occur as the oxidation and which as the reduction, on the basis of their relative E° values.
- Consistency in using the European sign convention should be secured.

Critical details

- Depending on the electrode potential values, the possibility of the solvent (water) being involved in the half-reactions of the electrochemical cell must also be considered:

In anode (− in a galvanic, +in an electrolytic cell):

$2H_2O \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$ oxidation (acid solutions) $E^\circ = +1.23V$

$4OH^-_{(aq)} \rightarrow O_{2(g)} + 2H_2O + 4e^-$ oxidation (basic solutions) $E^\circ = +0.40V$

- In cathode (+ in galvanic, in electrolytic cell):

$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ reduction (acid solutions) $E^\circ = 0V$

$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$ reduction (basic solutions) $E^\circ = -0.83V$

It is important to realize that the three studies reported here were carried out within the specific context of the Greek higher educational system, with its distinctive features, such as:

- traditional didactic methods of teaching
- lack of compulsory attendance at lectures by the students and,
- in principle, an unlimited ability to resit examinations

There are, of course, many approaches that can be used to motivate students to engage more actively with their courses, rather than merely passively attending the lectures.

It has been reported,* for instance, that the introduction of student-centered voluntary workshop tutorials in a large first year physics course (based on informal cooperative groupings with structured worksheets and short hands-on activities) resulted in about 80% of the students attending more than two-thirds of the tutorials.

- M. Sharma, A. Mendez, J. O'Byrne, **The relationship between attendance in student-centred physics tutorials and performance in university examinations** I

  International Journal of Science Education, 2005, 27,1375–1389.

- By discounting the students who had attended very few tutorials, it was found, on average, that exam marks improved significantly with increased tutorial attendance.

- Students' attendance at lectures should be regular if not compulsory, projects and exercises should be assigned by all instructors, and this should be followed by constructive feedback to the students.

- The introduction of tutorials, exploitation of the internet, and the promotion of collaborative learning, are all likely to contribute to motivating and engaging students.

An example of a problem

You are given the following galvanic cell at 298 K:

(-)Pt |$Fe^{2+}_{(aq)}$ (*a*=0.90), $Fe^{3+}_{(aq)}$(*a*=0.10) | |$Mn^{2+}_{(aq)}$ (*a*=0.10) |$MnO_{2(s)}$ |Pt (+)

(2A): Write the spontaneous reaction that takes place in this cell. Also calculate the standard cell potential difference Δ*E*° for the cell, and

(2B): Calculate the chemical equilibrium constant for the overall cell reaction at 298K.

An example of a problem

You are given the following galvanic cell at 298 K:

(-)Pt | $Fe^{2+}_{(aq)}$ (a=0.90), $Fe^{3+}_{(aq)}$(a=0.10) || $Mn^{2+}_{(aq)}$ (a=0.10) | $MnO_{2(s)}$ | Pt (+)

(2A): Write the spontaneous reaction that takes place in this cell. Also calculate the standard cell potential difference ΔE^{o} for the cell, and

(2B): Calculate the chemical equilibrium constant for the overall cell reaction at 298K.

- Data: $Fe^{3+}_{(aq)}/Fe^{2+}_{(aq)}$, $E^{o}=+0.77V$; $MnO_{2(s)}/Mn^{2+}_{(aq)}$, $E^{o}=+1.23V$

Solution

- Write the spontaneous reaction that takes place in this cell.
- Also calculate the standard cell potential difference Δ*E*° for the cell.

- the two half reactions that take place in the galvanic cell:

Oxidation at the negative electrode

ALTERNATIVELY:

Oxidation is the half reaction with the smaller algebraically *E*° , that is the one with *E*° = +0.77V (+0.77 < +1.23).

Hence, the two half reactions are:

(-) oxidation: $Fe^{2+} \rightarrow Fe^{3+} + 1e^-$ **(1)** $E_1^\circ = +0.77\,V$

(+) reduction: $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ **(2)** $E_2^\circ = +1.23\,V$

HENCE: Spontaneous overall reaction **2 X (1) + (2) (*n* = 2)**
(balancing the electrons in the two parts of the chemical equation):

$$2Fe^{2+} + MnO_2 + 4H^+ + \cancel{2}e^- \rightarrow 2Fe^{3+} + Mn^{2+} + 2H_2O + \cancel{2}e^-$$

$\Delta E^\circ = +1.23 - (+0.77) = +0.46\,V$. ($\Delta E^\circ > 0$ for a spontaneous reaction.)

(2): **Calculate the chemical equilibrium constant for the overall cell reaction at 298K.**

- **The Nernst equation at equilibrium that corresponds to the overall spontaneous reaction that takes place in the galvanic cell is:**
- $\Delta E = \Delta E^{\circ} - (RT/2F)\log Q_r$

$\Delta E = \Delta E° - (RT/2F)\log Q_r$

At equilibrium: $\Delta E = 0$, hence

$0 = \Delta E° – (RT/2F)\log K$

(at 298K)

$0 = +0.46\text{V} - (0.05916/2)\log K \rightarrow$

$\log K = 0.46 / (0.05916/2) = +15.55$

$\rightarrow K = 10^{+15.55} = 2.82\text{X}10^{15}$.

(For a spontaneous reaction, $K >> 1$).

The case of non-spontaneous reactions

- $Ag^+(aq) + 1e^- \rightarrow Ag(s)$ (1) $E_1° = +0.80$ V
- $AgCl(s) + 1e^- \rightarrow Ag(s) + Cl^-(aq)$ (2) $E_2° = + 0.22$V

$E_1° > E_2°$ → (1) is the reduction and (2) is the oxidation.

- (1) – (2): $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ $\Delta E° = +0.80 - 0.22 = 0.58 > 0$ (spontaneous reaction)

- (2) – (1): $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ $\Delta E° = +0.22 - (+0.80) = -0.58 < 0$ (non-spontaneous reaction)

At equilibrium: $\Delta E = 0$, hence

Nernst equation at 298K: $0 = \Delta E° - (RT/1F)\ \log K_{sp} \rightarrow 0 = -0.58 - 0.05916\ \log K_{sp}$

$\rightarrow \log K_{sp} = -0.58 / (-0.05916) = -9.804$

$K_{sp} = 10^{-9.804} = 1.57 \times 10^{-10}$

($K_{sp} \ll 1$)

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Grazie

Σας ευχαριστώ