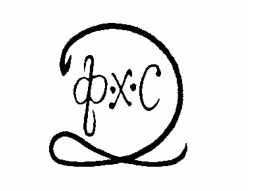

PHYSICAL CHEMISTRY 2016

13th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume I

B E L G R A D E
September 26 - 30, 2016

ISBN 978-86-82475-34-7
Title: Physical Chemistry 2016 (Proceedings)
Editors: Željko Čupić and Slobodan Anić
Published by: Society of Physical Chemists of Serbia, Studentski trg 12-16, 11158, Belgrade, Serbia.
Publisher: Society of Physical Chemists if Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: "Jovan", Printing and Publishing Company; 200 Copies.
Number of pages: 6+502; Format B5; printing finished in September 2016

Text and Layout: "Jovan"

200 - *Copy printing*

PHYSICAL CHEMISTRY 2016

13th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry

Organized by

The Society of Physical Chemists of
Serbia

in co-operation with

Institute of Catalysis Bulgarian Academy of Sciences

and

Boreskov Institute of Catalysis Siberian Branch of
Russian Academy of Sciences

and

University of Belgrade, Serbia:

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MICHAEL PUPIN AND PHYSICAL CHEMISTRY

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ABSTRACT

Michael Pupin is a great Serbian-American inventor, professor and scientist; best known for his huge contributions to the development of modern telecommunication and X-ray imaging. Less is known that his doctoral dissertation falls within a scope of physical chemistry. Pupin´s doctoral dissertation, entitled *Osmotic pressure and his relationship to free energy* was conducted under the mentorship of Helmholtz; can be considered as a pioneer theoretical research in a particular field of physical chemistry, chemical thermodynamics. Aim of this study is to draw public attention on the contribution of the celebrated Pupin to physical chemistry

FROM EUROPEAN SCHOOLS TO COLUMBIA COLLAGE

Mihajlo Pupin, Anglicized as Michael Idvorsky Pupin was born on October 9th, 1854, Idvor, Military frontier of the Austria Empire (now in Republic of Serbia) – died March 12th, 1935, New York, USA [1]. His formal education has begun in the village primary school of Idvor. Since he demonstrated marked mental energy and capacity, his secondary education has continued in Pančevo and Prague. During school days in Prague, Pupin met František Ladislav Rieger (1818-1903) and František Palacký (1798-1876); as he wrote "the great apostles of Panslavism and of nationalism of in Bohemia" [2]. Torn between personal aspiration toward higher education and social phenomena of nationalistic enthusiasm resulted in less then average grades. Pupin admits "I never during my whole year's stay in Prague sent a report home on my school work, because I never did more than just enough to prevent my dropping to the lower grade" [2].

Death of his father, mother's insistence to continue his education despite newly created situation and Rieger's advice to leave nationalistic engagement and devoted himself to the higher education, have done major influence on his firm decision to leave Europe, and go to USA. In this endeavor, Pupin was all alone. In order to cover transpiration expenses, he sold his books, watch, clothes. Pupin has left Europe on March 12th, 1874 in an immigrant ship. There on the ship, in order to survive coldness, Pupin

has applied the second low of thermodynamics instinctively and unknowingly (*the transfer of heat goes from the hot object to the cold object*). Namely, in order to survive coldness he placed himself alongside to the warm some-stack. He wrote, "If it had not been for the warm smoke-stack I should have died of cold" [2].

Due to his intellectual skills, Pupin successfully passed rigorous immigrant cross-examination, and entered the States. During next five years, he was forced to earn for his living, mostly throughout hard labor. Spare time, was reserved for self-education and education at night classes of the Cooper Union. On the last week of September 1879, he took entrance examination at *the Columbia Collage in the city of New York* [2]. He was so brilliant at examination that he managed to enroll at Columbia Collage, released from all tuition fees.

FROM COLUMBIA COLLAGE TO EUROPEAN UNIVERSITIES

His collage career begins in autumn 1879, at the Columbia Collage. As freshmen, Pupin has won first prize in competitive examination in Greek and mathematics. During sophomore year, Pupin has established himself as an excellent wrestler and boxer. Parallel with that, another Pupins virtue was reviled, that is the ability for qualitative tutoring (coaching) of students who failed in their collage examinations (Greek, Latin, mathematics). He was so good in this, that he earn reputation as a doctor for *lame duck* [2]. These were the first steps in his future successful academic carrier. Pupin has graduated in 1883, under the mentorship of Lewis Morris Rutherford (1816-1892), and become *Bachelor of Art*. Being a great student, he was appointed as the first to hold a John Tyndall Fellowship. This fellowship was established due to donation of John Tyndall (1820-1893.) to the Columbia Collage.

Pupin has continued his education on the University of Cambridge (1883-1885). There he began studies in mathematical physics under the precept or ship of Edward Routh (1831-1907). Under Routh he obtained mastery of dynamical methods [3]. During postgraduate studies at Cambridge, Pupin has become especially interested in research work of Michael Faraday (1791-1867), James Clerk Maxwell (1831-1879) and Herman von Helmholtz (1821-1894).

Eager to study experimental physics, Pupin obtained permission to continue postgraduate studies at Fredrich Wilhelms University in Berlin. He attended the course on experimental physics given by Helmholtz, and also lectures on the theory of electricity and magnetism given by Gustav Kirchhoff (1824-1887). Pupin has written: "A new physical science was attracting much attention in Germany at that time, the science of physical

chemistry" [2]. He become interested for *this new science*, realizing that research of Josiah Willard Gibbs (1839-1903), from the Yale University, was far ahead if it is compared with achievements obtained by "the alleged German fathers of this new science" [2]. Helmholtz and Pupin had agree that "It was clean-cut little discovery" [2]. Helmholtz had encouraged Pupin to investigate these findings in more details, suggesting that he might find material for research leading to doctoral dissertation. As Pupin writes "I embraced the suggestion and started an experimental research, at the same time studying the theories of Gibbs, Helmholtz, and other authorities, mostly German, on physical chemistry" [2].

PROMOTIONAL EXAM AT FREDRICH WILHELM UNIVERSITY

Priori to public defense of dissertation, Pupin has taken promotional oral exam on July 15th 1889, members of the Commission were Helmholtz, physicist August Kundt (1839-1894), mathematician Lazarus Fucks (1833-1902) and philosopher Eduard Zeller (1814-1908). The exam was a combination of oral exposition on views regarding three theses (selected by a candidate) and the discussion. As stated by Pupin, in its autobiography [2]: "The three theses which, according to old German custom, every candidate seeking promotion to the dignity of a doctor of philosophy must frame and defend publicly are given here, in order to show my final mental attitude which was formulated by my scientific studies in Europe.

I. Institutions in Physics in the preparatory schools should be as much as possible a practice one.
II. The Thermodynamics methods of Gibbs, von Helmholtz, and Plank form most reliable foundation for the study of those physical processes which we cannot analyzed by ordinary dynamics.
III. The Electromagnetic Theory of Light deserves more attention that it has received so far in university lecture".

First thesis came from realization that during his graduated studies on the Columbia Collage and postgraduate studies at the Cambridge University he receives no practical experience in physical laboratory. Further Pupin admits [2]: "I had no knowledge of physics acquired from my own conscious efforts in a physical laboratory". Consequently, Pupin skeptically claims that, "this was the real secret of my inability to understand Maxwell's physics; I longed for work in a real physical laboratory …". This thesis was also inspired by a Frederick Bernard (1809-1889), the president of Columbia Collage, who recognize that "young student in America at that time lacked a knowledge of visible things and not information about them – knowledge acquired by the learner's own conscious efforts, not crammed

into his mind in set forms of words out of books" [2]. During his first address to Helmholtz, Pupin informs professor that he never had an opportunity to work in a physical laboratory. Helmholtz suggested that Pupin "should make up this deficiency as soon as possible" claiming that "a few experiments successfully carried out usually lead to results more important than all mathematical theories" [2].

Second thesis, as Pupin writes "summed up my admiration for the new science of physical chemistry first stared by our own Josiah Willard Gibbs (1839-1903)" [2]. This tribute came from Pupin´s great respect for Gibbs´s work in a field of physical chemistry.

Third thesis is dedicated to the Farady-Maxwell electromagnetic science. To understand reason-way, one must have in mind that Pupin has studied Farady´s and Maxvell´s work well, and had become their huge admirer. Circumstantially, Pupin was present at a historically important event, which occurred at the end of 1887, during the meeting of Physical Society of Berlin (today's German Physical Society). There, Helmholtz solemnly announced that his former student, and at that time professor Heinrich Hertz (1857-1894) conclusively proved the existence of electromagnetic waves, verifying Farady-Maxwell electromagnetic theory. Impact of this discovery was so powerful on Pupin that it paved a way of his future scientific interests.

OVERVIEW OF DOCTORAL DISSERTATION

The title of Pupin´s doctoral dissertation is *Osmotic pressure and his relationship to free energy* (in original *Der osmotische Druck und seine Beziehung zur freien Energi*e) [4]. Mentor of the dissertation was Helmholz. Public defense was conducted on July 20th 1889. As opponents on public defense, following colleagues are citied on the frontal page: physicist August Raps (1865-1920), PhD candidate Arthur Webster (1863-1923) and PhD candidate Vladimir Michelson (1860-1927), Fig. 1. Webster and Pupin were colleagues from Ph.D. studies, and are among founders of American Physical Society (1899).

The dissertation is written in German, on 42 pages, and divided into eight sections: I Introduction, II History, III Concept of the free energy, IV General characteristics of the free energy of salt solutions, V Heat of Dilution, VI Osmotic pressure and its importance, VII Free energy of diluted salt solutions, VIII. Considerations about the internal constitution of a salt solution. Additionally, Thesis and Biography are presented at the last pages of dissertation. [4]

Der osmotische Druck
und seine
Beziehung zur freien Energie.

INAUGURAL-DISSERTATION

VON DER PHILOSOPHISCHEN FACULTÄT

NEBST DEN BEIGEFÜGTEN THESEN

am 20. Juli 1889

Michael Pupin

OPPONENTEN:
Hr. Dr. phil. August Raps.
Cand. phil. Arthur Gordon Webster.
Cand. phil. Wladimir Michelson.

BERLIN.

Осмотски притисак
и
његов однос према слободној
енергији

ИНАУГУРАЛНА ДИСЕРТАЦИЈА

ФИЛОЗОФСКОМ ФАКУЛТЕТУ

20. јула 1889. године.

Михајло Пупин

ОПОНЕНТИ
г. др фил. Аугуст Рапс
г. канд. фил. Артур Гордон Вебстер
г. канд. фил. Владимир Михелсон

БЕРЛИН

Figure 1. Front page of Pupin´s doctoral dissertation [4].

In the first section, *Introduction*, Pupin elaborates the aim of dissertation; that is to theoretically derive some characteristic related to the composition of salt solutions from the features of the Hemlohtz free energy (F), which is the thermodynamic function of the state. Two studies are citied in this section. Helmholtz´s paperwork from 1882, entitled *On the Thermodynamics of Chemical Processes*, in which the concept of the free energy is defined; and Wilhem Pfeffer´s report from 1877, which concerns investigation on the osmotic pressure (Π).

In the next section, *History*, Pupin quotes several scientific papers of importance. Kirchhoff´s work from 1858, which considers theoretical investigation of some features of salt solution (mainly heat of dissolution), from the thermodynamic viewpoint. Gibbs's paper from 1875-1878, (entitled *On the equilibrium of heterogeneous substances)*, in which analogy between some features of ideal gases and diluted salt solutions is given. Due to complex mathematical language, which outcome from his eager for more general conclusions, this work was incomprehensible by most of chemist and thus avoided. François Massie´s (1832-1896) work from 1876, who also had studied the concept of the free energy. Pierre Duhem´s (1861-1916) book from 1886; in which applied methods of Massie, Gibbs and Helmoltz are presented. Max Plank´s (1858-1947) work on the features of highly

dissolute salt solution, observed from the principles of the increasing entropy of the spontaneous processes. Studies of Wilhelm Ostwald (1853-1932), Jacobus van´t Hoff (1852-1911) and Svante Arrhenius (1859-1927), editors of the first scientific journal specialized for physical chemistry *Zeitschrift fur Physikalische Chemie* (first issued in 1887). These three scientists are considered as founders of modern physical chemistry. Wather Nernst´s (1864-1941) work also published in *Zeitschrift fur Physikalische Chemie*.

Quality of presented literature in the dissertation proves that Pupin has manage to gather all important articles and books, which either explicitly or implicitly elaborates problematic of modern aspects in the chemical thermodynamics of salt solutions. Today, when we are looking at these articles, and the authors, we consider them as a part of chemical thermodynamics history. Being their contemporaries, one must think of Pupin as a privileged man, who have work on his dissertation in a decade when history of the chemical thermodynamics, thereby physical chemistry was made.

In the third section, *Concept of the free energy*, Pupin mathematically defines the free energy from the first and the second low of thermodynamics [4]:

$$dQ = dU + \sum P_\alpha \, dp_\alpha \tag{1}$$

$$dQ = \Theta \, d\mathrm{S} \tag{2}$$

Q denotes the heat, U denotes the internal energy, p_α denotes parameters defining the state of the body and P_α denotes the force by which system opposes to the internal modification of system represented by p_α, Θ denotes the absolute temperature and S denotes the entropy. By coupling above equations, and presented them in the form where S and P_α are unambiguous functions determined by Θ and p_α, he obtained [4]:

$$P_\alpha = -\frac{\partial}{\partial p_\alpha}\left(U - \Theta \mathrm{S}\right) = -\frac{\partial F}{\partial p_\alpha} \tag{3}$$

U-ΘS is defined as Helmholze free energy (F). Thereupon, he showed that $dF \geq 0$ is sufficient condition for thermodynamic equilibrium. Notation that used in the dissertation is typical for Helmholtz´s marking method [5].

In next section, *General characteristics of the free energy of salt solutions*, Pupin mathematically shows that [4]:

$$\frac{\partial}{\partial h}\left(-\frac{\partial F}{\partial w}\right) \succ 0 \tag{4}$$

w denotes mass of salt solution, h denotes ration w⁄s, were s denotes mass of salt. He concludes that the force, equation (4), by which salt solution attracts solvent (water) must be negative, also. Hence, the force, by which salt solution attracts ions of salt, declines with concentration, becoming zero when salt solution becomes saturated.

In the section *Heat of Dilution*, he establishes relation between the heat of dissolution and the free energy. By considering changes of the free energy with increasing dilution, he was able to show an analogy between equations which show that both the gas pressure of ideal gases and the osmotic pressure of diluted salt solution are proportional on absolute temperature.

In the last section, *Osmotic pressure and its importance*, Pupin deals with phenomenon of osmotic pressure, giving precisions mathematics explanation of this phenomena and description of experiments according to which it was possible to obtained equation which extract analogy between ideal gas and diluted salt solution [4]:

$$\Pi V = \alpha s \Theta \qquad (5)$$

Π denotes the osmotic preassure, V denotes the volume, α denotes constant whish depends on the nature of salt and s denotes mass of salt.

Figure 2. Picture of Michael Idvorky Pupin take around 1890.

CONCLUSION

Doctoral dissertation of Michael Idvorsky Pupin entitled *Osmotic pressure and his relationship to free energy,* represents theoretical investigation in the field of chemical thermodynamics. Conducted under mentorship of

Helmholtz, this dissertation was publicly defended on July 20th 1889, just two years after appearance of the first scientific journal specialized for physical chemistry *Zeitschrift fur Physikalische Chemie* (first issued in 1887). Physicochemical community has paid practically no attention on this doctoral dissertation. It remains to be seen whether this study will provoke constructive analysis and criticism regarding scientific importance of Pupin´s doctoral dissertation.

Acknowledgement
This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grants no. 172015). The author would like to thank Mrs. Aleksandra Ninković Tašić for her generous support.

REFERENCES

[1] K. Snježana, Život i doprinos Mihajla I. Pupina fizici i hemiji, Diplomski rad, Univerzitet u Novom Sadu, Prirodno-Matematički fakultet, Departman za fiziku, Novi Sad, 2006. (in Serbian)
[2] M. I. Pupin, From Immigrant to Inventor, Charles Scribner´s Sons, New York, 1925.
[3] A. P. Wills, Science, 1935, **81**, 475-479.
[4] M. I. Pupin, *Der osmotische Druck und seine Beziehung zur freien Energi*e, Inaugural Dissertation, Frederich Wilhelm Univerzität zur Berlin, Berlin, 1889 (in German). M. I. Pupin, Monografije, Osmotski pritisak i njegov odnos prema slobodnoj energiji, Zavod za udžbenike i nastavna sredstva, Beograd, 1997, (Serbian translation).
[5] S. Bordoni, The European Physical Journal H, 2013, **38,** 617-660.

CIP - Каталогизација у публикацији - Народна библиотека Србије, Београд

544(082)
66.017/.018(082)
502/504(082)
663/664:658.56(082)
615.31:547(082)

INTERNATIONAL Conference on Fundamental and Applied Aspects of Physical Chemistry (13 ; 2016 ; Beograd)
Physical Chemistry 2016 : proceedings. Vol. 2 / 13th International Conference on Fundamental and Applied Aspects of Physical Chemistry, Belgrade, 26-30 September 2016 ; [editors Željko Čupić and Slobodan Anić]. - Belgrade : Society of Physical Chemists of Serbia, 2016 (Belgrade : Jovan). - IV, 507-930 str. : ilustr. ; 24 cm

Tiraž 200. - Bibliografija uz svaki rad.

ISBN 978-86-82475-33-0

1. Society of Physical Chemists of Serbia (Beograd)
a) Физичка хемија - Зборници b) Наука о материјалима - Зборници c) Животна средина - Заштита - Зборници d) Животне намирнице - Контрола квалитета - Зборници e) Фармацеутска хемија - Зборници
COBISS.SR-ID 225802508