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Quantal Aspects in Chemistry and Physics

A tribute to the memory of Professor Couceiro da Costa

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3. Professor Couceiro da Costa: The Pionner in the Teaching of Quantum Chemistry in Portugal

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3.1 Couceiro da Costa: The scientist

Ruy Gustavo Couceiro da Costa graduated in Physico-Chemical Sciences with high honours at the University of Coimbra in 1922. During his studies, he proved he had a bright mind with a special aptitude to science. In 1920, he was invited to join the chemical staff of the University of Coimbra as an assistant lecturer. Soon he displayed a propensity to interpret chemistry in both physical and mathematical grounds and an ability to delve deeply into scientific concepts. He was awarded his PhD in 1927 and in 1936 he was appointed professor of physical chemistry, a subject taught in the last year of the chemical graduate courses.

His PhD thesis was prepared in the *Chemical Physics Department of the Hydrological Institute of the College of France* and in the *Department of Chemistry of the University of Coimbra*. It deals with the analysis of gases emanated from Portuguese mineral water springs. Experimentation is the dominant feature of the work. Delicate glass blowing manipulations were involved to make the apparatus and devices used in the sampling, separation, identification and quantification of the components of the gaseous mixtures.

In those days, besides a thesis, the candidate for the doctorate degree had to propose three topics of chemistry and three of physics to be defended in

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the examination. The subjects chosen by Couceiro da Costa were theoretical open questions of utmost importance at the time. The pieces of work presented in his PhD examination showed immediately his scientific qualities: a talent to do experimental and theoretical research, a belief in both of these scientific approaches and his pleasure to undertake either of them. As an empiricist, he considered experiment the root of knowledge. Nevertheless he thought that generalisation could only be taken following a mathematical model as the inductive way. At the end of the lecture that he was invited to deliver on the commemoration of the 50$^{\text{th}}$ anniversary of the *Real Sociedad Española de Física y Química*, in 1953, he said: "The problems require quantitative solutions, otherwise we fall into the arbitrariness, which means the loss of prestige of theory."

It is not common to find someone who so easily take off the 'lab jack' after finishing a fine experiment and held the slide rule – the calculation tool of the time – to establish the theoretical explanation for the results or devise a new theory for a subject, popular at the time.

At a glance, the publications of Couceiro da Costa, considering their dispersion throughout the analytical and physical chemistry fields, may appear as resulting from pure serendipity. This though would not be quite correct. Indeed, he had three aims in mind while planning his research: to rationalise concepts based on inadequate scientific grounds, to closely follow the frontiers reached by the progress of science or use science to serve the society, contributing to the progress of industry and human welfare. And, underlying these aims, were the concepts that teaching should result in the student receiving a solid and modern scientific preparation and the idea that the knowledge and university laboratories should be put at the service of the country that pays for them.

The application of thermodynamics to the study of the distillation and crystallisation of a two-components liquid mixtures and the theorization of the analytical titration procedures illustrate the first aim. In the former paper, $P-x$ and $T-x$ diagrams for liquid-vapor and liquid-solid binary systems were interpreted from the work performed by van't Hoff machines (a piston pump closed by a membrane permeable only to one of the components) in a thermodynamic cycle formed by two isotherms and two adiabatic operations. The different types of theoretical diagrams explained the curves obtained from the experimental data.

The second paper referred to above deals with the theoretical interpretation of the volumetric techniques of the analytical chemistry. The analytical procedure is equated in terms of the equilibria occurring in solution and the properties with physical meaning are given by the derivatives of the deduced function in the different points of the titration.

The thixotropy of the vanadium pentoxide, published in 1934, is an up-to-date review of the colloidal state, in which he included research of his authorship. Colloids were known from Graham in 1860 who coined the name. However, until the end of the 19th century, colloidal solutions were considered as systems of enigmatic behavior compared with that of true solutions. The discovery of the role they played in aspects related with life, industry, etc., and the invention of new instruments increased the interest in this field. The research was initiated in inorganic colloids and was extended later to organic species. By the 1920s, about half of the papers submitted to *The Journal of Physical Chemistry* were related with the colloidal state. Between 1947 and 1951, this journal adopted the designation *The Journal of Physical and Colloid Chemistry*. It returned to the original name with the launching of periodicals especially dedicated to the matter. The work of Couceiro da Costa was of topical interest at the time.

Another evidence of his awareness about the recent acquisitions of science is the paper on the quantum mechanics in the prediction of chemical activity, published in 1954, after a conference given in Lisbon before the *Portuguese Chemical Society*.

During the period between the two world wars, great progress was achieved in theoretical organic chemistry. Famous chemists left their names linked to the electronic interpretation of the structure and reactions of organic compounds, especially in U.K. This scientific movement and the importance of the matter led to the appearance of a new discipline which was called “Physical Organic Chemistry” after the title of Hammett’s monograph that was published in 1940.

Two British chemists gave impressible contributions for this success: Robert Robinson and C. K. Ingold. Ingold published his theory in vol. 5 of *The Chemical Reviews* (1934) in a paper entitled "The mechanism of an electronic theory of organic reactions". This theory gave rise to a controversy that lasted for years. A heated debate with Robinson became famous because it was a struggle between two influential scientists. Ingold was accused of plagiarism of Robinson's pioneering work published in 1926 in Journal of the Chemical Society.

The controversy abated and by 1939 Ingold's ideas gained general acceptance. "Structure and mechanism in organic chemistry", published by Ingold in 1953, one of the four hundred and forty three publications authored or coauthored by him, was a reference book for decades.

The paper of Couceiro da Costa addressed the prediction of reactions between hydrocarbons with nucleophylic, electrophylic and radical molecular groups. He used quantum mechanics as research method. The effects of resonance, orientation in substituted benzene compounds and π-complexes were discussed. The main aim of his work was to show the potentialities of the molecular orbital theory in predicting reactions. It is a modern piece of work, both in respect to the focused topic and the novelty of the method employed. To underline the power of the quantal methods in relation to the older electronic theories he added the remark that the success of Ingold and Robinson with so modest data available, as to the values for dipole moments and refractivities was only possible because both were gifted scientists.

Besides aspects of pure chemistry, Couceiro da Costa published some papers on the composition and the evolution of the physical properties of mineral waters with time. He did very fine work on the trace analysis of metals using colorimetry, absorption spectrophotometry and atomic emission spectrometry in the early days of the development of physical methods of analytical chemistry. The laboratory methods he used were not applications of standard techniques, but rather procedures settled on physical chemical grounds, improving their analytical selectivity and sensitivity.

Backroft (1867, 1953), the influential American scientist, president of the

American Electrochemical Society and of the American Chemical Society, founder of the Journal of Physical Chemistry and its editor for decades, divided scientists into two groups: diligent “accumulators” and inspired “guessers”. Couceiro da Costa was included in the later category.

3.2 Couceiro da Costa: The head of the Department of Chemistry

In 1937, Couceiro da Costa was appointed head of his department. A lot of difficulties were waiting for him: poor, almost inexistent research activity, antiquated and exiguous installations, and insufficient financing for equipment, chemicals and journals. His predecessor, Prof. Egas Pinto Basto, did not accept the situation of the department and it was him who took the first steps to improve the situation. But, he died early. It was Couceiro da Costa who gave effectively the decisive contribution to the progress of the department. New graduates were sent abroad with scholarships to do research in English and American universities, where most of them got a PhD degree. Upon their return to Portugal, they carried on their research programs, giving rise to research teams which guided students and young graduates towards science.

Meanwhile, the teaching and research laboratories were equipped with modern instruments, purchased with money from different public and private funds. The library subscribed to the most important chemical journals published worldwide. Old volumes, sometimes complete collections of the subscribed periodicals were acquired. The library grew from a room that kept a few textbooks to an excellent teaching and research support facility. The scientific panorama of the department changed.

In spite of the efforts made to install research, teaching was also considered the most important university function. There was not so much concern in preparing the students for problem-solving, but rather to give them a good chemical preparation on both theoretical and laboratory sides. The main goal of university teaching was effectively the education of the mind for science.

In Portugal, the authorities responsible for education never believed in the role of science in human progress. Thus, the fraction of GNP allocated to higher education and to R&D was always insufficient. With Couceiro da Costa, the budget increased substantially. Despite his prestige and the circle of influential acquaintances he fought hard to overcome the difficulties caused by the shortage of funds. Once being accused of being too ambitious, he argued: "It is quite natural to intend that our laboratories are at least similar to the most modest ones of advanced countries; with this income we are quite far from this goal."

The laboratories of the Faculty of Sciences dated from the end of the 18^{th} century. The evolution of science, the increasing number of courses and chairs, the growing number of students made these laboratories quite unsatisfactory to meet these demands. The old *Laboratorio Chimico* was one of the first to be built especially for chemistry, in the eighteenth century. It was a beautiful edifice of magnificent architecture, but too narrow for the modern chemical activity. Instruments occupied all corners; the journals were kept in bookcases covering the walls of the lecture theater and all along the corridors. A new laboratory was, in fact, desperately needed.

In 1934, the government decided to reinstall the University of Coimbra, building new edifices and modernising some others. Couceiro da Costa devoted himself with great enthusiasm to the planning of new installations. He visited various European universities to collect information on laboratories and on the organization of recent departments of chemistry. Unfortunately, he did not assist in the construction, but he left the outline of a new laboratory large enough to be used as a chemical laboratory for the time being. The available area of the new building is 16000 m^2 over a total of six floors. Before the reduced number of chemistry students today it is considered by some people as being too big; the reality is that the university and the country is not proceeding in the correct way so as to bring more students to science.

In 1952, he faced a new challenge with respect to laboratory installations and, once again, he overcame it. Among the criticism of many, the approval of a few, and the indifference of the majority, Portugal decided to introduce the study of nuclear science to the university. In October of that year, the *Comissão Provisória de Energia Nuclear do Instituto de Alta Cultura* was created. In its program was scheduled the foundation of research centers associated to the universities. Couceiro da Costa could not loose this opportunity, all the more because he had been an ardent supporter of this project. However, it was not possible to install something else in the old edifice, and the new one would not be ready in time. Therefore, in a quite a short time, he built an annex with a few rooms equipped to carry out work with radioactive materials *(Centro de Estudos de Química Nuclear e Radioquímica)* in the landscaped space at the side entrance of the *Laboratorio Chimico*.

This extension of the main building was pulled down recently to install what is called *Museu da Ciência e da Técnica da Universidade de Coimbra*. It had no value from an architectural point of view, but it was really an historical document. Its place is now just an open air space.

3.3 Couceiro da Costa: The professor of physical chemistry

Aside from a few other chemical courses, Couceiro da Costa taught during his career two subjects: “inorganic chemistry” and “physical chemistry”. The former was taught in the first year of the undergraduate chemical courses and it was really an introduction to the study of chemistry. The program gave a good grounding in chemical fundamentals without using much mathematics. The latter, taught in the last year of the degree, was a deep interpretation of chemistry as science. The syllabus of “physical chemistry” was devised at the time of the development of this discipline. To get a better idea about his merit as a lecturer, it is useful to revisit the most important steps in the awakening of this chemical method.

Chemistry is a branch of science that had to travel a long journey before getting the statute of a scientific discipline. In this context, science is understood as a body of knowledge that, through observation/perception, induction and deduction reasoning, establishes laws able to explain the natural world. The history of chemistry is indeed rather peculiar insofar as the chemical phenomena accompanying very closely the life of man from the very beginning, took a long time to reach the status of mature science. It remained for millennia as a set of separate acquirements and techniques but without a theoretical matrix joining them together.

In spite of the progress of experimental chemistry during the first scientific revolution (17th-18th centuries), this situation remained unaltered. Lavoisier's work contributed very little to change that. Chemists, physicists and philosophers noted this imperfection. Kant, in the *Metaphysische Anfangsgruünde der Naturwissenschaft* (1786) and in the preface of the 2nd edition of *Kritik der Reinen Vernunft* (1787) characterised chemistry as a set of very useful techniques but not as a true science, because the deductive method could not be applied to the subject matter of chemistry. Later, Maxwell criticised the deficiency of rigor, clearness and abstraction in chemistry. In Helmholtz's opinion, it was not advanced rationally.

Chemistry and physics grew separately but by the middle 1800's both disciplines started to converge. Since the 17th century, heat became an important concept in natural philosophy. It was related with the power generated by the steam machines that later propelled the industrial revolution. In chemistry, heat produced transformations of matter like calcination, hardly understood. Thus, it was natural that scientists raised the questions about the nature of heat.

In the first half of the 19th century, two theories found audience. One admitted that heat was matter. It appeared in phlogiston as matter of a substance determining all chemical transformations. Lavoisier tabled heat as an element, the caloric. Carnot considered the caloric as matter able to produce work while moving from a hot to a cold reservoir. In contrast, the kinetic theory admitted that heat was the result of particle motions, atoms and molecules. The development of thermodynamics proved that heat was, in fact, a manifestation of energy.

With the discovery of the second law of thermodynamics, in 1850, and its enunciate in terms of entropy, 15 years later, thermodynamics was established. Gibbs, in his renowned work "On the Equilibrium of Heterogeneous Substances", published in 1878, adapted thermodynamics to the interpretation of chemical systems. The work of Gibbs remained largely unknown for a long time because it appeared in the modest *Journal of the Connecticut Academy of Sciences* and was written in difficult mathematical terms. The great European scientists: Maxwell, van der Walls, van't Hoff and Le Châtelier, were deeply impressed as soon as they made acquaintance with Gibbs' monumental work and became its most active promoters.

Thermodynamics was then applied to the chemical phenomena, being the first approach of physical chemistry. In 1887, Oswald and van't Hoff launched the *Zeitschrift für Physikalische Chemie*, the first journal specially dedicated to the new discipline.

Physical chemistry grew rapidly in sciences related with chemistry and by the turn of the century its study was part of the university curricula. In Portugal, it was introduced in the university as a one semester course in 1911. At the time, it was also created another semester course dedicated to the study of thermodynamics.

In the United States, the importance of theoretical and practical physical chemistry was soon perceived. This gave rise to a movement to qualify people in this field. Many graduates were sent to good research centers in Europe. Paris, Leipzig, Heidelberg and Berlin received American chemists in short visits or in longer stays to run research projects. From 1889 to 1904, forty two American graduates attended Ostwald laboratories in Leipzig. When they returned to their country, many of them became influential lecturers and research leaders. As a corollary of this intense activity, a journal dedicated to physical chemistry, *The Journal of Physical Chemistry*, was launched by the American Chemical Society in 1896.

Lewis, an old student of Leipzig, went back to MIT in America and in 1912 was invited to lead the California Institute of Technology (CALTECH). Some colleagues and students followed him and in a few years CALTECH left the position of a modest institute and became one of the best world research centers. One of the most active areas at the time in CALTECH was thermodynamics. In 1923 Lewis and one of the colleagues who came with him from MIT, Randall, wrote the concise and comprehensive book, "Thermodynamics and Free Energy of

Chemical Substances", which became a reference in chemical thermodynamics. This book was a valuable agent to make the Gibbs' work known amongst scientists.

The kinetic theory of heat was not forgotten. Various scientists tried to explain the properties of ideal gases by mechanics. They did not succeed until Maxwell, who in 1860 was able to establish a distribution law of the particles against velocity at a given temperature. The theory based on the mechanics and statistics explained various properties of the gases such as pressure, free mean path, viscosity and diffusion.

However, the triumph of Maxwells' theory was not the interpretation of the behavior of the gases but rather for being the first with a new approach to interpret the physico-chemical phenomena, latter called statistical physics or statistical mechanics. This science allows the determination of the macroscopic properties of matter from the information taken from the microscopic properties, atoms or molecules. The publication of Maxwells' work called the attention of Boltzmann and both, in friendly concurrence, improved the previous theory and obtained a more general distribution law, which was known as the Maxwell-Boltzmann distribution law.

Boltzmann progressed his research trying to establish a link between mechanics and thermodynamics. He attempted to base the second law of thermodynamics on mechanical grounds. From the mechanical statistical treatment of more complex gaseous systems under an external force field he derived the famous H function, which had the particularity to decrease with time, and tended to a constant value as the system approached the stationary state. Boltzmann admitted then that H was related to the entropy. The H theorem was the mechanical version of the second law. He set up the equation $S = k \ln W$, relating the entropy with the number of microstates of the system under consideration.

The apparent contradiction for the explanation of irreversibility by mechanics, gave rise to opened and inflamed discussions that did not affect the foundations of statistical thermodynamics.

Gibbs, in 1902, cut-off the links of the statistical physics with the primitive roots as systems of particles with certain properties and developed it as rational mechanics. With Gibbs, statistical mechanics was complete in classical terms, applicable to any system, and ready to receive the new mechanics that was coming.

Late in the 19^{th} century, physicists were attempting to interpret the distribution law for the thermal radiation emitted by a hot body. The Rayleigh-Jeans equation accounted for the experimental results at long wavelengths (low temperatures) but failed to explain the spectrum at short wavelengths. In this region, classical physics predicted a thermal emission of a hot body at an infinite rate (ultraviolet catastrophe). In the University of Berlin there was an active group working on this subject, among them, Max Planck. He obtained an equation able to explain the full spectrum of the thermal radiation emitted by a black body. In the deduction of this law he admitted that the radiation was in thermal equilibrium with a set of harmonic oscillators. The results could only be explained considering that the energy of each oscillator would be given by the equation, $E = nh\nu$, where n is an integral number, h a universal constant later called after him and ν the frequency of the radiation. That is, the energy of each oscillator was quantized being $h\nu$ the quantum of energy. It is very likely that Planck did not become aware of the importance of his quantum theory that he announced to the Berlin Physical Society on 14^{th} of December of 1900. He took it as being some sort of mathematical trick that enable him to explain the results observed for the black-body radiation. He did not realize that it was a turning point in the history of the physics.

Hertz discovered that the light was capable to eject electrons from metals (1887) and Leonard in 1902 observed that the maximum value of the energy of the electrons was related to the frequency of the radiation. The latter author also verified that the effect is observed only at frequencies above a certain limit, and further that the threshold frequency was different for every metal. According to classical electromagnetism the energy of the ejected electrons should be dependent not on the frequency but rather on its intensity. Three years later, Einstein interpreted the photoelectric effect; part of the kinetic energy of a quantum of the radiation was transferred to the electron of the target which acquires enough energy to leave the metal. The quantum, $h\nu$, of the radiation was called by Einstein, photon. The radiation behaves as a wave and sometimes as a particle. The idea of light quanta contradicted the wave theory from the Maxwells' equation.

The wave-particle duality gave rise to great controversies and quarrels, which ended in 1924 with Broglies' investigation. The French physicist proved that effectively an electromagnetic wave corresponds to a corpuscle and the corpuscles, as electrons, behave as a wave. He deduced an equation relating the velocity, v, of an electron of mass, m, with the corresponding wavelength, $\lambda = h/(mv)$. Davidson and Gurner obtaining diffraction patterns using electrons confirmed the De Broglies' theory experimentally.

Meanwhile (1913) Bohr had the stroke of genius to apply the quantum theory to the atom. Inspired in the periodic law of Mendeleev, according to which a determined energy level could only contain a certain number of electrons, he developed his well-known atomic model, based on the quantum theory.

A puzzle for the scientists of that time was to explain why the orbiting electron did not loose energy and fall towards the nucleus as predicted by the classical electromagnetic theory. The Bohr atom explained the emission spectrum of the hydrogen but was not able to interpret the spectra of multi-electron elements. Refinements were added to the Bohr model as proposed by Sommerfeld and Broglie. The latter admitted that an electron in an orbit could be considered as a wave around the nucleus and will only be observed in the situation that permits a standing wave.

With de Broglie, the old quantum theory was at the end after standing for twenty-five years as an opened question. However, it produced a rich harvest for the second phase of the development of quantum mechanics. Heisenberg announced the discovery of this theory in 1925 in a paper published in *Zeitschrift für Physik*. He founded it in a rather unfamiliar form for physicists, the matrix mechanics. Six months after Heisenberg's paper, Schrödinger published in *Annalen der Physik* a different version of the theory describing the quantum state of the electron by a wave function. Soon, it was realised that both versions were equivalent, which means that the quantum mechanics was discovered twice in six months time.

Quantum mechanics was a wonderful creation of outstanding physicists, gifted and privileged minds with credentials in mathematics and physics and knowledge of chemistry. Chemistry, with its roots in the microscopic world, took advantage of it and experimented, making great progress during the development of the theory. A new science was developed in the chemical field and the progress was such that by 1940s it gave birth to Quantum Chemistry, also called Theoretical Chemistry. Physical Chemistry had then three research methods available to the study of systems at equilibrium: thermodynamics, statistical mechanics and quantum mechanics.

The academic career of Couceiro da Costa (1920-1955) elapsed during the development of the physical chemistry. When he arrived at the University of Coimbra, chemical thermodynamics was a recent method applied to chemistry, statistical mechanics were just taking its first steps, quantum statistical and quantum mechanics were in development.

By the 1920s, physics passed over the greatest crisis of its history due to the conflicts between quantum theory, Newtonian mechanics and Maxwellian electromagnetism. Causality, a fundamental scientific assumption that passed untouched through the development of the statistical mechanics, was to be renounced to the understanding of the new ideas and facts. Complementarity, in some aspects, accepted principles of the classical physics while rejected them in some others.

Before this situation, it is surprising as a young man that had just arrived at university was capable of recognising the importance of the revolution and who followed it closely. Soon, he introduced these new ideas at the undergraduate level what is an assertion of his idea on the aim of university teaching that it was to prepare the students for the forthcoming world. To do this, the professor has to lead his students to the scientific frontiers of knowledge.

Making a plea to my memory and with the collaboration of my colleague Professor J. Providência, both old students of Couceiro da Costa, we reproduced the topics of the program of "physical chemistry" from 1937s on and we present it in Appendix I. This program was taught when the first books of quantum chemistry were just being published.

3.4 Couceiro da Costa: The man

Couceiro da Costa was born in January of 1901 in Praia (Cabo Verde) in a distinguished family. His father was magistrate and diplomat and when the republican regime rose to power he was appointed governor of the Portuguese-India State. His maternal uncle was professor of chemistry in the University of Coimbra. He began his schooling in India and finished it in Portugal with distinction (19 in 20). He obtained his degree at the University of Coimbra in 1922 with honours. Still a student, he was invited to join the university as an assistant lecturer and obtained his doctoral degree in 1927. In 1934, he was promoted to full professor and held the cathedra of "physical chemistry". Three years latter, he was appointed head of the Department of Chemistry, a post that he held until his death in 1955, at the age of fifty four. He married Maria Helena Wittnich Carrisso in 1938 and they had a son and a daughter.

Couceiro da Costa was a kind and educated man. He was tender-hearted with human problems, keenly interested in the professional situation of assistants and technical staff. His jovial nature made him a wonderful fellow worker and a friend although keeping the deferential barriers created by his prestige and personality. The pleasant atmosphere he created in the Department of Chemistry was also characterised by deep respect to ethical principles, justice and dedication to the university cause.

A social-minded person, he enjoyed a break late in the afternoon to have coffee with his colleagues. This was an opportunity to talk about the work in progress, science or just to comment on the affairs of every day life. His opinion always deserved to be listened to.

He was quite rigorous in what to the laboratory work is concerned. He used to say that a student that was not well-prepared would never be a skilful experimenter. For those, experience does not teach; on the contrary, it just made the faults more apparent.

When someone did his job negligently he lost his temper and reacted immediately. Soon though, he forgot the incident and proceeded calmly with what he was doing. He did not bear any grudges.

The intellectual achievements never overshadowed his natural simplicity and education. He was approachable by the qualified students and encouraged them to take an academic career. To get a place to work with him was an honour given his reputation and rigorous selection criteria. The daily work with him was a permanent lesson. When he discovered something rather interesting in the work he had in hand he called his collaborators and with great enthusiasm explained what he had just found. I have never met someone with such a deep critical insight into the fundamental concepts of chemistry.

Apendix 1 Program of the physical chemistry course taught by Couceiro da Costa in the 1940s

- *Classical statistical mechanics*: Phase space, Liouville's theorem. Statistical equilibrium. Maxwell-Boltzmann distribution law. Mean values in statistical distribution. Principles of the energy equipartition. Axioms of Gibbs statistical mechanics.
- *Quantum statistics*: Indistinguishability of identical particles. Quantum statistics: Bose-Einstein and Fermi-Dirac statistics. Comparison of the three statistics. Examples of Bose-Einstein and Fermi-Dirac systems. Electron gas in metals. Heat capacity of solids. Real gases. Quantum statistics in the resolution of apparent discrepancies between theory and experiment.
- *Statistical thermodynamics:* Entropy and probability. Boltzmann's H theorem. Partition functions: translational, rotational and vibrational partition functions. Monoatomic and diatomic molecules.
- *Quantum mechanics*: Quantum theory. The Bohr-Sommerfeld atom and the primitive quantum theory. Hamilton-Jacobi theory of integrable systems. Quantum mechanics: de Broglie, Heisenberg, Schrodinger. Inter-

pretation of the wave function. The theory of the chemical bond. The hydrogen molecular ion and hydrogen molecule. Heitler and London theory of the chemical bond

Apendix 2 Selecta Bibliográfica de Ruy Gustavo Couceiro da Costa

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- "Análise dos gases espontâneos das nascentes de águas minerais", *Dissertação de doutoramento* (Imprensa da Universidade, Coimbra, Portugal, 1927).
- *Teses de Física e Química* que se propõe defender no exame de Doutoramento Ruy Gustavo Couceiro da Costa.
  Química:
    I. *O facto de os electrólitos fortes se afastarem da lei de Guldberg e Waage não invalida a teoria de Arrhenius.*
    II. *A pressão e a temperatura podem considerar-se propriedades específicas.*
    III. *A dissolução, susceptível de saturação, é um fenómeno químico.*

  Física:
    I. A teoria das ondulações do éter é insuficiente.
    II. A pressão osmótica não pode ser explicada pelo bombardeamento, geralmente admitido, da membrana semi-permeável.
    III. A formação de soluções coloidais, de partículas sólidas, é contrária ao segundo princípio da termodinâmica. (Imprensa da Universidade, Coimbra, Portugal, 1927).
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