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ELEMENTOS PARA UMA NOVA BIOGRAFIA DE WILHELM OSTWALD

Letícia dos Santos Pereira

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LETÍCIA DOS SANTOS PEREIRA

ELEMENTOS PARA UMA NOVA BIOGRAFIA DE WILHELM OSTWALD

Tese apresentada ao Programa de Pós-Graduação em Ensino, Filosofia e História das Ciências, da Universidade Federal da Bahia e da Universidade Estadual de Feira de Santana, para obtenção do título de Doutora em Ensino, Filosofia e História das Ciências.

Orientador: Prof. Dr. Olival Freire Jr.
Coorientadora: Prof.a Dr.a Gisela Boeck

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LETÍCIA DOS SANTOS PEREIRA

ELEMENTOS PARA UMA NOVA BIOGRAFIA DE WILHELM OSTWALD

Tese apresentada como requisito parcial para obtenção do grau de Doutora em Ensino, Filosofia e História das Ciências, área de concentração Contribuições da História e Filosofia para o Ensino de Ciências, pela Universidade Federal da Bahia e Universidade Estadual de Feira de Santana.

____

Prof. Dr. Olival Freire Júnior (orientador)
Universidade Federal da Bahia

____

Prof.a Dr.a Gisela Boeck (co-orientadora)
Universidade de Rostock

____

Prof. Dr. Artur José Santos Mascarenhas (avaliador externo)
Universidade Federal da Bahia

____

Prof. Dr.a Márcia Helena Mendes Ferraz (avaliador externo)
Pontifícia Universidade Católica de São Paulo

____

Prof. Dr. Climério Paulo da Silva Neto (avaliador externo)
Universidade Federal do Oeste da Bahia

____

Prof. Dr. José Luís de Paula Barros Silva (avaliador interno)
Universidade Federal da Bahia

LETÍCIA DOS SANTOS PEREIRA

ELEMENTOS PARA UMA NOVA BIOGRAFIA DE WILHELM OSTWALD

Resumo: A História das Ciências contemporânea nos mostrou que a ciência é um empreendimento coletivo. Isso aconteceu quando os historiadores da ciência abandonaram as histórias de longa duração, as hagiografias científicas e as narrativas whig para escrever narrativas retratando a complexidade da produção do conhecimento em diferentes contextos. Contudo, a historiografia mostra ser possível apresentar a ciência através de histórias de indivíduos que, sendo eles atores da história, são pontos de interseção e materialização das diversas esferas sociais que se relacionam com a prática científica. Talvez por esta razão o gênero biográfico seja tão recorrente na história das ciências. Somado a isso, alguns personagens são tão cativantes que somos frequentemente tentados a escrever sobre suas trajetórias. Um exemplo desses personagens é químico báltico-alemão Wilhelm Ostwald (1853-1932). Imerso em um contexto de profundas mudanças sociopolíticas, científicas e filosóficas, Ostwald é um dos personagens mais complexos e importantes da história da química do final do século XIX e início do XX, sendo retratado em diversos trabalhos biográficos. Estas biografias o apresentam como um personagem multifacetado e, até certo ponto, contraditório: ao mesmo tempo que ressaltam o seu papel na popularização da físico-química, seus êxitos nessa área são pouco explorados, em nosso entendimento. Ostwald é eventualmente lembrado devido ao prêmio Nobel de Química recebido em 1909, apesar da superficial apresentação dos seus trabalhos em catálise, considerados a razão de sua nomeação pelos historiadores. A sua oposição ao atomismo e relação com o paradigma energeticista também é destacada nesses trabalhos biográficos, mas sem grande destaque sobre como a Energética influenciou suas pesquisas físico-químicas. Tais problemas nos mostram que a biografia de Wilhelm Ostwald possui muitas lacunas, o que impede os historiadores da ciência e o público em geral compreender o seu legado. Buscando preencher algumas dessas lacunas, esta tese busca responder algumas questões sobre a trajetória de Ostwald que não estão presentes ou são pouco exploradas na literatura. Com base em trabalhos anteriores,

identificamos três questões não esclarecidas pelas principais biografias sobre Ostwald: 1. Como os livros-texto escritos por Ostwald contribuíram para a popularização da Físico-química moderna? 2. Quais foram as contribuições de Ostwald para o campo da catálise? 3. Quais as motivações para a indicação de Ostwald ao prêmio Nobel de Química entre os anos de 1904 e 1909? Para responder estas questões, foi necessário o suporte das biografias sobre Ostwald e de uma ampla literatura sobre História da Química/Ciências. Somada a estas obras, foi necessária a busca por fontes primárias, em especial, suas publicações em periódicos, livros-texto, correspondências e a documentação relativa ao prêmio Nobel de Química, constituída por cartas de nomeação e relatórios do comitê de premiação. Por fim, esperamos que esta pesquisa contribua para motivar historiadores a revisitar a biografia de Wilhelm Ostwald sem repetir algumas premissas que obscurecem nossa compreensão sobre seu legado na ciência.

Palavras-chave: Wilhelm Ostwald; Biografias Científicas; Catálise; Prêmio Nobel; Livros-texto de Química.

LETÍCIA DOS SANTOS PEREIRA

ELEMENTS FOR A NEW BIOGRAPHY OF WILHELM OSTWALD

Abstract: The Contemporary History of Science has shown us that science is a collective enterprise. This change in historiography happened when historians of science abandoned panoramic histories, scientific hagiographies and whig narratives to write narratives portraying the complexity of knowledge production in several contexts. However, historiography shows to be possible presenting the production of science through histories of individuals that, being themselves historical actors, they are the materialization and intersection points of the many social spheres connected to scientific practice. Maybe for this reason the biographical writings are so recurrent in history of sciences. Additionally, some characters are so fascinating that we are frequently seduced to write about their trajectories. An example of these characters is the Baltic-German chemist Wilhelm Ostwald (1853-1932). In a context of deep sociopolitics, scientific and philosophical changes, Ostwald is one of the most complex and controversial figures of chemistry at the turn of the nineteenth to the twentieth century, being portrayed in several biographical works. These biographies show him as a multifaceted and, to a certain extent, contradictory character: at the same time that they highlight Ostwald's role in popularization of physical chemistry, his achievements in this field are little explored in our viewpoint. Ostwald is eventually remembered for his Nobel Prize of Chemistry granted in 1909, despite the superficial presentation of his works in catalysis, which are considered the reason of his nomination by historians. His opposition to atomism and his relationship with energetic paradigm also is stressed in the biographies, but without much emphasis on how Energetics influenced his physico-chemical research. Such problems show us that Wilhelm Ostwald's biography has many gaps, which prevents historians of science and the general public from understanding his legacy. Trying to fill some of these gaps, this doctoral thesis aims to answer some questions about Ostwald's trajectory, which are not present or are little explored by literature. Based on previous works, we identify three questions not elucidated by the main biographies of Ostwald: 1. How Ostwald's textbooks contributed for popularization of modern physical chemistry? 2. What are Ostwald’s contributions to the research on catalysis? 3. What were the motivations for Ostwald's appointment to the Nobel Prize for Chemistry between 1904 and 1909? To answer these questions it was necessary the support of the main biographies about Ostwald and a varied literature on history of chemistry and history of science, in general. Also it was necessary to search primary sources, as Ostwald’s scientific articles, textbooks, correspondences and the documents concerning the Nobel Prize of Chemistry, namely nomination letters and reports from Nobel committee of chemistry. Finally, we hope that our research can motivate historians of science to revisit Wilhelm Ostwald’s biography without repeating some premises that obscure our understanding about his legacy in science.

Keywords: Wilhelm Ostwald; Scientific Biography; Catalysis; Nobel Prize; Chemistry Textbooks.

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INTRODUÇÃO

Revisitando a Biografia de Wilhelm Ostwald

A História das Ciências contemporânea nos mostrou que a ciência não é uma atividade feita por gênios, mas sim um empreendimento coletivo, que envolve as relações sociais, política, contexto econômico e as visões de mundo em diferentes momentos históricos. Essa mudança historiográfica aconteceu quando os historiadores da ciência abandonaram as histórias de longa duração, as hagiografias científicas e as narrativas *whig*.[1] Em vez disso, eles começaram a escrever narrativas retratando a complexidade da produção do conhecimento em diferentes períodos e contextos.

Contudo, a historiografia mostra ser possível apresentar a produção da ciência através de histórias de indivíduos que, sendo eles atores da história, são pontos de interseção e materialização das diversas esferas sociais que se relacionam com a prática científica. Por esta razão, a despeito de muitas críticas e opiniões contrárias, o gênero biográfico seja tão recorrente na história das ciências.[2]

Deste modo, mesmo que os historiadores reconheçam a ciência como uma atividade coletiva, alguns de seus praticantes têm uma história de vida tão cativante e interessante que os historiadores são seduzidos por suas trajetórias. Um exemplo desses personagens é químico báltico-alemão Wilhelm Ostwald (1853-1932).

Ostwald viveu no epicentro das mudanças e descobertas científicas que ocorreram entre os séculos XIX e XX, participando ativamente dos debates científicos, epistemológicos e políticos de seu tempo. As biografias sobre Ostwald nos mostram um personagem multifacetado e, até certo ponto, contraditório.[3] Nessas biografias, o pioneirismo de Ostwald na físico-química, como um dos responsáveis pela popularização dessa disciplina através da

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[1] BUTTERFIELD, Herbert. *The Whig Interpretation of History*. New York: Norton, 1965.

[2] Sobre o papel das biografias na história das ciências, ver: SHORTLAND, Michael; RICHARD, Yeo (eds.). *Telling lives in science: Essays on scientific biography*. Cambridge: Cambridge University Press, 1996; FIGUEIRÔA, Silvia F. M. A propósito dos estudos biográficos na história das ciências e das tecnologias. *Fênix*, v.4, n.3, p.13. 2007.

[3] Entre os trabalhos sobre a vida de Wilhelm Ostwald, destacamos: DOMSCHKE, Jan-Peter. *Wilhelm Ostwald: Chemiker, wissenschaftstheoretiker, Organisator*. Urania Verlag, Leipzig, Jena, Berlin, 1982; HIEBERT, Erwin; KÖRBER, Hans-Günther. Ostwald, Wilhelm. In: GILLISPIE, Charles Coulston; HOLMES, Frederic (ed). *Dictionary of Scientific Biography*. New York, Charles Scribner's Sons, 2007; ERTL, Gerhard. Wilhelm Ostwald: Founder of Physical Chemistry and Nobel Laureate 1909. *Angewandte Chemie International Edition*, 48, 2009. p. 6600-6606.

publicação do *Zeitschrift für Physikalische Chemie*, é frequentemente destacado.[4] É também mencionada nessas obras a relação entre Ostwald e os químicos Svante Arrhenius e Jacobus Henricus Van't Hoff, cujos trabalhos são considerados a base da físico-química do século XIX. No que compete aos trabalhos científicos de Ostwald, esses escritos apresentam com poucos detalhes suas pesquisas sobre autocatálise e equilíbrio químico, que resultaram na elaboração da Lei de Diluição dos Ácidos (também conhecida como Lei de Ostwald) e na sua nomeação ao Prêmio Nobel de Química em 1909.

Figura 1 - Friedrich Wilhelm Ostwald (1853-1932) aos 50 anos (Fotografia publicada no *Zeitschrift für Physikalische Chemie*, n. 3, 1903).

[4] HAPKE, Thomas. *Die Zeitschrift für Physikalische Chemie*: Hundert Jahre Wechselwirkung zwischen Fachwissenschaft, Komunikationsmedium und Gesselschaft. Verlag Tragott Bautz, Herzberg, 1990.

A oposição de Ostwald ao atomismo também é destacada nesses trabalhos biográficos. Ostwald escreveu diversos livros e artigos afirmando que a teoria atômica seria inadequada para a ciência moderna e defendendo a criação de uma nova ciência baseada na Energética - um programa científico que visava unificar e reinterpretar as diferentes ciências através da ideia de energia e de leis fenomenológicas que descrevessem suas transformações.[5] As biografias relatam que Ostwald e os físicos Pierre Duhem e Georg Helm se dedicaram à criação de abordagens energeticistas para as ciências, mas sem sucesso. Além disso, eles receberam duras críticas de importantes nomes da comunidade científica, sendo Max Planck e Ludwig Boltzmann os mais notórios. A confiança de Ostwald em relação à Energética era tão forte que, mesmo quando este programa foi gradualmente abandonado pelos seus adeptos na comunidade científica no início do século XX, Ostwald continuou a defendê-la, embora como uma filosofia particular.

De um ponto de vista político, Ostwald é descrito por essas obras como um pacifista e universalista. Essas características o fizeram participar da Liga dos Monistas Alemães e se envolver na criação de variadas associações internacionais. Contudo, Ostwald e a maioria dos cientistas alemães apoiaram a entrada da Alemanha na Primeira Guerra Mundial, o que resultou no isolamento dos mesmos pela comunidade científica internacional.

Sendo Ostwald tema de diversos trabalhos biográficos, qual a necessidade de revisitar a sua história? Em outras palavras, o que ainda há na vida de Ostwald que continue merecendo a atenção dos historiadores da ciência?

Em relação às biografias sobre Ostwald publicadas até 2005, a historiadora da ciência Bernadette Bensaude-Vincent argumenta que:

> "A despeito de sua tremenda energia e atividade em sua longa carreira, Wilhelm Ostwald é uma figura negligenciada na história da ciência. Não há sequer uma biografia decente. Entre os historiadores da química, parece existir um consenso que tende a negar a criatividade de Ostwald."[6]

Obviamente, estas biografias foram determinadas pelas tendências historiográficas do seu tempo. Algumas delas foram influenciadas pelas disputas ideológicas durante a Guerra

[5] DELTETE, Robert J. Wilhelm Ostwald's Energetics 1: origins and motivations. *Foundations of Chemistry*, v. 9, n.1, 2007. p.3-56.

[6] BENSAUDE-VINCENT, Bernadette. Revisiting the controversy on Energetics. In: GÖRS, Britta; PSARROS, Nikolaos; ZICHE, Paul. (org.) Wilhelm Ostwald at the Crossroads Between Chemistry, Philosophy and Media Culture. Leipziger Universitätsverlag, 2005. p. 26.

Fria[7] e Ostwald até recebeu uma biografia escrita quando ele estava em plena atividade científica – um trabalho hagiográfico realizado pelo seu pupilo Paul Walden.[8] Contudo, o que Bensaude-Vincent se refere é ao papel limitado dado às contribuições de Ostwald pelos historiadores em diversos compêndios de história da química: Ostwald é apresentado muitas vezes como um cientista excêntrico cuja contribuição mais importante foi a defesa da físico-química. Esta imagem atribuída à Ostwald está presente não apenas em compêndios, mas também em suas biografias.

Tais retratos biográficos se opõem à relevância que Ostwald teve em seu próprio tempo, como relatado por seus contemporâneos, que o descreviam como um químico cuja importância atravessou as fronteiras disciplinares da sua ciência e responsável por atrair diversos químicos jovens e experientes para uma nova forma de produzir conhecimento em química.[9]

Certamente, escrever uma biografia sobre um personagem tão complexo quanto Ostwald não é simples. É possível pensar que apenas o próprio Ostwald poderia escrever sobre sua vida. De fato, ele fez isso: Entre 1926 e 1927 Ostwald publicou o *Lebenslinien*, sua autobiografia dividida em três volumes. Este trabalho recebeu recentemente uma edição traduzida para o inglês, realizada pelo químico Robert Jack e pelo químico e historiador da ciência Fritz Scholz.[10] O trabalho de tradução e edição realizado por Scholz e Jack foi bem recebido pelos historiadores da ciência, mas os próprios editores reconheceram que "nós [Jack e Scholz] discutimos intensamente - algumas vezes de forma acalorada - os detalhes da tradução, porque não é uma tarefa simples tornar o texto de Ostwald compreensível para leitores de língua inglesa contemporâneos."[11]

A partir das principais biografias sobre Ostwald e do seu *Lebenslinien*, identificamos algumas lacunas e silenciamentos referentes ao legado de Ostwald. Primeiramente, esses trabalhos biográficos precisam de mais detalhes sobre as contribuições de Ostwald para a Físico-Química e a relação dessas pesquisas com a Energética. Em segundo lugar, é necessário entender o papel de Ostwald no processo de organização conceitual da Físico-Química. Em particular, devemos considerar a contribuição dos seus trabalhos pedagógicos, como seus livros-texto, para tal organização conceitual. Por fim, as obras sobre

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[7] RODNYJ; N. I.; SOLOWJEW, J. I. *Wilhelm Ostwald.* Leipzig: B.G. Teubner, 1977.
[8] WALDEN, Paul. *Wilhelm Ostwald*. Engelmann, Leipzig, 1904.
[9] SERVOS, John W. *Physical Chemistry from Ostwald to Pauling*: The Making of a Science in America. (Princeton: Princeton University Press, 1990), 53-99.
[10] JACK, Robert Smail; SCHOLZ, Fritz (eds.). Wilhelm Ostwald: The Autobiography. Springer, 2017.
[11] JACK; SCHOLZ, *Wilhelm Ostwald: The Autobiography*. p. x-xi.

a vida de Ostwald discutem pouco sobre as razões de sua premiação com o Nobel de Química, um relevante reconhecimento da comunidade científica pelos seus trabalho. Estas lacunas nos motivaram a escrever esta tese, que tenta elucidar cada uma dessas questões.

Pelo exposto, podemos afirmar que Ostwald e seu legado é um tema de pesquisa desafiador - frase esta que é tão verdadeira quanto clichê. Contudo, falta de bom senso e frases clichês são coisas que sobram em uma jovem estudante de licenciatura em Química que se interessou pela complexa biografia de Wilhelm Ostwald. Tento apresentar na seção seguinte as motivações para a escrita desta tese e minha aproximação com a trajetória de Wilhelm Ostwald.

Trajetória Acadêmica e Aproximação com o Tema da Pesquisa: Notas Autobiográficas

Wilhelm Ostwald é um personagem recorrente em minhas pesquisas desde o início da minha trajetória acadêmica. Lembro-me dos professores de História da Química da UFBA, Maria da Conceição Oki e Edilson Moradillo, comentando sobre sua recusa em aceitar a Teoria Atômica, sobre sua tentativa em construir uma ciência livre de entidades inobserváveis e sua postura positivista. Acabei abordando sua biografia indiretamente em meu Trabalho de Conclusão de Curso, no qual apresentei a influência das ideias positivistas para a rejeição ao atomismo no século XIX.[12]

O levantamento bibliográfico realizado ainda durante o meu TCC indicou haver poucos trabalhos sobre o legado científico de Ostwald, especialmente em língua portuguesa. Em contrapartida, havia uma diversa literatura sobre a postura energeticista de Ostwald e seu envolvimento na controvérsia atômica. Tal constatação foi corroborada por outros colegas professores de química, em especial o professor Dr. José Luís Silva, que também incentivou a realização desta pesquisa.

Durante o mestrado, o contato com a literatura em língua inglesa ampliou os horizontes da pesquisa, e me revelou um personagem complexo, difícil de ser bem compreendido se analisado de forma fragmentada, isto é, dissociando sua prática científica da sua visão de mundo energeticista. Encorajada pelo meu orientador, prof. Dr. Olival Freire Júnior, dei o

[12] PEREIRA, Letícia dos Santos, *Auguste Comte, Ernst Mach e Wilhelm Ostwald: a Influência do Positivismo na Controvérsia sobre o Atomismo no Século XIX*. 50 f. Trabalho de Conclusão de Curso (Licenciatura em Química) - Universidade Federal da Bahia, Salvador, 2013.

primeiro passo para compreensão da relação entre a ciência e a filosofia ostwaldiana na minha dissertação de mestrado.[13]

Todavia, o mestrado trouxe-me respostas insuficientes, além de mais perguntas sobre Ostwald e seu legado: Quais foram e sobre o que tratavam as pesquisas de Ostwald sobre catálise? Por que, a despeito da pouca fama desses trabalhos, ele é considerado pelos historiadores um dos principais representantes da pesquisa em catálise no século XIX? Por qual razão Ostwald recebeu o Nobel de Química apenas em 1909, visto sua contínua nomeação desde 1904? Estas e outras perguntas foram o ponto de partida para esta pesquisa de doutoramento.

Contudo, dar continuidade à pesquisa significava enfrentar alguns problemas. Como apresentado anteriormente, Wilhelm Ostwald não é um personagem simples de ser estudado e a literatura sobre o mesmo é tão diversificada quanto complexa. Apropriar-se da extensa literatura em curto tempo e garantir originalidade para a tese foram os primeiros desafios identificados por mim. Além disso, havia uma barreira linguística a ser superada, visto que as principais fontes se apresentavam em língua alemã, que eu não dominava. Superados esses problemas, ainda seria preciso obter apoio financeiro para a realização da pesquisa, visto que a mesma demandava a busca por fontes primárias em arquivos na Suécia e Alemanha.

Devido a estes obstáculos, fui tomada por um lampejo de bom senso e abandonei esta pesquisa ainda no início do doutorado. Mas como eu disse, foi realmente apenas um lampejo: logo retomei as perguntas que me guiaram nesta pesquisa e busquei solucionar os problemas para a execução do trabalho.

O contato com a literatura me permitiu identificar quais das minhas perguntas iniciais ainda não haviam sido respondidas ou satisfatoriamente abordadas por outros pesquisadores - o que justificou a escolha do título da pesquisa, visto que não abordamos completamente o período de vida de Wilhelm Ostwald, selecionando apenas alguns episódios e elementos do seu trabalho.

Para além da falta de bom senso e frases clichês, preciso reconhecer que tenho um pouco de sorte. Em 2015, participando da *International Conference on History of Chemistry* (10th ICHC), conheci a professora Dr.a Gisela Boeck, da Universidade de Rostock, responsável pela coordenação da sessão na qual eu estava apresentando meu trabalho. Mesmo

[13] PEREIRA, Letícia dos Santos. *Considerações sobre o Energeticismo e a Catálise na obra de Wilhelm Ostwald.* 74f. Dissertação de Mestrado, Universidade Federal da Bahia (Programa de Pós-graduação em Ensino, Filosofia e História das Ciências). 2015.

que o contato que estabelecemos na conferência tenha sido bastante superficial, ela demonstrou simpatia ao trabalho, me incentivou a visitar os arquivos sobre o Ostwald na Alemanha e se colocou à disposição para uma eventual ajuda.

Figura 2 - Apresentação de Trabalho no 10th International Conference on the History of Chemistry (ICHC), Aveiro - Portugal. Acima: Fotografia dos participantes do evento, a professora Gisela Boeck ocupa o centro da fotografia. Abaixo, à esquerda: apresentação da minha comunicação, intitulada *A Nobel for Energetics? Revisiting Wilhelm Ostwald Nobel Prize of Chemistry*. Abaixo, à direita: eu, em primeiro plano, sendo arguida pelos participantes e a professora Gisela Boeck, atrás, em segundo plano.

Meses após o meu retorno ao Brasil, foi lançado o edital do PROBRAL, projeto da Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES, cujo objetivo era fomentar o intercâmbio científico entre grupos de pesquisa brasileiros e alemães. Sendo a professora Gisela Boeck meu único contato na Alemanha, eu e o professor Olival Freire Jr. entramos em contato com a mesma a fim de escrever um projeto sobre história das ciências a fim de concorrer a este edital. A escrita do projeto também agregou outros pesquisadores da UFBA e de outras instituições alemãs que estavam pesquisando outros episódios e personagens da História das Ciências. Entretanto, apesar da qualidade das pesquisas e do esforço coletivo para a escrita e conclusão da proposta, nosso projeto não foi aprovado pela

CAPES. Deste modo, tivemos que procurar outros meios de financiar minha viagem para Alemanha.

Se passou quase um ano desde nossa tentativa frustrada de conseguir financiamento via PROBRAL. Nesse período, consegui ser aprovada no concurso da Universidade Federal do Recôncavo da Bahia - UFRB, saindo da condição de doutoranda à beira do desemprego para me tornar a quimera Professora-Estudante. Apesar da melhoria significativa ocasionada por um emprego dessa natureza, deparei-me com um exaustivo cotidiano, ao me dedicar simultaneamente à pesquisa de doutorado e às novas responsabilidades do trabalho docente em uma universidade localizada a 240 km da minha cidade. Dada a minha nova rotina, eu já considerava a missão de pesquisa na Alemanha inviável.

Entretanto, a situação se tornou mais favorável pouco tempo depois: em meados de 2016, conseguimos acesso às cartas de nomeação a favor da premiação de Wilhelm Ostwald ao Nobel de Química, enviadas pelo Centro de História das Ciências da Academia Real de Ciências da Suécia. Contudo, ter acesso às fontes não era o suficiente, visto que muitos dos documentos recebidos estavam escritos em sueco e norueguês. Felizmente, graças à recursos do Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq, conseguimos contratar um tradutor para traduzir nossas fontes para a língua inglesa. Estas fontes tornaram esta pesquisa viável, apesar da nossa dificuldade naquele momento em conseguir financiamento para a realização da minha missão de pesquisa na Alemanha.

Em Junho de 2016, a CAPES divulgou o edital de bolsas do Programa de Doutorado Sanduíche no Exterior - PDSE. Nesta seleção, eu consegui uma bolsa de pesquisa com duração de quatro meses - um período curto, mas que poderia ser bem aproveitado. A professora Gisela Boeck novamente colaborou conosco nesta seleção, ao aceitar a posição de orientadora estrangeira da pesquisa e concordar com minha ida para a Universidade de Rostock.

Além de aceitar colaborar com uma estudante de doutorado que mal conhecia, a professora Gisela Boeck resolveu visitar o Brasil, com recursos próprios, para estreitar os laços com nosso grupo de pesquisa, ministrar uma disciplina de curta duração em nosso programa de pós-graduação e, obviamente, conhecer o verão soteropolitano.[14]

[14] A passagem da professora Gisela pela UFBA foi registrada pela equipe do Edgard Digital, portal online de notícias da comunidade universitária. Ver: TOURINHO, Fernanda. Descobertas científicas na química e curiosos casos históricos. *Edgar Digital*. Publicado em 03 Março 2017. Disponível em: http://www.edgardigital.ufba.br/?p=1411 Acesso em 13 Abril 2019. Além desta matéria, a professora Gisela Boeck publicou em nosso portal de notícias um pequeno texto sobre a biografia da química alemã Else Hilschberg, primeira mulher a se formar em Química na Universidade de Rostock. Ver: BOECK, Gisela. Else

Figura 3 - Professora Gisela Boeck ministrando curso de curta duração no PPGEFHC durante visita à Salvador (Fonte: TOURINHO, Fernanda. *Edgar Digital*. 03 Março 2017. Disponível em: http://www.edgardigital.ufba.br/?p=1615. Acesso em 13 Abril 2019).

No início de Abril de 2017, deixei Salvador e viajei para Rostock, onde fui recebida pela família da professora Gisela Boeck, que gentilmente me acolheu em sua casa. O contato com a Família Boeck contribuiu muito para minha aprendizagem do idioma alemão, em especial o esposo da professora Gisela, Erich Boeck, que por não dominar a língua inglesa, acabou me me estimulando a aprender o idioma alemão (ele também me ensinou a falar "cerveja" em tcheco, o que foi de grande ajuda em viagens posteriores). Mesmo que eu não tenha apropriado completamente o idioma alemão, o que aprendi foi suficiente para a realização da pesquisa, me comunicar com a população local e pedir informação aos transeuntes ao me perder pelas cidades que visitei.

Tão importante quanto aprender alemão, foi estabelecer contato com novos lugares e culturas. A Família Boeck me ajudou a criar relações com o espaço e a cultura germânica, introduzindo-me à cultura do século XIX por meio de visitas à museus, igrejas, cidades, monumentos, dentre outros ambientes. Gentilmente, Gisela e Erich me apresentaram lugares nos quais Wilhelm Ostwald e outros químicos nasceram, viveram, trabalhavam, passavam

Hirschberg, uma cientista pioneira assassinada em Auschwitz. *Edgar Digital.* Traduzido por Denise Scheyerl. Publicado em 03 Março 2017. Disponível em: http://www.edgardigital.ufba.br/?p=1528. Acesso em 13 de Abril de 2019.

férias... para mim, que pretendia compreender e reconstruir a vida de um personagem tão complexo, o contato com esses lugares foi fundamental.

Graças à professora Gisela Boeck, a minha estadia na Alemanha permitiu o contato com diferentes pesquisadores do campo da Química e da História da Química. Em Dresden, visitei o professor Dr. Horst Hartmann, responsável pela Coleção de Corantes da Universidade Técnica de Dresden e estudioso da Teoria das Cores desenvolvida por Ostwald. Em Großbothen, conheci o professor Jan-Peter Domschke, um dos biógrafos de Wilhelm Ostwald e responsável pela publicação do *Mitteilungen der Wilhelm-Ostwald-Gesellschaft zu Großbothen*, publicação periódica que reúne os trabalhos de diferentes pesquisadores dedicados à investigação do legado de Wilhelm Ostwald. Em Leipzig, visitei o professor Lothar Beyer e o diretor do Instituto Wilhelm Ostwald de Físico-química e Química Teórica, Dr. Knut R. Asmis. Na Universidade de Greifswald, conheci o professor Dr. Fritz Scholz, um dos responsáveis pela tradução da autobiografia de Wilhelm Ostwald para a língua inglesa e historiador da Físico-química.

Figura 3 - Memórias da missão de pesquisa na Alemanha (Abril à Julho de 2017). *Acima, à esquerda*: Haus Energie, em Großbothen, onde Ostwald viveu os últimos dias de sua vida. Hoje esta casa abriga o museu em memória de Ostwald que faz parte do *Wilhelm Ostwald Park*. *Acima, à direita*: Lápide de Wilhelm Ostwald e sua família, também localizada no *Wilhelm Ostwald Park*. *Abaixo, à direita*: Parte do acervo do Wilhelm Ostwald Museum, em Großbothen. *Abaixo, à esquerda*: A autora e a professora Gisela Boeck em visita ao *Wilhelm Ostwald Institute für Physikalische und Theoretischen Chemie*, na Universidade de Leipzig. O auditório retratado na fotografia é o mesmo no qual Ostwald ensinou Físico-química durante seus anos como professor em Leipzig (Fotos do acervo pessoal da autora).

Minha missão de pesquisa também permitiu acesso aos arquivos de Wilhelm Ostwald, disponíveis na Academia de Ciências de Berlim. Neste arquivo consegui ter acesso à manuscritos, correspondências, fotografias e outros documentos relativos às pesquisas de Ostwald. Entretanto, obtive diversas fontes que não foram utilizadas nesta pesquisa, mas que possivelmente subsidiarão trabalhos futuros sobre este químico.

Em Julho de 2017, finalizei minha missão de pesquisa e retornei ao Brasil. A despeito da saudade da minha família e da minha vontade de comer um acarajé, os quatro meses que passei na Alemanha foram inesquecíveis devido ao aprendizado, à beleza dos lugares e às pessoas incríveis que conheci. Após o meu retorno, reassumi meu trabalho na UFRB e passei os últimos meses dando aulas e escrevendo esta tese, que agora segue para defesa pública. Nas seções abaixo, apresento algumas considerações sobre o uso de biografias na História das Ciências, assim como as fontes utilizadas e a estrutura desta tese.

O Gênero Biográfico e a História: Reflexões Metodológicas

Situadas entre o campo da história e a literatura, as biografias certamente são um dos tipos de narrativa mais antigos e controversos. Na Antiguidade clássica, a biografia tinha fins artísticos e retóricos e destinava-se a ilustrar a história de deuses e heróis. Na Idade Média, a biografia também possuiu um papel moralizante, ao apresentar a vida dos santos e cavaleiros como um modelo de conduta para os demais indivíduos. Posteriormente, as biografias seriam utilizadas para destacar o legado dos “grandes-homens” (políticos, cientistas, monarcas, dentre outros), considerados os heróis de uma nação.[15]

As biografias científicas também se prestaram a este papel de exaltação do legado dos seus principais representantes. De acordo com Söderqvist, apesar dos autores destas obras considerarem estes escritos como trabalhos históricos, é notório o uso dessas obras para

[15] ALMEIDA, Francisco A. A biografia e o ofício do historiador. *Dimensões*. v. 32, 2014, p. 292-313; PRIORE, Mary Del. Biografia: quando o indivíduo encontra a história. *Topoi*, v. 10, n. 19, 2009. p. 7-16.

outros fins, dentre os quais, servir de exemplo moral aos demais cientistas, reforçando a equivocada imagem dos cientistas enquanto seres excepcionais, sujeitos que trabalham alienados em relação às questões políticas, econômicas e culturais, e que supostamente abdicaram da vida comum em prol da ciência.[16] A defesa desta imagem de cientista está atrelada a outras narrativas que apresentavam uma visão positivista da ciência, que a considerava uma atividade neutra e dogmática, na qual sua objetividade e universalidade seriam produto de sua própria lógica e método, transcendentes ao valores e ações humanas.[17] Sob este ponto de vista, fazia sentido considerar a existência de uma pretensa continuidade entre os trabalhos de diferentes cientistas ao longo de séculos, sem levar em conta o contexto sócio-cultural de suas descobertas.

Em momentos diferentes, a narrativa biográfica seria colocada de lado tanto pela História, quanto pela História das Ciências. Os representantes da Escola dos *Annales*, em especial aqueles da segunda geração, não tinham interesse nas narrativas centradas no indivíduo, visto que o tempo da vida humana era demasiadamente curto quando comparado com as grandes e lentas transformações da sociedade.[18] Para além disso, a relação das biografias com a criação de mitos heróicos desde a Antiguidade, fez com que os historiadores vinculados aos *Annales* a compreendessem como um gênero ultrapassado e decrépito.[19]

No campo da história das ciências, algo semelhante aconteceu após a Segunda Guerra Mundial. Söderqvist mostra que os historiadores da ciência deste período consideravam as biografias científicas exemplos de narrativas anedóticas, hagiográficas e alienadas de um contexto mais amplo.[20] Mesmo que alguns dos historiadores interessados em biografias se preocupassem em destacar mais o desenvolvimento intelectual, o contexto sócio-histórico, e o legado científico dos biografados do que as minúcias de sua vida, a exemplo do trabalho de

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[16] SÖDERQVIST, Thomas. 'No genre of history fell under more odium than that of biography': The delicate relations between scientific biography and the historiography of science. The history and poetics of scientific biography, 2007. p. 241-262; KRAGH, Helge. *Introdução à Historiografia da Ciência*. Porto: Porto Editora, 2001.

[17] KRAGH. *Introdução à Historiografia da Ciência*. p. 119-131. SHAPIN, Steven. *Nunca Pura*: Estudos Históricos de Ciência como se Fora Produzida por Pessoas com Corpos, Situadas no Tempo, no Espaço, na Cultura e na Sociedade e Que Se Empenham por Credibilidade e Autoridade. Tradução de Erick Ramalho. Belo Horizonte, MG: Fino Traço, 2013.

[18] ROBERTS, Michael. A Escola dos Annales e a Escrita da História. In: LAMBERT, Peter; SCHOFIELD, Phillipp (ed.). História - Introdução ao Ensino e à Prática. Trad. Roberto Cataldo Costa. Rio Grande do Sul: Penso, 2011.

[19] ALMEIDA. *Dimensões*. p. 292-293.

[20] SÖDERQVIST. *The history and poetics of scientific biography*. p. 251-255.

Alexandre Koyré sobre Galileu Galilei,[21] a rejeição dos historiadores da ciência pelas biografias científicas mostrava-se reticente.

A interação entre historiadores, antropólogos e sociólogos interessados na prática científica resultou na emergência de novos problemas, objetos e abordagens para o campo da História da Ciência entre as décadas de 1960 e 1970, resultando na emergência de novas perspectivas historiográficas, como a História Social e História Cultural das Ciências.[22] De acordo com estes novas correntes, o historiador da ciência deveria compreender a prática científica como um fenômeno cultural e dinâmico, buscando compreender como o conhecimento produzido é socialmente validado; os valores e pressupostos sócio-culturais desta atividade; a relação da ciência com a sociedade e a economia, dentre outros elementos.[23] Frente a esta nova e robusta agenda, as biografias científicas ficaram à margem do interesse de grande parte dos historiadores.

Contudo, mesmo marginalizada, alguns historiadores levantaram-se em sua defesa, produzindo trabalhos biográficos importantes, como o projeto *Dictionary of Scientific Biography*,[24] coordenado pelo historiador da ciência Charles Coulston Gillispie (1918-2015) no final da década de 1960.[25] Mesmo tendo surgido em um contexto no qual as biografias científicas eram vistas com desconfiança, a obra contribuiu para que historiadores revissem sua opinião sobre este gênero e refletissem sobre as potencialidades da narrativa centrada no cientista e seu legado, como mostra o historiador da ciência Thomas Hankins em sua defesa do gênero biográfico:

> "In defence or biography, however, I only wish to point out that its work is far from done. Especially in the history of science, where there are so many major figures who still lack adequate treatment, there is great opportunity for the biographer, The opportunity lies not merely in the large number of important individuals whose lives remain to be described, but more significantly in the contribution that biography can make to the history of science itself. A fully integrated biography of a scientist which includes not only his personality, but also

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[21] KOYRÉ, Alexandre. *Études galilèennes*. Paris: Hermann, 1939.

[22] PESTRE, Dominique. Por uma nova História Social e Cultural das Ciências: novas definições, novos objetos, novas abordagens. *Cadernos IG/UNICAMP*, v. 6, n. 1, Campinas, 1996, p. 3-56.

[23] VIDEIRA, Antônio A. P. Historiografia e história da ciência. *Escritos* (Fundação Casa de Rui Barbosa). v. 1, 2007. p. 111-158.

[24] GILLISPIE, Charles C. (ed.) *Dictionary of Scientific Biography*. New York: Charles Scribner's Sons, 1970–1980. 16 vols. Supplement II, editado por Frederic Lawrence Holmes, 2 vols., 1990.

[25] NYE. *Isis*. p. 322–323; HANKINS, Thomas L. In Defence of Biography: The Use of Biography in the History of Science. *History of Science*, v. 17, n. 1, 1979. p. 1–16.

his scientific work and the intellectual and social context of his times, is still the best -way to get at many of the problems that beset the writing of history of science. When the *Dictionary of Scientific Biography* was in the planning stages it was argued that a reference work in the history of science could better be arranged according to subjects rather than according to individuals, Biography won out in the final decision, however, and it is a decision that we need not regret. As the editors point out, science is created by individuals, and however much it may be driven by forces from outside, these forces work through the scientist himself. Biography is the literary lens through which we can best view this process."[26]

As críticas de historiadores às biografias também não impactaram na sua popularidade, produção e rentabilidade. No caso das biografias científicas, os historiadores Mary J. Nye e Thomas Söderqvist concordam que a publicação e demanda por este tipo de obra no período após a Segunda Guerra Mundial era grande, em especial textos sobre a vida de célebres figuras científicas, como Charles Darwin, Marie Curie e Albert Einstein.[27] Enquanto obra artística-literária, as biografias se mostraram um dos gêneros de maior sucesso, em especial na Europa, como aponta a historiadora Mary del Priore:

> "Enquanto os historiadores preferiram rejeitar os ídolos individuais e os recortes cronológicos dados pelo tempo de uma existência, escritores se tornaram, então, os grandes biógrafos: Guy de Pourtalés. Gide, Michel de Leiris, André Maurois, no mundo literário francês. Lytton Strachey e Antonia Fraser, no anglo-saxão, entre outros. Convite à viagem artificial no passado, fortemente ligada aos fatos, a maior parte das biografias era acrítica e lançava suas raízes no terreno das paixões coletivas. Elas correspondiam a um público ávido de fatos históricos, de acontecimentos sensacionais ou de enigmas insolúveis: na França, por exemplo, o caso do Colar da Rainha ou a desaparição do tesouro dos templários. A paixão pela biografia crescia e fez nascer o romance genealógico de Claude Simon e Georges Perec. Ou ainda a autobiografia psíquica de um Hermann Broch. Havia sede desse gênero, notadamente no mundo europeu e anglo-saxão."[28]

A biografia recuperou importância paulatinamente, devido a novas formas de pensar a relação entre o indivíduo e o seu contexto. Contrariando as narrativas sociológicas das

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[26] HANKINS. *History of Science*. p. 13-14.

[27] NYE, Mary J. Scientific Biography: History of Science by Another Means? *Isis*, v. 97, n. 2, 2006. p. 322–329; SÖDERQVIST, Thomas. Introduction: A New Look at the Genre of Scientific Biography. In: *The History and Poetics of Scientific Biography*. Routledge, 2016. p. 17-32.

[28] PRIORE. *Topoi*. p. 8.

décadas anteriores, alguns historiadores mostraram ser possível reconstruir a sociedade e a cultura de uma determinada época por meio de narrativas centradas em indivíduos. Um dos principais exemplos é a Micro-história italiana.

Surgida no final da década de 1970, a Micro-história mostrou como a investigação centrada em indivíduos comuns pode nos auxiliar na compreensão de um contexto cultural mais amplo, visto que a ação do sujeito no mundo reflete a mentalidade e as práticas sociais de determinada época e local.[29] O maior exemplo desse movimento é o clássico *O Queijo e os Vermes* (1976) do historiador italiano Carlo Ginzburg, obra que nos apresenta a vida de Menocchio, moleiro italiano processado pela Santa Inquisição no século XVI. A partir dos documentos do processo de Menocchio, Ginzburg reconstrói a mentalidade do seu personagem e de sua época, mostrando como mudanças sociais importantes - Reforma Protestante, expansão marítima, descoberta de novos continentes - eram incorporadas à visão de mundo e cultura de indivíduos comuns.[30]

Outro exemplo da mudança de perspectiva em relação à narrativa biográfica é oriundo de um dos representantes da Escola dos *Annales*. O retorno ao gênero biográfico pela historiografia tradicional se deve muito ao historiador francês Jacques Le Goff, responsável pela biografia de Luís XI da França, o santo rei.[31] Antes crítico deste tipo de narrativa, Le Goff percebeu a potencialidade do gênero e a defendeu que a biografia como apoio para a análise das estruturas sociais e culturais.[32]

De modo semelhante, as biografias científicas resgataram seu prestígio de outrora a partir da década de 1980, quando foram incorporadas aos propósitos da História Cultural e Social das Ciências. A biografia científica começou a ser então utilizada como *ancilla historiae*, isto é, uma história auxiliar, utilizada para uma melhor compreensão dos elementos sociais e culturais da prática científica, a partir da trajetória dos cientistas e dos seus êxitos.[33]

Mas será que este seria o único valor das biografias científicas para a História das Ciências? De acordo com Söderqvist, não. Este autor coloca outras diferentes razões para a escrita biográfica, que transcendem ao propósito colocado pelos historiadores vinculados à História Cultural e Social. Além do uso das biografias como *ancilla historiae*, Söderqvist

[29] LEVI, Giovanni. Sobre a micro-história In: BURKE, Peter (org). A escrita da história: novas perspectivas. São Paulo: Editora da UNESP, 1992. p. 133-161; BARROS, José D.'Assunção. Sobre a feitura da micro-história DOI10. 5216/o. v7i9. 9336. OPSIS, v. 7, n. 9,2007. p. 167-186.
[30] GINZBURG, Carlo. *O queijo e os vermes*. São Paulo: Companhia das Letras, 2006.
[31] LE GOFF, Jacques. *Saint Louis*. Paris, Gallimard, 1996.
[32] ALMEIDA. *Dimensões*. p. 295-296.
[33] SÖDERQVIST. *The History and Poetics of Scientific Biography.* p. 255-258.

destaca o papel das biografias para reconhecer o aspecto humano da prática científica. Por mais que a ciência seja uma atividade coletiva, alguns indivíduos se destacam pelo seu papel na descoberta de fenômenos, na construção de teorias e conceitos, e criação e aperfeiçoamento de métodos de pesquisa.[34]

Mais do que isso, Söderqvist aponta que as biografias possuem uma dimensão existencialista relevante. Segundo este autor, muitas vezes as biografias científicas limitam-se a contextualizar o trabalho científico do biografado a partir do contexto sócio-histórico no qual este se insere, contudo, o trabalho do cientista também pode ser compreendido frente a sua própria vida, a particularidade de sua própria existência.[35] Utilizando como exemplo sua própria pesquisa sobre a vida do imunologista britânico Niels Jerne, Söderqvist apontou que "quanto mais mergulhava no arquivo, mais a vida pessoal e privada de Jerne se movia para o centro do trabalho biográfico. Em vez de ver um cientista de sucesso que também era um homem problemático, comecei a ver um homem problemático que também era um cientista de sucesso."[36] Em síntese, a perspectiva existencialista do trabalho biográfico, conforme defendida por Söderqvist, mostra os êxitos científicos como uma entre os diversos aspectos de um personagem cuja história de vida possui um valor intrínseco, que não pode ser reduzido apenas ao seu legado para a ciência.

Pessoalmente, concordo com a perspectiva de Söderqvist. Quando Ostwald entrou no meu horizonte de interesses, ainda durante o mestrado, o objetivo inicial da minha pesquisa era apresentar o legado científico de um personagem, destacando seus trabalhos sobre catálise, a relação destes com sua filosofia energeticista e o reconhecimento destas pesquisas. Porém, o contato com as fontes e a literatura me fez perceber que o valor de Ostwald para a ciência não poderia ser mensurado apenas pelo que ele descobriu, teorizou ou conceituou.

Olhando para outros problemas nesta tese, percebo que compreender o papel de Ostwald como pesquisador, professor, filósofo, escritor e inspiração para os jovens químicos - elementos que são abordados nos artigos que compõem esta tese - contribuem para uma melhor percepção da sua importância para a ciência, mas também não nos apresenta adequadamente Ostwald em sua complexidade e humanidade. Por esta razão, reconhecemos

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[34] Söderqvist aponta sete utilidades para a narrativa biográfica em sua obra, as quais não foram completamente exploradas aqui. Para conhecer estas utilidades apontadas pelo autor, ver: SÖDERQVIST, Thomas. The seven sisters: Subgenres of bioi of contemporary life scientists. *Journal of the History of Biology*. v. 44, n. 4, 2011. p. 633-650.

[35] Agradeço aqui ao meu orientador, Olival Freire Jr., por chamar minha atenção para a profundidade deste uso das biografias apontado por Söderqvist.

[36] SÖDERQVIST. *Journal of the History of Biology*. p. 645.

que esta tese não consiste em uma biografia do indivíduo Wilhelm Ostwald, mas tenta apresentar alguns elementos biográficos que consideramos essenciais para compreender a sua importância para a Química.

Estrutura da Tese e Fontes

Como mencionado anteriormente, a partir do contato com a literatura e as pesquisas biográficas sobre o trabalho de Ostwald, foi possível identificar algumas questões que não possuíam resposta clara nessas obras. Cada uma destas questões resultou em um artigo, que constitui cada um dos capítulos desta tese. Uma descrição de cada um desses artigos é apresentada a seguir.

Primeiramente, é necessário entender o papel de Ostwald no processo de organização conceitual e popularização da Físico-Química e da Química Geral. Em particular, devemos considerar o papel de suas contribuições literárias para o treino de jovens químicos, como os seus diversos livros-texto. A análise de sua obra literária é um trabalho necessário, porém difícil, dada a sua vasta produção e às frequentes modificações sofridas por seus livros a cada nova edição publicada. Escolhemos então analisar o seu primeiro livro, o *Lehrbuch der allgemeinen Chemie* (1886-1887). Este livro-texto, inicialmente concebido para ser um material de apoio ao trabalho de Ostwald como professor do *Riga Polytechnikum*, tornou-se a representação da organização conceitual da química e um meio de divulgação das teorias físico-químicas. Somado a estes elementos, o *Lehrbuch* reflete os trabalhos iniciais de Ostwald sobre o tema da afinidade química, os quais foram profundamente influenciados pelo paradigma mecanicista, aspecto pouco explorado na literatura. Esta discussão é abordada no primeiro artigo desta tese, intitulado *Wilhelm Ostwald e o Lehrbuch der Allgemeinen Chemie (1885-1887) Construindo e Popularizando a Físico-química*.

Em segundo lugar, os trabalhos biográficos carecem de detalhes sobre as contribuições de Ostwald para a Físico-Química e a relação dessas pesquisas com a Energética. Com base em pesquisa anterior, acreditamos que o elo entre energeticismo e a ciência ostwaldiana possa ser encontrado analisando seus trabalhos sobre catálise.[37] Nossa tentativa em elucidar esta temática é apresentada em nosso segundo artigo, intitulado *Teaching and Thinking on Catalysis: Wilhelm Ostwald and his Catalysis Research (1890-1906)*.

[37] PEREIRA, *Considerações sobre o Energeticismo e a Catálise na obra de Wilhelm Ostwald.* 2015.

Por fim, a nomeação de Ostwald ao Prêmio Nobel de Química é um episódio que ainda motiva debates. Enquanto autores atribuem aos seus trabalhos no campo da catálise como a principal razão de sua nomeação, outros afirmam que a catálise foi uma fachada para um prêmio baseado no conjunto de sua obra. Entretanto, a história de Ostwald e o Nobel de Química transcende as razões para sua nomeação em 1909 e os aspectos políticos da mesma. As nomeações a favor da candidatura de Ostwald ao prêmio podem ajudar na compreensão dos principais méritos de Ostwald e desmistificar alguns discursos frequentes sobre sua candidatura, como por exemplo a suposta influência negativa do antiatomismo para sua premiação.[38] Estas questões foram exploradas por nós no artigo *A Nobel for What? Revisiting Wilhelm Ostwald's Nobel Prize in Chemistry*.

Utilizamos nesta pesquisa uma variada literatura sobre Ostwald e seu legado científico e filosófico, em grande parte constituída por textos biográficos[39] e trabalhos históricos sobre as principais pesquisas, teorias e controvérsias que permeavam a físico-química, e a química de modo geral, no fim do século XIX.[40]

Contudo, foi necessário a apropriação de outras leituras sobre diferentes elementos da cultura científica. Dentre essas obras, destacamos a literatura sobre premiações e celebrações científicas;[41] sobre a história dos Livros-texto e sua utilização como fontes para a história das

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[38] Um resumo deste trabalho foi explorado por nós, ainda de forma inicial, na *25th International Conference on History of Science and Technology* (25th ICHST), no qual focamos em cartas de nomeação enviadas por químicos norte-americanos.

[39] Algumas das principais biografias utilizadas foram ERTL, *Angewandte Chemie*, 2009; ZOTT, *Angewandte Chemie*, 2003; HIEBERT; KÖRBER, *Ostwald, Wilhelm*, 1989. Também destacamos a autobiografia de Wilhelm Ostwald traduzida e editada pelos pesquisadores Robert Jack e Fritz Scholz: JACK; SCHOLZ, *Wilhelm Ostwald: an autobiography*, 2017.

[40] ZECCHINA, Adriano; CALIFANO, Salvatore. *The Development of Catalysis*: A History of Key Processes and Personas in Catalytic Science and Technology. John Wiley & Sons, 2017; NYE, Mary J. *Before big science*: the pursuit of modern chemistry and physics, 1800 - 1940. Cambridge, Mass. [u.a.]: Harvard University Press, 1999. BENSAUDE-VINCENT; Bernadette; STENGERS, Isabelle. *História da Química*. trad. Raquel Gouveia, Lisboa: Instituto Piaget, 1992.

[41] FELDMAN, Burton *The Nobel Prize:* A History of Genius, Controversy, and Prestige. New York: Arcade, 2013; FRIEDMAN, Robert M. *The Politics of Excellence:* Behind the Nobel Prize in Science. New York: Times Books, 2001; CRAWFORD, Elisabeth *The Beginnings of the Nobel Institution*: The Science Prizes, 1901-1915 (Cambridge: Cambridge University Press), 2001.

ciências;[42] materiais sobre controvérsias científicas;[43] instituições científicas e institucionalização da ciência;[44] e relações entre ciência e indústria.[45]

As fontes utilizadas nesta pesquisa foram obtidas em arquivos localizados na Alemanha e Suécia. Os relatórios e cartas de indicação do prêmio Nobel de Química entre 1904 e 1909 utilizados nesta pesquisa encontram-se no arquivo do Centro para História das Ciências da *Royal Academy of Sciences of Sweden* (Real Academia de Ciências da Suécia, KVA). Estas fontes foram solicitadas à KVA em Dezembro de 2015 e recebidas por correspondência em meados de 2016.

As demais fontes utilizadas nesta pesquisa foram obtidas durante já mencionada missão de pesquisa na Alemanha no primeiro semestre de 2017. Em visita aos *Archiv der Berlin-Brandenburgischen Akademie der Wissenschaften* (Arquivos da Academia de Ciências de Berlim, ABBAW) obtivemos correspondências não-publicadas entre Ostwald e seus ex-alunos e colaboradores, assim como textos raros.[46] Na Universidade de Rostock, conseguimos acesso a correspondências publicadas[47] e diferentes periódicos do final do século XIX, em especial, os volumes do jornal *Zeitschrift für Physikalische Chemie*, revista fundada por Ostwald em 1887. Deste e de outros periódicos, realizamos um levantamento dos trabalhos sobre catálise de sua autoria e de ex-alunos e colaboradores. Ainda em Rostock, obtivemos acesso aos volumes do livro *Lehrbuch der allgemeinen Chemie*, foco de um dos artigos desta tese.[48]

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[42] SIMON, JOSEP. Textbooks. In: LIGHTMAN, BERNARD (ed.) A Companion to the History of Science. Chichester, UK; Malden, MA: John Wiley & Sons, 2016. 400-413; LUNDGREN, Anders; BENSAUDE-VINCENT, Bernadette (ed.) Communicating chemistry: textbooks and their audiences, 1789-1939. Canton, MA: Science History Publications, 2000.

[43] COFFEY, Patrick *Cathedrals of Science*: The Personalities and Rivalries That Made Modern Chemistry. London: Oxford University Press, 2008; KRAGH, Helge. A Sense of Crisis: Physics in the fin-de-siècle Era. in: SALER, Michael. *The Fin-de-Siècle World* New York, Routledge, 2014. p. 441-455.

[44] LENOIR, Thimothy. *Instituindo a ciência*. A produção cultural das disciplinas científicas. São Leopoldo: Unisinos, v. 27, 2003.

[45] LESCH, John (ed.). The German chemical industry in the twentieth century. Chemists and chemistry, v. 18, Dordrecht: Kluwer Academic Publishers, 2000.

[46] OSTWALD, Wilhelm. Zur Geschichte der Chemischen Lehrbücher. *Chemischen Novitäten*, v. 1, n. 1, p. 2-6, 1904.

[47] ZOTT, Regine *Fritz Haber in seiner Korrespondenz mit Wilhelm Ostwald sowie in Briefen an Svante Arrhenius.* Berliner Beitrage zur Geschichte der Naturwissenschaften und der Technik, 20. Berlin: ERS Verlag, 1997.

[48] OSTWALD, Wilhelm. *Lehrbuch der allgemeinen Chemie* (erster Band - Stöchiometrie, zweiter Band - Verwandtschaftslehre), erste ausgabe, Leipzig: Engelmann, 1885-1887; OSTWALD, Wilhelm. *Lehrbuch der allgemeinen Chemie* (erster Band - Stöchiometrie; zweiter Band, erster Teil - Chemischen Energie; zweiter Band, zweiter Teil - Verwandtschaftslehre) zweite ausgabe, Leipzig: Engelmann, 1891-1902.

WILHELM OSTWALD E O LEHRBUCH DER ALLGEMEINEN CHEMIE (1885-1887)

Construindo e Popularizando a Físico-química

Resumo: Elementos da cultura científica, os livros-texto cumprem objetivos que transcendem o ensino e popularização da ciência. Estas obras podem servir como instrumento de organização de disciplinas, assim como para a sua institucionalização, ao colaborar para a formação dos seus praticantes. Este é o caso do *Lehrbuch der allgemeinen Chemie* (Livro-texto de Química Geral), escrito pelo químico báltico-alemão Wilhelm Ostwald e publicado entre 1885 e 1887. O *Lehrbuch* foi uma resposta aos anseios de Ostwald em organizar novas ideias químicas, em especial aquelas voltadas à Teoria de Afinidades. Entretanto, a escrita de Ostwald foi além seus objetivos iniciais, tornando esta obra um marco importante para a organização da moderna Físico-química, que na época de sua publicação começava a se apresentar como uma disciplina independente e bem definida. Partindo da literatura e dos dois volumes que compõem a primeira edição do *Lehrbuch*, neste artigo apresentamos as motivações de Ostwald para a escrita do *Lehrbuch* e seu impacto na organização da Físico-química.

Palavras-Chave: Livros-texto; Wilhelm Ostwald; Literatura Científica; Institucionalização da Ciência.

Introdução

As narrativas sobre a origem da Físico-química refletem sua complexidade. As narrativas mais tradicionais apontam que o estabelecimento da Físico-química enquanto uma disciplina independente - isto é, com programas de pesquisa, escolas e uma base teórico-conceitual própria - ocorreu devido aos esforços de três químicos: o holandês Jacobus Henricus van't Hoff (1852-1911), o sueco Svante Arrhenius (1859-1927) e o báltico-alemão Wilhelm Ostwald (1853-1932). De acordo com esta narrativa, a criação do periódico

Zeitschrift für Physikalische Chemie, fundado por van't Hoff e Ostwald e editado pelo último, marcaria o surgimento desta nova disciplina no início de 1887.

Entretanto, historiadores apontam esta visão sobre o surgimento da Físico-química é um mito fundador, criado pelos seus próprios praticantes para legitimar diferentes formas de se produzir ciência surgidas no final do século XIX, como mostrado pela historiadora Diana Barkan.[49] Outros estudiosos apontam que o termo *físico-química* já era comum ao vocabulário dos químicos no século XVII, e mostram que a narrativa mitológica em torno de Ostwald, Arrhenius e van't Hoff oculta o papel de antigas teorias, práticas e campos de pesquisa que constituíram esta disciplina e que, em sua maioria, surgiram de modo independente e em períodos anteriores à institucionalização desta disciplina.[50]

Entretanto, o historiador John Servos apresenta um olhar diferente sobre a origem desta disciplina, destoando da narrativa simplista sobre o papel destes três químicos, e ao mesmo tempo se contrapondo às críticas dos historiadores que apontaram a dívida da Físico-química oitocentista com diferentes práticas e teorias químicas anteriores. Servos defende que Arrhenius, van't Hoff e Ostwald devem ser considerados os principais responsáveis pela construção das instituições culturais da Físico-química, necessárias para o sucesso desta disciplina:

> "Jacobus Henricus van't Hoff, Svante Arrhenius and Wilhelm Ostwald founded the discipline of physical chemistry. They did not invent the name, nor did their ideas lack precursors; their theories were not without flaws, and their conception of physical chemistry was not without ambiguities and internal tensions. Nevertheless, these three chemists created the discipline. Etymologically, discipline is derived from the Latin *disciplina*, a word meaning instruction or training (...) When applied to science in modern times, the word implies a certain coherence of aims and techniques maintained through transmission from teacher to student. The content of the science may change over time, but there is a genetic link among its practitioners, the methods they use, and the questions they ask. To maintain this continuity, institutions are necessary: schools in which techniques are practiced and honed; societies in which workers meet and renew their ties; journals in which results are exposed to public scrutiny. Van't Hoff, Arrhenius and Ostwald created

[49] BARKAN, Diana K. A Usable Past: Creating Disciplinary Space for Physical Chemistry. In: *The Invention of Physical Science*: Intersections of Mathematics, Theology and Natural Philosophy Since the Seventeenth Century. Essays in Honor of Erwin N. Hiebert. Boston Studies in the Philosophy of Science, vol. 139. Dordrecht: Kluwer Academic Publishers, 1992. p. 175-202.

[50] NYE, Mary Jo. *Before big science*: the pursuit of modern chemistry and physics, 1800 - 1940. Cambridge, Mass. [u.a.]: Harvard University Press, 1999; LAIDLER. *The World of Physical Chemist*. 1993;

physical chemistry in this sense. They systematized their predecessors' work and developed new concepts and techniques that served as growing points for subsequent research. They brought physical chemistry to the attention of their contemporaries (...). And together with their students, they founded the laboratories and journals through which the new discipline grew and prospered. They gave coherence and continuity to what had been diffuse and sputtering traditions of study."[51]

Contudo, ao aceitarmos a posição de Servos, nos vemos face a uma importante questão: se no início da década de 1880, estes químicos sequer se conheciam, como eles instituíram até o final desta mesma década uma nova disciplina científica? Escolas não se consolidam tão rapidamente, comunidades científicas internacionais muito menos. Periódicos científicos não têm utilidade se não houver uma comunidade de leitores interessados nas pesquisas neles publicadas.

De fato, o reconhecimento da Físico-química enquanto uma disciplina institucionalizada foi notavelmente rápido, o que nos sugere a existência de um ambiente científico favorável a emergência deste novo campo disciplinar. Alguns autores apontam como justificativa para o rápido reconhecimento desta disciplina o contexto sócio-econômico alemão, que favoreceu o desenvolvimento da Físico-química devido a maior relação entre o setor industrial em expansão, as instituições científicas e os interesses políticos nacionais.[52] Entretanto, também nos parece necessário encontrar elementos internos à prática científica que tenham favorecido a emergência desta disciplina.

A própria Diana Barkan nos aponta um caminho em seu trabalho: esta historiadora mostra como escritos produzidos por importantes físico-químicos entre 1890 e 1915 contribuíram para a fundação de uma narrativa sobre o surgimento da Físico-química.[53] Nos apropriando de seu argumento, acreditamos que obras voltadas ao treinamento dos químicos e divulgação desta ciência, publicadas em um período anterior, desempenharam um papel importante na institucionalização da Físico-química, abrindo caminho para jovens cientistas que trouxeram consigo novas ideias e abordagens para a Química.

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[51] SERVOS, John W. *Physical Chemistry from Ostwald to Pauling*: the Making of a Science in America. Princeton: Princeton University Press, 1990. p. 20.

[52] NYE, Mary Jo. *From Chemical Philosophy to Theoretical Chemistry*. Berkeley, Los Angeles, London: University of California Press, 1993; SÁNCHEZ-RON, José Manuel El poder de la ciencia: historia social, política y económica de la ciencia - siglos XIX y XX. Barcelona: Crítica, 2007. LENOIR, Timothy. *Instituindo a ciência*: A produção cultural das disciplinas científicas. São Leopoldo: Unisinos, v. 27, 2003.

[53] BARKAN. A Usable Past. p. 175-202.

Dentre estas obras, destacamos o livro-texto *Lehrbuch der allgemeinen Chemie*, escrito por Wilhelm Ostwald. Publicado entre 1885 e 1887, o *Lehrbuch* foi o primeiro livro-texto escrito por este químico. Sua escrita foi iniciada pouco tempo após a conclusão de seu doutorado na Universidade de Tartu, enquanto seu segundo volume foi publicado quando Ostwald já havia se estabelecido como um dos mais importantes jovens pesquisadores de sua época.

Inicialmente concebido com objetivos pedagógicos, este livro se tornou o cartão de visitas das novas pesquisas sobre afinidade química desenvolvidas por Ostwald, Arrhenius e van't Hoff, que viriam a ser a base de trabalhos fundamentais desta ciência. Ao mesmo tempo, Ostwald utilizou seu livro para defender sua visão mecanicista (e reducionista) da Química, ao chamar a atenção dos seus contemporâneos para as diferentes forças - posteriormente chamadas de energias - que atuam sobre a matéria. Esta obra também contribuiu para aproximar diferentes áreas do conhecimento que viriam a constituir a Físico-química - como a Eletroquímica, a Termoquímica e a Fotoquímica, campos de pesquisa autônomos que após a década de 1880 foram incorporadas ao guarda-chuva disciplinar da Físico-química.

Tais características do *Lehrbuch* exemplificam bem as múltiplas funções dos livros-texto na ciência.[54] Os livros-texto são um tipo de escrito comum e necessário à cultura escolar e científica que nos permite compreender como a ciência se desenvolve por meio do ensino e da divulgação científica: os livros-texto nos ajudam a entender como o ensino de ciências era pensado e executado em diferentes contextos e para diferentes audiências, como cientistas em formação ou o público geral.[55] Além disso, estes livros refletem os elementos teórico-conceituais considerados válidos pelos praticantes de uma determinada disciplina, por mais que eventualmente debates ou controvérsias sejam retratadas em textos dessa natureza.[56] Até o início do século XIX, os livros-texto eram um dos mais populares meios de comunicação científica, o que faz desses escritos fontes importantes para entendermos a

[54] Nós não esgotaremos essas razões neste texto. Uma síntese sobre as vantagens e potencialidades da investigação histórica dos livros-texto pode ser encontrada em: SIMON, Josep. Textbooks. In: LIGHTMAN, Bernard (ed.) *A Companion to the History of Science*. Chichester, UK; Malden, MA: John Wiley & Sons, 2016. 400-413; BROOKE, John Hedley. Introduction: the study of chemical textbooks. In: LUNDGREN, Anders; BENSAUDE-VINCENT, Bernadette. (ed.) *Communicating chemistry*: textbooks and their audiences, 1789-1939. Canton, MA. Science History Publications. 2000. p. 1-18.

[55] GORDIN, Michael D. Beilstein Unbound: The Pedagogical Unraveling of a Man and his Handbuch. In: KAISER, David (ed.). *Pedagogy and the Practice of Science*: Historical and Contemporary Perspectives. Cambridge, MA and London. MIT Press. 2005. p. 11-40; ORLAND, Barbara. The Chemistry of Every-day Life: Popular Chemical Writing in Germany. In: LUNDGREN, Anders; BENSAUDE-VINCENT, Bernadette. (ed.) *Communicating chemistry*: textbooks and their audiences, 1789-1939. Canton, MA. Science History Publications. 2000. p. 327-366.

[56] Discutiremos o papel de livros-texto nas controvérsias científicas em trabalho futuro.

disseminação de novas ideias científicas, assim como o surgimento de novos campos de pesquisa.[57]

Neste primeiro artigo, apresentaremos a origem e as características da primeira edição do *Lehrbuch der allgemeinen Chemie*.[58] Pretendemos apresentar as motivações de Ostwald para a escrita deste livro e mostrar seu papel para a organização e popularização da Físico-química, a partir da aproximação de diferentes campos de pesquisa por meio do interesse comum de compreender as afinidades químicas. Também pretendemos mostrar como a escrita de Ostwald reflete o paradigma mecanicista no qual este químico foi treinado, fazendo-o valorizar no início de sua carreira as explicações atomistas, cinético-moleculares. Como fontes para a realização desta pesquisa, utilizamos a primeira edição do *Lehrbuch der allgemeinen Chemie* (1885-1887), assim como a autobiografia de Wilhelm Ostwald. Também utilizaremos a literatura sobre o desenvolvimento da Química e, especificamente, da Físico-química no século XIX.

Apresentaremos inicialmente a trajetória acadêmica de Ostwald, tentando compreender suas motivações para a escrita de um livro-texto ainda no início de sua carreira. Em seguida, apresentaremos o primeiro volume do *Lehrbuch*, destacando elementos característicos da escrita de Ostwald e sua abordagem para os conteúdos. Posteriormente, mostraremos o impacto dos trabalhos dos químicos Svante Arrhenius e Jacobus Henricus van't Hoff nas ideias de Ostwald sobre afinidade química. O impacto desses trabalhos sobre Ostwald e seu *Lehrbuch* é discutido na seção seguinte, na qual tentamos mostrar como Ostwald aproxima áreas com relativa autonomia entre si - a termoquímica, eletroquímica e fotoquímica - em torno do problema das afinidades químicas, agregando campos de pesquisa que se tornaram parte da moderna Físico-química.

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[57] KAISER, David. Making Tools Travel: Pedagogy and the Transfer of Skills in Postwar Theoretical Physics. In: KAISER, David (ed.). *Pedagogy and the Practice of Science: Historical and Contemporary Perspectives*. Cambridge, MA and London. MIT Press. 2005. p. 41-74; GAVROGLU, Kostas; SIMÕES, Ana. One Face or Many? The role of Textbooks in Building the New Discipline of Quantum Chemistry. In: LUNDGREN, Anders; BENSAUDE-VINCENT, Bernadette. (ed.) *Communicating chemistry*: textbooks and their audiences, 1789-1939. Canton, MA. Science History Publications. 2000. p. 415-449.

[58] Este é o primeiro de dois artigos que buscam resgatar a importância do Lehrbuch der allgemeinen Chemie para a formação da cultura científica da Físico-química. O segundo artigo ainda está em processo de escrita e depende de uma nova visita aos arquivos da Academia de Ciências de Berlim e, por esta razão, não compõe o texto final desta tese.

Formação Inicial de Ostwald e Origens do Lehrbuch

Filho de um construtor de barris e uma dona de casa, ambos de origem alemã, Wilhelm Ostwald nasceu na cidade de Riga, atual Letônia, em 1853. Então parte do Império Russo, a cidade de Riga congregava diferentes povos do Leste e do Centro da Europa, em especial os alemães, que trouxeram a cultura germânica para o centro das esfera cultural da cidade.[59]

Ostwald foi educado em uma escola religiosa com orientação técnica, criada com o objetivo de formar estudantes aptos para ingressar no recém-criado Instituto Politécnico de Riga.[60] Esta formação técnica despertou seu interesse para a investigação científica e pavimentou seu posterior ingresso no curso de química na Universidade de Tartu (atual Estônia) em 1872.

O ingresso de Ostwald na Universidade de Tartu foi importante para o desenvolvimento de suas pesquisas em físico-química, visto que os químicos de Tartu não compartilhavam da mesma agenda dos químicos das principais universidades da Inglaterra, França e Alemanha, onde predominava a pesquisa em química orgânica, que havia se desenvolvido notavelmente nas últimas décadas graças às contribuições de nomes como Liebig, Perkin, Hofmann e Kekulé.[61] Estes e outros químicos mostraram como a química poderia transformar a sociedade, permitindo a produção de substâncias já conhecidas e outras completamente novas que poderiam ser utilizadas como medicamentos, tinturas e outros produtos sintéticos.[62] Frente às novidades surgidas neste campo, não é difícil compreender porque a química orgânica dominava a agenda dos químicos experientes e, consequentemente, o interesse dos jovens químicos em formação.

Contudo, a Universidade de Tartu não possuía nenhum químico que se dedicasse a esta área. Ostwald relata em suas memórias que havia um certo mal estar entre os químicos que se dedicavam à Química Inorgânica e Analítica e os químicos orgânicos, visto que estes últimos

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[59] OSTWALD, Wilhelm. Lebenslinien. In: JACK, Robert S.; SCHOLZ, Fritz (ed.). *Wilhelm Ostwald: the Autobiography*. Springer International Publishing, 2017. p. 3-10.

[60] OSTWALD, Lebenslinien. In: JACK; SCHOLZ, *Wilhelm Ostwald*. p. 11-12.

[61] Ver SCHUMMER, Joachim. Wilhelm Ostwald. In: *Encyclopaedia Britannica*, Encyclopaedia Britannica Inc., accessed January 2, 2018 https://www.britannica.com/biography/Wilhelm-Ostwald; HIEBERT; KÖRBER. *Dictionary of Scientific Biography*. p. 456-457. Sobre o desenvolvimento da Química Orgânica na Alemanha, França e Inglaterra, ver: NYE, Mary Jo. *Before big science*: the pursuit of modern chemistry and physics, 1800 - 1940. Cambridge, Mass. [u.a.]: Harvard University Press, 1999. p. 1-27; MILAGRE, A. S. K. A produção do conhecimento em química e suas relações com aspectos sociais, políticos e econômicos: considerações históricas. *Epistéme*, v. 1 n. 2, 1996. p. 119-128.

[62] ABELSHAUSER, Werner; VON HIPPEL, Wolfgang; JOHNSON, Jeffrey Allan; STOKES, Raymond G. *German Industry and Global Enterprise: BASF: The History of A Company.* Cambridge: Cambridge University Press, 2004. BENSAUDE-VINCENT, Bernadette; STENGERS, Isabelle. *História da Química*. trad. Raquel Gouveia. Lisboa: Instituto Piaget, 1992. p. 207-257.

eram mais requisitados pelas universidades e ocupavam as melhores posições acadêmicas, o que gerava conflitos e competição entre os representantes dessas áreas.[63]

O curso de Química da Universidade de Tartu seguia a tradição da Química Analítica e Inorgânica, seguindo o legado de célebres representantes destas áreas, como Antoine Lavoisier (1743-1894) e, em especial, Claude Louis Berthollet (1748-1822).[64] Além da Química Analítica, os trabalhos de Berthollet eram voltados às afinidades químicas e ao equilíbrio de reações - temas que foram frequentemente explorados pelos químicos da Universidade de Tartu.[65] A pesquisa de Berthollet também promoveu a relação de dependência teórica da Química para com a Mecânica newtoniana, visto sua defesa de que as afinidades seriam uma força de natureza mecânica, similar às forças gravitacionais, e por ter introduzido a ideia de equilíbrio mecânico às reações químicas.[66]

Ostwald manteve estreita relação com o químico Carl Schmidt (1822-1894), que havia estudado com Justus von Liebig (1803-1873) e Friedrich Wöhler (1800-1882), figuras importantes da Química Orgânica. Entretanto, Schmidt era essencialmente um químico analítico, dedicando sua pesquisa à análise química mineral, sendo responsável por orientar Ostwald e introduzi-lo à Química Analítica.[67] Segundo Past, Schmidt também teria sido o responsável por despertar o interesse de Ostwald pela história das ciências, algo que se mostraria útil para a escrita do *Lehrbuch*.[68] Outro professor de fundamental relevância na trajetória de Ostwald em Tartu, foi o assistente de Schmidt, o químico Johann Lemberg (1842-1902). Interessado em mineralogia e química inorgânica, é creditado à Lemberg o interesse de Ostwald pelas pesquisas sobre cinética e equilíbrio químico de reações, assim como pelos métodos de medida das afinidades químicas, consideradas as forças responsáveis pela ocorrência das transformações químicas.[69]

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[63] OSTWALD, Lebenslinien. In: JACK; SCHOLZ, *Wilhelm Ostwald* p. 53.

[64] PAST, Velo The Emergence of Physical Chemistry. In: Vihalemm Rein. (Ed.) *Estonian Studies in the History and Philosophy of Science*. Boston Studies in the Philosophy of Science, v. 219. Dordrecht: Springer, 2001. p. 35-50. <https://doi.org/10.1007/978-94-010-0672-9_3>

[65] PAST, Velo. *Estonian Studies in the History and Philosophy of Science*. p. 37-44.

[66] QUÍLEZ, Juan. From Chemical Forces to Chemical Rates: A Historical/Philosophical Foundation for the Teaching of Chemical Equilibrium. *Science & Education*, v. 18, n. 9, 2009. p.1203-1251. <https://doi.org/10.1007/s11191-006-9048-4>

[67] PAST, Velo. *Estonian Studies in the History and Philosophy of Science*. p. 39.

[68] PAST, *Studia Philosophica*, p. 20.

[69] KIM, Mi G. Biography: Wilhelm Ostwald (1853-1932). *Hyle*. 12, 1, 2006, p. 141 – 148; HIEBERT; KÖRBER. *Dictionary of Scientific Biography*. p. 456-457. Sobre o desenvolvimento das ideias sobre afinidade química no século XIX, ver NYE, Mary Jo. *From Chemical Philosophy to Theoretical Chemistry*. Berkeley, Los Angeles, London: University of California Press, 1993. p. 105-138.

Estimulado por Schmidt e Lemberg, Ostwald desenvolveu métodos para a avaliação das afinidades químicas - forças de atração responsáveis pela união dos constituintes da matéria e sua transformação - de diferentes compostos inorgânicos, baseado nas variações de volume e índice de refração dos sistemas antes e após a ocorrência de reações químicas. O uso destes métodos para determinação da afinidade química foi o tema de suas pesquisas de mestrado e doutorado em Tartu, defendidos em 1877 e 1878, respectivamente.[70] Estas pesquisas alcançaram um público mais amplo, tornando-o relativamente conhecido na comunidade científica com apenas 26 anos de idade.[71]

Além de Schmidt e Lemberg, Ostwald manteve estreito contato com o físico Arthur von Öttingen, também professor em Tartu. Öttingen foi responsável por introduzir Ostwald ao estudo da termodinâmica e por estimulá-lo a aplicar as leis de energia aos fenômenos químicos.[72] Além disso, Öttingen o admitiu como assistente de laboratório em 1875, o que colaborou para o seu contato com a física de modo geral, e com as atividades de ensino, visto que seu trabalho compreendia ministrar algumas aulas e preparar e executar experimentos para os graduandos.[73] Posteriormente, Ostwald tornou-se assistente de Schmidt, também colaborando em suas atividades de pesquisa e ensino.

De acordo com Past, foi Schmidt que sugeriu a Ostwald a escrita de um livro-texto sobre química geral.[74] Porém, analisando a autobiografia de Ostwald, nos parece que esta sugestão foi feita em tom de brincadeira, não como um conselho a ser levado a sério.[75] Todavia, Ostwald acatou a "sugestão" de seu mentor e começou a amadurecer a ideia de escrever seu próprio livro-texto, especialmente durante seu doutoramento, quando precisou

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[70] Ostwald explorou o método volumétrico para medidas de afinidade química durante o seu mestrado. Em seu doutorado, ele incorporou a sua pesquisa métodos ópticos, mas estes não alcançaram tamanha notoriedade. Ambos métodos foram descrito em HIEBERT; KÖRBER. *Dictionary of Scientific Biography*. p. 457-458. Ver também OSTWALD, Wilhelm. *Volumchemische Studien über Affinität*. Magisterdissertation, Dorpat, H. Laakmann, 1877; OSTWALD, Wilhelm. *Volumchemische und Optisch-chemischen Studien über Affinität.* Doktordissertation, Dorpat, H. Laakmann, 1878.

[71] O químico escocês M. M. Pattison Muir leu os trabalhos de Ostwald sobre afinidade química e encontrou ideias compatíveis com a Lei de Ação de Massas proposta pelos noruegueses Cato Guldberg (1836-1902) e Peter Waage (1833-1900). Pattison Muir escreveu um artigo apresentando ambos os trabalhos na revista Philosophical Magazine, o que trouxe um rápido reconhecimento ao trabalho de jovem Ostwald. MUIR, Matthew M. P. Chemical Affinity. *Philosophical Magazine*, Sept. 1879. p. 181-203.

[72] DELTETE, Robert J. Wilhelm Ostwald's Energetics 1: Origins and Motivations. *Foundations of Chemistry*, 9, 1, p. 3-56, 2007. p. 13-15.

[73] OSTWALD, Lebenslinien. In: JACK; SCHOLZ, *Wilhelm Ostwald*. p. 60-61.

[74] PAST, Velo. Wilhelm Ostwald and Physical Chemistry at the University of Tartu. *Studia Philosophica*, IV (40), Tartu, 2004. p. 19-25.

[75] OSTWALD, Lebenslinien. In: JACK; SCHOLZ, *Wilhelm Ostwald*. p. 68.

ministrar um curso de Físico-química na Universidade de Tartu.[76] Todavia, a escrita do *Lehrbuch* iniciou-se apenas em 1880, dois anos após a conclusão do seu doutorado.

Em 1879, dividindo seu tempo entre a pesquisa e o trabalho, Ostwald casou-se com Helene von Reyher, também oriunda de uma família alemã de Riga. De acordo com Ostwald, a vida conjugal e o nascimento do seu primeiro filho exigiram a busca por um emprego melhor. Graças à indicação de Schmidt, ele foi contratado como professor de química na Escola Politécnica de Riga em 1881.[77]

Esta experiência foi importante para que Ostwald percebesse a importância do uso de uma linguagem simples e objetiva na exposição de suas ideias para a melhor compreensão das suas ideias pelo público:

> "I got a lot out of this teaching experience. Since the pupils didn't have much background in the subjects I was forced to restrict myself to a more basic level of explanation than I used in the university lectures and the experience of doing things this way in the school in turn flowed back to improve my university lectures. I learned here the importance of simplicity and clarity in presentation and when later I wrote textbooks these were the qualities for which they were praised."[78]

Portanto, percebe-se que as motivações iniciais de Ostwald para a escrita do *Lehrbuch* eram de natureza pedagógica: a sua relação com a sala de aula, ainda enquanto estudante em Tartu, o direcionou para a escrita de um livro-texto próprio. Entretanto, não foi apenas a atividade docente que mostrou a Ostwald a necessidade em escrever um livro-texto. Imerso em um contexto de profundas mudanças na Química, Ostwald sentia que os livros-texto disponíveis eram muito antigos ou pouco colaboravam para que os leitores tivessem uma visão geral da Química e seus fundamentos. Em outras palavras, Ostwald achava que a escrita de livros-texto contribuía para a sistematização do conhecimento químico.

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[76] Ostwald não deixa claro em sua autobiografia se essas aulas eram necessárias para a obtenção do grau de doutor, ou uma das suas atribuições como assistente. Ver: OSTWALD, Lebenslinien. In: JACK; SCHOLZ, *Wilhelm Ostwald*. p. 71-72.
[77] OSTWALD, Lebenslinien. In: JACK; SCHOLZ, *Wilhelm Ostwald*. p. 83-61.
[78] OSTWALD, Lebenslinien. In: JACK; SCHOLZ, *Wilhelm Ostwald*. p. 80.

Sistematizar a Química é Preciso: Stöchiometrie (1885)

O século XIX testemunhou um crescimento exponencial na produção de literatura científica: os historiadores Sally Shuttleworth e Berris Charnley afirmam que o número de periódicos científicos existentes no mundo aumentou de 100 títulos para cerca de 10 mil na transição para o século XX.[79] Outros tipos de literatura científica, como obras de popularização, manuais e livros-texto também surgiram em abundância.[80] Em muitos casos, tal proliferação deveu-se não apenas ao crescimento do mercado editorial, mas também ao próprio desenvolvimento de uma ciência cada vez mais especializada e geograficamente descentralizada, gerando diversas publicações locais e de maior grau de especificidade.[81] Ao mesmo tempo, as novidades oriundas dos laboratórios químicos tornavam os periódicos científicos meios de comunicação cada vez mais necessários.

Em meio a este festim editorial, alguns químicos expressavam críticas à excessiva criação de periódicos científicos. Um deles foi o químico russo-alemão Friedrich Beilstein (1938-1906), que afirmava que a criação de revistas cada vez mais locais e especializadas poderia dificultar a disseminação de novas ideias e impedir o próprio desenvolvimento da ciência, visto que trabalhos inovadores poderiam ser perdidos em meio a uma diversidade de artigos publicados em periódicos cada vez mais locais e com pouco alcance.[82]

O aumento no número de livros-texto, por outro lado, não era recebido com as mesmas críticas. Há duas razões para isso: primeiramente, a proliferação de livros-texto causava um impacto menor na comunicação científica, pois atendiam principalmente às necessidades pedagógicas e de popularização científica, não sendo o principal meio de divulgação de pesquisas inéditas.[83] Em segundo lugar, a escrita de livros-texto pode ser compreendida como

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[79] SHUTTLEWORTH, Sally; CHARNLEY, Berris. Editorial: Science periodicals in the nineteenth and twenty-first centuries. *Notes and Records*: The Royal Society Journal of the History of Science, v. 70, n. 4, 2016. p. 297–304.

[80] KNIGHT, David M. Scientists and Their Publics: Popularization of Science in the Nineteenth Century. In: NYE, Mary Jo (ed.). *The Cambridge History of Science*: The modern physical and mathematical sciences. v. 5, Cambridge: Cambridge University Press, 2002.

[81] SHUTTLEWORTH; CHARNLEY. *Notes and Records*. p. 297–304; TOPHAM, Jonathan R. The scientific, the literary and the popular: Commerce and the reimagining of the scientific journal in Britain, 1813–1825. *Notes and Records:* The Royal Society Journal of the History of Science v. 70, n. 4, 2016. p. 305-324; CORSI, Pietro. What do you mean by a periodical? Forms and functions. *Notes and Records:* the Royal Society Journal of the History of Science. v. 70, n. 4, 2016. p. 325-341.

[82] GORDIN, Michael D. Beilstein Unbound: The Pedagogical Unraveling of a Man and his Handbuch. In: KAISER, David (ed.). *Pedagogy and the Practice of Science*: Historical and Contemporary Perspectives. Cambridge, MA and London. MIT Press. p. 11-40. 2005.

[83] Sobre os diferentes papéis dos Livros-texto na História da Química, ver: BROOKE, John H. Introduction: the study of chemical textbooks. In: LUNDGREN, Anders; BENSAUDE-VINCENT, Bernadette. (ed.)

um exercício contrário à pulverização do conhecimento criticada por Beilstein, devido a natureza sistematizadora dessa atividade: escrever livros-texto exige um esforço de síntese frente ao conhecimento científico, que precisa ser selecionado, organizado e muitas vezes simplificado para atingir fins didáticos. Em várias passagens de sua autobiografia, Ostwald ilustra este argumento, ao relatar as dificuldades enfrentadas e estratégias utilizadas para produzir um texto que fosse simples, acessível e que sintetizasse várias pesquisas de forma lógica.[84]

Devido seu contato com a literatura química, Ostwald conhecia os principais livros-texto de química de sua época. Essas obras, escritas por químicos importantes como Jöns J. Berzelius (1779-1848), Hermann Kopp (1817-1892) e Leopold Gmelin (1788-1853), poderiam fornecer para Ostwald um modelo de apresentação dos conteúdos.[85] Entretanto, Ostwald se mostrava insatisfeito com os materiais disponíveis, que estavam há muito tempo obsoletos ou representavam muito mais compilações de artigos do que uma síntese didática do conhecimento químico.[86]

Sua dificuldade em estabelecer uma organização lógica para a apresentação dos conteúdos em seu livro, o levou até os trabalhos do psicólogo e filósofo Wilhelm Wundt (1832-1920), chegando a se corresponder com este pensador para buscar uma solução para o problema. Entretanto, Ostwald afirmou não ter conseguido colocar em prática todos os conselhos recebidos de Wundt.[87]

Apesar do seu esforço para escrever um livro que fosse, de fato, didático e sistemático, Ostwald era consciente de que o trabalho literário e pedagógico era pouco valorizado pelos químicos, incluindo seus mentores, Schmidt e Lemberg. Tal fato foi como relatado por Ostwald em suas memórias:

Communicating chemistry: textbooks and their audiences, 1789-1939. Canton, MA. Science History Publications. p. 1-18. 2000.

[84] OSTWALD, Lebenslinien. In: JACK; SCHOLZ, *Wilhelm Ostwald*. p. 71-71; 82; 107.

[85] BERZELIUS, Jöns J. *Lehrbuch der Chemie*. Traduzido por Friedrich Wöhler. Dresden e Leipzig: Arnoldischen Buchhandlung, 1825-1841; BUFF, Heinrich L.; KOPP, Hermann; ZAMMINER, Friedrich. *Graham-Otto's ausführliches Lehrbuch der Chemie*. 4. Aufl.: Lehrbuch der physikalischen und theoretischen Chemie. Braunschweig : Vieweg, 1863. Gmelin foi autor de diversos manuais, que posteriormente foram publicados em colaboração com o químico Karl Kraut, e após sua morte, foi editado por outros químicos a exemplo de Alexander Naumann, responsável pelo volume de Química Inorgânica. ver: NAUMANN, Alexander (ed.). *Gmelin-Kraut's Handbuch der Anorganischen Chemie*. Heidelberg: Carl Winter's Universitätsbuchhandlung, 1877.

[86] OSTWALD, Lebenslinien. In: JACK; SCHOLZ, *Wilhelm Ostwald*. p. 71; 108-109.

[87] OSTWALD, Lebenslinien. In: JACK; SCHOLZ, *Wilhelm Ostwald*. p. 107.

Both of them despised the writing of books and saw the heart of science firmly placed in experimental work which was to be described as tersely and dispassionately as possible. Neither of them recognised the value for the advance of knowledge of ordering and summarising what was known, although there were numerous examples where the publication of a textbook had brought the results from disparate areas into context and had often made the development of the field possible. I did recognise this and the success of my textbook soon became a further example of this rule.[88]

De fato, a escrita de livros-texto pode eventualmente resultar em produções científicas originais. Em 1869 foi apresentada a lei periódica proposta por Dmitrii Mendeleev (1834-1907), elaborada durante a escrita do seu livro-texto *Osnovy Khimii* (Princípios de Química).[89] Apesar disso, o caso de Mendeleev parece ter sido um ponto fora da curva: a valorização da pesquisa experimental e seus resultados parecia se sobrepor a outras atividades relevantes para o fortalecimento da ciência, como a teorização e o ensino.[90]

Em meio a este contexto de desvalorização do trabalho literário e pedagógico na Química, e ciente dos desafios para a escrita de um livro-texto original, Ostwald publicou o primeiro volume do seu *Lehrbuch der allgemeinen Chemie*.[91]

No prefácio do *Lehrbuch*, Ostwald apresenta suas motivações e objetivos, afirmando que seu livro destinava-se a todos os interessados em Físico-química ou, como preferia chamar esta disciplina, Química Geral:[92]

"The present book is a result of the author's wish, to get a complete overview of an area to whom he has dedicated his interest and activity since the beginning of his scientific career. Such a compilation will not be unpleasant to the experts, especially since for sometime the importance of the so-called physical, or rather, I

[88] OSTWALD, Lebenslinien. In: JACK; SCHOLZ, *Wilhelm Ostwald*. p. 108.

[89] MENDELEEV, Dmitrii Ivanovich. *Osnovy Khimii.* Cast' pervaja, S.-Peterburg: 1869. Sobre o desenvolvimento da Lei Periódica de Mendeleev durante a escrita de seu livro, ver BROOKS, Nathan M. Dmitrii Mendeleev's Principles of Chemistry and the Periodic Law of the Elements. In: LUNDGREN, Anders; BENSAUDE-VINCENT, Bernadette (ed.). *Communicating chemistry*: textbooks and their audiences, 1789-1939. Canton, MA: Science History Publications, 2000. p. 295-309.

[90] Posteriormente, o próprio Ostwald se tornaria exemplo da pouca valorização das atividades teóricas e pedagógicas na química em ocasião das suas indicações ao Prêmio Nobel de Química entre 1904 e 1909. Ver o Capítulo 3 desta tese: *A Nobel for What? Revisiting Wilhelm Ostwald Nobel Prize of Chemistry.*

[91] OSTWALD, Wilhelm. *Lehrbuch der allgemeinen Chemie*. bd. 1: Stöchiometrie. Leipzig: Verlag von W. Engelmann, 1885.

[92] Apesar das origens distintas, os termos *Química Geral*, *Físico-química* e *Química Teórica* eram considerados sinônimos no século XIX, conforme afirmado por Patrick Coffey em *Cathedrals of Science*. p. 10-11.

would say, general chemistry for the further development of our science is increasingly appreciated."[93]

A estratégia finalmente adotada por Ostwald para a apresentação dos conteúdos foi a utilização de uma abordagem histórica, pois ele acreditava que a História da Química refletiria o próprio desenvolvimento lógico desta disciplina.[94] Entretanto, tais narrativas partiam de uma perspectiva linear e cumulativa do desenvolvimento da ciência, que compreendia o passado da Química como uma marcha progressiva para uma ciência cada vez mais objetiva, socialmente útil e verdadeira, visão comum em sua época.[95]

Ostwald também acreditava ser necessário diferenciar as teorias das hipóteses científicas em seu livro-texto, afirmando no prefácio do seu *Lehrbuch* que "às primeiras, concedi o mais amplo espaço, e às segundas, de acordo com a natureza do assunto, [as apresentei] como resultado da experiência e limitadas por ela."[96]

Em meio a uma profusão de publicações relatando novas descobertas e teorias, selecionar os conteúdos a serem apresentados no *Lehrbuch* certamente foi um problema para Ostwald. Quais conteúdos mereciam uma abordagem mais profunda? Quais poderiam ser suprimidos ou reduzidos? As respostas para tais questões perpassam pela imagem da Química defendida por Ostwald, em especial, sobre os objetos mais fundamentais desta ciência, em seu ponto de vista.

É importante destacar que a despeito do valor de sua autobiografia para compreendermos sua visão de mundo e opinião sobre os fundamentos da Química, Ostwald usa a lente do Energeticismo - programa científico-filosófico o qual viria a ser adepto a partir

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[93] "*Das vorliegende Buch ist dem Bedürfnisse des Verfassers entsprungen, sich eine möglichst vollständige Übersicht über ein Gebiet zu verschaffen, welchem er seit dem Beginne seiner wissenschaftlichen Laufbahn vorwiegend sein Interesse und seine Thätigkeit gewidmet hat. Den Fachgenossen wird eine derartige Zusammenstellung nicht unwillkommen sein, insbesondere da seit einiger Zeit in zunehmendem Masse die Bedeutung der sogenannten physikalischen, oder, wie ich lieber sage, allgemeinen Chemie für die Weiterentwicklung unserer Wissenschaft gewürdigt wird*." OSTWALD, *Lehrbuch* v. 1, p. vii. Tradução nossa.

[94] OSTWALD, *Lehrbuch* v. 1, p. viii.

[95] A abordagem histórica empregada por Ostwald assemelha-se a visão positivista de Auguste Comte. Entretanto, não é possível afirmar que Ostwald era assumidamente positivista entre 1877 e 1887. De qualquer modo, algumas concepções que rodeavam as ciências da natureza desde o século XVII serviram à filosofia positivista de Auguste Comte e, a partir de seus trabalhos, ganharam um novo fôlego e atingiram outros públicos. Portanto, é possível que as ideias de Ostwald sobre o desenvolvimento da química sejam reflexo do espírito de sua época. Sobre a relação entre a Química e o Positivismo, assim como a relação de Ostwald com essa filosofia, ver BENSAUDE-VINCENT, Bernadette; SIMON, Jonathan. *Chemistry the Impure Science*. London: Imperial College Press, 2008. p. 175-184.

[96] Trecho completo: "*Was ich bei der Ausführung meines Buches beständig im Auge gehabt habe, ist die sorgfältige Trennung des thatsächlich Beobachteten von den Hypothesen und Theorien. Ersterem habe ich den breitesten Raum gewährt, letztere, der Natur der Sache gemäss, als Ergebnis der Erfahrung und begrenzt durch diese dargestellt.*" OSTWALD, *Lehrbuch* v. 1, p. viii. Tradução nossa.

de 1890 - ao descrever os objetos e propósitos da Química em suas memórias, fazendo uma leitura anacrônica do seu passado. Assim, para compreendermos o que Ostwald considerava ser os fundamentos da Química, optamos por analisar a tradição de pesquisa química em que ele estava inserido, nos baseando na obra de Mary Jo Nye, *From Chemical Philosophy to Theoretical Chemistry* (1993).

Sob influência de Schmidt e Lemberg, Ostwald foi treinado seguindo uma tradição mecanicista de Química. Os seus objetos de estudo - afinidades, cinética e equilíbrio de reações - já sugerem sua vinculação com o programa mecanicista. Nye mostra em uma breve revisão da literatura que a Química setecentista era organizada em torno de problemas oriundos de ideias mecanicistas, como o flogisto e a Teoria de Afinidades.[97] Apesar de ter perdido espaço para a Química Orgânica a partir dos anos 1830, o programa mecanicista de Química foi reiterado no século XIX por químicos como John Dalton (1766-1844), Berzelius e Justus von Liebig (1803-1873), este último professor de Schmidt e um dos ídolos científicos de Ostwald:[98]

> "Liebig, too, saw the aim of chemistry as the search not only to consolidate the truth of chemical proportions but to study the causes of the regularity and constancy of these proportions. Liebig took the cause of chemical action to lie in Newtonian-type atoms and forces of the Berzelian variety, that is, spherical atoms and electrical affinity forces. This is a problem-solving tradition focused on atoms and powers, or mechanism and materialism."[99]

Deste modo, refletindo em seu livro a tradição mecanicista e materialista desta ciência, Ostwald deu destaque em seu primeiro livro ao tema da composição da matéria e das proporções químicas, isto é, os estudos estequiométricos. Essa relação com o programa mecanicista também se refletiu no subtítulo do primeiro volume do *Lehrbuch*, intitulado *Stöchiometrie* (Estequiometria). A estrutura deste livro, assim como os conteúdos apresentados neste volume, são apresentadas no Quadro 1.

[97] Ver a revisão realizada por NYE. *From Chemical Philosophy to Theoretical Chemistry*. p. 34-36.
[98] Ostwald mostra em diversos escritos sua admiração por Berzelius e Liebig. Ostwald considerava-os exemplos de dois arquétipos de cientistas, o romântico (Liebig) e o clássico (Berzelius), devido às suas diferentes trajetórias. Ver: OSTWALD, Lebenslinien. In: JACK; SCHOLZ, *Wilhelm Ostwald*. p. 379-380.
[99] NYE. *From Chemical Philosophy to Theoretical Chemistry*. p. 64.

Quadro 1 - Estrutura do *Lehrbuch der allgemeinen Chemie* (Volume 1)[100]

Volume 1: Stöchiometrie (1a edição, 1885)	
Primeiro Bloco - Razões de Massa dos Compostos Químicos Capítulo 1. Leis Gerais - Teoria Atômica Capítulo 2. Pesos dos Elementos Químicos *Segundo Bloco - Estequiometria de Substâncias Gasosas* Capítulo 1. As Propriedades Gerais dos Gases Capítulo 2. A Lei de Gay-Lussac e a Hipótese de Avogadro Capítulo 3. A Teoria Cinética dos Gases Capítulo 4. O Calor Específico dos Gases Capítulo 5. As Propriedades Ópticas dos Gases *Terceiro Bloco - Estequiometria de Substâncias Líquidas* Capítulo 1. Propriedades Gerais dos Líquidos Capítulo 2. Relações entre os Estados Gasoso e Líquido Capítulo 3. Razões Volumétricas de Líquidos Capítulo 4. Soluções Capítulo 5. Refração em Líquidos Capítulo 6. Rotação do Plano de Polarização Capítulo 7. Capilaridade	Capítulo 8. Viscosidade de Líquidos Capítulo 9. Difusão e Osmose Capítulo 10. Condutividade Elétrica e Eletrólise Capítulo 11. Magnetismo Capítulo 12. Calor Específico dos Líquidos *Quarto Bloco - Estequiometria de Substâncias Sólidas* Capítulo 1. Propriedades Gerais dos Sólidos Capítulo 2. Volume dos Sólidos Capítulo 3. Cristais Capítulo 4. Isomorfia e Polimorfia Capítulo 5. Propriedades Ópticas de Sólidos Capítulo 6. Mudanças no Estado de Agregação Capítulo 7. Calor Específico Capítulo 8. Condutividade Térmica e Elétrica Capítulo 9. Adsorção *Quinto Bloco - Sistemática* Capítulo 1. A Escolha dos Pesos Atômicos Capítulo 2. A Lei Periódica Capítulo 3. Teoria Molecular Capítulo 4. Teoria de Compostos Químicos

Ostwald iniciou o primeiro capítulo de seu livro apresentando cronologicamente o desenvolvimento das leis ponderais, resgatando os trabalhos de Joseph Proust (1754-1826), Jeremias Richter (1762-1807), John Dalton (1766-1844) e outros. Em seguida, Ostwald introduziu a hipótese atômica de John Dalton e sua relação com as leis ponderais, seguida por um capítulo dedicado às determinações de massa atômica dos elementos químicos. Apesar de se referir aos átomos como uma hipótese ao longo de sua explanação,[101] Ostwald reforçou o valor do atomismo em seu livro, afirmando que a hipótese de Dalton conseguia explicar as relações de massa dos compostos químicos de forma satisfatória, rápida, concisa.[102]

Dando continuidade, Ostwald dedicou o segundo, terceiro e quarto bloco do *Stöchiometrie* à apresentação e discussão de propriedades físico-químicas de gases, líquidos e sólidos, respectivamente, sumarizando diversos trabalhos referentes à características físico-químicas de materiais em cada um destes estados de agregação. Neste quesito, o

[100] OSTWALD. *Lehrbuch* v. 1, p. xvi-xv. Tradução Nossa. Para melhor entendimento da estrutura do livro e compreensão deste artigo, utilizamos a expressão *Bloco* em lugar da tradução literal da palavra alemã *Buch* (Livro) para designar os agrupamentos dos capítulos.

[101] Apesar de considerar o atomismo uma hipótese, o segundo capítulo do seu livro é intitulado *Atomtheorie* (Teoria Atômica). Provavelmente, Ostwald cometeu um pequeno deslize na sua tentativa em diferenciar as teorias científicas de hipóteses.

[102] OSTWALD, *Lehrbuch* v. 1, p. 14-15.

Lehrbuch se diferencia significativamente dos demais livros de sua época, como aqueles escritos por Gmelin e Berzelius. Enquanto estes livros apresentavam um caráter descritivo e normativo, com capítulos específicos para cada um dos elementos químicos conhecidos e as substâncias químicas derivadas, organização baseada em elementos e substâncias químicas conhecidas, Ostwald optou por destacar propriedades físico-químicas dos materiais em diferentes estados físicos, discutindo variadas propriedades dessas substâncias, assim como experimentos encontrados na literatura e seus resultados.

Nos último bloco de seu livro, intitulado *Sistemática*, Ostwald apresentou tópicos relacionados à composição da matéria, as propriedades periódicas dos elementos, e as teorias de constituição molecular. Ao introduzir esses temas, Ostwald retomou o debate sobre a natureza da matéria, ao discutir as vantagens e desvantagens da hipótese atômica em relação à teoria de equivalentes para definir a composição das substâncias químicas. Ele ainda apresentou as principais ideias defendidas em sua época sobre composição química, como a Teoria dos Radicais, a Teoria dos Tipos e a Teoria de Valência, conectando esta última a trabalhos recentes, como a representação tetraédrica para o carbono proposta por van't Hoff.

Ostwald concluiu seu livro afirmando que a Teoria de Valência e a Química Estrutural direcionaram os químicos até a questão sobre quais forças são responsáveis por unir os átomos para formar novas substâncias. Entretanto, ele destacou que este problema só poderia ser compreendido sob a luz da Teoria de Afinidade, a ser discutida no segundo volume da obra:

> "If one asks oneself, whereby the development of the structural schemata, which is apparently ahead of chemistry, can be brought about to a representation of the spatial relation of the atoms, then only one way seems to lead to this result, the investigation of the forces acting between the atoms. (...) But the discussion of these relations belongs to the theory of affinity, to which the second volume of this work is to be dedicated."[103]

Possivelmente, devido a extensão desta obra, Ostwald tenha sido aconselhado a dividir seu livro-texto em dois volumes, facilitando a publicação do mesmo. De qualquer modo, tal

[103] "*Fragt man sich schliesslich, wodurch die der Chemie offenbar bevorstehende Entwicklung der Strukturschemata zu einer Darstellung der räumlichen Beziehung der Atome sich wird bewirken lassen, so scheint nur ein Weg zu diesem Resultat führen zu können, die Erforschung der zwischen den Atomen wirkenden Kräfte. (...) Die Erörterung dieser Verhältnisse aber gehört der Verwandtschaftslehre an, welcher der zweite Band dieses Werkes gewidmet sein soll.*" OSTWALD, *Lehrbuch* v. 1, p. 833. Tradução nossa.

decisão permitiu que Ostwald entrasse em contato e agregasse ao seu texto os trabalhos de Svante Arrhenius e Jacobus H. van't Hoff, que viriam a ser fundamentais para o estabelecimento de uma nova compreensão do problema da afinidade química.

As Pesquisas Sobre Afinidade Química no Século XIX e o impacto dos trabalhos de Arrhenius e van't Hoff

A Teoria de Afinidade química é originária dos antigos conhecimentos práticos sobre o comportamento químico da matéria que, no início do século XVIII, foram incorporados à interpretação mecanicista da natureza.[104] A ideia de relações, poderes ou forças atuando sobre os materiais esteve presente nos trabalhos de filósofos clássicos, alquimistas e posteriormente, filósofos naturais como René Descartes (1596-1650), Nicolas Lémery (1645-1715), Isaac Newton (1642-1727) e Étienne Geoffroy (1672-1731).[105]

A concepção newtoniana sobre as afinidades recebeu grande destaque ao longo do século XVIII e em parte do XIX. Ao final da edição de 1717 do seu tratado *Opticks,*[106] Newton conjecturou a existência de forças de atração e repulsão atuando sobre os constituintes da matéria e ocasionando suas transformações, estabelecendo assim uma analogia entre a força de atração gravitacional e as reações químicas.[107] De forma independente, Geoffroy elaborou a primeira tabela de *relações químicas*[108] em 1718, refletindo uma tradição mecanicista cartesiana sobre as transformações da matéria, que posteriormente foi eclipsada pelo programa mecanicista newtoniano.

Enquanto uma ferramenta teórica química, as afinidades serviam para prever e explicar a ocorrência de alguns tipos de reações (majoritariamente, reações químicas de simples e dupla troca), assim como permitiam aos químicos sistematizar as diversas reações químicas conhecidas desde a Antiguidade com base nas forças relativas entre os diferentes compostos

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[104] QUÍLEZ, Juan. The Role of Theories in Early Studies of Chemical Equilibria. *Bull. Hist. Chem*, v. 31, n. 2, 2006. p. 45-57; KIM, Mi G. *Affinity, That Elusive Dream: a Genealogy of the Chemical Revolution* Cambridge. MIT Press. 2003; BROCK, William H. *The Norton history of chemistry*. New York: W.W. Norton, 1993.
[105] As diferentes correntes que constituíram a ideia de afinidades químicas no século XVIII são retratadas pela historiadora Mi Gyung Kim em *Affinity, That Elusive Dream*. 2003.
[106] NEWTON, Isaac. *Opticks, or, a Treatise of the Reflections, Refractions, Inflections and Colours of Light*. 2ª edição revisada, Londres: 1717.
[107] BENSAUDE-VINCENT; STENGERS. *História da Química*. p. 67-69.
[108] Geoffroy utiliza o termo *Rapport*, que pode ter diferentes significados, a exemplo de relação e afinidade. ver KIM. *Affinity*. p. 113.

químicos.[109] Esse conhecimento sobre as reações foi sistematizado nas Tabelas de Afinidade Química, instrumentos que representavam as substâncias químicas conhecidas e que eram organizadas de acordo com a intensidade das forças relativas de afinidade entre diferentes substâncias.[110]

Apesar do programa newtoniano na Química ter perdido espaço a partir da década de 1830, as afinidades ainda eram uma ferramenta teórica importante. Com a emergência da Termoquímica e Eletroquímica no século XIX, os conceitos de *força* e *afinidade química*, vinculados a uma tradição newtoniana de ciência, foram vinculados - e posteriormente substituídos - pelos conceitos de *energia* e *trabalho*, conceitos surgidos no campo da Termodinâmica clássica.[111]

Alguns cientistas foram importantes para iniciar tal mudança conceitual: entre as décadas de 1850 e 1860, os químicos Julius Thomsen (1826-1909) e Marcellin Berthelot (1827-1907) promoveram a ideia de que as afinidades seriam manifestações do calor liberado pelas reações químicas, contribuindo para um compreensão das afinidades em bases termoquímicas.[112] Em 1882, o físico Hermann von Helmholtz (1821-1894) introduziu considerações termodinâmicas ao analizar as reações químicas envolvidas em uma bateria galvânica, propôs que a afinidade química seria equivalente ao trabalho máximo realizado por uma reação química reversível.[113] Tais contribuições fizeram com que os químicos interessados em determinar as forças de afinidade direcionassem seus estudos às relações de energia, mesmo que, em um primeiro momento, estes químicos e físicos dessem uma abordagem mecânica às suas pesquisas, preferindo utilizar o termo *força* em vez do termo *energia*.[114]

Ao mesmo tempo, percebeu-se que as afinidades não dependiam apenas da natureza das substâncias envolvidas em uma transformação química: Berthollet havia percebido ainda no

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[109] KIM. *Affinity*. p. 132-141.

[110] MOCELLIN, Ronei C. O "sonho newtoniano" de Guyton de Morveau. *Circumscribere*, v. 10, 2011. p. 22-39; BENSAUDE-VINCENT, Bernadette; STENGERS, Isabelle. *História da Química*. trad. Raquel Gouveia. Lisboa: Instituto Piaget, 1992. p. 83-84, 101-106.

[111] NYE. *From Chemical Philosophy to Theoretical Chemistry*. p. 117-118. Sobre o conceito de "energia" ver: MÜLLER, Ingo. *A History of Thermodynamics*: The Doctrine of Energy and Entropy. Berlin Heidelberg: Springer-Verlag GmbH, 2007. p. 9-46.

[112] DOLBY, R. G. A. Thermochemistry versus Thermodynamics: The Nineteenth Century Controversy. *History of Science* v. 22, n. 4, 1984. p. 375-400. SCHELAR. *Chymia*. p. 99-124;

[113] KRAGH, Helge. Between physics and chemistry: Helmholtz's route to a theory of chemical thermodynamics Helge Kragh In: CAHAN, David (ed.). *Hermann Von Helmholtz and the Foundations of Nineteenth-Century Science.* University of California Press, 1993. http://www.jstor.org/stable/10.1525/j.ctt1pnwfn.

[114] Um exemplo pode ser encontrado nos trabalhos do próprio Helmholtz. Em seu "Über die Erhaltung der Kraft" (1847), no qual Helmholtz refere-se à "força" ao discutir sobre a energia cinética. Ver: MÜLLER, Ingo. *A History of Thermodynamics*. p. 9-10; 24-26.

fim do século XVIII a dependência das afinidades com as massas dos reagentes, levando-o a propor que fatores físicos seriam determinantes para as afinidades entre os corpos químicos.[115] Tal constatação contribuiu para a elaboração de métodos para avaliar quantitativamente as afinidades das substâncias químicas, a partir de relações entre afinidades e propriedades físicas das substâncias - a exemplo do calor específico, densidade, índice de refração, entre outras.[116] Nesse contexto, emergem as pesquisas volumétricas e ópticas de Ostwald sobre afinidade química, responsáveis por alavancar sua carreira.

Apesar dos seus trabalhos iniciais terem recebido destaque por parte comunidade científica, Ostwald era apenas mais um dentre outros químicos interessados nesse tema que vinham fazendo importantes descobertas nas últimas décadas sobre este campo de pesquisa. Um destes químicos era o estudante sueco Svante Arrhenius (1859-1927).

Durante seu doutorado na então provinciana Universidade de Uppsala, Arrhenius foi orientado pelo químico inorgânico Per Teodor Cleve (1840-1905) e pelo físico Tobias Thalén (1827-1905), mas não se interessava pelas linhas de pesquisa de nenhum destes cientistas. Seu interesse inicial era determinar pesos moleculares de açúcares a partir da condutividade destas substâncias em solução, porém este tema acabou se tornando obsoleto antes que Arrhenius pudesse concluir suas pesquisas, devido ao método de medida de pesos moleculares a partir dos pontos de fusão e ebulição das substâncias, proposto por François-Marie Raoult (1830-1901).[117]

Arrhenius redirecionou sua tese ao comportamento de eletrólitos, compreendidos como substâncias que em meio aquoso são capazes de conduzir eletricidade.[118] Em sua tese de doutorado, intitulada *Recherches sur la conductivité galvanique des électrolytes*,[119] ele realizou diversas medidas de condutividade de ácidos, bases e sais em diferentes graus de

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[115] QUÍLEZ, Juan. From Chemical Forces to Chemical Rates: A Historical/Philosophical Foundation for the Teaching of Chemical Equilibrium. *Science & Education,* v. 18, 2009. p. 1203–1251. https://doi.org/10.1007/s11191-006-9048-4

[116] NYE, Mary Jo. *Before big science: the pursuit of modern chemistry and physics, 1800 - 1940*. Cambridge, Mass. [u.a.]. Harvard University Press. 1999. p. 95.

[117] WISNIAK, Jaime. François-Marie Raoult: Past and Modern Look. *The Chemical Educator*. v. 6, n.1, 2001. p. 41-49. https://doi.org/10.1007/s00897000432a

[118] COFFEY. Patrick. *Cathedrals of Science*: The Personalities and Rivalries That Made Modern Chemistry. London. Oxford University Press. 2008. p. 11-13

[119] ARRHENIUS, Svante. *Recherches sur la conductibilité galvanique des électrolytes.* Kongl. Boktryckeriet, 1884.

diluição e em solventes distintos.[120] A partir destes valores, ele pôde determinar a condutividade das soluções de cada substância em diferentes condições.[121]

Figura 1 - Svante Arrhenius enquanto doutorando da Universidade de Uppsala, 1878 (fotografia extraída de ARRHENIUS, Gustaf; DAHLGREN, Caldwell; WOLD, Svante. *A Tribute to the Memory of Svante Arrhenius (1859-1927)*. Stockholm: Royal Swedish Academy of Engineering Sciences, 2008.

Dentre as conclusões e hipóteses resultantes de sua pesquisa, duas merecem nosso destaque: Arrhenius percebeu que a força dos ácidos, isto é, de maior afinidade química, era diretamente proporcional à condutividade dessas substâncias em solução, sendo possível avaliar a afinidade de um ácido medindo a passagem de corrente elétrica pela solução.[122] Porém, para que as moléculas conduzissem corrente elétrica, seria necessário que elas estivessem em um estado apto para tal, chamado por Arrhenius de *estado ativo*. Arrhenius também afirmou que estas moléculas em estado ativo seriam as responsáveis pela afinidade química dos ácidos em solução, visto que ácidos fortes, isto é, de maior afinidade química frente a um reagente definido, apresentavam maior condutividade.[123] Todavia, Arrhenius não conseguiu explicar satisfatoriamente o que despertaria o estado ativo das moléculas.

O trabalho de Arrhenius foi mal recebido pelos seus orientadores, que atribuíram à sua tese uma nota mediana, com a qual dificilmente ele conseguiria uma posição como professor

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[120] ARRHENIUS. *Recherches sur la conductibilité galvanique des électrolytes.* p. 5-18.
[121] SNELDERS, H. A. M. Arrhenius, Svante. In: GILLISPIE, Charles Coulston; HOLMES, Frederic L. (ed.). Dictionary of Scientific Biography. 13. New York. Scribner. 1981. p. 298.
[122] ARRHENIUS. Recherches sur la conductibilité galvanique des électrolytes. p. 19-45.
[123] COFFEY, *Cathedrals of Science*. p. 14.

em alguma universidade.[124] Insatisfeito com repercussão negativa do seu trabalho e acreditando que suas hipóteses tinham fundamento, Arrhenius enviou cópias de sua tese para vários químicos na Europa. Um destes químicos foi Ostwald.

Em 1884, um ano antes da publicação do *Lehrbuch*, Ostwald recebeu uma cópia da tese de Arrhenius. Apesar do estranhamento inicial, Ostwald percebeu que os resultados de Arrhenius guardavam semelhança com os valores de afinidade química que obteve utilizando o método volumétrico. Assim, mesmo discordando de alguns aspectos do trabalho, Ostwald reconheceu o valor da abordagem empregada por seu colega sueco:

> "(...) What he'd written was so contrary to everything that was known and accepted that at first I thought it must be nonsense. But then I saw that the obviously very young author had presented some calculations of the chemical affinity of the acids which agreed with the values that I'd already reached from a completely different starting point. Finally, having read the paper in detail I convinced myself that (...) he had looked at the problem in a much more generally applicable way and had, to some extent, even solved parts of it."[125]

Em vez de considerar Arrhenius um adversário, Ostwald optou por colaborar com o colega sueco. Após um período de intensa correspondência entre estes químicos, Ostwald resolveu visitar Arrhenius em Uppsala no verão de 1884, estabelecendo uma duradoura amizade.[126] Durante sua estadia, ele fez o possível para defender as ideias sobre dissociação eletrolítica de seu amigo, mal recebidas devido a avaliação realizada por Thalén e Cleeve. Ostwald também fez uma rápida menção à Arrhenius no primeiro volume do seu livro, mas sem destacar seu método para medida de afinidades. Estes trabalhos seriam apresentados detalhadamente no segundo volume da obra.

Contudo, o trabalho de Arrhenius não foi o único a exercer profundo impacto nas ideias de Ostwald sobre afinidade química. Outra obra de fundamental importância foi o livro *Études de dynamique chimique*,[127] escrito pelo químico holandês Jacobus Henricus van't Hoff (1852-1911). Trabalhando na Escola Veterinária de Utrecht, van't Hoff já havia ganhado considerável notoriedade pela sua proposta de representação espacial tetraédrica para as

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[124] COFFEY. *Cathedrals of Science*. p. 14.

[125] OSTWALD, *Lebenslinien*. In: JACK; SCHOLZ, *Wilhelm Ostwald: the Autobiography*. p. 114.

[126] As correspondências entre Ostwald, Arrhenius e van't Hoff foram publicadas pelo historiador da química Hans-Günther Körber. Ver: KÖRBER, Hans-Günther (ed.). *Aus Dem Wissenschaftlichen Briefwechsel Wilhelm Ostwalds*: 2. Teil. Berlin: Akademie-Verlag, 1969.

[127] VAN'T HOFF, Jacobus H. *Études de dynamique chimique.* Amsterdam: Frederik Muller, 1884.

moléculas orgânicas, também desenvolvida de forma independente por Joseph Le Bell (1847-1930).[128] Posteriormente, van't Hoff deixou a estereoquímica em segundo plano e direcionou seu interesse para o equilíbrio químico das reações e a afinidade química, utilizando uma abordagem termodinâmica para os mesmos.

Publicado em 1884, os *Études* mostram como a termodinâmica aliada aos estudos cinéticos poderiam ser utilizadas para compreender os fatores determinantes para a ocorrência das reações químicas.[129] Além de aplicar a Termodinâmica fenomenológica às reações químicas em equilíbrio, van't Hoff mostrou que as forças de afinidade química eram equivalentes à quantidade de trabalho realizado por uma reação química.[130] Tal conclusão é semelhante àquela obtida por Helmholtz em 1882, entretanto, o trabalho de van't Hoff possuiu um ponto de partida completamente distinto - reações químicas em equilíbrio - tornando seu trabalho completamente original.

Enquanto buscava materiais sobre afinidade química para a conclusão do segundo volume do *Lehrbuch*, Ostwald encontrou os trabalhos de van't Hoff sobre afinidade química, conforme relatado em sua autobiografia:

> "(...) I was getting the last part of the textbook ready. This was the most difficult section of the book because it should describe the current state of knowledge about the field of chemical affinity. Shortly before this, I'd read a publication that caused me even more headaches than had that of Arrhenius. It was entitled *Études de dynamique chimique* and had been written by J. H. van't Hoff. It described both theoretical and experimental studies of the laws governing the rates of chemical reactions. (...) the author had made considerably greater advances in the application of thermodynamics to chemistry than had Horstmann—or I."[131]

Assim como ocorreu com Arrhenius, Ostwald estabeleceu comunicação com van't Hoff, de modo que ainda em 1886, estes químicos começaram a planejar a publicação de outro

[128] BELTRAN, Maria Helena Roxo. O tetraedro de Van't Hoff: algumas considerações sobre o papel dos modelos na história da química e no ensino. *IX Enpec-Encontro Nacional de Pesquisa em Educação em Ciências*–Águas de Lindóia, 2013; ROCKE, Alan J. Kolbe Versus the "Transcendental Chemists": the Emergence of Classical Organic Chemistry, *Ambix*, v. 34, n. 3, 1987. p. 156-168, DOI: 10.1179/amb.1987.34.3.156; MEIJER, E. W. Bert. Jacobus Henricus van't Hoff; Hundred years of impact on stereochemistry in the Netherlands. *Angewandte Chemie International Edition*, v. 40, n. 20, p. 3783-3789, 2001.

[129] SERVOS. *From Ostwald to Pauling*. p. 25-30; RAMBERG, Peter. Jacobus Henricus van't Hoff. *Encyclopædia Britannica*. Encyclopædia Britannica, inc., August 26, 2018. <https://www.britannica.com/biography/Jacobus-Henricus-van-t-Hoff> accessed 05 November 2018;

[130] SNELDERS, Henricus A. M. van 't Hoff, Jacobus Henricus. In: GILLISPIE, Charles Coulston; HOLMES, Frederic L. (ed.). Dictionary of Scientific Biography. 13. New York. Scribner. 1981. p. 577-580.

[131] OSTWALD, *Lebenslinien*. In: JACK; SCHOLZ, *Wilhelm Ostwald*. p. 123.

importante marco para a institucionalização da Físico-química, o *Zeitschrift für Physikalische Chemie* (Revista de Físico-química), o primeiro periódico especializado em Físico-química do mundo, editado por Ostwald e van't Hoff, cujo primeiro número foi publicado em Fevereiro de 1887.[132]

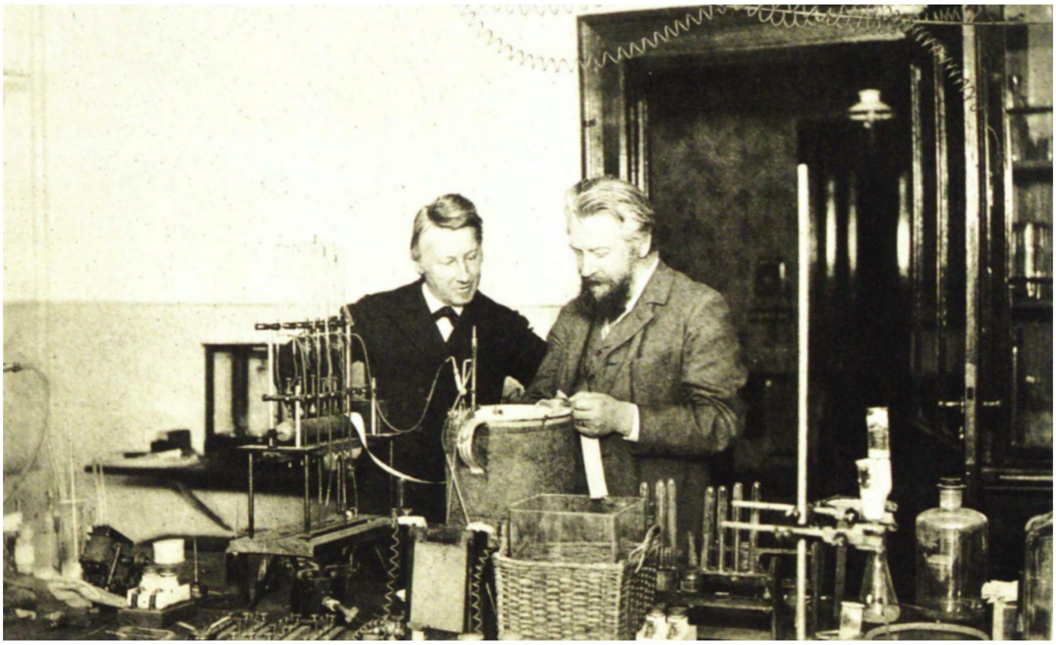

Figura 2 - Wilhelm Ostwald recebe Jacobus Henricus van't Hoff em seu laboratório em 1900 (fotografia publicada no *Zeitschrift für Physikalische Chemie*, v. 9, n. 50, 1905).[133]

A interação entre Ostwald, Arrhenius e van't Hoff contribuiria posteriormente para o estabelecimento da base teórico-conceitual e metodologias empregadas pela físico-química moderna, a exemplo da relevante Teoria de Dissociação Eletrolítica proposta por Arrhenius em 1887, elaborada a partir dos trabalhos de van't Hoff sobre pressão osmótica.[134]

Mas antes desta teoria se tornar popular e os químicos se voltarem ao comportamento dos íons em solução, as pesquisas sobre afinidade química aproximaram alguns dos campos de investigação que formaram a moderna Físico-química e permitiram à Arrhenius, van't Hoff

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132 HIEBERT, Erwin N. Developments in physical chemistry at the turn of the century. In: BERNHARD, Carl G.; CRAWFORD, Elisabeth; SÖRBOM, Per (org.) *Science, Technology & Society in the Time of Alfred Nobel*. Oxford: Pergamon Press, 1982. p. 106-107; HAPKE, Thomas. *Die Zeitschrift für Physikalische Chemie*: Hundert Jahre Wechselwirkung zwischen Fachwissenschaft, Komunikationsmedium und Gesselschaft. Herzberg: Verlag Tragott Bautz, 1990.

133 Sobre esta fotografia, assim como outras tiradas na mesma ocasião, ver FOULK, C. W. The Ostwald-van't Hoff photograph and other memories of Ostwald's laboratory. *Journal of Chemical Education*. v. 11, n. 6, 1934. p. 355-359. doi:10.1021/ed011p355.

134 DE MOURA SOUZA, Felipe; ARICÓ, Eliana Maria. Teorias ácido-base no século XX e uma análise reflexiva do trabalho científico. *Educación química*, v. 28, n. 4, 2017. p. 211-216; COFFEY. Cathedrals of Science, p. 20-23.

e Ostwald tornarem-se seus principais representantes. Deste modo, mais do que aproximar diferentes campos de pesquisa, Ostwald sintetizou o conhecimento até então produzido sobre as afinidades químicas e promoveu seus próprios trabalhos - assim como os de Arrhenius e van't Hoff - nas páginas da segunda edição do seu *Lehrbuch*.

Entre Forças e Energias, sob o Mecanicismo: Verwandtschaftslehre (1887)

Tendo como objetivo central do segundo volume do *Lehrbuch* introduzir e explicar a Teoria de Afinidades Químicas, Ostwald se viu impelido a apresentar diferentes tipos de fenômenos que influenciam na ocorrência das reações químicas. Alguns deles já eram conhecidos há muito tempo, como o calor. Outros fenômenos tiveram sua relação com as transformações químicas percebida apenas no início do século XIX, como a luz, a eletricidade e o magnetismo.

Ao longo deste mesmo século, campos de pesquisa se organizaram em torno da interação entre as reações químicas e de diferentes formas de energia.[135] Alguns destes campos foram a Termoquímica, a Eletroquímica e a Fotoquímica; áreas cujo objetivo era compreender como diferentes manifestações energéticas - o calor, a eletricidade e a luz - influenciavam na transformação da matéria, isto é, nas afinidades das substâncias químicas. Deste modo, cada uma destas subdisciplinas mostrou a necessidade de compreender as afinidades químicas sob outras bases, contribuindo para o abandono das ideias mecanicistas sobre as afinidades.

Ao mesmo tempo, muitos dos praticantes destes campos de pesquisa, responsáveis pela formulação de suas leis e teorias, compreendiam os seus respectivos fenômenos de interesse a partir de um paradigma mecanicista. Não por acaso, fenômenos como o calor, a eletricidade, a luz e as próprias reações químicas tentaram ser compreendidos a partir de explicações de base mecânica ao longo da história.[136]

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[135] Além dos já citados *Before Big Science* (1999) de Mary Jo Nye, e *The World of Physical Chemistry* (1993) de John Laidler, que mostram o desenvolvimento destes campos de pesquisa, podemos indicar as seguintes leituras: SCHELAR, Virginia M. Thermochemistry and the Third Law of Thermodynamics. *Chymia*. v. 11, 1966. p. 99-124; KRAGH, Helge. Confusion and controversy: Nineteenth-century theories of the voltaic pile. BEVILACQUA, Fabio; FREGONESE, Lucio (ed.) *Nuova Voltiana,* Studies on Volta and his Times, v. 1, Milão: Hoepli, 2000. p. 133-157.

[136] Há várias pesquisas sobre estas teorias, de modo que apresentaremos apenas alguns textos aqui: SABRA, Abdelhamid I. *Theories of light: from Descartes to Newton*. CUP Archive, 1981; FRANKEL, Eugene. Corpuscular Optics and the Wave Theory of Light: The Science and Politics of a Revolution in Physics. *Social Studies of Science*, v. 6, n. 2, 1976. p. 141–184. https://doi.org/10.1177/030631277600600201; GOMES, Luciano

Utilizando as afinidades químicas como um elo entre campos de pesquisa diferentes, Ostwald publicou o segundo volume do seu *Lehrbuch der allgemeinen Chemie* no início de 1887, livro este que recebeu o subtítulo de *Verwandtschaftslehre* (Teoria de Afinidades).[137] Este livro foi dividido em duas partes: a primeira, foi intitulada de *Chemischen Energie* (Energia Química), dado o seu objetivo em mostrar as relações entre diferentes formas de energia e as reações químicas. Já a segunda parte consiste em uma aprofundada apresentação sobre a pesquisa referente às Afinidades Químicas, e por isso recebeu o mesmo nome que o subtítulo da obra, *Verwandtschaftslehre*. A estrutura do livro é apresentada no Quadro 2.

Quadro 2 - Estrutura do *Lehrbuch der allgemeinen Chemie* (Volume 2)[138]

Verwandtschaftslehre (1ª edição, 1887)	
Parte 1 - Energia Química	Parte 2 - A Teoria de Afinidades
Primeiro Bloco - Termoquímica Capítulo 1. A Energia Capítulo 2. Aspectos Gerais sobre Termoquímica Capítulo 3. Termoquímica de Não-Metais Capítulo 4. Formação de Sais em Soluções Aquosas Capítulo 5. Termoquímica de Metais Capítulo 6. Termoquímica de Compostos Orgânicos Capítulo 7. A Segunda Lei Geral da Teoria Mecânica do Calor *Segundo Bloco - Fotoquímica* Capítulo 1. Aspectos Gerais Capítulo 2. Actinometria Capítulo 3. As Leis do Efeito Fotoquímico Capítulo 4. Fotoquímica Especial Capítulo 5. Hipóteses sobre a Fotoquímica *Terceiro Bloco - Eletroquímica* Capítulo 1. Bases Gerais Capítulo 2. Força Eletromotriz Capítulo 3. Relações de Massa entre Energia Química e Elétrica Capítulo 4. Fluxo de Eletrólitos	*Primeiro Bloco - História da Teoria de Afinidades* Capítulo 1. História das Teorias Químicas Capítulo 2. História das Antigas Determinações de Afinidade Capítulo 3. História das Modernas Determinações de Afinidade *Segundo Bloco - Mecânica Química* Capítulo 1. Cinética Química Capítulo 2. Equilíbrio Químico Capítulo 3. Dissociação Capítulo 4. Aplicação da Teoria Mecânica do Calor ao Problema do Equilíbrio Químico Capítulo 5. Influência da Temperatura nos Estados de Equilíbrio e Taxas de Reação Capítulo 6. Influência da Teoria Cinético-Molecular na Mecânica Química *Terceiro Bloco - Medidas de Afinidade Química* Capítulo 1. Métodos Capítulo 2. A Afinidade entre Ácidos e Bases Capítulo 3. Coeficientes de Afinidade Específicos Capítulo 4. Relações Eletroquímicas Capítulo 5. Influência da Natureza, Composição e Constituição das Substâncias sobre suas Afinidades

Carvalhais. A ascensão e queda da teoria do calórico. *Caderno brasileiro de ensino de Física*, v. 29, n. 3, 2012. p. 1030-1073; LIVENS, George Henry. The theory of electricity. Cambridge University Press, 2016.

[137] OSTWALD, Wilhelm. *Lehrbuch der allgemeinen Chemie*. v. 2, Verwandtschaftslehre. Leipzig: Verlag von W. Engelmann, 1887.

[138] OSTWALD, Wilhelm. *Lehrbuch der allgemeinen Chemie*. Bd: 2, Verwandtschaftslehre. Leipzig: Verlag von W. Engelmann, 1887. Tradução nossa. Para melhor entendimento da estrutura do livro e compreensão deste artigo, utilizamos a expressão *Bloco* em lugar da tradução literal da palavra alemã *Buch* (Livro) para designar os agrupamentos dos capítulos.

Ostwald iniciou seu livro diferenciando-o do volume anterior, *Stöchiometrie*. Defendendo a necessidade em se compreender fenômeno químico em si, Ostwald defende a investigação sobre como as reações químicas acontecem e quais suas causas, justificando a importância de se debruçar sobre a Teoria de Afinidades Químicas:

> "The relations which exist between the different properties of the same substance, as well as between the corresponding properties of different substances, and whose epitome constitutes Stoichiometry, presuppose the considered substances as such. But the substances are not immediately given and unchanging; they arise and are transformed in manifold ways. The study of the processes conditioning and accompanying these transformations is the task of Affinity Theory. Thus, while Stoichiometry deals with the rational knowledge of what has become of the chemical world, Affinity is concerned with the exploration of becoming."[139]

Ainda no primeiro capítulo, Ostwald apresenta brevemente as origens da Teoria de Afinidades. Em sua narrativa, ele ressaltou que esta teoria possui origem mecanicista, mas que ao longo do século XIX, ela recebeu contribuições importantes vindas da Eletroquímica e Termoquímica. Entre essas contribuições, Ostwald destacou a determinação do equivalente mecânico do calor e o desenvolvimento da Lei de Conservação da Energia para uma nova compreensão sobre as afinidades químicas, visto que graças à estes trabalhos:

> "It was realized that it was useless to make tentative assumptions about the nature of a force whose laws were unknown and whose intensity could not be measured. Instead, it was found in the recognition that the effects of chemical affinity in the last instance are equivalent to the effects of any other forces, especially the mechanical ones, a means of obtaining the generally valid propositions without knowing the particular nature of these laws."[140]

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[139] "*Die Beziehungen, welche zwischen den verschiedenen Eigenschaften desselben Stoffes, sowie zwischen den entsprechenden Eigenschaften verschiedener Stoffe bestehen, und deren Inbegriff die Stöchiometrie bildet, setzen die betrachteten Stoffe als solche fertig gebildet voraus. Die Stoffe aber sind nichts unmittelbar gegebenes und unveränderliches; sie entstehen und verwandeln sich in mannigfaltiger Weise. Die Erforschung der Vorgänge, welche diese Umwandlungen bedingen und begleiten, ist die Aufgabe der Verwandtschaftslehre. Während also die Stöchiometrie die rationelle Kenntnis des in der chemischen Welt Gewordenen zum Gegenstande hat,'befasst sich die Verwandtschaftslehre mit der Erforschung des Werdens*." OSTWALD. *Lehrbuch* v. 2, p. 1. Tradução Nossa.

[140] "*Man sah ein, dass es zwecklos ist, vorläufige Annahmen über die Natur einer Kraft zu machen, deren Gesetze man nicht kannte, und deren Größe man nicht zu messen vermochte. Statt dessen fand man in der Erkenntnis, dass die Wirkungen der chemischen Verwandtschaftskräfte in letzter Instanz gleichwertig sind den Wirkungen irgendwelcher anderer Kräfte, insbesondere der mechanischen, ein Mittel, durch Anwendung der*

Deste modo, Ostwald se distanciou dos interesses de alguns dos seus antecessores que buscavam definir a natureza das forças de afinidade química, e defendeu a busca das leis da Afinidade Química por meio de relações de correspondência ou equivalência com outros tipos de forças ou energias que poderiam ser medidas. Deste modo, Ostwald explorou a relação das afinidades com outras formas de energia na primeira parte do seu livro, refletidas nos blocos *Termoquímica*, *Fotoquímica* e *Eletroquímica* (ver Quadro 2). Estes blocos também serviram para introduzir as bases teóricas de pesquisas que seriam apresentadas na segunda parte do *Lehrbuch*.

A Termoquímica recebeu atenção especial no *Lehrbuch*. Além de introduzir os principais fundamentos teóricos desta área, Ostwald apresentou uma compilação de dados termoquímicos para variadas substâncias, o que tornou esta obra não apenas um livro-texto, mas também um *handbook*. Mas para além dos dados termoquímicos, Ostwald faz neste bloco uma relevante revisão sobre a relação entre calor e afinidade química, resgatando os trabalhos do químico suíço Germain Henry Hess e dos já citados Julius Thomsen e Marcellin Berthelot, estes últimos responsáveis por estabelecer a crença de que o calor liberado nas reações químicas seria equivalente à afinidade química entre as substâncias reagentes. Além de apresentar seus trabalhos, Ostwald comparou os valores obtidos por estes químicos para calores de reação de diferentes processos químicos. Destaca-se também sua apresentação para as Leis da Termodinâmica - chamadas por Ostwald de Primeira e Segunda Lei Mecânica do Calor.

Em seguida, Ostwald apresentou a área da Fotoquímica. Apesar deste campo não ter fornecido teorias ou conceitos importantes para a consolidação para a Teoria de Afinidades Químicas, ele mostra, a partir das reações químicas envolvidas no Daguerreótipo,[141] como a luz pode afetar as afinidades químicas das substâncias. Ostwald também apresentou alguns métodos ópticos, a exemplo da Actinometria; discutiu os processos de absorção e emissão da luz pelas substâncias químicas; apresentou leis matemáticas para estes fenômenos; apresentou

allgemein gültigen Sätze auch ohne Kenntnis der besonderen Beschaffenheit jener eine Reihe von wirklichen Gesetzen zu erlangen." OSTWALD. *Lehrbuch*, v. 2, p. 4. Tradução Nossa.

[141] A daguerreotipia foi o primeiro método fotográfico criado. A produção das imagens se dava pela exposição de uma chapa de cobre, revestida de prata sensibilizada pelo vapor de iodo, que em contato com a luz transforma os cristais de iodeto de prata em prata metálica, da qual a imagem era revelada pelo vapor de mercúrio e fixada com hipossulfito de sódio. Sobre a história desse processo fotográfico, ver: SANT'ANNA, Caroline V. Do daguerreótipo às manipulações artísticas: uma breve história da fotografia brasileira. In: *Cultura Visual*, n. 16, dezembro/2011, Salvador: EDUFBA, p. 47-57.

uma síntese das pesquisas recentes sobre Fotossíntese e introduziu algumas hipóteses sobre a influência da luz sobre os constituintes da matéria.

Na parte de seu livro destinada à Eletroquímica, Ostwald mostrou como diferentes tipos de energia - elétrica, química e térmica - estavam envolvidas nos fenômenos eletroquímicos, com base no princípio de conservação da energia. Em sua apresentação sobre a eletrólise e o comportamento químico de eletrólitos, Ostwald apresentou as contribuições de diversos químicos e físicos para o entendimento dos fenômenos eletroquímicos, como as Leis da Eletrólise de Michael Faraday (1791-1867), as de Helmholtz sobre força eletromotriz os trabalhos de August Horstmann (1842-1929), pioneiro na utilização da Termodinâmica fenomenológica para avaliar o equilíbrio das reações químicas e as afinidades químicas dos reagentes.

Mesmo aproximando diferentes tipos de energia aos fenômenos químicos, Ostwald é notavelmente mecanicista em sua obra. Seu discurso ao longo do seu *Lehrbuch* sugere que ele compreendia a Físico-química uma ciência de bases mecânicas, e que a Eletroquímica, a Termoquímica e a Fotoquímica seriam desdobramentos do paradigma mecanicista. Estas áreas, por sua vez, teriam o objetivo de compreender como diferentes fenômenos energéticos interferiam na dinâmica das reações químicas. Indícios desta postura reducionista são encontrados na segunda parte do *Lehrbuch*, dedicada à Teoria de Afinidades Químicas, que apresentaremos a seguir.

A segunda parte do *Lehrbuch* se inicia a apresentação do desenvolvimento histórico da Teoria de Afinidades. Seguindo uma linha do tempo que abrange desde a Antiguidade clássica até o século XIX, Ostwald apresentou as principais hipóteses e teorias utilizadas para explicar as transformações químicas. Ele resgatou as ideias de filósofos gregos sobre a transformação da matéria e seguiu sua cronologia passando pelo corpuscularismo alquímico, as ideias mecanicistas sobre afinidade química, pelo dualismo eletroquímico berzeliano, pelas investigações quantitativas da metade do século XIX, até chegar ao seu tempo, concluindo convenientemente sua narrativa nas contribuições feitas por Arrhenius, van't Hoff e por ele próprio para o campo das afinidades químicas.[142]

[142] Ostwald apresenta as ideias mais antigas sobre as Afinidades Químicas nos dois primeiros capítulos da segunda parte do *Lehrbuch* (Capítulo 1. História das Teorias Químicas, Capítulo 2. História das Antigas Determinações de Afinidade). Os seus próprios trabalhos, assim como os de contemporâneos, como por exemplo as pesquisas de Cato Guldberg e Peter Waage, Arrhenius e van't Hoff, foram apresentados em um capítulo em separado (Capítulo 3. História das Modernas Determinações de Afinidade) e retomadas diversas vezes ao longo do livro.

A abordagem histórica comum à escrita de Ostwald se aliou no segundo volume do *Lehrbuch* ao frequente uso da escrita em primeira pessoa. Ainda que seja possível perceber o uso de uma narrativa pessoal ainda em seu *Stöchiometrie*, foi no segundo volume do *Lehrbuch* que Ostwald a utilizou de forma mais frequente. Tal estilo de apresentação - que evidencia a opinião do autor e destaca o relato pessoal dos eventos - certamente teve um papel importante na promoção de Ostwald, Arrhenius e van't Hoff como os principais representantes da Físico-química ainda em seu processo de institucionalização.

Ostwald não escondia em sua narrativa o desejo de publicizar os trabalhos desenvolvidos por ele e seus companheiros. Ele apresentou uma síntese de suas investigações sobre medidas de afinidade química, assim como apresentou os *Études* de van't Hoff e a criticada tese de doutoramento de Arrhenius sobre condutibilidade elétrica, defendendo que estes trabalhos solucionaram antigos problemas da Teoria de Afinidade Química.[143]

Os *Études* de van't Hoff receberam grande destaque no *Lehrbuch*. Ostwald afirmou que van't Hoff era um importante "criador de hipóteses frutíferas e originais"[144] e, portanto, ele dedicou um amplo espaço para apresentar a abordagem termodinâmica das reações em equilíbrio químico proposta por este químico holandês, assim como sua abordagem para as afinidades químicas:

> "In the last part [of *Études*] the affinity is discussed. From measurements of Pfeffer on the osmotic pressure of saline solutions against pure water, the affinity to the latter is measured in mechanical measure. Thermodynamic considerations lead to consistent results from the reduction in vapor pressure that such solutions show relative to pure water. Further considerations provide an expression of the work that affinity can afford. It corresponds to the above given expression for the work convertible part of the heat, if for the upper temperature the transition point, that is to say the temperature at which the chemical process in question can be voluntary in both senses, is used. The application of this formula to the electromotive forces gives a principal agreement with the results of Braun.
>
> This review illuminates the very significant advancement that chemical mechanics has experienced through the book of van't Hoff. Of course, some of the author's conclusions still require confirmation and experimental basis, but the wealth of ideas and the variety of applications has an undoubted and lasting word."[145]

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[143] OSTWALD. *Lehrbuch*. v. 2. p. 760-768.
[144] OSTWALD. *Lehrbuch*. v. 2. p. 611.
[145] Trecho completo: "*Im letzten Teile wird die Affinität besprochen. Aus Messungen von "Pfeffer" über den osmotischen Druck von Salzlösungen gegen reines Wasser wird die Affinität zu letztcrem in mechanischem Mass gemessen. Entsprechende thermodynamische Betrachtungen führen zu übereinstimmenden Ergebnissen aus der*

Além de apresentar um resumo dos *Études*, Ostwald apresentou os métodos para determinação do fator de correção *i* por van't Hoff, ao aplicar a lei dos gases ideais para soluções. Os trabalhos de van't Hoff sobre o fator *i* seriam sumarizados em um artigo publicado no *Zeitschrift* [146] e a partir destas pesquisas, Arrhenius viria desenvolver sua Teoria de Dissociação Eletrolítica, apresentada poucos meses após a publicação do *Lehrbuch*.

As pesquisas de Arrhenius sobre condutividade elétrica também foram defendidas por Ostwald ao longo da sua apresentação histórica sobre a Teoria de Afinidades. Ostwald mostrou como os valores de condutividade elétrica obtidos por Arrhenius estavam em concordância com os resultados de sua própria pesquisa, o que indicava a validade do método empregado por Arrhenius:

> "The material on which Arrhenius was able to base his theory, and especially the preceding proposition, was not a great one, yet it was enough to prove the undoubted parallelism of the two magnitudes.
>
> At the same time I had begun experimenting with the analogy between the reaction velocities I measured at that time and the electrical conductivities of various acids determined by Kohlrausch and Lenz. After Arrhenius' work (whose theoretical part was handed over to the Swedish Academy in June 1883) was published in 1884 and became known to me, I was soon able to compare it to 34 different acids whose affinity and velocity coefficients I had measured by different methods of the electrical conductivity and found, in confirmation of the theorem of Arrhenius, a close parallelism of both."[147]

Verminderung des Dampfdruckes, den solche Lösungen im Verhältnis zu reinem Wasser zeigen. Weitere Betrachtungen ergeben einen Ausdruck für die Arbeit, welche die Affinität leisten kann. Derselbe entspricht dem oben gegebenen Ausdruck für den in Arbeit verwandelbaren Teil der Wärme, wenn für die obere Temperatur der Übergangspunkt, dass heißt die Temperatur, bei welchem der fragliche chemische Vorgang in beiderlei Sinn freiwillig verlaufen kann, eingesetzt wird. Die Anwendung dieser Formel auf die elektromotorischen Kräfte ergiebt eine prinzipielle Übereinstimmung mit den Ergebnissen von Braun. Aus diesem Überblick erhellt die sehr bedeutende Förderung, welche die chemische Mechanik durch das Buch von van't Hoff erfahren hat. Freilich bedürfen manche Schlussfolgerungen des Autors noch sehr der Bestätigung und experimentellen Durcharbeitung, doch hat die Fülle der Ideen und die Mannigfaltigkeit der Anwendungen einen unzweifelhaften und dauernden Wort." OSTWALD. *Lehrbuch*. v. 2. p. 613.

[146] VAN'T HOFF, Jacobus H. Die Rolle des osmotischen Druckes in der Analogie zwischen Lösungen und Gasen. *Zeitschrift für Physikalische Chemie*, v. 1, n. 1, 1887. p. 481–508.

[147] "*Das Material, auf welches Arrhenius seine Theorie und speziell den vorstehenden Satz stützen konnte, war kein grosses, doch genügte es immerhin, um den unzweifelhaften Parallelismus beider Grössen zu erweisen. Zu derselben Zeit hatte ich begonnen, die Analogie, welche sich zwischen den damals von mir gemessenen Reaktionsgeschwindigkeiten und den von Kohlrausch und Lenz bestimmten elektrischen Leitfähigkeiten verschiedener Säuren herausstellte, experimentell zu verfolgen. Nachdem Arrhenius' Arbeit (deren theoretischer Teil der schwedischen Akademie im Juni 1883 übergeben wurde) 1884 veröffentlicht und mir bekannt geworden war, konnte ich alsbald an 34 verschiedenen Säuren, deren Affinitäts-, resp. Geschwindigkeitskoeffizienten ich nach verschiedenen Methoden gemessen hatte, den Vergleich mit der elektrischen Leitfähigkeit durchführen und*

Ostwald afirmou ter provado a validade da hipótese da proporcionalidade entre afinidade e condutividade elétrica ao comparar os resultados obtidos pelos métodos volumétrico e eletroquímico para as afinidades de 34 ácidos diferentes.[148] Frente à correspondência entre os valores obtidos por Arrhenius e os seus próprios, ele afirmou que "o fato da lei é incontestável, e apenas surge a questão de quais desvios existentes podem ser explicados."[149]

Ostwald ainda apresentou em seu livro a hipótese das moléculas eletricamente ativas, ideia fundamental para o desenvolvimento da Teoria de Dissociação Eletrolítica, apresentada à comunidade científica alguns meses após a publicação do *Lehrbuch*:

> "The author concludes from his own measurements that in the state of extreme dilution all salts of the same base have the same conductivity. The same thing must be valid to the 'hydrogen salts', the acids, which he attributes to the great differences that exist at medium dilutions, that only part of the molecules are in the 'active' state, that is, participate in the processes of the double exchange could. With increasing dilution, this fraction becomes larger and larger, becoming one at infinite dilution. On the cause of the ineffective state, he hypothesizes that it is due to a 'complexity' of the molecules, a conglomeration of them to larger aggregates."[150]

Contudo, mais do que apresentar e defender os trabalhos de outros químicos, o *Lehrbuch* foca nas opiniões e no trabalho de Ostwald. Suas pesquisas iniciais, assim como as mais recentes, sobre afinidades químicas e cinética de reações são apresentadas em várias partes do livro. Dando destaque ao desenvolvimento dos seus métodos volumétrico e óptico

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fand, in Bestätigung des Satzes von Arrhenius, einen engen Parallelismus beider." OSTWALD. *Lehrbuch*. v. 2. p. 608. Tradução nossa.

[148] Ostwald apresenta em seu livro uma tabela com os valores obtidos utilizando ambos os métodos. ver OSTWALD. *Lehrbuch*, v. 2. p. 823-824.

[149] Trecho completo: "*Doch ist die nahe Beziehung der Werte so schlagend, dass das Thatsächliche des Gesetzes ausser Zweifel steht, und nur die Frage aufzuwerfen ist, wodurch die vorhandenen Abweichungen erklärt werden können*." OSTWALD. *Lehrbuch*, v. 2. p. 824.

[150] "*Aus eigenen Messungen zieht der Autor den Schluss, dass im Zustande äusserster Verdünnung alle Salze derselben Basis das gleiche Leitvermögen haben. Dasselbe muss konsequenterweise auch für die 'Wasserstoffsalze', die Säuren, gelten. Die bei mittleren Verdünnungen vorhandenen grossen Unterschiede führt er darauf zurück, dass nur ein Teil der Molekeln im 'aktiven' Zustande sei, d. h. sich an den Vorgängen des doppelten Austausches beteiligen könne. Mit zunehmender Verdünnung wird dieser Bruchteil immer grösser, um bei unendlicher Verdünnung gleich Eins zu werden. Über die Ursache des unwirksamen Zustandes stellt er die Hypothese auf, dass sie in einer 'Komplexität' der Molekeln, einer Zusammenhäufung derselben zu grösseren Aggregaten beruhe*." OSTWALD. *Lehrbuch*. v. 2. p. 822. Tradução Nossa.

para avaliar as afinidades de ácidos e bases, Ostwald explica as vantagens destes em relação ao método calorimétrico, utilizado por Berthelot e Thomsen em suas pesquisas:

> "The original method of determining the distribution of a base between two competing acids that Thomsen had formed is difficult to accomplish and requires much substance. The 'volum-chemical' method which I applied to it is much easier: it presupposes only such tools, which are present everywhere, since it is only a matter of determining specific weights (or volumes) of homogeneous liquids, and permit the experiments to be carried out with fifty times smaller amounts of substance, while the results obtained by thermochemical means request a superior amount. A third method [O método óptico de Ostwald], which I based on the determination of the refractive indices, makes it possible to limit the amounts of substance even further (to a few centigrams), but is related to accuracy of the volumetric method."[151]

Outros trabalhos também foram apresentados, como suas pesquisas sobre a hidrólise de amidas e ésteres, processos estes catalisados por ácidos. Apesar da afinidade química ser o foco destas pesquisas, Ostwald fez importantes considerações sobre a cinética química dessas reações, que viriam a introduzi-lo ao tema da catálise, campo no qual se dedicaria na década seguinte.[152]

A despeito da importância dada ao estudo das diferentes formas de energia para compreensão das afinidades químicas, Ostwald reforça uma imagem da Química enquanto uma ciência mecanicista, dedicada à compreensão da dinâmica da matéria. Tal concepção está expressa no bloco *Mecânica Química*, no qual apresenta os estudos sobre cinética e o equilíbrio de reações químicas, assim como explicações atomísticas e cinético-moleculares para as transformações químicas. Na conclusão de seu livro, Ostwald revela sua visão mecanicista de mundo, ao afirmar que "o objetivo de fazer da Química um capítulo da

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[151] "*Das ursprüngliche Verfahren, die Verteilung einer Base zwischen zwei konkurrierenden Säuren zu ermitteln, welches Thomsen ausgebildet hatte, ist schwierig auszuführen und erfordert viel Substanz. Die 'volumchemische' Methode, welche ich darauf anwandte, ist sehr viel leichter; sie setzt nur solche Hilfsmittel voraus, welche überall vorhanden sind, da es sich nur um die Bestimmung spezifischer Gewichte (resp. Volume) von homogenen Flüssigkeiten handelt, und gestattet die Versuche mit fünfzigmal geringeren Stoffmengen auszuführen, während die Resultate an Genauigkeit den auf thermochemischem Wege erhaltenen überlegen sind. Eine dritte Methode, welche ich auf die Bestimmung der Brechungskoeffizienten gründete, gestattet die Stoffmengen noch weiter (auf einige Centigramme) einzuschränken, steht aber in Bezug auf Genauigkeit der volumchemischen nach*." OSTWALD. *Lehrbuch*. v. 2. p. 606. Tradução Nossa.

[152] Apesar de ter investigado diferentes reações catalíticas, seu objetivo nestas pesquisas foi determinar afinidades relativas de ácidos que atuavam como catalisadores destes processos, assim como testar a validade de ferramentas teóricas como a Lei de Ação de Massas para estes fenômenos.

Mecânica Aplicada (...) não paira mais diante de nós em uma distância enevoada, mas avançou para uma proximidade previsível."[153]

O estudo sobre as relações de energia mudaria a carreira de Ostwald poucos anos depois, quando ele tornou-se adepto da Energética, um programa de pesquisa antimecanicista que pretendia unificar e reinterpretar as ciências em termos da ideia de energia e suas transformações.[154] A virada energeticista na carreira de Ostwald influenciou profundamente a segunda edição do *Lehrbuch*, publicada entre 1891 e 1902, que será discutida em artigo futuro.

Considerações Finais

O *Lehrbuch der allgemeinen Chemie* não é considerado o mais importante livro-texto de Ostwald, assim como também não é considerado seu maior êxito literário.[155] Também pesa à primeira edição do *Lehrbuch* sua relativamente rápida obsolescência, visto que este livro foi publicado antes da elaboração das teorias que formaram o núcleo teórico-conceitual da moderna Físico-química, em especial a Teoria de Dissociação Eletrolítica de Arrhenius. Entretanto, o *Lehrbuch* exemplifica a importância dos livros-texto para a ciência, auxiliando na comunicação e educação científica, e no estabelecimento de tradições de pesquisa.

Inicialmente concebido com objetivos pedagógicos, essa obra ganhou diferentes propósitos a medida em que Ostwald consolidava sua carreira de pesquisador. Seu contato com a literatura química de sua época, o levou a sistematizar os resultados de diferentes pesquisas químicas surgidas em décadas anteriores à sua publicação, em especial aquelas voltadas a estudo das reações químicas, focando em seu livro desde as relações

153 "*Das Ziel, die Chemie zu einem Kapitel der angewandten Mechanik zu gestalten, schwebt angesichts dieser Thatsachen nicht mehr in nebelhafter Ferne vor uns, sondern es ist in absehbare Nähe gerückt*." OSTWALD. *Lehrbuch*. v. 2, p. 893. Tradução nossa.

154 Ver: DELTETE, Robert J. Wilhelm Ostwald's Energetics 1: Origins and Motivations. *Foundations of Chemistry*, v. 9, n. 1, 2007. p. 3-56.

155 Frequentemente o *Grundriss der allgemeinen Chemie* (1889) é mencionado como o mais famoso livro-texto de Ostwald. Esta obra foi traduzida para diversos idiomas e responsável por popularizar as ideias ionistas para um público mais amplo. Ver: OSTWALD, Wilhelm. *Grundriss der allgemeinen Chemie.* Leipzig: W. Engelmann, 1889. Por outro lado, é comumente destacada a importância do jornal *Zeitschrift für Physikalische Chemie* como a maior contribuição literária de Ostwald, devido a importância deste jornal para a institucionalização da Físico-química, publicização de novas teorias e defesa da abordagem ionista. Sobre este jornal, ver: HAPKE, Thomas. Die Zeitschrift für Physikalische Chemie: Hundert Jahre Wechselwirkung zwischen Fachwissenschaft, Komunikationsmedium und Gesselschaft. Verlag Tragott Bautz, Herzberg, 1990.

estequiométricas entre reagentes e produtos até as causas das reações químicas e os fatores determinantes para sua ocorrência.

O destaque destinado às afinidades químicas no *Lehrbuch* reflete o interesse de Ostwald pelo tema - foco de suas pesquisas iniciais - assim como representa um ponto de interseção entre diferentes campos de pesquisa que se tornaram parte da Físico-química. O destaque dado às afinidades químicas, cinética e equilíbrio de reações também mostram o quanto Ostwald estava imerso em um contexto epistemológico mecanicista, apesar do crescente interesse de Ostwald pela Termodinâmica e pelas relações de energia.

O contato com os trabalhos de van't Hoff e Arrhenius também tornou o *Lehrbuch* um cartão de visitas do trabalho destes químicos. No caso de Arrhenius, tal contribuição foi mais dramática, visto que este químico foi severamente criticado por seus pares e acabou encontrando apoio às suas pesquisas por meio de Ostwald, que mostrou o valor de sua abordagem eletroquímica por meio de artigos e do seu livro-texto.

A organização e a forma de exposição dos conteúdos no *Lehrbuch* também merece destaque. A explanação histórica apresentada por Ostwald para os conceitos e teorias da Físico-química reflete uma visão de desenvolvimento científico linear e cumulativo, própria das correntes filosóficas positivistas em voga na sua época. A narrativa histórica apresentada por Ostwald pode ser encarada como um primeiro passo em direção à construção dos mitos sobre o surgimento da Físico-química destacados por Diana Barkan.

É preciso salientar que o impacto do *Lehrbuch* não ficou restrito à formação dos jovens químicos. Assim como sugerido por Ostwald no prefácio do seu livro, o *Lehrbuch* atingiu os químicos mais experientes, como indicam as frequentes menções a este livro nos artigos publicados no *Zeitschrift*, desde sua fundação.[156] Devido ao sucesso da obra, Ostwald foi aconselhado pelo seu editor a escrever uma segunda edição deste livro, que viria a ser publicado entre 1891 e 1902.

Por fim, o *Lehrbuch der allgemeinen Chemie* é um exemplo da importância que os livros-texto possuem para o estabelecimento da cultura científica. Esta obra desempenhou um papel significativo na comunicação científica, apresentando e organizando o conhecimento

[156] É possível encontrar menções ao *Lehrbuch der allgemeinen Chemie* no *Zeitschrift* desde seu primeiro número. Ver: LEHMANN, Otto. Über Krystallisation von Gemengen. *Zeitschrift für Physikalische Chemie*, v. 1, n. 1, p. 15–26. Trabalhos publicados em outros periódicos científicos, como o *Chemiker Zeitung* também mencionam o *Lehrbuch*. Ver: KEISER, H. B. Ueber die Verbrennung abgewogener Mengen von Wasserstoff und über das Atomgewicht des Sauerstoffs. *Chemiker Zeitung*. 25 Julho, 1887. p. 2323-2324.

produzido em sua época sobre as as transformações químicas para uma audiência mais ampla e diversificada, colocando estes temas sob os holofotes dos químicos do final do século XIX.

TEACHING AND THINKING ON CATALYSIS

Wilhelm Ostwald and his Catalysis Research (1890-1906)

Abstract: Even not being the creator of catalysis concept, the Baltic-German chemist Wilhelm Ostwald (1853-1932) took catalysis for the forefront of chemical research. He started to investigate this phenomenon in 1890's and contributed in different ways for its popularization. His interest on catalysis, however, was related by the possibility to work in a field which he do not use mechanistic theories and show the value of his energetic approach for science. Simultaneously, Ostwald's tentatives to prove the value of energetic worldview turned catalysis a popular subject, calling the attention of the German chemical industries and spreading catalysis by means of his writings and teaching, stimulating several investigations on this subject in his laboratory. Analyzing Ostwald's autobiography, textbooks and papers written by him and his students, we intend to present in this work Ostwald's contributions to catalysis research, its teaching and popularization, highlighting his achievements, obstacles and failures in catalysis area.

Key-words: Catalysis; Wilhelm Ostwald; Chemical Industry; Scientific Training.

Introduction

Catalysis is recognized as one of the most important branches of chemical research. The discovery and domain of catalytic processes have dramatically changed our world. The development of catalysts was fundamental to the development of the modern society based on large-scale industrial production, which was determinant for the economic development of many countries in the 20th century (Hagen, 2015). Additionally, catalysis has shown its importance in minimizing the environmental problems derivatives from the capitalist society, optimizing chemical processes and is an important tool in Green Chemistry area (Anastas, Kirchhoff and Williamson, 2001).

Chemical process accelerated due to the presence of strange substances were known since Antiquity and many of those reactions were investigated by philosophers and chemists across the time. However, catalysis research is considerably recent: systematic investigations on catalysis date from the end of eighteenth century, period in which these chemical reactions were investigated as isolated phenomena and chemists tried to provide different explanation for each known catalytic process (Wisniak, 2010; Kilani, Batis and Chatrette, 2001).

Analysing these investigations, in 1835 the swedish chemist Jöns Jacob Berzelius (1779-1848) unified them through the concept of catalysis (from Greek, *kata* = down and *lyein* = loosen) and explained catalysis existence due to the action of a chemical force, the catalytic force, able to "awake" the latent affinities of chemical bodies (Zecchina and Califano, 2017, p. 5-6; Wisniak, 2010, p. 60). However, his ideas on the nature of catalysis were not so appreciated by the chemists, as for example, the German chemist Justus von Liebig, who saw catalytic force as a kind of artificial vital force (Bensaude-Vincent and Stengers, 1992, p. 301).

The catalytic phenomena came back to spotlights in last decade of nineteenth century, but now far from affinities forces and grounded on the modern theories of physical chemistry. One of the responsibles for this change was the Baltic German chemist Wilhelm Ostwald (1853-1932), professor of Physical Chemistry at University of Leipzig and a great enthusiast of catalytic research. His laboratory became the most important center of catalysis research in the end of nineteenth century, being his former students prominent researchers in catalytic area. In 1909, Ostwald received the Nobel Prize of Chemistry in recognition of his contributions to Physical Chemistry science, including catalysis works.

However, these contributions for catalysis are not clear in literature. Some authors stressed that Ostwald's works on catalysis were the main reason of his award, especially his efforts to renew catalysis and catalyst concepts, regarded as his main contribution to this field (Zott, 2003; Hiebert and Körber, 1981; Bancroft, 1933). The definitions to catalysis and catalyst were his first step towards developing a theory for catalysis occurrence, but he never reached this aim. Sketches of these ideas on catalysis and its nature could be found in his papers (Ostwald, 1901a; 1901b; 1902; 1907) and textbooks, as for example the popular second edition of his *Lehrbuch der allgemeinen Chemie* (1891-1902). On the other hand, Ostwald published few papers on experimental works, as the tentative to develop a catalytic process for production and oxidation of ammonia, and autocatalysis' investigation (Zecchina; Califano, 2017; Ertl, 2009; Hiebert and Körber, 1981).

Also strong critics to Ostwald's catalysis works are found in literature. The historian

James R. Partington affirmed that Ostwald's ideas on catalysis were "a revival of Mitscherlich's contact theory" (Partington, 1961, p. 599) and his supposed theory of catalysis was actually a set of superficial analogies for the action of catalyst in chemical reactions (Idem, p. 600). Consenting to these critics, the historian Robert Friedman also affirms that Ostwald's catalysis investigations were a "smoke screen" for hiding the real reasons of his Nobel award - his lifetime achievements (Friedman, 2001, p. 37).[157]

For us, it is not possible to comprehend Ostwald's works on catalysis, as well as its limitations, without understanding the theoretical ground which these investigations established. Under the light of changes occurred in Ostwald's worldview and scientific convictions at the last decade of nineteenth century, it is possible to better evaluate the value of Ostwald's theoretical contributions to catalysis. Simultaneously, it is necessary to highlight a relevant factor behind his small number of published experimental writings: the role of his students as performers of catalysis research developed in his laboratory. Finally, it is necessary highlight Ostwald's attempts to solve industrial problems, namely ammonia and nitric acid synthesis, which were an important step forward to supply the need for Nitrogen derivatives in Germany. In this paper we intend to discuss these elements of Ostwald's achievements in catalysis field.

First, we look at Ostwald's initial investigations on catalysis, which concerned the autocatalysis' problem. In the two following sections, we discuss the relation between Ostwald's interest in catalysis and his adoption to Energetics, trying to show how energetic ideas permeated his proposal to this subject, pointing also some limitations of his energetic viewpoint. Finally we discuss his experimental works in this field, stressing the collective aspect of the catalysis research at Leipzig laboratory coordinated by him as well as his efforts for German chemical industry.

Ostwald's approximation to catalytic studies

Son of German immigrants, Wilhelm Ostwald was born in Riga, an old Baltic city in Latvia, which was strongly influenced by German culture. In 1710, Riga was taken by Russian Tzar Peter the Great, becoming part of the Russian Empire. Such annexation changed dramatically the social structure of the city and its administrative sphere, which adapted to

[157] We discussed the motivations of Ostwald's supporters to Nobel Prize in the third paper of this doctoral thesis.

Russia's bureaucracy, including the scholar curriculum. For this reason, Ostwald received an instruction very different from those available in Germany.

This difference became more significant in his university's life. In 1872, Ostwald joined the University of Tartu, in Estonia. Built at 1632, the University of Tartu is one of the most ancient universities in the European East. Despite its importance, the chemical training in Tartu was outdated if compared to German universities. Beyond technical and structural problems in the chemistry laboratories, the contact with organic chemistry was quite limited in Ostwald's student time (Ostwald, 1926 in Jack and Scholz, 2017, p.53).

Despite these problems, Tartu was a stimulating place for Ostwald develop his interest in some subjects which were underestimated in Germany and proved to be important for the further development of chemistry, as the theory of chemical affinity. In the nineteenth century, stimulated by the rise of thermochemistry and electrochemistry, chemists started to investigate how physical properties could be used to measure chemical affinity and define its nature (Nye, 1999). Interested in this subjects, Ostwald started his career trying to determine the chemical affinity between inorganic acids and bases by changes in total volume of reactants in neutralization reactions. Later, he expanded the research using an optical method to determine affinity. The results of these investigations were published in his master and doctoral thesis (Ostwald, 1877; 1878).

In 1881 Ostwald became professor at Riga Polytechnic School. There he continued to develop his research, proposing values of chemical affinity of some catalytic reactions, as for example, the hydrolysis of esters occurred in presence of inorganic acids, a typical catalytic reaction (Ostwald, 1883). One year later, he received a copy of Arrhenius' doctoral work, in which he determined chemical affinity of electrolytes using measurements of their conductivities. Despite an initial suspction, Ostwald assumed that Arrhenius "had looked at the [chemical affinity] problem in a much more generally applicable way and had, to some extent, even solved parts of it" (Ostwald, 1926, in Jack and Scholz, 2017, p. 114). In 1886, Ostwald became aware of van't Hoff's *Études de Dynamique Chimique* (1884), which also impacted his research on affinity bringing a thermodynamic view to chemical affinity problem.

The collaboration among these scientists resulted in two important works: van't Hoff's description of the behavior of diluted solutions using a approach similar to kinetics theory of gases; and Arrhenius' theory of electrolytic dissociation, which postulated the existence of electric charged particles, called ions (Coffey, 2008). Arrhenius' works made Ostwald consider the measuring of electrical conductibility as an useful form to determine chemical affinity and basing his dilution law of acids, an empirical law that describes the variation of conductibility according to the concentration for weak acids solutions (Zott, 2003; Laidler, 1995).

In 1887, Ostwald became professor at University of Leipzig. There he was well succeeded in establish a physico-chemical research program based on the electrolytic dissociation theory developed by Arrhenius, from which he derived his Dilution Law (Ertl, 2009, Laidler, 1995). Using Arrhenius ideas, he continued to investigate chemical affinity of catalytic processes, as for example the reaction involving iodidric and bromic acids (Ostwald, 1888). In addition to experimental work, he also had a fruitful career as journal editor of *Zeitschrift für Physikalische Chemie*,[158] textbook writer and professor. His efforts for popularizing Physical Chemistry made him a reference in this discipline, and his laboratory the most relevant school for physico-chemical training in the last quarter of nineteenth century (Servos, 1990).

Even present in his initial works, catalysis did not constituted the central subject of these investigations. At that time, Ostwald was yet occupied on chemical affinity and the new approaches for this subject, especially those derived from Arrhenius' theory. He became to investigate catalytic phenomena strictly just in 1890, due to the investigation of the Belgian engineer Paul Henry, who was working in Ostwald's laboratory, and the Finnish chemist Uno Collan (Ostwald, 1926 in Jack and Scholz, 2017, p. 285).

Both chemists investigated if a chemical substance could catalyse its own reactions. Under Ostwald's supervision, Henry analyzed the catalytic conversion of solutions of γ-oxovaleric acid[159] into valerolactone. This chemical process is catalysed by strong acids, which accelerate the chemical conversion.

Henry tried to describe the rate of reaction using a equation of first order, which was not appropriated to experimental data. Ostwald and Henry noticed that the rate of reaction was proportional to the square of the concentration of γ-oxovaleric acid, what means its conversion to valerolactone is described for a rate equation of second order (Ostwald, 1890). Analysing the problem, they noticed that a part of γ-oxovaleric acid was ionized in water

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[158] From now on appointed only *Zeitschrift* in this paper.

[159] According to International Union of Pure and Applied Chemistry (IUPAC), the current name for this substance is 4-oxopentanoic acid.

forming hydrogen ions, which also played a role as catalyst. Ostwald and Henry concluded that γ-oxovaleric acid can act as its own catalyst. Based on this process, Ostwald proposed the term autocatalysis, defined as "the catalysis of a substance on itself" (Ostwald, 1890).[160]

One year later, Collan published the first paper explicitly on catalysis in *Zeitschrift*, reinforcing the arguments in favor to autocatalysis existence and proposing some improvements to Ostwald and Henry's experimental procedures (Collan, 1891). One year later, Henry's paper on autocatalysis was published, however, Ostwald was not present as one of the authors (Henry, 1892).

The research on autocatalysis represents a starting point to Ostwald's investigations on catalysis. A little later, catalysis became one the main Ostwald's scientific interests, being not only a new area for physico-chemical investigation in which he could use his scientific expertise, but also a showcase for Ostwald's new approach based on Energetics.

Energetics applied to Catalysis

Some years before paying attention to catalysis phenomena, Ostwald dedicated himself to themes from a mechanistic tradition of chemistry, as represented by his investigations on chemical affinities. In his first writings, as for example the *Lehrbuch der allgemeinen Chemie*, Ostwald highlighted the role of mechanical theories for chemical science, defending the use of atomic hypothesis and kinetic theories (Ostwald, 1885, p. 14-15).

However, Ostwald was enthusiastic with thermodynamics since he was a student in Tartu, where his physics professor Arthur Öttingen introduced Ostwald to thermodynamic writings and its application for chemical problems. Ostwald became more interested in this topic after the publication of van't Hoff's *Études de dynamique chimique*, which this chemist presented a thermodynamic interpretation of chemical affinity, relating it to the amount of work that could be produced by a reversible chemical reaction (Snelders, 1989). Another influence was Arrhenius' electrolytic dissociation theory, introducing new ideas on the nature of matter in solution.

Ostwald would give a different approach to the affinity problem, inspired on Arrhenius' ion theory and van't Hoff's thermochemical approach to chemical reactions in equilibrium.

[160] Nowadays autocatalysis is defined as "a chemical reaction in which a product (or a reaction intermediate) also functions as a catalyst." (IUPAC, 1997).

Even grounded to some extent on an corpuscular perspective, Arrhenius' and, especially, van't Hoff's works showed to Ostwald new tools and methods to solve chemical problems (Coffey, 2008; Deltete, 2007).

At this point, phenomenological Thermodynamics exerted a deep influence on Ostwald's thinking, especially after 1887, due to his contact with Gibbs' writings, which showed to be possible to analyze chemical processes for macroscopic and measurable quantities, focusing in the energetic changes of the system (Ostwald 1926 *apud* Jack; Scholz, p. 179; Deltete, 2007, p. 44). Slowly he embraced a thermodynamic approach for his chemical research, which changed his perspective about the basis of chemical sciences: for Ostwald, besides understanding the matter and its nature and properties, Chemistry should look to energies involved in chemical process.

At the same time, anti-materialist ideas such as Ernst Mach's positivism, influenced a significant part of the scientists (including Ostwald) who had many criticisms and were disappointed with mechanistic science. Those elements played an important role in Ostwald's rupture with kinetic-molecular theories in favor of a new comprehension of the physical reality based on Energetics, an anti-mechanistic scientific program which sought to unify and reinterpret science in terms of energy and its transformations (Kragh, 2014; Deltete, 2005; Hiebert and Körber, 1981).[161]

However, Ostwald minimized these contextual elements and presented a "spiritual conversion" to Energetics in his autobiography. According to his memories, the conversion to Energetics occurred in 1890 during a stay in Berlin, where he experienced a catharsis that made him conceive the central role of energy in the world:

> "In the early morning I left the hotel and went into the Tiergarten Park. There in the sunlight of a wonderful spring morning, I experienced a real Pentecost, an effusion of the holy spirit. The birds were singing in all the trees, golden-green leaves shimmered against a light blue sky, butterflies opened and shut their wings while sunning themselves on the flowers and I wandered through this springtime landscape in an exalted state. I saw everything with new eyes and felt that I'd never experienced delight and wonder like this before. I can only compare my feelings then with those of my first love which lay 10 years behind me. In my mind the plan for a complete energetic concept of the world unfolded effortlessly and joyfully. (...) Then slowly the great town awoke and took me back into its din and dust. As soon

[161] The origins of Energetics and its influence on Ostwald's scientific and personal life was explored by a serie of papers written by the historian of science Robert J. Deltete (Deltete, 2007a; 2007b; 2008).

> as was reasonably possible I visited some of the experts and tried to explain my views to them. (...) I should add that never again did I undergo such a thing and never again experienced such concentrated joy - even though I was lucky enough to be granted many exhilarating - and also some harrowing - births of substantial new ideas." (Ostwald, 1926 apud Jack; Scholz, 2017, p. 231-233).

The joy of his insight, however, was not enough to convince his colleagues of the value of his ideas, and they kept a reserved posture. Despite the support from prominent scientists as the physicists Georg Helm (1851-1923) and Pierre Duhem (1861-1916), and some interest of some pupils as Theodore Richards (1868-1928) and Arthur Noyes (1866-1936), Energetics was heavily criticized by the scientific community, gradually diminishing the support to this program, until its abandon (Kim, 2006, Deltete, 2005). However, the initial criticisms and reservations made Ostwald feel challenged to apply energetics to chemical research:

> "I returned to my routine work mentally strengthened by this experience and tried to pin the ideas down in the daily round of discussion with my co-workers. Here as well I was met with both passive and active resistance. This spurred me on to apply the energetic prism to all of the problems being dealt with in the lab so as to try to show its practical usefulness." (Ibdem, p. 233).

One of these problems was catalysis. Despite some kinetics hypothesis, catalytic phenomena was poorly understood. Since Berzelius' conceptual synthesis in 1834, some chemists tried to solve the enigma of catalysis occurrence, as Friedrich Schönbein who put forth the hypothesis that a catalyst accelerate reactions through the formation of intermediate products by its mere presence (Zecchina and Califano, 2017, p. 6), and Georges Lemoine and his explanation on the action of *les corps poreux* (Lemoine, 1877). However, despite these works, catalysis was still an underexplored topic, potentially fruitful and open to new scientific investigations.

Additionally, catalysis appeared in an opportune moment to Ostwald. Between 1891 and 1895, he tried to develop his theory of energy and convince scientific community about the applicability and advantages of an energy-based science (Deltete, 2007a; 2007b). Energetics constituted the core of Ostwald's worldview after the 1890's, what explains his continuous defense of the Energetics, applying its principles to other areas of knowledge until the end of his life (Hiebert; Körber, 1981, p. 463). The gaps and problems of Energetics were not an obstacle in Ostwald’s viewpoint and, despite all critics, he believed that Energetics could be useful to solve chemical problems, as catalysis.

Ostwald’s energeticist approach for catalysis could be characterized by some elements. First, the defense of the central role of energy changes and the use - or simply mention - of energeticist laws and concepts to describe catalytic phenomena. Second, Energetics approach was based in an anti-mechanistic stance, represented by his antiatomism view and rejection to kinetics-molecular theories. Ostwald argued that mechanistic approaches had resulted in little progress in catalysis field due to the use of naive models and hypothesis about reality:

> “[...] I recalled the naive drawings which a prominent worker at that time had published in order to "visualize" the catalytic effect (...) the drawings showed how the sharp edges of the glass splinters cut the gas molecules into atoms which were then able to combine freely (...) I therefore took the opportunity offered to me by many reports, etc. to combat those injurious hypotheses and draw attention to the incomparably greater effectiveness of the simple definition of catalysis based on measurable facts.” (Ostwald, 1909a).

As result of this refuse to use hypothetical entities as atoms and molecules to interpret catalytic phenomena, Ostwald defended a phenomenological method and the appreciation of measurable quantities for catalysis. His epistemological posture is closer to positivist ideas of Auguste Comte (1798-1857) and Ernst Mach (1838-1916), who Ostwald admired and was sympathetic with their doctrines (Ostwald, 1926 in Jack and Scholz, 2017).

An example of the application of Energetics to catalysis can be found in the elaboration of his definition of catalysis, that appeared at the first time in an abstract published in 1894 in his *Zeitschrift für Physikalische Chemie*. Writing the abstract section for the *Zeitschrift*, he made criticisms to the paper *Über den Wärmewert Bestandteile der Nahrungsmittel* (On the value of heats of combustion of foodstuffs) of the German agricultural chemistry Friedrich Stohmann (1832-1897). In this paper, Stohmann presented his own view of catalysis, defining it as “a process of movement of the atoms in a molecule of a labile body which follows the entrance of the energy emitted from one body into another and leads to the formation of more stable bodies with loss of energy" (Stohmann, 1894). Ostwald strongly disagreed with this definition, criticizing its hypothetical basis and his considerations on energy involved in the process:

> "The abstractor has several objections to make to this definition. First, the assumption of a 'condition of movement of the atoms in a molecule' is hypothetical and therefore not suitable for purposes of definition. Also, that is plainly not a loss of energy. What is more, in describing characteristic conditions of catalysis, a loss of free energy can follow under conditions even of absolute energy uptake." (Ostwald, 1894, p. 705).

Despite atomic theory had been proved an important tool for chemistry, Ostwald argued that Stohmann's view based on a kinetic nature for catalysis was "hypothetical and therefore not suitable for purposes of definition" (Ostwald, 1894, p. 705), suggesting that definitions in chemistry should be based entirely on directly observable chemical phenomena.

Ostwald refused to go beyond phenomena and based his concept only in facts and quantities that could be experimentally obtained, freeing him from a mechanistic view that was unable to contribute to the description of catalytic phenomena in his viewpoint. For this reason, Ostwald proposed a phenomenological concept for catalysis, free from atomic premisses, affirming that it was "the acceleration of a chemical reaction, which proceeds slowly, by the presence of a foreign substance" (Ostwald, 1894, p. 705).

Ostwald's reinforced in several writings his rejection to kinetic-molecular hypothesis, considering it a naive realistic interpretation of chemical phenomena. At this point, Ostwald referred specially to visual representations of atoms and molecules used to explain catalysis and other chemical processes, which present properties without experimental support, as stressed by Ostwald some years later, when he received the Nobel Prize of Chemistry:

> I recalled the naive drawings which a prominent worker at that time had published in order to "visualize" the catalytic effect of pounded glass on the combination of the constituents of detonating gas with moderate heating; the drawings showed how the sharp edges of the glass splinters cut the gas molecules into atoms which were then able to combine freely. And there was more of that sort of thing such as the late Lémery with his spikes and hooks on the atoms. I therefore took the opportunity offered to me by many reports, etc. to combat those injurious hypotheses and draw attention to the incomparably greater effectiveness of the simple definition of catalysis based on measurable facts which states that catalysis is a chemical acceleration brought about by the presence of substances which do not appear in the reaction product. (Ostwald, 1909a).

It is also necessary to stress that radical phenomenology is frequently considered a sterile approach in many cases in history of science. The positivist idea of a objective science purely based on observables and measurable quantities proved to be insufficient to comprehend the natural world still in Ostwald's time, as demonstrated by the organic synthesis program and the research on atomic structure, which had corpuscular premises. However, for catalysis, Ostwald's claims to free catalysis research from the current atomistic theories showed to be a relevant step to bring catalysis to modern era. The power of his phenomenological view of catalysis can be perceived by the similarities between Ostwald's concept and those currently accepted.[162]

Returning to Ostwald's 1894 abstract - which became a summary on his ideas about catalysis - he presented some considerations on the nature of these phenomena, as his disagreement on the notion of catalysis as a kind of force, which opposed to Berzelius' notion of catalytic force, which reinforces his opposition to mechanics and its derived concepts. For Ostwald, catalysis should be investigated through energetic paradigm, namely the transformations of energy and the energetic laws:

> "It is therefore misleading to consider catalytic action as a force which produces something which would not occur without the substance which acts catalytically; still less can it be assumed that the latter performs work. It will perhaps contribute to an understanding of the problem if I especially mention that time is not involved in the idea of chemical energy; thus if the chemical energy relations are such that a definite process must occur, then it is only the initial and final states, as well as the whole series of intermediate given states which must be passed through, which must occur, but in no way is the time during which the reaction takes place of concern. Time is here dependent on conditions which lie outside the two laws of energetics.
>
> The only form of energy which contains time in its definition is kinetic energy, which is proportional to the mass and the square of the velocity. All cases in which such energies take a fixed part are therefore completely determined in time if the conditions are given; but all cases in which the vibrational energy does not play this role are independent of time, that is, they can occur without violating the laws of energy in any given time. Catalytic processes are empirically found to be of the type in which this last property is observed; the existence of catalytic processes is to me

[162] According to IUPAC, catalyst is "a substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called catalysis." (IUPAC, 1997).

> therefore a positive proof that chemical processes cannot have a kinetic nature." (Ostwald, 1894, p. 705-706).

Despite these elements, Ostwald was aware of some limitations of energetic approach. His insistence in showing that time was not involved in catalysis was due to the fact that time was related to kinetic energy, a manifestation of energy which Ostwald could not understand without using mechanical concepts and quantities. In other words, Ostwald knew that "Energetics' principles did not determine on its own the time or velocity of a chemical reaction." (Ostwald, 1909b, p. 289). Additionally, he often modified his concepts, as for example, of catalyst, for which three different definitions could be found in his writings (Laidler, 1987). A more mature definition of catalyst, including a general overview for catalysis, can be found in the second edition of Ostwald's *Lehrbuch*:

> "The essence of catalytic processes, as far as it is concerned, has been described as an acceleration of the rate of reaction by one of the substances present, without altering its quantity. As long as the catalytically active substance or catalyst is neither changed, increased or nourished by the substances present at the beginning of the reaction, nor by the resulting substances, its influence is valid only in relation to the value of the velocity coefficient, but not in reference to the character of the formula for the time course of the process"[163] (Ostwald, 1902, p. 262. Our translation).

Once Ostwald's energy theory was never developed further than a draft and his ideas on catalysis and its nature was in continuous change, it is not so easy to understand his ideas about the nature of catalysis, since his concepts and ideas were modified for a writing to another. Despite this, we try in the following section to present Ostwald viewpoint to some theories concerning catalysis occurrence.

[163] *Das Wesen katalytischer Vorgänge ist soweit es hier in Betracht kommt, bereits als eine Beschleunigung der Reaktionsgeschwindigkeit durch einen der anwesenden Stoffe ohne Änderung von dessen Menge gekennzeichnet worden. So lange der katalytisch wirksame Stoff oder Katalysator weder durch die zu Beginn der Reaktion vorhandenen, noch durch die entstehenden Stoffe verändert, vermehrt oder vermindert wird, macht sich sein Einfluss nur in Bezug auf den Wert des Geschwindigkeitskoëffizienten geltend, nicht aber in Bezug auf den Charakter der Formel für den zeitlichen Verlauf des Vorganges.*

Organizing and Explaining Catalysis

Ostwald stood out in catalysis also because of his proposals on how to organize catalytic phenomena and the promotion of theories to explain them. Besides the kinetic-molecular explanations to catalysis, which Ostwald rejected by reasons previously pointed, there was at that time other hypothesis for the occurrence of catalytic phenomena. We explore these ideas based on Ostwald's paper *On Catalysis* (Ostwald, 1902), in which he presented an overview of the main explanations proposed for catalysis occurrence.

Until Berzelius' synthesis, different manifestations of catalysis were investigated as phenomena unrelated to each other. Fermentation, metallic surface reactions, and several organic reactions accelerated by the increase of small amounts of acids were considered as having distinctive natures. Only in 1935 the proposed concept of catalysis unified these processes as under the same class of chemical phenomenon.

Ostwald organized the catalytic reactions into four groups: catalysis in supersaturated solutions, homogeneous catalysis, heterogeneous catalysis, and action of enzymes. Additionally, each of these catalytic processes would have a different origin, and therefore, they were explained differently.

The first kind of catalysis referred to precipitation of supersaturated solutions.[164] He defended that precipitation was a kind of catalytic phenomena which occurred in solutions of solids and gases in liquid systems. In his viewpoint, a small fraction of solute or any material that could disturb the chemical system in determined conditions of temperature and pressure would act as a catalyst in formation of precipitate substances:

> "The theory of all these phenomena is known. In all cases we have the formation of a system the stability of which is not the greatest possible under the given conditions of temperature and pressure. There are, on the contrary, other more stable conditions which are characterised by the fact that in them a new phase, that is a physically different component with other properties, makes its appearance. In the case of a supersaturated solution of Glauber's salt, this is the solid salt; in supersaturated soda-water, it is carbonic acid gas. As a rule such a new phase does not appear spontaneously if the supersaturation is not too great, and the system behaves as if it were in equilibrium ; but if a small quantity of the absent phase

[164] Nowadays, precipitation of solutes from a supersaturated solution is not considered a catalysis phenomenon, just a physical process resulting of instability of supersaturated system.

comes in contact with the metastable system, the action is set going and the new phase increases until equilibrium is reached." (Ostwald, 1902, p. 522).

These considerations on the nature of the so-called catalytic precipitation justifies Partington's affirmation which considers Ostwald's ideas on catalysis as a revival of Eilhard Mitscherlich's contact theory, according to which a catalyst promote the acceleration of a chemical reaction by its mere presence in chemical system. Indeed, Ostwald showed to be open for such ideas for some catalytic phenomena, but, as we will see, he considered other explanations for catalysis and kept a reserved posture to the proposed theories.

One of them was intermediate reactions theory, initially used to explain some examples of homogeneous catalysis, another kind of catalytic phenomenon in which reagents and catalyst are involved in only one phase.

The theory of intermediates was proposed by the French chemists Nicolas Clément (1779-1842) and Charles Bernard Désormes (1771-1862) in the beginning of nineteenth century. Working at sulphuric acid industrial production, Clément and Désormes proposed that the process for obtaining sulphuric acid started by the catalyst (saltpeter) action and occurred with successive reactions involving intermediate products.

Ostwald was sympathetic to the idea of intermediates because of its experimental ground, considering this view as the oldest and most important way to interpret catalytic processes (Ostwald, 1902, p. 524). However, he affirmed that this hypothesis was not generalizable for all catalytic phenomena and, focusing in Clément and Désormes' example, affirmed not be possible to determine if catalyst forms an intermediate or a by-product:

> "In confronting a catalytic phenomenon, we seek for the possible intermediate product in the formation of which the catalyst could take part, and we consider the problem essentially solved when we can fix upon such. If we succeed, indeed, in getting some of the assumed intermediate products from the materials, the view is considered to be proved. Whether such a substance is truly an intermediate product, and not merely some bye-product, is a question which is hardly raised and still less answered." (Ibidem, p. 524).

Even though the existence of intermediates did not contradict Energetics laws in Ostwald's viewpoint, he did not support this hypothesis. Ostwald affirmed not to be possible to explain catalytic retarding by the theory of intermediates (Ibdem, p. 524). Additionally, his energetic worldview prevented him to support any explanation to catalysis far from experimental facts. According to him, there was no experimental proof that intermediate reactions could make the chemical process faster than a direct reaction:

> "There is thus no contradiction of general laws, if we assume that a certain course of reaction takes place more quickly through an intermediate substance than it does directly. Nothing can be said for, but something against, the view that this is generally the case. (...) No catalytic acceleration is explained, unless it is also shown that the intermediate reactions actually take place more rapidly than the direct reactions, under the given conditions. Up to now, no case of this kind has been satisfactorily investigated. and no such explanation actually proved for a given case. I certainly hope that this gap will not long remain, as investigations directed to this point are approaching their conclusion." (Ostwald, 1902, p. 524).

Besides intermediate theory, another explanation for homogeneous catalysis was proposed by the young German-Swedish chemist Hans von Euler-Chelpin (1873-1964), a professor at the University of Stockholm who would be one of the winners of the Nobel Prize in 1929 for his investigations on enzymes and alcoholic fermentation (Nobel Prize, 2018). Pupil of famous scientists as Emil Fischer (1852-1919) and Max Planck (1858-1947), Euler interested in physical chemistry after his doctoral formation, going to Göttingen in 1896 to work at Walther Nernst's laboratory and, one year later, he took an assistant position at Arrhenius' laboratory at Stockholm Hogsköla (Friedman, 1993, p. 173-174).

In 1901, Euler published a paper in *Zeitschrift* proposing a theory affirming that the common cause of the various known reactions was the propagation of the ions involved in the reaction. Assuming that all chemical reactions involving ions, and the concentration of active ions presents in a reaction would be determinant for the speed of the process, Euler defended that catalysis was a phenomenon in which the catalyst could change the concentration of the ions in a chemical system, thus affecting the speed of the chemical reactions:

> "All these phenomena, referred to as catalysis, are based on a common process, as will be shown in this introductory and in the following treatises: the multiplication of one or more of the types of molecules by which the (non-accelerated) reaction takes place, that is to say in use the electrochemical

principles on the entire field of chemistry, the increase of the incoming ions in the reaction."[165] (Euler, 1901, p. 644. Our translation).

Ostwald was sympathetic to Euler's ideas, but he had some reservations about this theory, affirming that it could not explain all catalytic processes, as autocatalysis. Ostwald also pointed some other discrepancies between of this theory and experimental data, namely the increase of speed of reaction by the simultaneous action of two catalysts:

> "There appears to be one difficulty in the fact, often observed, that two catalysts acting together effect a much greater acceleration than would be calculated from the sum of their separate effects. It is not obvious how, by the simultaneous action of the two catalysts, so much larger quantities of reactive ions could be formed than these can form acting apart." (Ostwald, 1902, p. 524).

Among most explored examples of catalytic processes in nineteenth century were the reactions in metal surfaces, common examples of heterogeneous catalysis. It occurs when a chemical change happens at or near an interface between phases of a system. These phenomena were investigated by several chemists between nineteenth and twenty century, as Georg Bredig (1868-1944) a colloidal catalysis researcher and Ostwald's former pupil.

Working as Ostwald's assistant in Leipzig, Bredig developed a relevant work on catalysis using colloidal solutions of metals as catalysts. Deeply influenced by old ideas on contact theory from the beginning of century, this research led him to develop a different viewpoint on the nature of catalysis and to conclude that catalysis would be a physical phenomenon, dependent of physical state of reagents, as related by Ostwald:

> "If we suppose that in the gaseous system, at a given temperature, one part is replaced by a liquid or acquires a density corresponding to the liquid state, then in this part the reaction will take place proportionately more quickly, and the liquid part of the materials will be converted into the final products. If then the liquefying or condensing source is of such a nature that it goes on condensing fresh quantities of materials as fast as the old are being used, these will react quickly and the result is acceleration of the reaction. That such is the case in the action of platinum on gases

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[165] "Allen diesen als Katalysen bezeichneten Erscheinungen liegt, wie in dieser einleitenden und in folgenden Abhandlungen gezeigt werden soll, ein gemeinsamer Vorgang zu Grunde: die Vermehrung einer oder mehrerer derjenigen Molekülarten, durch welche die (nicht beschleunigte) Reaktion vor sich geht, dass heisst bei Anwendung der elektrochemischen Prinzipien auf das Gesamtgebiet der Chemie, die Vermehrung der in die Reaktion eingehenden Ionen."

> is quite possible. I do not wish to assert by this representation that the catalytic action takes place in such a way, but only to point out a possibility as to how it might take place. We should then have the simplest and purest case of an accelerating intermediate reaction to which I have already referred." (Ostwald, 1902. p. 524).

As well as Bredig, Ostwald assumed heterogeneous catalysis as a phenomenon resulted by changes in physical states of reagents. He considered the catalytic effect of metals in gas-phase reactions as result of the adsorption of gaseous reagents for porous metals, which combined to heating favored the chemical reaction (Zecchina; Califano, 2017, p. 26). But despite agreeing with this explanation for surface catalysis, Ostwald affirmed it was necessary to carry out more investigations on all of these presented hypotheses - especially the defenders of kinetic hypothesis (Ostwald, 1902, p. 524).

The last kind of catalysis pointed by Ostwald is the enzymatic action. Enzymes were long investigated apart from chemical laws and theories due to vitalist ideas on substances from living organism (Zecchina and Califano, 2017, p. 270-272). Despite vitalism, many chemists contributed to enzymes' science, as Anselme Payen (1795–1878) and Jean-François Persoz (1805–1868), who discovered diastase, and Charles Cagniard de la Tour (1777–1859), who developed investigations on yeast action in fermentation processes. These are just a little example of the number of investigations about enzymes and their reactions.

At Ostwald's time, important discoveries were made on enzymatic action. One of them was the discovery of the stereospecificity of enzymes acting in substrates, in 1894, by the German organic chemist and Nobel Prize winner Hermann Emil Fischer (1852-1919), and the research on free-cell fermentation carried by Eduard Buchner, awarded with the Nobel Prize of chemistry in 1907 (Hunter, 2000, p. 92-99).

Ostwald stressed the importance of enzymes to understand physiological process and life process in its totality. Mentioning Bredig's investigations, Ostwald affirmed that contemporary scientists showed that inorganic catalysts and enzymes to have the same kind of action, but that the research involving the latter was predominantly qualitative, due to its reactivity in which result loss of catalytic power (Ostwald, 1902, p. 525). On Fischer's achievements, Ostwald was a little reluctant in agreeing with stereochemical explanation proposed by him:

> "The beautiful investigations of E. Fischer have shown that at any rate the very slight differences which nowadays we know in chemistry as stereochemical can

bring about alteration in the action of a given enzyme. As to whether this rests on the asymmetric character of the enzyme itself or on other grounds appears to me not to have been decisively ascertained." (Ostwald, 1902, p. 526).

If Ostwald had been so careful to adopt a explanation to catalysis nature as presented above, he had not the same reservation to establish relations among catalysis, energetics and physiological processes, namely fever symptoms, and characteristics of living-systems, as memory and adaptation (Domschke; Hansel, 2000, p. 41-42).

Despite the presence of some elements from Ostwald's catalysis classification in nowadays science, a large part of his ideas on catalysis are obsolete nowadays. Works from the first half of twentieth century showed the need of a kinetic-molecular comprehension allied to thermodynamics to the understanding of chemical reactions, especially catalysis.

Teaching Catalysis: the Research Group at Leipzig Institute (1894-1906)

Like no other scientist in that time, Ostwald stimulated the experimental research on catalysis, leading a significative number of students and assistants to get involved in this area. Under his supervision, several students developed research on catalysis in their doctorate thesis and *Habilitationsarbeiten*. Additionally, some pupils and co-workers, who initially investigated different subjects, turned to catalysis after their formation or after leaving the laboratory, as for example Robert Luther (1868-1945) and Alwin Mittasch (1869-1953). Thus, it is reasonable to suppose that the number of catalysis' scientists formed in Ostwald's laboratory is bigger than described in Table 1.

Table 1 - Some researchers involved in catalysis investigations working at Ostwald's laboratory (1890-1906)*

Chemist	Position/Period	Research in catalysis
Aleksandr Adrejeviĉ Titow	Ph.D. student (1901-1904)	Negative catalysis (inhibitors) in homogeneous systems
Arthur Slator	Ph.D. student (1901-1903)	Catalysis of chloride and benzol reaction (with Luther)
Carl A. Ernst	Ph.D. student (1897-1901)	Catalysis of blast gas due to colloidal Platinum
Carl Drucker	Ph.D. student (1895-1900) and assistant (1905-1911)	Catalysis in non-homogeneous systems

Colin Garfield Fink	Ph.D. student (1903-1907)	Heterogeneous catalytic reactions (under Bodenstein's supervision)
Georg Bredig	Ph.D. student (1889-1894) and assistant (1895-1901)	Colloidal Platinum and heterogeneous catalysis
George Senter	Ph.D. student (1903-1907)	Blood enzymes (with Luther)
Heinrich F. Wilhelm Ohlmer	Ph.D. student (1899-1904)	Catalysis by silica (under Bodenstein's supervision)
Heinrich K. W. Schade	Visiting researcher (1906-1907)	Fermentation of sugar without enzymes
Johannes Brode	Ph.D. student (1901-1903)	Catalysis by the reaction between hydrogen peroxide and hydrogen iodide (under Bredig's supervision)
Kikunae Ikeda	Visiting researcher (1899-1901)	Catalytic poisoning (with Bredig)
Max E. A. Bodenstein	Assistant (1900-1904)	Ammonia catalytic synthesis and heterogeneous catalysis
Mieczysław Centnerszwer	Ph.D. student (1891-1898)	Catalytic influence of different gases and vapors on the phosphorus oxidation
Nikolai Alexandrowitsch Schilow	Visiting student (1896-1897/1901-1904)	Catalytic phenomena in the oxidation of hydrogen iodide and bromic acid
Oskar Gros	Ph.D. student (1898-1901 under Luther supervision) and assistant (1902-1903)	Catalytic photographic method (Catatypie)
Otto Eberhard H. Brauer	Ph.D. student (1895-1900) and assistant(1901-1902)	Ammonia and nitric acid catalytic synthesis
Paul Henry	Visiting researcher (1899-1902)	Autocatalytic conversion of lactones and oxoacids
Rudolf Ihle	Visiting researcher (1894-1898)	Catalytic influence of nitrous acid
Rudolf von Berneck Müller	Visiting researcher (1898-1900)	Platinum catalysts and heterogeneous catalysis (with Bredig)
Samuel Lawrence Bigelow	Ph.D. student (1895-1898)	Catalytic effects of the atmospheric oxygen
Thomas Francis Rutter	Ph.D. student (1904-1906)	The catalytic characteristics of Vanadium (under Luther's supervision)
Thomas Slater Price	Ph.D. student (1896-1898)	Catalysis of potassium persulfate and potassium iodide reaction
Wilhelm Dietz	Ph.D. student (1902-1906)	Reversible catalysis in heterogeneous system (under Bodenstein's supervision)
Wilhelm Karl Federlin	Ph.D. student (1897-1902)	Transmission catalysis (under Luhter's supervision)
Willem Reinders	Ph.D. student (1900-1901?)	Heterogeneous catalysis (under

Bredig's supervision)

*Informations displayed in the table were extracted from Vatterott (1997); Hammer (1999; 1998); Pludra (2002; 2000) and Facius and Pohle (1997).

The research at the laboratory focused mainly on inorganic processes. Using Ostwald's classification for catalytic phenomena, his students frequently dedicated to heterogeneous and homogeneous catalysis. Some investigations concerned catalytic poisoning or negative catalysis (catalytic inhibitors). Enzymatic reactions were also studied, even not being a so popular topic in the group. One of these was the investigation on sugar fermentation developed by the physician and chemist Heinrich K. Wilhelm Schade (1876-1935), who spent two semesters in Ostwald's laboratory (Schade, 1907).

The relation between Ostwald and his students in the development of their research is not very clear in literature. Frequently, his concepts on catalyst and catalysis, as well his tentatives to explain the nature of catalytic phenomenon are pointed as his main contributions for the area, as well as few experimental works on autocatalysis and the production of nitric acid. Indeed, the publications about to catalysis published by his students and assistants did not present him as co-author. His collaboration was mentioned in endnotes, acknowledging him for his role as teacher and advisor, as for example, in Bigelow's paper:

> "I am happy to take this opportunity to express my sincere gratitude to my esteemed teacher, Mr. Prof. Dr. Ostwald, for the support and advice he has given me in the course of this work. I also feel obliged to thank Dr. G. Bredig and Dr. R. Luther for her kind interest (Bigelow, 1898, p.532. Our translation)."[166]

As Ostwald diverted from experimental activity from 1895, due to extreme weariness as well as a growing interest in subjects out of scope of experimental chemical research, his assistants became more necessary to helping in his teacher duties. He was gradually turning away from laboratory and his teaching activities, delegating them to assistants, what explains their growing presence in central positions of catalytic research. It is evident in the acknowledgements of the paper on negative catalysis written by the Russian chemist Alexander Andrejewitsch Titow (1878-1961):

[166] *"Mit Freuden ergreife ich an dieser Stelle die Gelegenheit, meinem hochverehrten Lehrer, Herr Prof. Dr. Ostwald, meinen innigsten Dank für die Unterstützung und die Ratschläge auszusprechen, welche er mir im Laufe dieser Arbeit in so reichem Mass hat zu teil werden lassen. Herrn Dr. G. Bredig and Dr. R. Luther fühle ich mich ebenfalls für ihr freundliches Interesse zu Dank verpflichtet."*

> "My highly esteemed teacher, Mr. Prof. W. Ostwald, I express my deepest gratitude for the suggestion for the work and the benevolence always testified to me. Mr. Subdirector Dr. Luther, under whose direction the work was carried out, I also owe my warmest thanks. Finally I thank the assistants of the institute, the Privatdozent Dr. Bodenstein, Dr. Fredenhagen and especially Dr. Böttger sincerely for numerous advice and their always friendly congeniality (Titow, 1903, p. 683. Our translation).[167]

However, Ostwald's role in the catalytic research developed in his laboratory is deeper: a clue of his contribution was given by Harry Clary Jones (1865-1916), one of his American pupils. In a review on Ostwald's biography,[168] Jones pointed a relevant characteristic of Ostwald's style:

> "The fertility of Ostwald's mind in new ideas can not have failed to impress anyone who had been with him even for a short period, and also the unusual freedom with which suggestions, often of very great importance, were made to anyone who had the desire and ability to work them out in the laboratory. And when the work was done the student was told to publish the investigation as if the whole was his own. The result is that a large part of the work done in Ostwald's laboratory does not bear his name, although the original suggestion came from him, and every stage of the investigation was under his daily scrutiny." (Jones, 1904, p. 822).

This affirmation led us to reconsider the scientific production in Leipzig: a large part of chemical works from Institute of Physical Chemistry, including catalysis works, was product of Ostwald's scientific creativity. Indeed, in some writings from his laboratory, it is possible to see Ostwald as an active head of catalytic research, coordinating and directing his students to subjects of his own interest, as demonstrated by Bigelow, who developed a study on catalytic oxidation of sodium sulphite "at the suggestion of Mr. Prof Ostwald." (Bigelow, 1898, p. 494). However, it seems that Ostwald did not impose completely his interests to students, as suggested in Titow's work, who affirmed that "(...) when I was asked by Prof. Ostwald to investigate more closely the phenomena of negative catalysis, it seemed most appropriate to

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[167] *"Meinem hochverehrten Lehrer, Herrn Prof. W. Ostwald, sage ich den tiefsten Dank für die Anregung zu der Arbeit und das mir gegenüber stets bezeugte Wohlwollen. Herrn Subdirektor Dr. Luther, unter dessen Leitung die Arbeit ausgeführt wurde, bin ich ebenso meinen wärmsten Dank schuldig. Endlich danke ich den Assistenten des Instituts, Herrn Privatdozent Dr. Bodenstein, Dr. Fredenhagen und. besonders Herrn Dr. Böttger aufrichtig für zahlreiche Ratschläge und ihr stets freundliches Entgegenkommen."*

[168] Paul Walden, *Wilhelm Ostwald* (1904).

continue Bigelow's work and, if necessary, to make more accurate measurements by improving the experimental conditions.” (Titow, 1903, p. 644).

Even when he moved away from experimental activity, Ostwald did not delegate completely the supervision of catalytic research to his assistants. The catalysis’ subject had a privileged position in his scientific horizont, which was not affected by his breakdown:

> “In this way I was able to show that my creative scientific streak was still intact - and this was the most important result for me. I was thus able to put aside the worry that I’d lost the ability to provide my students with projects and the means to attack them. In particular this work had started for me the new and fruitful field of catalysis in which I could employ as many co-workers as I wanted.” (Ostwald, 1926 apud Jack; Scholz, 2017, p. 263).

His status as reference in catalysis field led former students to come to him and discuss about their own investigations, as Titow, Max Bodenstein (1871-1942), Eberhard Bauer (1875-1958) and Thomas Price (1875-1949).[169] Price, an Ostwald’s former student, spent one year in Arrhenius’ laboratory developing a study on the reaction between ethyl alcohol and hydrochloric acid (Price, 1901). One of Price’s hypothesis for the equilibrium values of this chemical change was the catalytic influence of hydrogen ions in chemical system, idea which led him to consult his old master:

> “First, as regards of my work in Stockholm I managed to get through two theses there and it is about the second that I wish to consult you. The subject is the interaction of ethyl alcohol and hydrochloric acid. When I began the “Arbeit” my idea was to investigate the velocity of reaction, but before this could be done, I had to obtain reliable figures to equilibrium constant (...) I also find that constant of equilibrium depends on the amount of hydrochloric acid present (...) It seems to me that the explanation depends on the catalytic influence of the H^+ ions of the acid. This influence of H^+ ions is known to be a specific one, and as we may consider the direct and reverse reactions in ester formation are quite separated from each other, the catalytic influence of H^+ ion may be different in each case and thus bring about the variation of k (equilibrium constant) with the amount of acid present.” (Price, 1899).

[169] These documents were part of Wilhelm Ostwald’s archives kept in Archiv der Berlin-Brandenburgischen Akademie der Wissenschaften (ABBAW).

Ostwald's influence on catalysis can also be evaluated through the mentions to his writings about the subject. A large part of the papers on catalysis published in *Zeitschrift* mention Ostwald's definitions for catalysis and catalyst, as well as descriptions of specific catalytic phenomena proposed in his *Lehrbuch.*[170] Additionally, there are frequent mentions to techniques, scientific instruments present in other Ostwald's writings, as his *Hand- und Hilfsbuch zur Ausführung physiko-chemischer Messungen* (Ostwald, 1893).

On the other hand, concerning the presence of Energetics in these works from Ostwald's pupils and assistants, our analysis did not find energetic considerations in these works. However, the anti-mechanistic atmosphere from Ostwald's laboratory can be noticed in some works wrote by his students, as Bigelow's affirmation that "in contrast to mechanics, where the acceleration of a process at the same time implies an energy consumption, (...) the catalytic phenomena provide a means to do twice as much and more in a given time, free of charge, than would otherwise be possible."[171] (Bigelow, 1898, p. 493). Despite some conceptual mistakes, Bigelow's statement represents the belief that the catalysis did not have a mechanical nature, an idea defended by Ostwald in his writings (Ostwald, 1902; 1909b; 1894).

Even not adopting the thinking of their master entirely, the students were responsible of promoting catalytic research - and their diverse nationalities suggest that this area crossed the boundaries of German Empire. Indeed, former students who worked on catalysis continued their investigation in institutions and industries in Germany as well as in other countries.[172]

[170] Concerning nomenclature, the terms "catalysis" and "catalyst" were more utilized by the chemists in their papers. However, Bredig and some of his students used the expression "inorganic ferments" to designate metallic catalysts, as platinum. This use came from Berzelius' analogy between the action of metals in catalytic reactions and the yeast action in sugar conversion to carbonic gas and alcohol (Bredig; von Berneck, 1899). The term "enzyme", also used by chemists, had a more specific definition, concerning on biological substances, which act as catalyst in biochemical process.

[171] *"Im Gegensatz zur Mechanik, wo die Beschleunigung eines Prozesses zugleich einen Energieverbrauch in sich schliesst, also nur durch einen Mehraufwand von Arbeit zu beschaffen ist, zeigt es sich hier, dass die katalytischen Erscheinungen ein Mittel in die Hand geben, um kostenlos in gegebener Zeit, das Doppelte und mehr zu leisten, als es sonst möglich wäre."*

[172] Besides his American students who were responsible to institutionalize the branches of Physical Chemistry in United States, Ostwald contributed directly for the formation of catalysis researchers in America, teaching catalysis for American chemists in 1905, during his period as exchanged professor at University of Harvard (Ostwald, 1927 apud Jack; Scholz, 2017, p. 405).

Achievements and failures in Chemical Industry

As result of important changes in the scientific training and modernization of research institutions, German chemical industries suffered a remarkable expansion in the second half of nineteenth century, represented specially by large-scale production of synthetic dyestuffs, drugs and fertilizers (Sánchez-Ron, 2007; Lenoir, 2003; Johnson, 2000; 1990). In 1887, when Ostwald assumed the chair of physical chemistry in Leipzig, there was more than 4000 chemical plants employing 82000 workers on German territory, and less than ten years later, the number of industries was superior to 6000 in which worked around 120000 employees (Sánchez-Ron, 2007, p. 81). The advances in organic chemistry and its synthesis program played a central role in this panorama, but it is necessary reinforce the importance of physical chemistry for the improvement of industrial processes.

Even being an academic chemist, Ostwald was not indifferent to chemical industry, especially because he was aware how politics and industrial financial investment can improve scientific and technological development, as for example the creation of the *Physikalisch-Technische Reichsanstalt* (Imperial Institute of Physics and Technology, abbreviated, PTR), a technical-scientific institution supported by the industrial Werner Siemens (1816-1892), founder of Siemens and Halske company, and the German government. The PTR aimed to train physicists and to supply the demand of skilled labor for companies of precision instruments and technology in general (Sánchez-Ron, 2007; Pfetsch, 1970). Another example of this fruitful relationship among science, politics and industry was the foundation of *Deutsche Elektrochemische Gesellschaft*[173] (German Electrochemical Society), an organization formed by industrialists, chemists, engineers and technicians for the promotion of electrochemical research and its technological applications. The society was founded in 1894 having Ostwald as first chairman (Jaenicke, 1994).

The relationship among chemistry, politics and industry also was fruitful to solve the saltpeter importation, a chemical substance necessary of the development of German chemical industry, army, and food supply.

Nitrogen is a relevant nutrient for vegetable life that is absorbed from the soil by the roots of plants. Despite nitrogen composes around 78% of air, the plants cannot absorbed it, being necessary to convert nitrogen gaseous to other substances accessible to vegetables,

[173] The society change its name after Robert Bunsen's death, calling *Deutsche Bunsen-Gesellschaft für Angewandte Physikalische Chemie*. In 1936 the society was rename again, calling *Deutsche Bunsen-Gesellschaft für Physikalische Chemie*. See Jaenicke (1994).

process called nitrogen fixation. However, the nitrogen fixation is a natural and slow process, involving microorganism and determined environment conditions. Another source of nitrogen for plants are nitrates, usually called saltpeter. Nitrates are chemical substances used for the production of two different and fundamental products for Imperial Germany: fertilizers, for increasing the food production, and explosives, for war.

Germany as well as other countries had no large reserves of nitrates salts, which were exported from South America, especially from Chile (Smil, 2001). The dependence of Chilean saltpeter for agriculture and military needs led Germany susceptible to elevated costs of importation and commercial locks - as occurred during the First World War. Facing these problems, industrials and scientists tried to solve the problem turning atmospheric nitrogen "fixable," and one the ways to reach this objective was producing ammonia through the reaction between nitrogen and hydrogen gases, but the tentatives had no good results (Ibdem, 2001).

Ostwald was aware on the costs to obtain saltpeter from South America, and the investigations concerning nitrogen fixation (Zecchina; Califano, 2017). As editor of *Zeitschrift*, Ostwald was deeply informed on chemical literature. Therefore, it is not strange that he knew on the research of César-Mansuète Despretz (1791-1863) and collaborators, who produced nitrogen and hydrogen gases by the decomposition of ammonia in contact with an incandescent iron wire catalyst. Facing Despretz's results, Ostwald believed to be possible obtaining ammonia through the inverse reaction using atmospheric nitrogen (Ostwald, 1926 apud Jack; Scholz, 2017; Hiebert; Körber, 1981). Therefore, Ostwald applied ideas on catalysis and the ionist theories on chemical equilibrium to the ammonia synthesis.

As other experimental works, appears again the collective aspect of his research. The involved experiments for producing ammonia were executed by his assistants Max Bodenstein and Eberhard Brauer (Domschke; Hansel, 2000). The following experimental procedure also was submitted as patent for Ostwald in March of 1900:

> "(...) I have discovered that the fusion of free nitrogen and hydrogen can be achieved at a measurable rate at the low temperatures of 250–300 °C in the presence of appropriate contact substances or catalysts. The reaction rate increases rapidly as the temperature is increased. Metals, such as iron or copper, which have been treated to give them a large surface area, serve as the catalysts. The synthesis is not complete but rather leads to an equilibrium and the amount of ammonia produced is therefore dependent on the ratio of the amounts of the input nitrogen and hydrogen.

> To achieve complete synthesis it is necessary to remove the ammonia from the reaction mixture and this can be done by dissolving it in water or acid. For this purpose the gas mixture can be recycled, if necessary after cooling and then using the recovered heat once more." (Ostwald, 1926 apud Jack; Scholz, 2016, p. 298).

The first results of the research were enthusiastic: a small amount of ammonia was detected for Ostwald's assistants, leading Ostwald to contact some chemical industries, as Hoechst and Badische Anilin & Soda Fabrik (BASF). To confirm Ostwald's results, the direction of BASF company designated the young chemist Carl Bosch (1874-1940) - who further made Haber's method for conversion of nitrogen to ammonia industrially viable - to confirm the results of Ostwald's catalytic synthesis (Smil, 2001).

Despite Ostwald's excitement, Bosch's analysis concluded that Ostwald's process was unsuccessful. The formed ammonia did not come from atmospheric nitrogen, but from traces of nitrogen present in all commercial iron catalysts (Sánchez-Ron, 2007; Domschke; Hansel, 2000). Informed on the results, Ostwald initially deny the conclusions of Bosch's analysis, but new experiments carried out in his laboratory confirmed the report from BASF (Smil, 2001, p. 64). Facing the facts, he suspended the patent request for ammonia synthesis.

In his autobiography, Ostwald affirmed not to have seen the breakdown of his financial expectations of millionaire contracts with chemical industries as a great loss (Ostwald, 1926 apud Jack; Scholz, 2017). He had opportunity to return to his research on ammonia some years later, when Fritz Haber, at that time a recently formed chemist, consulted him about a possible collaboration with an Austrian chemical industry:

> "An Austrian company has written repeatedly to me in recent times to hear my opinion on whether it is possible to combine nitrogen and hydrogen in large catalytic ammonia. (...) a foreign college told me at the congress in Berlin that you, honored Privy Councilor, had studied this question and encouraged it to the development of a technically feasible way. Therefore, I ask you to let me know if it is pleasant for you to get the Austrian company to contact you. It leads me to the idea that you might want to when a well-funded and honorable company takes charge of the technical implementation, while this company could be nothing more

valuable than having you as a consultant."[174] (Haber, 1903 apud Zott, 1997. Our translation).

Ostwald did not answer Haber's letter and never came back to his ammonia synthesis investigations. In 1908, Haber and his assistant Robert Le Rossignol (1884-1976) synthesized ammonia using a similar method to Ostwald's, which was well-successful due the development of a high-pressure apparatus and a suitable catalyst for the conditions of pressure and temperature - between 550–600 °C (Lenoir, 2003; Smil, 2001). For this reason, some years later Ostwald affirmed to be the intellectual father of ammonia industry (Ostwald, 1926 apud Jack; Scholz, 2017, p. 298).

An unfolding of these efforts to obtain ammonia was Ostwald's process to produce nitric acid from catalytic oxidation of ammonia. The experiments were took by Brauer, and consisted in put ammonia and air in contact to a platinum catalyst to produce nitrogen dioxide, which was further converted in nitric acid. This time the result of the investigation was successful, and the successives adjustments and improvements of the process increased the rentability of the reaction to 85%, turning the so-called Ostwald-Brauer process advantageous (Zecchina; Califano, 2017, p. 32).

One more time, Ostwald negotiated with chemical industries and applying a new patent for his nitric acid synthesis process. Initially he tried to deal with large companies as BASF, Hoechst and Bayer, but the negotiations were unsuccessful. According to Abelshauser and others (2004), BASF company did not approve Ostwald's proposal due to his very expensive demands. Due to the rejection of big chemical industries, Ostwald dealt with the German entrepreneur and industrialist Max von Duttenhofer (1843-1903), who supported the implementation of a small pilot plant for nitric acid production in an abandoned explosives fabric close to Berlin, which noticed its first production of nitric acid in 1902 (Domschke; Hansel, 2000).

In parallel to the implantation of industrial process, a new setback appeared for Ostwald: Ostwald and Brauer's patent was denied by Imperial Patent Office due to the

[174] *"Eine österreichische Firma hat mir wiederholt in neuerer Zeit geschrieben, um meine Meinung darüber zu hören, ob es sich für sie empfiehlt, Stickstoff und Wasserstoff in großen katalytisch zu Ammoniak zu vereinigen. (...) Nun hat mir ein ausländischer College beim Congreß in Berlin erzählt, daß Sie, hochgeehrter Herr Geheimrat, diese Frage studiert und bis zur Ausarbeitung eines technisch gangbaren Weges gefördert hätten. Ich bitte Sie deshalb mich wissen zu lassen, ob es Ihnen angenehm ist, wenn ich die österreichische Firma veranlasse, sich an Sie zu wenden. Es leitet mich dabei der Gedanke, daß es Ihnen vielleicht erwünscht ist, wenn einen kapitalkräftige und ehrenwerte Firma die technische Durchführung in die Hand nimmt, während dieser Firma nichts wertvoller sein könnte als Sie zum Berater zu haben."*

existence of an old patent very similar submitted by the French chemist Frédéric Kuhlmann (1803-1881) in 1838 (Kaden, 2013). According to Alwin Mittasch (1953), a Bodenstein's former student and catalysis specialist of BASF, Ostwald did not know on Kuhlmann's discovery, developing the same technique independently. Later BASF asked to the Patent Office to develop its own similar process, based on Kuhlmann-Ostwald proposals (Abelshauser *et al.*, 2004). On the other hand, Ostwald and Brauer patented their ammonia-oxidation process in England, Austria and the United States (Kaden, 2013).

Additionally, there was other problems concerning Ostwald-Brauer process. The necessary platinum catalyst was very expensive and not suitable for the high temperature of process (Abelshauser *et al.*, 2004). The situation became worse after Duttenhofer death in the summer of 1903, when his successors refused in maintaining contract with Ostwald, resulting in the close of nitric acid industrial plant.

One more time looking for supporters, Ostwald negotiated with the chemist and director of the company *Chemische Fabrik Griesheim-Elektron*, Bernhard Lepsius (1854-1934), who permitted the continuity of the nitric acid production in Griesheim am Main, and later in Gerthe, due to a deal with the coal mine *Chemische Werke of Kohlenzeche Lothringen* to obtain cheap ammonia, which was a byproduct of coking process (Szöllösi-Janze, 2000). In 1906, Brauer enlarged the industrial plant, obtaining 300 kg of nitric acid per day (Domschke; Hansel, 2000).

However, the nitric acid produced through Ostwald-Brauer process was not enough to supply German market and turn the saltpeter importation unnecessary. The expensive platinum catalyst and the costs to purify ammonia from coking were the main obstacles for its large-implementation. In 1914, BASF developed a method to synthesize nitric acid from ammonia using a cheaper catalyst developed by Mittasch and Christoph Beck (1887–1960), turning Ostwald-Brauer process obsolete few years later (Abelshauser *et al.*, 2004; Smil, 2001).

Some Final Remarks

Even not being the creator of catalysis concept, Ostwald took catalysis for the forefront of chemical research when he started to investigate this phenomenon. Motivated by his objective to prove the value of Energetics, Ostwald found in catalysis a scientific area to apply his ideas on energy, free from mechanistic and realistic views that was unable, according to him, to contribute to the description of catalytic phenomena. Ostwald highlighted the importance of Energetics in his works on catalysis during his Nobel lecture in 1909:

> "It was not until somewhat later when I personally turned to energetics and thus freed myself from hypothetical ideas from which no direct, experimentally verifiable conclusions can be derived, that I also felt the need to put an end to the stagnation in which the study of catalytic phenomena had ended up as a result of such ideas. (Ostwald, 1909a)"

If energetic theory and its precepts were at the same time motivation and basis for Ostwald's scientific approach, on the other hand, energetics can be seen as an obstacle for his tentatives to explain catalytic reactions, since the nature of catalysis goes beyond the description purely phenomenological.

Even considered a kind of theorist of catalysis, Ostwald had an expressive experimental production in collaboration of his students and assistants, being tacitly present in many works on catalysis published by the members of his laboratory. On the other hand, the investigations directed to chemical industry, which were openly credited to Ostwald, suffered with various technical limitations concerning suitable catalysts and adaptation and expansion of processes for industrial production, being supplanted by processes developed by a new generations of physico-chemists in the first decades of twentieth century.

Ostwald's efforts to turn catalysis a popular subject worked well: he was successful to spread catalysis field in Germany and other countries by means of his writings and teaching, since Ostwald and his laboratory are a common point among the trajectories of relevant catalytic chemists who contributed for the development of the area in the following years.

After his retirement, catalysis area flourished with the development of new theories, the improvement of industrial processes, and the development of cheaper and more efficient catalysts. These modern chemical wonders showed in little time the insufficiness of some Ostwald's ideas on the occurrence of catalysis. However, the relatively rapid obsolescence of his ideas contrasts with his concept of catalysis, which still so useful that it remains in the main chemistry textbooks.

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A NOBEL FOR WHAT?

Revisiting Wilhelm Ostwald's Nobel Prize in Chemistry

Abstract: The historical narratives on the Nobel Prize of Chemistry granted to the Baltic-German chemist Wilhelm Ostwald (1853-1932) hardly address the strong support Ostwald received and the reasons presented in their nomination letters. Considering the literature on his laureate works and political aspects of his nomination, and defending to be relevant presenting the reasons pointed by these nominators in order to understand Ostwald's legacy in chemistry, in this work we present and discuss the nomination letters sent in Ostwald's favor in Nobel Prize editions between 1904 and 1909. Analysing these letters and dialoguing with the literature, we argue that, for Ostwald's supporters, his most relevant achievements concerned to extra-laboratorial activities, as his role as teacher and organizator of chemical science, for example. We will also try to demystify some frequent discourses on Ostwald's nomination, as the negative influence of his antiatomist posture and the central role of catalysis for his nomination.

Keywords: Wilhelm Ostwald; Nobel Prize; Nomination letters; Scientific Prizes.

Introduction

The Nobel Prize in Chemistry awarded to the Baltic-German chemist Wilhelm Ostwald (1853-1932) was a special episode in his life. The prize was already recognized as a traditional and internationally relevant event that honored reputable scientists from the main scientific institutions of the world working in the *rocket science* of their time.

To be a prize-winner, it was necessary to be indicated by permanent or invited nominators. The letters sent by the proponents were analysed and the applications were evaluated by the responsible committees. The recommended candidates were evaluated by the members of its respective sections of the Academy of Sciences of Sweden and finally, the winners were chosen in a plenary of Academy.[175] Nobel Prize' statute established also some directions to select the winners: only recent works and, in chemistry case, only scientists who made relevant discoveries or improvements for chemistry could be awarded.[176]

In 1909, Ostwald was included in this select group of intellectuals that received such relevant public recognition in a very particular situation: he was retired since 1906, when he gave up his outstanding Laboratory of Physical Chemistry at Leipzig University to dedicate himself to chemistry, philosophy, energetics, color theory and other subjects free of academic responsibilities.[177] His scientific partners, Jacobus Henricus van't Hoff (1852-1911) and Svante Arrhenius (1859-1927), who developed the main theories of modern discipline of physical chemistry, had received the Nobel Prize in Chemistry in 1901 and 1903, respectively. Of this foundation group, only Ostwald had not yet been laureate.

At the time of the prize, Ostwald's contributions to physical chemistry had diminished considerably and his main experimental works, even being a solid basis for the further development of this discipline, were eclipsed by works from other scientists. Additionally, some of his philosophical positions and scientific interests were, it seems, at least, as eccentric, if not controversial. Ostwald was, for a long time then, reluctant to accept the value of atomic theory and its derived models and theories in a period when physicists and chemists were already discussing topics as atomic structure and radioactivity. Since the late nineteenth century, the energetics program defended by him was in subtle decline, being abandoned by science in the following decades. Ostwald was one of the few scientists who continued to defend energetics, but without its initial scientific ambitions.[178]

Beyond his scientific beliefs and philosophy, it is fact that Ostwald had a strong reputation and his name was fit to be considered for the Nobel prize. He was one of physical chemistry pioneers, being the main responsible for its institutionalization and popularization, and for breaking resistance to important theories in the field, such as Arrhenius' electrolytic dissociation theory.[179] Ostwald also developed both theoretical and practical works concerning

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[175] Elisabeth Crawford "Introduction," in *Science, Technology & Society in the Time of Alfred Nobel*, org. Carl G. Bernhard, Elisabeth Crawford, and Per Sörbom (Oxford, Pergamon Press, 1982), 307-310.

[176] Elisabeth Crawford and Robert M. Friedman "The prizes in Physics and Chemistry in the context of Swedish science: a working paper," in *Science, Technology & Society in the Time of Alfred Nobel* org. Carl G. Bernhard, Elisabeth Crawford and Per Sörbom (Oxford, Pergamon Press, 1982), 313.

[177] Gerhard Ertl, "Wilhelm Ostwald: Founder of Physical Chemistry and Nobel Laureate 1909," *Angewandte Chemie International Edition*, 48, no. 36 (August 2009): 6600-6606, https://doi.org/10.1002/anie.200901193.

[178] Robert J. Deltete "Energetics," in *The Oxford guide to the history of physics and astronomy* ed. John L. Heilbron (Oxford, Oxford University Press, 2005), 104-105.

[179] Joachim Schummer "Wilhelm Ostwald," in *Encyclopaedia Britannica*, Encyclopaedia Britannica Inc., accessed January 2, 2018 https://www.britannica.com/biography/Wilhelm-Ostwald.

several subjects mentioned in nomination letters in his support from 1904 until 1909, when he finally received the Nobel Prize of Chemistry.

Since his first nomination, scientific community believed Ostwald's time to be laureate was coming but, as years went by, Ostwald's claim became harder to be attended. Therefore, when his luck dramatically changed and Ostwald said that he was surprised to receive the prize,[180] it was not false modesty - he was being completely honest.

Nobel statement indicates that he was awarded for his works on catalysis, chemical equilibrium and rates of reaction. However, some historians, as we will see, attribute his prize especially to his catalysis research, while others claim that Ostwald received the Prize for political reasons, arguing that his lifetime achievements played a more important role than any discovery or improvement. Each view is based in a valid perspective and some of them are somehow complementary, but important actors of the editions that Ostwald was nominated are not well represented in those historical narratives – the scientists who thought Ostwald worthy of the prize, his nominators.

Subjectivity plays an important role in any award. Nominators tend to support his friends, scientific partners, masters or important figures in their respective areas. Nevertheless, some of the subjective reasons for these choices need to be translated in the letters by means of factual achievements to be shared and evaluated. Additionally, these personal motivations could also be perceived by similarities among candidates and supporters that the historical work can demonstrate, as nationality, shared institutions, collective work, public expression of affection, scientific hierarchy and others.

Besides these psychological and occasional components, his supporters and their nomination letters show us the importance of his extra-laboratorial achievements for chemistry: activities that are fundamental for the institutionalization of scientific fields and their further development, but are frequently underestimated by practitioners. The reasons pointed by Ostwald's supporters demonstrate the great value of Ostwald's teaching, literary and philosophical activity, which were considered as fundamental for chemistry as laboratorial works.

In this paper we present who were Ostwald nominators and their reasons to support his candidacy. Based on the Nobel Prize archives, previous literature and other documents, we

[180] Nobelstiftelsen *Nobel lectures: chemistry 1901-1921*. Amsterdam: Elsevier, 1966. Available in: "Wilhelm Ostwald - Nobel Lecture: On Catalysis". Nobelprize.org. Nobel Media AB 2014. Web. 17 May 2018. <http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1909/ostwald-lecture.html>

present some aspects of these attempts to prize Ostwald that could be relevant to understand why he was a good candidate for the Nobel and mainly the importance of his extra-laboratorial achievements for the chemists that supported his candidacy.

Initially, we briefly review the literature concerning Ostwald Nobel Prize. Following, we present chronologically the nomination letters, discussing the grounds for his nominations from 1904 until his award in 1909 and try to understand why they were pointed as his most relevant contributions. Finally, we look at Ostwald's award in 1909 from the perspective of the reasons pointed by his supporters.

Ostwald's Nobel Prize: A Review

Writings on History of Chemistry are synthetic on the reasons for Ostwald prize. In general, it is only presented the Nobel Prize statement "in recognition of his works on catalysis and for his investigations into the fundamental principles governing chemical equilibria and rates of reaction."[181] This statement encompasses nearly all the themes to which Ostwald devoted himself in his all scientific life, but it is not clear on what specifically were these works, so it is possible to consider that he was recognized for his lifetime chemical investigations.

To Ostwald himself and to some authors, the prize was given especially for his works on catalysis, which he considered the "most personal and momentous contribution to chemistry." [182] He demonstrated in many occasions the personal importance of this subject along his autobiography – in which catalysis was the theme of an entire chapter – and also along his Nobel lecture, entitled *On Catalysis:*

> "It has pleased no less than surprised me that of the many studies whereby I have sought to extend the field of general chemistry, the highest scientific distinction that there is today has been awarded for those on catalysis. The award has pleased me because in my innermost being I used to, and still do, consider this part of my

[181] "The Nobel Prize in Chemistry 1909". Nobelprize.org. Nobel Media AB 2014. Web. 26 Jan 2018. <http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1909/>

[182] Wilhelm Ostwald, *Lebenslinien*, Klasing, Berlin, 1926/1927. The quotation was extracted from Robert S. Jack and Fritz Scholz *Wilhelm Ostwald: The Autobiography* (Springer International Publishing, 2017), 484.

work the one in which the personal quality of my method of work is most definitely shown up and which I therefore have more at heart than all the others."[183]

However, even in his autobiography, his contributions for catalysis were not so detailed. He presented an overview of his first works involving catalysis, including the conceptual change developed by him and his view on the relation between catalysis and energetics, but his other experimental contributions were not explored. He also highlighted his efforts to solve the problem of ammonia synthesis and the causes of his failure.

Some authors stressed that catalysis played an important role for Ostwald's prize not due to a single discovery or improvement in this field, but for his manifold investigations and for his efforts to renew catalysis concept, which was considered by the German historian Regine Zott as the main reason to award him:

> "He [Ostwald] was able to derive a valid definition, according to which a catalyst does not induce a process, but accelerates it without appearing in the final product; in this way important advances in chemical kinetics were stimulated. It was mainly for his work on catalysis, but also in part for his work on chemical equilibria and rates of reaction, that he received the Nobel Prize in 1909."[184]

Could a conceptual change be recognized for the Nobel Prize? This kind of improvement normally was not strong enough to support a Nobel candidacy at that time. Experimental discoveries or improvements were a ground more suitable to a possible candidate to the Chemistry prize, even if Ostwald's definitions for catalysis and catalyst are still useful and present in many contemporary textbooks of General Chemistry.

A particular feature of Ostwald's definition for catalysis is the absence of an atomistic basis. Rejecting mechanistic theories, as atomism, Ostwald developed new concepts for catalyst and catalysis that did not appeal to unverifiable entities as atoms. Wilder Bancroft, who was Ostwald's former student and wrote two posthumous articles on his teacher's life, had personal contact with him and his research group during this time as student in Leipzig. In his biographical articles, he presents a view on Ostwald achievements in catalysis field.

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[183] Nobelstiftelsen, *Nobel lectures*.
[184] Regine Zott "Friedrich Wilhelm Ostwald (1853–1932), Now 150 Years Young…," *Angewandte Chemie International Edition* 42, no 34 (September 2003): 3992, https://doi.org/10.1002/anie.200330059.

> "(…) In 1891 Ostwald wrote a review of a paper by Stohmann in which he gave the modem definition of catalysis: 'Catalysis is the acceleration by the presence of a foreign substance of a chemical reaction which is taking place slowly.' In 1909 Ostwald was awarded the Nobel prize in chemistry for his work on catalysis. This shows that it was possible for him to receive the highest recognition for work without making use of atomistic conceptions. It may be urged that the great feature of Ostwald's work was rather qualitative than quantitative, that catalysis was to be considered as accelerating an already existent reaction rather than as starting in otherwise non-existent reaction. The answer to this is that neither van't Hoff nor anybody else had seen this before Ostwald and that it was a number of years after Ostwald had formulated it before people accepted it."[185]

Ostwald's beliefs in Energetics led him try to create a phenomenological approach to catalysis' area, as the historian J. R. Partington highlighted:

> "His own work on catalysis had led him to formulate phenomena in a manner which emphasised the observed facts and minimised the unverified (or unverifiable) and unnecessary hypothetical interpretation of them. This method of approach was typical of his outlook."[186]

If Ostwald had attained to his goal to develop a catalysis' theory based on energeticist ideas, he would have a useful proof of the scientific value of Energetics and indicate that reforming chemistry in energy terms was possible. However, he soon perceived that energeticist considerations were not enough to understand catalytic phenomena[187] and, with the slow decline of Energetics among scientific community, Ostwald's objective to reform chemistry turned harder to reach.

Besides his conceptual contribution to catalysis, he performed also experimental works. He developed studies on catalytic action of acids that were used to measure the strength of these substances and helped to convince the scientific community about the value of Arrhenius' electrolytic dissociation theory.[188] Another product of his research in catalysis was the development of catatypie, a kind of photographic method based on catalysis, performed

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[185] Wilder D. Bancroft "Wilhelm Ostwald, the great protagonist: Part II," *J. Chem. Educ.* 10, no. 10 (1933): 609, https://doi.org/10.1021/ed010p609

[186] James R. Partington *A History of Chemistry* v.4 (London: Macmillan, 1961), 597.

[187] Wilhelm Ostwald, *L' Évolution d'une science, la chimie*, trans. Marcel Dufour (Paris: Ernest Flammarion, 1909), 288-289.

[188] Keith J. Laidler "Chemical Kinetics and the Origins of Physical Chemistry" *Archive for History of Exact Sciences* 32, no. 1 (1985): 64.

with the chemist Oskar Gros (1877-1947) and, before Fritz Haber could obtain ammonia from the catalytic reaction between hydrogen and nitrogen gases, Ostwald and the chemists Eberhard Brauer (1875-1958) and Max Ernst August Bodenstein (1871-1942) dedicated themselves to synthesizing ammonia, but the catalyst and the conditions of reaction were not suitable for the process.[189]

Ostwald and Brauer returned to nitrogen compounds industry few years later, proposing a way to convert ammonia in nitrates. The chemist Alwin Mittasch, remarked that Ostwald-Brauer industrial process for oxidation of ammonia contributes to the increasing of nitrate-based substances production, as fertilizers and explosives in Germany, but the popularization of their method was interrupt by the First World War in 1914.[190]

However, even if Ostwald's contributions to catalysis field could be considered sufficient to Nobel committee to grant for him the prize, historians have argued that he received the prize due to Svante Arrhenius' influence on the members of the Nobel Prize Committee of Chemistry.[191,192,193,194]

Arrhenius and Ostwald had a strong personal and scientific relationship. Ostwald was one of the first enthusiasts of Arrhenius' thesis on electrical conductivity that suffered strong opposition by the physicists from University of Stockholm. Ostwald understood the potential of Arrhenius' ideas and became himself one of their most important advocates, using the theory in his works on chemical affinity of acids and bases.[195] When Ostwald became the editor of *Zeitschrift für Physikalische Chemie*[196] (Journal of Physical Chemistry), he contributed for the adoption of Arrhenius ideas through the divulgation of ionist works and

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[189] Erwin N. Hilbert and Hans-Günther Körber "Ostwald, Wilhelm" in *Dictionary of Scientific Biography* org. Charles Coulston Gillispie and Frederic L. Holmes 15, Supplement I (New York: Scribner, 1981), 461- 462.

[190] Alwin Mittasch *Salpetersäure aus Ammoniak: geschichtliche Entwicklung der Ammoniakoxydation bis 1920.* (Weinheim/Bergstr: Verlag Chemie, 1953), 52-57.

[191] Crawford and Friedman "Introduction," 317-320.

[192] Robert M. Friedman *The Politics of Excellence: Behind the Nobel Prize in Science* (New York: Times Books, 2001), 34-37.

[193] Elisabeth Crawford *The Beginnings of the Nobel Institution: The Science Prizes, 1901-1915* (Cambridge: Cambridge University Press), 2001.

[194] Burton Feldman *The Nobel Prize: A History of Genius, Controversy, and Prestige* (New York: Arcade, 2013), 207-209.

[195] Patrick Coffey *Cathedrals of Science: The Personalities and Rivalries That Made Modern Chemistry* (London: Oxford University Press, 2008), 3-37.

[196] From now on appointed only *Zeitschrift* in this paper.

defending them from oppositionists, what turned this journal into the tribune and vehicle of new chemical theories.[197]

Arrhenius was also one of the first Ostwald's assistants at the University of Leipzig, where he stayed until 1891 when he took a position at Stockholm Högskola. However, his stay there was short: in 1901, Arrhenius was elected member of Royal Swedish Academy of Sciences and turned member of Nobel Committee of Physics. In this position, he was able to be indicated as rector of the Nobel Institute for Physical Research, where he stayed until retirement in 1927. The rise of his status in scientific community and specially the Nobel of Chemistry he was granted in 1903 "brought out the worst in Arrhenius."[198] Besides his overbearing posture, Arrhenius used his influence on the Nobel institution to favor some candidates and to preclude rivals and enemies in Nobel prize choices, as Paul Ehrlich and Walther Nernst.[199]

Even being personal friends and scientific partners, only in 1909 Arrhenius supported Ostwald for the Nobel Prize. One reason pointed out by historians for this delay was Ostwald's insistence in denying atomic theory. Admittedly an atomist, Arrhenius was an important figure in Ostwald's conversion to atomic theory in 1908, convincing him of the importance and validity of the Brownian movement theory, which is based in an atomic nature of matter. Ostwald's change contributed, according to some authors, to Arrhenius' support for his awards.[200,201] Additionally, Arrhenius knew that it was already time to put some energy in his old-friend candidacy: Ostwald's main works were already old and, since his retirement, his research and influence in the new paths of Chemistry in the twentieth century were diminishing. If Ostwald did not receive the Nobel soon, he would be left behind.

With the help of the organic chemist and member of chemistry committee Oskar Widman (1852-1930), Arrhenius made Ostwald a strong candidate for the prize in 1909: Widman was responsible for identifying possible opponents and neutralizing the arguments against Ostwald candidacy at the committee meetings. Arrhenius was responsible for writing

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197 Erwin N. Hiebert "Developments in physical chemistry at the turn of the century," In: *Science, Technology & Society in the Time of Alfred Nobel* org. Carl G. Bernhard, Elisabeth Crawford, and Per Sörbom (Oxford, Pergamon Press, 1982), 97-115.
198 Coffey, *Cathedrals of Science*, 32.
199 Coffey, *Cathedrals of Science*, 36-37 and 156-162.
200 Elisabeth Crawford "Arrhenius, the Atomic Hypothesis, and the 1908 Nobel Prizes in Physics and Chemistry," *Isis* 75 no. 3 (1984): 503-522.
201 Feldman, *The Nobel Prize*, 201-209.

a report on Ostwald's achievements that was signed and presented by Widman for the committee:

> "(...) It was, after all, Ostwald's lifetime contributions—not the official justification—that were the real reason for the prize. Arrhenius accepted Widman's strategy. When Widman received Arrhenius's "excellent report," he used it almost verbatim; the only changes highlighted yet more clearly the catalytic studies. The tactic worked; Ostwald received the 1909 Nobel Prize in chemistry."[202]

About Ostwald's catalysis works, the historian Robert Friedman affirmed that these works were a "smoke screen" used by Arrhenius and Widman to justify his nomination.[203] This opinion came from the analysis of the historian J. R. Partington on Ostwald's contributions to catalysis, which argues that Ostwald had no theory of catalysis, having proposed just superficial analogies for the action of catalyst in chemical reactions.[204]

Even Ostwald's prize being an example of institutional politics in scientific celebrations and awards, the political factor could not minimize his extremely productive career. Ostwald was pointed as Nobel Prize candidate from 1904, when he still strongly opposed atomic theory, to 1909, when Arrhenius and Widman focused in his candidacy (Table 1). The historian Regine Zott presented some correspondences showing that Ostwald had a considerable support among important scientists, that criticized Nobel statutory rules and considered Ostwald's merits should be prized, independently of its age.[205]

Table 1 - Wilhelm Ostwald's Nominators (1904 - 1909)[206]

Year	Nominators	Institution*
1904	Paul Walden Maximilian von Glasenapp	Riga Polytechnic Institute
1905	Theodore Richards	Harvard University
1906	James Walker	University College, Dundee
	Arthur Noyes	Massachusetts Institute of Technology
1907	Heinrich Goldschmidt	

[202] Friedman, *Politics of Science*, 37.
[203] Friedman, *Politics of Science*, 37.
[204] Parttington, *A History of Chemistry*, 600.
[205] Zott "Friedrich Wilhelm Ostwald," 3993-3994.
[206] "Nomination Database". Nobelprize.org. Nobel Media AB 2014. Web. 14 Mar 2018. http://www.nobelprize.org/nomination/archive/show_people.php?id=6913

	Waldemar Brögger Johan Vogt Thorstein Hiortdahl	University of Christiania (today University of Oslo)
1908	Jacobus H. van't Hoff Hans Landolt Hermann Thoms	University of Berlin
	Emil Constam	Zürich Polytechnic School
	Heinrich Goldschmidt Waldemar Brögger Johan Vogt Thorstein Hiortdahl	University of Christiania (today University of Oslo)
1909	Georg Bredig	University of Heidelberg
	Jacobus H. van't Hoff	University of Berlin
	Svante Arrhenius	Nobel Institute of Physics

* At nomination year

Therefore, it is necessary to know what were the reasons behind the support to Ostwald. Was catalysis the main reason for his nomination or did other achievements play a more important role in his prize? What discovery or improvement made Ostwald receive support for six uninterrupted years? In other words, for his supporters, he received a Nobel for what?

Nobel Prize of Chemistry in 1904: national and institutional relationships

Ostwald is considered a German prize-winner, but his nationality is a difficult question: he was born in Riga, an historical Hanseatic city that was constituted by different groups from Central and East Europe. In 1721, the Latvian city turned into a domain of Russian Empire, which dominated the government structure and public institutions, despite the large parcel of German immigrants that composed the aristocratic and intellectual sphere of the city and dictated the social mores.[207]

Being a Baltic-German made Ostwald quite different from his German colleagues. His adaptation to German society and university was very difficult and he affirmed that he felt as a foreigner during the entire period in Leipzig.[208] Additionally, his scientific trajectory was

[207] Ostwald *Lebenslinien*, 3-5.
[208] Ostwald *Lebenslinien*, 190.

also singular. Historians agree that Ostwald' scientific training in a peripheral institution as University of Tartu, where the contact with organic chemistry was quite restricted, was fundamental for his interest in the creation of new chemical methods and disciplines.[209]

Sharing his intellectual background, the Latvian chemist Paul Walden (1863-1957) and the Baltic-German chemical engineer Maximilian (von) Glasenapp (1841-1923) were invited nominators in 1904. Both Walden and Glasenapp worked at Riga Polytechnic School, where Ostwald started his scientific career.

Walden finished his chemistry course at Riga Polytechnic School in 1882 with distinction and started his scientific career as Ostwald's assistant. Working together, they determined the relation between basicity and molar electroconductivity (now known as Ostwald-Walden rule).[210] In 1891, he obtained his Ph.D. at University of Leipzig under Ostwald supervision. He returned to Riga Polytechnic Institute[211] in 1893 as a professor, where he stayed until 1906. In 1904, Walden published a biography of Ostwald, which was the basis for his nomination letter.[212]

Walden argued that Ostwald deserved the Nobel for a series of achievements. They are enumerated and summarized under three general reasons: First, Ostwald should receive the Nobel for his experiments on chemical affinity, electrochemistry and his theoretical and experimental works on catalysis. Second, for his activity as writer in physical chemistry area and, third, for his efforts in the training of physical chemists that made his laboratory at University of Leipzig the most important school in this area at the time.[213]

The theory of chemical affinity was a product of an ancient practical knowledge on the chemical behavior of substances and the mechanistic modern science from seventeenth century. It explained the occurrence of replacement reactions, using the idea of attraction and

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209 Mi Gyung Kim "Biography: Wilhelm Ostwald (1853-1932)," *Hyle* 12, no. 1, (2006): 141 - 148.

210 Jānis Stradiņš "Walden, Paul," in *Dictionary of Scientific Biography* org. Charles Coulston Gillispie and Frederic L. Holmes 14, (New York: Scribner, 1981),124-125.

211 In 1862 the Riga Polytechnical School was established. It works until 1895, when it turned the polytechnical Institute of Riga in 1896. From 1918 until 1919 it was called Baltic Technical University. In 1919, it was incorporated as a technical faculty in the School of Latvia, which turned in 1923 the University of Latvia. However, in 1958 it returned to be a technical faculty, which was again from 1958 to 1986 Polytechnic Institute. Then, the institution was called Polytechnic Arvīds-Pelše Institute Rīga (Arvīda Pelšes vārdā nosauktais Rīgas politechniskais instituts). In 1990, it became finally the Technical University of Riga. See more in "Technische Universität Riga," Wikipedia, Die freie Enzyklopädie. Accessed in June 1, 2018, https://de.wikipedia.org/w/index.php?title=Technische_Universit%C3%A4t_Riga&oldid=178305901

212 Paul Walden, *Wilhelm Ostwald* Engelmann, Leipzig, 1904.

213 Paul Walden to Nobel Committee of Chemistry 09 January 1904, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.

repulsion forces among chemical bodies.[214] Based in the affinity idea, chemists as Éttiene Geoffroy and Torbern Bergman elaborated tables in which chemical bodies were organized according to their relative affinities one each other.[215]

Despite the problems on this theory pointed by many chemists in the turn of the nineteenth century, affinity was useful to predict the occurrence of a considerable number of chemical reactions and the tables were a powerful pedagogical tool.[216] In nineteenth century, stimulated by the rise of thermochemistry and electrochemistry, chemists started to investigate how physical properties could be used to measure chemical affinity and define its nature.[217]

Interested in determining the chemical affinity of inorganic substances, Ostwald started his career trying to determine chemical affinity between inorganic acids and bases by changes in total volume of reagents in neutralization reactions. Later, he expanded the research using an optical method to determine affinity. The results of these investigations were published in his master thesis in 1877[218] and his doctoral thesis in 1878.[219]

Ostwald's work on chemical affinity changed in 1884 due to his contact with Arrhenius' dissociation theory and later with van't Hoff ideas. These works influenced Ostwald research, making him consider the measuring of electrical conductibility as a relevant form to determine chemical affinity, as in the case of his dilution law, an empirical law that describes the variation of conductibility according to the concentration for weak acids' solutions.[220]

Walden was the first to mention Ostwald's works on catalysis as a ground for the prize. He highlighted the synthesis of nitric acid from ammonia and the theoretical efforts to change the catalysis concept, the importance and involvement of Ostwald' students in catalytic research carried out in his laboratory, and his efforts for "directing the attention of chemical researchers in this field by spoke and writing to a new explanation and justification of the nature of catalysis."[221]

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[214] Mi G. Kim *Affinity, That Elusive Dream: a Genealogy of the Chemical Revolution* (Cambridge: MIT Press, 2008), 2-16.
[215] Bernadette Bensaude-Vincent and Isabelle Stengers, *História da Química* trad. Raquel Gouveia, (Lisboa: Instituto Piaget, 1992), 83-84, 101-106.
[216] Kim, *Affinity*, 135-136, 256-258.
[217] Mary Jo Nye *Before big science: the pursuit of modern chemistry and physics, 1800 - 1940*. (Cambridge, Mass. [u.a.]: Harvard University Press, 1999), 95.
[218] Wilhelm Ostwald, *Volumchemische Studien über Affinität*. Magisterdissertation, Dorpat, H. Laakmann, 1877.
[219] Wilhelm Ostwald, *Volumchemische und Optisch-chemischen Studien über Affinität*. Doktordissertation, Dorpat, H. Laakmann, 1878.
[220] Keith J. Laidler *The World of Physical Chemistry* (Oxford: Oxford University Press, 1995), 279.
[221] "*[...] er I/ die Aufmerksamkeit der chemischen Forscher auf dieses Gebiet durch Wort und Schrift lenkte, II/ eine neue Erklärung und Begründung des Wesens der Katalyse schuf, III/ eigene experim. Forschungen ausführte [...]*" Paul Walden to Nobel Committee of Chemistry.

Among his scientific merits, Walden highlighted some laboratory devices developed by Ostwald or improved by him, as the pycnometer, the thermostat, the viscometer apparatus developed for measuring the internal friction of liquids, the arrangement for measuring electrical conductivity, the drop electrodes and others.[222]

Walden also presented a panoramic view on Ostwald's contributions for the popularization and teaching of physical chemistry, highlighting his activity as editor of *Zeitschrift*, writer and founder of a relevant school of physico-chemists in University of Leipzig.[223] Walden highlighted some writings of the very extensive Ostwald's bibliography, consisting of forty-five books embracing history of chemistry, textbooks, handbooks and other subjects; more than 500 scientific papers and 5000 reviews.[224]

The hagiographical letter sent by Walden contrasts with the discrete message written by the Baltic-German chemist Maximilian (von) Glasenapp. Born in Kurland, city belonged to Russian Empire, Glasenapp studied chemistry at Riga Polytechnic School between 1867 and 1870, where he became professor of chemistry eight years later.[225] Working on technical and industrial subjects, he developed works for Silicon industries and investigated physico-chemical properties of cements, fermentation process and agricultural chemistry. As Ostwald, Glasenapp dedicated himself to editing scientific periodicals. From 1882 until 1914, he was editor of *Rigasche Industrie-Zeitung*, an engineer and technology journal.[226]

Different from Walden's long letter, Glasenapp was synthetic in his letter, arguing that Ostwald should be awarded for the sum of his lifetime achievements:

> "To draw out a particular work from the long series of his well-known and excellent literary products by this extraordinary productiven pioneer and advocate of physical chemistry, seems to be in vain here; in the case of a researcher like Wilhelm Ostwald, it is more a matter of the so admirable totality of the work and his brilliant accomplishments, which are in close connection one to each other."[227]

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[222] Paul Walden to Nobel Committee of Chemistry.
[223] Paul Walden to Nobel Committee of Chemistry.
[224] Schummer, *Biography of Wilhelm Ostwald.*
[225] I. Ja. Grosvald and Ju. Ja. Ėjduk "Žizn' i deiatel'nost' professora Maksimiliana Glazenappa," *Iz istorii estestvoznanija i techniki Pribaltiki* no. 1 (1968): 179-187.
[226] Grosvald and Ėjduk "Žizn' i deiatel'nost' professora Maksimiliana Glazenappa," 179-187.
[227] "*Ein besonderes Werk dieses so ausserordentlich productiven Bahnbrechers und Förderers der physikalischen Chemie aus der langen Reihe seiner allbekannten und vortrefflichen literarischen Erzeugnisse herauszugreifen, erscheint hier unthunlich; es kommt bei einem Forscher, wie Wilhelm Ostwald, vielmehr auf die so überaus fruchtbare Gesamtthätigkeit und auf seine gesammten glänzenden Leistungen an, die unter einander in engsten Zusammenhange stehen.*" Maximilian Glasenapp to Nobel Committee of Chemistry 10/23 January 1904, Nobel Archives,Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.

Both Walden and Glasenapp based their nominations in Ostwald's lifetime achievements, but these successes were not restricted to his experimental activities. They highlighted the importance of activities that normally are ignored by scientific awards, as teaching activity or literary work.

However, neither the concise letter from Glasenapp or the biographical stretch from Walden on Ostwald' successes was effective. Ignoring Ostwald's experimental and theoretical works, the report from Nobel committee considered that Ostwald's works were merely literary, refusing his candidacy:

> "Ostwald's merits are predominantly to be found in the area of scientific chemistry literature. (…) In these works, most of which have been published in several editions and in several languages, the author has, in an original and brilliant style, and from a physical chemistry viewpoint, discussed nearly all the important phenomena within inorganic and analytical chemistry, and detailed the inner connections between various groups of such phenomena. (...) Ostwald's position in present day scientific chemistry literature is rather similar to the position held by Berzelius during the 1820's and 1830's, and there can be no doubt that Ostwald above others should be considered in this year's awards assessment, if the prize in chemistry was awarded on literary merits in writings about the development of the science of chemistry in general."[228]

The Nobel of Chemistry in 1904 was granted for the Scottish William Ramsay for the discovery of inert elements in air that resulted in the creation of Noble Gases group in periodic system.

Nobel Prize of Chemistry in 1905 and 1906: Support from America

Ostwald kept being nominated for Nobel Prize in following editions, and in Nobel Prize editions of 1905 and 1906 he was supported by former pupils that had a central role in the dissemination of physical chemistry in scientific circles of Great Britain and United States.

Ostwald's laboratory received students from many countries and extended his methodology and influence around the world. Americans were one of the most representative

[228] Nobel Committee of Chemistry Report 1904. Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.

groups in his laboratory: he received 44 chemists from United States, a large part of which came to do Ph. D. studies, but others were just visitors that would like to learn the new theories of physical chemistry. Returning to United States, the students brought Ostwald's didactic, thinking and research approach that were assimilated and improved in the American universities and industries, which resulted in the rise of United States as an international potency in Physical and Theoretical Chemistry research in the twentieth century.[229]

Among the American chemists who worked at Ostwald's laboratory, Theodore Richards (1868-1928) and Arthur A. Noyes (1866-1936) were invited to be nominators in 1905 and 1906, respectively.

Richards was a brilliant pupil of Josiah Cooke (1827-1894) who finished his Ph.D. on measurements of atomic weights at the Harvard University in 1888, when he was just 20 years old. In 1895, Cooke died and Richards was pointed as Professor of physical chemistry at Harvard University. Trying to learn about the new physico-chemical theories, he went to Germany to meet some researchers, as Ostwald and Nernst.[230]

Richards was the first American to receive a Nobel Prize of Chemistry. He was laureate in 1914 for his precise measurements of atomic weights.[231] He also found differences between atomic weights of elements from different sources that lead him to corroborate the isotopes theory. Beyond his interests on atomic properties, Richards dedicated himself also to issues as thermochemistry and electrochemical properties of substances, on which Ostwald had great interest.[232]

As Nobel prize nominator, Richards suggested as candidates the German organic chemist Adolf von Baeyer (1835-1917) and Wilhelm Ostwald for the following reasons:

> "If the Prize is to be given for originality, and for contribution to the sum of human knowledge, I suggest that the Prize be awarded to Adolf von Baeyer, of München, for his contribution for his researches (sic) in synthetic organic chemistry. If, on the other hand, the Prize may be given for general influence on chemical thought, and for philosophical grasp of the subject, I suggest that the Prize be

[229] John W. Servos, *Physical Chemistry from Ostwald to Pauling: The Making of a Science in America*. (Princeton: Princeton University Press, 1990), 53-99.
[230] Dudley R. Herschbach "Theodore William Richards: Apostle of Atomic Weights and Nobel Prize Winner in 1914" *Angew. Chem. Int. Ed.* 53, no. 51 (2014): 13982-13987.
[231] "The Nobel Prize in Chemistry 1914". Nobelprize.org. Nobel Media AB 2014. Web. 17 May 2018. <http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1914/>
[232] Herschbach "Theodore William Richards," 13982-13985.

awarded to Wilhelm Ostwald, of Leipzig, for his codification and presentation of the subject."[233]

Richard's letter suggest us that he was not sure about statutory rules. The recommendations that the prize should be given to chemical discoveries or improvements was loose enough to permit this kind of doubt. If discoveries are easier to identify, an improvement, on the other hand, could be interpreted in many ways. Richards probably considered an improvement in chemistry, for example, a technical upgrading, a conceptual change, or even a new way to understand chemical science. His acknowledgement to Ostwald's philosophical contributions also show us that he considered theoretical works in a high degree and that they could be great enough to overwhelm a discovery or an experimental improvement.

Another aspect of Richards' nomination is the choice of two representatives of different scientific styles and disciplines. As Ostwald devoted himself to several subjects in physical chemistry, von Baeyer spent his entire academic life to organic synthesis. His fame in chemistry came from the growth of the synthesis program in organic chemistry field, in the third quarter of nineteenth century, when structural theories had shown its power to understand the behavior of organic compounds. In von Baeyer's laboratory in Munich, many substances were synthesized, including indigo, responsible for a revolution in dyes production.[234] When physical chemistry attracted the attention of young chemists by the end of 1880's, von Baeyer's laboratory continued to attract chemists from several countries interested in organic synthesis.

Although Ostwald had also been a successful experimentalist, having established chemical laws and developed considerable number scientific instruments, Richards mentioned only Ostwald's philosophy, but it is not clear what it is and its characteristics. What does "chemical thought" mean and what is that so influential philosophy that Ostwald developed?

Ostwald's philosophy could be seen as a complex amalgam of science, energetics, monism and positivist ideas that resulted in an unconventional worldview that guided in some way his scientific approach and interests after 1890. In 1905, he was engaged in showing the

[233] Theodore Richards to Nobel Committee of Chemistry 04 January 1905, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences (*in verbatim*).

[234] Laylin K. James *Nobel Laureates in Chemistry, 1901-1992* (Washington, D.C.: American Chemical Society and the Chemical Heritage Foundation, 1995): 30-34.

uselessness of atomic hypothesis and developing an energetic approach to chemistry, although the controversial repercussion of his ideas in the meeting of the Society of German Naturalists and Physicians in 1895 had diminished the interest of scientific community.[235] His driving philosophical question on what was the ground of all the sciences led him to consider energy concept as fundamental and to try reformulating the conceptual structure of chemistry by means of energetics and a phenomenological approach, dismissing what he considered as pure metaphysics. Following previous thinkers as Auguste Comte (1798-1857), Ostwald was trying to include other areas of human knowledge, as biological and social sciences and psychology in his systematization, using energy idea as the common point among natural and social phenomena.[236]

Probably Richards was referring to these characteristics of Ostwald's thinking in his letter, specially the reformulation of chemistry on a phenomenological basis. It is relevant to point that Ostwald and Richards - as many other scientists - had no reservations about discussing philosophical topics that emerged from their experimental works, as show us their correspondence:

> "My dear prof. Ostwald
>
> I enclose reprint the manuscript of a paper which is now being printed in the Proceedings of the American Academy. I hope that you may be able to print it soon in the Zeitschrift [für Physikalische Chemie]; and should be glad if you could print also the proceeding paper "The possible significance of changing atomic volume" which I send by this mail.
>
> I am afraid that you will not approve of a view so material, but to me it seems to reconcile the atomic hypothesis with Energetics, as well as with the philosophical doctrine of continuity. My colleagues here are even more convinced than I am of the extreme importance of the papers." [237]

This letter is an example of how philosophy could be useful when allied to chemistry and also suggests the existence of a group of chemists interested in these issues at Harvard.

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[235] Robert J. Deltete "Helm and Boltzmann: Energetics at the Lübeck Naturforscherversammlung" *Synthese* 119, no. 1, (1999): 45-68.
[236] Wilhelm Ostwald *Vorlesungen über Naturphilosophie: gehalten im Sommer 1901 an der Universität Leipzig*. Leipzig: Veit & Co., 1902.
[237] Theodore Richards to Wilhelm Ostwald, 17 January 1902. Archive of Academie of Sciences of Berlin, NL Ostwald, signature 2460, n. 106/29.

Not surprisingly, Ostwald was at Harvard University in 1905 as an invited professor, teaching, in addition to catalysis, his natural philosophy for chemistry students.[238]

But Nobel committee did not see Ostwald's natural philosophy as a sufficient reason to grant him the prize in 1905. The other candidate of Richards, Adolf von Baeyer, received the prize for a set of achievements in organic synthesis.

In 1906 Ostwald was nominated once more by an American pupil, the chemist Arthur Amos Noyes. Trained as organic chemist at Massachusetts Institute of Technology (M. I. T.), Noyes intended to work under von Baeyer' supervision at the University of Munich. He travelled to Germany in 1888, but there was no place for new students. Looking for other possibilities, he went to University of Leipzig to work with Johannes Wislicenus, but there he was attracted by Ostwald's lectures on physical chemistry and he decided to do his Ph. D under Ostwald's supervision.[239]

Noyes held the chair of Theoretical Chemistry at M. I. T. from 1899 to 1919. There, he build and directed the Research Laboratory of Physical Chemistry for sixteen years, establishing the basis of the graduate program of physical chemistry in the institution. Along his career, Noyes tried to determine physical chemical constants, to investigate the behavior of chemical reactions in equilibria, and to develop analytical methods. He is also recognized as textbooks writer and builder of institutions and research schools, just like Ostwald.[240,241]

Noyes purposed Ostwald's candidacy to Nobel of chemistry asserting that "after Professors van't Hoff and Arrhenius, he deserves most credit for the remarkable development of the modern science of physical chemistry."[242]

As Walden in 1904, Noyes also suggested that he should be nominated by a set of achievements, as much experimental achievements in chemistry as extra-laboratorial works, that could be considered those activities proper to science beyond research, as epistemological contributions, pedagogical and teaching activities, scientific divulgation and others. Noyes presented some of these Ostwald's extra-laboratorial achievements as a partial reason for his nomination:

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238 Ostwald, *Lebenslinien*, 401-432.
239 Servos, *From Ostwald to Pauling*, 58.
240 Servos, *From Ostwald to Pauling*, 83-84.
241 Pauling, Linus "Arthur Amos Noyes" *Memoirs of National Academy of Sciences*. 31 (1958): 322-348.
242 Arthur A. Noyes to Nobel Committee of Chemistry 16 January 1906, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.

> "It would seem to me that the prize, if granted to him, should be awarded upon this general basis – namely, for his many-sided contributions to the development of science of Physical Chemistry. He seems to me to deserve the prize not as a recognition of any specific original discovery, but partly on account of the wide variety of his physical-chemical researches, and mainly on account of the great value of his efforts in creating und systematizing the science of physical-chemistry through the publication of his 'Lehrbuch der allgemeinen Chemie', through the foundation of the 'Zeitschrift für Physikalische Chemie', through the creation of a school of younger investigators, through his constant efforts to enforce on the attention of contemporary scientists the recent developments in Physical Chemistry, and finally, through his vigorous support of energy considerations and of an empirical basis for the fundamental principles of the science, which must be recognized as highly valuable even by those who may think he has gone too far in his depreciation of molecular conceptions."[243]

In Noyes' letter there is no direct mention to any specific work in chemistry, but many mentions to Ostwald's efforts for organization, popularization and teaching of physical chemistry. As previous nominators, Noyes pointed the importance of Ostwald's role as spokesman of this discipline, his efforts in the training of young chemists and his so celebrated writings. However, the most peculiar achievement pointed by Noyes is Ostwald's "vigorous support of energy considerations." This statement refers to Ostwald' strong support to Energetics to the detriment of a mechanistic world view and its science, as atomic theory.

Energetics, the anti-mechanistic scientific program which sought to unify and reinterpret science in terms of energy and phenomenological laws describing its transformations, dominated Ostwald' scientific interests since the 1890's.[244] Ostwald was one of the main spokesman of energetics and supported it even after its abandonment by the scientific community in the beginning of twentieth century, when the program acquired a predominantly philosophical purport.

Although there are few mentions to Noyes relation with Energetics in literature, he was not indifferent to Ostwald's Energetics and, in some way, he was influenced by this program: the historian Mary Jo Nye argues that an energeticist approach in Noyes' teaching and

[243] Arthur A. Noyes to Nobel Committee of Chemistry 16 January 1906.
[244] Robert J. Deltete "Wilhelm Ostwald's Energetics 1: Origins and Motivations," *Foundations of Chemistry,* 9, no. 1, (2007): 3-56.

textbooks is noticeable.[245] However, his relation with Energetics did not prevent Noyes to criticize some ideas of Ostwald's energeticist theory, as for example, the rejection to use of atomic hypothesis in chemistry:

> "I had underlined some passages that I think may be of interest. As you will see, if you care to look the sheets over, I can not regard matter as "complex of energy" merely. Nor does it seems (sic) to me probable the atomic conception is of short life; its rejection at the present time would leave organic chemistry a chaos, and no other system of correlating of the facts of that science has as yet been so much as hinted at."[246]

Even not being a full energeticist, Noyes was not indifferent to Ostwald's Energetics, being at least sympathetic by this program. Therefore, it is visible that Noyes attributed high value to Ostwald's energetics as a scientific contribution, not only as a philosophy.

Ostwald's Energetics and his activities for the teaching and popularization of physical chemistry constituted, according to Noyes, a true, extraordinary and original improvement to the whole chemistry that should be recognized by Nobel Committee:

> "Permit me to express the opinion that a man who has contributed in so marked a degree to the systematization and extension of a body of knowledge is no less deserving of the highest scientific recognition than is the original discoverer of an important principle."[247]

Ostwald also received support in 1906 from the Scottish chemist James Walker (1863-1935), the first Ostwald's foreigner student in Leipzig. As a professor at the University College, in Dundee, he dedicated himself to electrochemistry and measurements of dissociation constants of organic acids and bases.[248] He is also responsible to spread the ionist ideas in English world through his translation of Ostwald's *Grundriss der allgemeinen Chemie* (1890)[249] and his own book *Introduction to Physical Chemistry* (1899).[250]

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245 Mary Jo Nye "From student for teacher: Linus Pauling and the reformulation of principles of chemistry in the 1930's" in *Communicating Chemistry: Textbooks and Their Audiences, 1789-1939* ed. Anders Lundgren and Bernadette Bensaude-Vincent (Canton, MA: Science History Publications/USA, 2000): 401.

246 Arthur A. Noyes to Wilhelm Ostwald 17 November 1896. Archive of Academie of Sciences of Berlin, NL Ostwald, signature 2171, n. 153/10.

247 Arthur A. Noyes to Nobel Committee of Chemistry 16 January 1906 (*in verbatim*).

248 James P. Kendall "Sir James Walker. 1863-1935," *Obituary Notices of Fellows of the Royal Society* 1 no. 4 (1935): 536-549.

249 Wilhelm Ostwald, *Outlines of General Chemistry*. London: Macmillan, 1890.

Different from Noyes, Walker indicated Ostwald for the prize based on his experimental investigations on chemical affinity of acids and bases, developed in the beginning of his career. However, he also mentioned Ostwald's role as teacher and writer as important contributions for chemistry:

> The special ground on which I make this proposal is Professor Wilhelm Ostwald's work on the affinity of acids and bases (…). Besides this special claim to consideration, there may be urged in favor of Professor Ostwald's candidature the circumstance that by his writings (in special by his Lehrbuch der allgemeinen Chemie) and by his teaching, he has founded a school of Physical Chemistry which has a deep and direct influence in all parts of the world.[251]

However, in 1906 the French chemist Henri Moissan received the Nobel of Chemistry for the isolation of fluorine element. Moissan received considerable international support during the previous year, but his candidacy was eclipsed by von Baeyer's supporters. In 1906, he received again strong support for the prize, but another candidate, the Russian chemist Dmitri Mendeleev, appeared as a possible candidate since the nominators saw the possibility to prize old works, as in the case of von Baeyer in the previous year.[252]

Discoveries of new elements and substances were commonly recognized as of highest scientific value, due to the potential developments in science and further products for industry. On the other hand, the periodic law of elements expressed through Mendeleev's periodic table represented one of the most relevant changes of the nineteenth century chemistry, organizing chemical elements known by then and predicting the existence of new ones. In this context, there was no place to prize pedagogical or philosophical achievements like those pointed by Ostwald's supporters.

Having four nominations and the majority of member's votes, Mendeleev was indicated as prize-winner by the Nobel committee of Chemistry. However, he had a powerful opponent in the Academy: Svante Arrhenius. Some years before, Mendeleev and Arrhenius had a public disagreement, due to the scepticism and criticism from the Russian chemist about Arrhenius'

[250] James Walker, *Introduction to Physical Chemistry*. London: Macmillan, 1899.
[251] James Walker to Nobel Committee of Chemistry 26 January 1906, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.
[252] Friedman, *Politics of Excellence*, 32-34.

electrolytic theory.[253] Apparently he saw Mendeleev's posture as a personal attack, for in 1906, Arrhenius and his circle of supporters strongly defended Moissan candidacy in the plenary of Royal Academy of Sciences to preclude Mendeleev from winning the chemistry prize, arguing that his works were too old to be nominated.[254] His efforts in avoiding Mendeleev's candidacy to the prize worked well and Moissan received the Nobel of Chemistry in 1906 for the discovery of fluorine.

The posture of Arrhenius and his fellows against the recommendation of Nobel committee of Chemistry highlighted Arrhenius' powerful position in the backstage of the chemistry prize choices, avoiding enemies and advancing colleagues. On this episode, the historian Robert Friedman argues that it represented a break of consensus which until then had been respect in the choices for the chemistry prizes.[255]

Nobel Prize of Chemistry 1907: The Christiania's group

In Nobel Prize edition of 1907, Ostwald received support from a particular group of professors from University of Christiania.[256] This group was composed by chemists and geologists who were interested in topics of inorganic chemistry and mineralogy. Physicochemical theories helped them to understand their topics. This group was composed by two Norwegian geologists, Waldemar Christopher Brögger (1851-1940) and Johan Hermann Lie Vogt (1858-1932), the chemist and politician Thorstein Hiortdahl (1839-1925) and by the Jewish chemist Heinrich Goldschmidt (1857-1937).

Even being different areas of knowledgement, chemistry and geology shared interests, techniques and theories for a long time, trying to understand and describe the formation of mineral compounds. Chemistry provided a theoretical and conceptual basis for the reactions involving minerals, which physical chemical theories proved to be useful for geological research. Brögger's works on the minerals of Norway[257] and Vogt's investigation on the

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[253] Carmen J. Giunta "Dmitri Mendeleev's Nobel-Prize-Losing Research," in *The Posthumous Nobel Prize in Chemistry Volume 1: Correcting the Errors and Oversights of the Nobel Prize Committee* (ACS Symposium Series, 2017), 31-49. http://dx.doi.org/10.1021/bk-2017-1262.ch003.

[254] Remembering this episode, the chemist and member of Nobel committee of Chemistry Otto Pettersson wrote in his memories that Arrhenius' posture was not in favor to Moissan, but against Mendeleev. See Giunta, "Dmitri Mendeleev's Nobel-Prize-Losing Research," 34-35 and Friedman, *Politics of Excellence*, 33-34.

[255] Friedman, Politics of Excellence, 32-34.

[256] Christiania is the old name of Oslo, Norway.

[257] Olaf Holtedahl "Brögger, Waldemar Cristopher," in *Dictionary of Scientific Biography* org. Charles Coulston Gillispie and Frederic L. Holmes 2 (New York: Scribner, 1981): 486- 487.

relation between physico-chemical properties and geological composition[258] were examples of the productive relation between geology and physical chemistry.

Also dedicated to geology and chemistry, the co-founder of Norwegian Chemical Society, Thorstein Hiortdahl used physical chemical frameworks to understand the formation of crystals, one of his scientific interests and, also like Ostwald, Hiortdahl was textbook writer and interested in history of sciences.[259]

Beyond the geologists, organic chemists started to consider physical chemistry necessary for their discipline too. The works of Heinrich Goldschmidt were considered an example of the fruitful approximation of these disciplines, due to his use of physical chemical methods and theories to understand organic reactions, like in his studies on kinetics of azo compounds and catalytic action of hydrogen and hydroxide ions for esterification and saponification reactions.[260]

All of these scientists defended Ostwald's candidacy for the large number of experiments carried out by him to prove the value of physico-chemical theories to the understanding of chemical substances and his laboratory methods (devices and improvements) developed to physico-chemical inquiries:

> "(…) It is generally acknowledged that Ostwald, during the time when he was director of the physical chemistry laboratory of Leipzig, not only carried out an extraordinary number of research experiments, which proved the veracity of the theories of physical chemistry, but also worked out the practical working methods nowadays employed by all physical chemists. Nearly everywhere where there is work done in the field of physical chemistry, Ostwald's methods are being used."[261]

In addition to his experimental merits, the group from Christiania also argued that Ostwald should be prize for his writings and pedagogical activity, as previous supporters also highlighted. Ostwald succeeded in spreading the new chemical ideas by means of his pedagogical and literary activity. Among his many writings, his textbooks stood out in

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[258] Christopher Oftedahl "Vogt, Johan Hermann Lie," in *Dictionary of Scientific Biography* org. Charles Coulston Gillispie and Frederic L. Holmes 14 (New York: Scribner, 1981): 58-59.
[259] Ove Kjølberg "Thorstein Hiortdahl," in *I Norsk biografisk leksikon* accessed May 17, 2018, https://nbl.snl.no/Thorstein_Hiortdahl.(2009, 13. februar)
[260] Alfred Stock "Sitzung am 11. Oktober 1937," *Berichte der deutschen chemischen Gesellschaft* 70, no. 11 (1937): 149-150.
[261] Thorstein Hiortdahl, Johan H. L. Vogt, Waldemar C. Brögger and Heinrich Goldschmidt to Nobel Committee of Chemistry 23 January 1907, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.

propagation of physico-chemical theories in the most varied and distant scientific circles. Maybe for this reason, Ostwald's textbooks were so famous in scientific community in general, transcended the boundaries of chemistry and turned into important basis for other sciences. The acknowledgement from Christiania's group for these pedagogical contributions reflects the idea that, if Arrhenius and van't Hoff had built the building of physical chemistry, Ostwald organized and turned it into a habitable place.

The supporters did not mentioned specifically what was the teaching method developed by Ostwald, but we can consider his textbooks as material examples of his pedagogical achievements. In their letter, these scientists stressed the relevance of two textbooks, the already mentioned *Lehrbuch der allgemeinen Chemie*[262,263] (1885 and 1887, 1st edition) and his *Grundlinien der Chemie*[264] (1889, 1st edition).

> "Likewise, the teaching method in the field of physical chemistry is nearly exclusively the work of Ostwald. (...) We will content ourselves with calling attention to his large 'Lehrbuch der allgemeinen Chemie' and his 'Grundlinien der Chemie'. The first edition of the former book was published at a time when the works of Van't Hoff and Arrhenius were not yet published and not yet known in wider circles. The second edition, which is constantly being reprinted, is a comprehensive codification of the results of physical chemistry, and far from just enumerating said results, it also thoroughly and critically evaluates them, and at the same time presents a number of brilliant ideas for further works. His 'Grundlinien' treats of inorganic chemistry in a new way, on the basis of physical chemistry, and has been generally acknowledged as an important improvement in the field of chemistry teaching pedagogy."[265]

Despite its importance for scientific training, communication and formation of scientific community, pedagogical activities normally plays a secondary role in science. Discoveries, methods or theories are still considered for some practitioners as the only possible products of scientific activity, ignoring the importance of writings with pedagogical purposes.[266] However,

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[262] Wilhelm Ostwald, *Lehrbuch der Allgemeinen Chemie.* I. Band: Stöichiometrie. Leipzig, W. Engelmann, 1885.
[263] Wilhelm Ostwald, *Lehrbuch der Allgemeinen Chemie*. II. Band: Verwandtschaftslehre. Leipzig, W. Engelmann, 1887.
[264] Wilhelm Ostwald, *Grundlinien der anorganischen Chemie.* Leipzig, W. Engelmann, 1900.
[265] Thorstein Hiortdahl, Johan H. L. Vogt, Waldemar C. Brögger and Heinrich Goldschmidt to Nobel Committee of Chemistry 23 January 1907.
[266] John Hedley Brooke "Introduction: the study of chemical textbooks," in *Communicating Chemistry: Textbooks and Their Audiences, 1789-1939* ed. Anders Lundgren and Bernadette Bensaude-Vincent (Canton, MA: Science History Publications/USA, 2000): 1-18.

historians[267] have shown that textbooks could be powerful frameworks to publicize new ideas and building research schools, as Ostwald's *Lehrbuch* was for ionic theory, for example.

The propagation of the physico-chemical theories contributed not only for the development of chemistry, but for the scientific fields in the chemistry boundaries that used the new chemical concepts and methods in their disciplines. Therefore, it is not peculiar that Ostwald's books have been so popular among practitioners of different branches of science, as geologists from Christiania. Mentions to his pedagogical writings in the nomination letter written by this particular group of supporters is a typical example of the pedagogical value of Ostwald's textbooks.

Neither Ostwald's pedagogical skills nor his method or experimental work could change the decision of academy, that continued to consider Ostwald achievements extra scientific or, as in the previous editions, merely literary. Among the nominees for 1907 prize, there was prominent experimental chemists, as Marcellin Berthelot, Walther Nernst, William Crookes, Giacomo Ciamician and others. The winner was the German chemist Eduard Buchner[268] (1860-1917) for his discovery of cell-free fermentation process.

Nobel Prize of Chemistry in 1908: the late conversion to atomism

Despite his actions for the establishment of new theories and disciplines, and his experimental and literary works, maybe Ostwald is best remembered today by his strong rejection to atomic theory. Adept of atomic theory in the beginning of his career, Ostwald became skeptical about the value of a corpuscular approach as his contact with phenomenological thermodynamics increased. Around the 1890's, his initial beliefs on a

[267] As a product of scientific culture, textbooks are a window for the past of science and its teaching, helping historians to understand the spread of scientific practices in different contexts, as well as its theories, methods and values. There is a increasingly literature defending and using textbooks as objects for historical analysis. See Josep Simon "Textbooks," in *A Companion to the History of Science* ed. B. Lightman (Chichester: Wiley-Blackwell, 2016): 400–413; Kathryn M. Olesko "Science Pedagogy as a Category of Historical Analysis: Past, Present, and Future," *Science and Education*, 15 no. 7–8 (2006): 863–880; David Kaiser (ed.), P*edagogy and the practice of science : historical and contemporary perspectives*, Cambridge, MIT Press, 2005. Lundgren and Bensaude-Vincent (ed.), *Communicating Chemistry: textbooks and their audiences, 1789-1939*, Canton: Science History Publications/USA, 2000.

[268] Despite his prize, Buchner was considered an ordinary chemist by some prominent colleagues. See Feldman, *The Nobel Prize*, 208 and Lothar Jaenicke "Centenary of the Award of a Nobel Prize to Eduard Buchner, the Father of Biochemistry in a Test Tube and Thus of Experimental Molecular Bioscience," *Angewandte Chemie International Edition* 46, no. 36, (2007): 6776-6782. doi:10.1002/anie.200700390.

mechanical worldview had already been abandoned and Ostwald started his crusade against mechanical entity realism by means of his energetics.[269]

But his adoption to phenomenological thermodynamics did not explain totally his change. The *zeitgeist* from the end of century, surrounded by anti-materialism ideas and a disappointment with mechanics also played a role in his and his fellows' antiatomist posture.[270] But while many of these antiatomists turned to other alternative paradigms, as phenomenological thermodynamics, electromagnetism or even the theoretical pluralism, Ostwald developed a particular interpretation of energetics that made him a difficult ally even for other critics to atomic theory, as Georg Helm and Ernst Mach.[271] Despite these difficulties among them, no one but Ostwald had the means to spread energetics in wide circles: he had *Zeitschrift*, his books and a group of young pupils that admired his ideas. These factors contributed for Ostwald to become the central figure of energeticist program.

In 1908, however, the situation had changed: energetics program lost adherence since the end of 1890's and the new scientific discoveries of the turn of century, as radioactivity, photoelectric effect and the electron had shown that, even complex reality could have an atomistic ground. Ostwald was certainly conscious of these new ideas, many of them reported in his *Zeitschrift*, but he still refused corpuscular theory. The science of new century took some time to change Ostwald's antimechanicist convictions, but in 1908 it finally got.

However, this change did not influence the support received by him in 1908 for the Nobel Prize. His conversion to atomism occurred in the summer of 1908, whereas the nomination letters in his favor were sent in January of the same year. In 1908 Ostwald received the largest number of nominations in all editions that he was indicated – five letters from eight scientists. The reasons pointed out for his nomination were not so different from the previous years, but the list of his supporters brings some surprises, as his Dutch colleague and then professor at University of Berlin, J. H. van't Hoff, that nominated him for the first time.

In his brief letter, van't Hoff argues that the main Ostwald's achievements concerned to extra-laboratorial activities, but knowing that these merits were not sufficient for Ostwald to

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[269] Deltete, "Wilhelm Ostwald's Energetics 1," 6-9.

[270] Helge Kragh "A Sense of Crisis: Physics in the fin-de-siècle Era," in *The Fin-de-Siècle World* ed. Michael Saler, (New York, Routledge, 2014): 441-455.

[271] Matthias Neuber "Uneasy allies: Ostwald, Helm, Mach and their Philosophies of science,"in *Wilhelm Ostwald at the crossroads between chemistry, philosophy and media culture*. ed. Britta Görs; Nikolaos Psarros and Paul Ziche, (Leipzig: Leipziger Universitätsverlag, 2005): 47-58.

be laureate, he emphasized Ostwald's experimental investigation on chemical affinity as the reason of his nomination:

> "I see as Ostwald's main merit the organization and promotion of physical chemistry, and then his *Lehrbuch*, the *Zeitschrift für Physikalische Chemie*, and the founding of the Electrochemical Society come into consideration. However, since the statutes of the Nobel Foundation may require more creative activity, I would like to emphasize Ostwald's works on determination of affinity which were concluded in the *Verhandlungen* Volume III, 170, 241, 369 in the *Zeitschrift für Physikalische Chemie*."[272]

Ostwald received support from another physical chemist, the Swiss Hans Landolt (1831-1910) from University of Berlin. Even not being considered as one of the representatives of modern physical chemistry, it is possible to see in his research an important characteristic of this discipline, relating chemical composition with physical properties of the substances,[273] as for example his works on the variations of luminosity from different gases produced in a Bunsen burner, and on the relation between specific refraction and molecular weights of organic compounds.[274]

Landolt's nomination is grounded in two achievements. First, Landolt considered Ostwald worthy of the prize due to "the important Dilution Law established by him"[275] fruit of his works on affinity. Second, Landolt pointed Ostwald's *Lehrbuch der allgemeinen Chemie* as an important contribution to chemistry, "which gave a major impetus to the great development of this discipline in modern times."[276] On the importance of this book, Landolt affirmed:

> "The main achievements of Ostwald are literary - already in 1884-87 years the first edition of his 2 volumes 'Lehrbuch der Allgemeinen Chemie' appeared, in

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[272] "*Das Hauptverdienst Ostwald's erblicke ich in der Organisation und Förderung auf dem Gebiet der physikalischen Chemie, und dann kommen wesentlich sein Lehrbuch, die Zeitschrift für physikalische Chemie und die Gründung der elektrochemischen Gesellschaft in Betracht. Da die Statuten der Nobelstiftung jedoch vielleicht mehr eine schöpferische Tätigkeit fordern, möchte ich besonders Ostwald's Arbeiten zur Bestimmung der Affinität hervorheben, welche in den Verhandlungen Band III, 170, 241, 369 in der Zeitschrift für physikalische Chemie ihren Abschluss fanden*." J. H. van't Hoff to Nobel Committee of Chemistry 28 January 1908, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.
[273] Servos, *From Ostwald to Pauling*, 11-13.
[274] Ruth G. Rinard "Landolt, Hans," in *Dictionary of Scientific Biography* org. Charles Coulston Gillispie and Frederic L. Holmes 7 (New York: Scribner, 1981): 619-620.
[275] Hans Landolt to Nobel Committee of Chemistry 26 January 1908, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.
[276] Hans Landolt to Nobel Committee of Chemistry 26 January 1908.

> which the never attempted hitherto unification of the branches of science described as theoretical chemistry and physical chemistry was carried out with great skill. There is no doubt that this book has become an essential cause for the astonishing upswing which general chemistry took since 1890, stimulating the research drive in this field to a high degree."[277]

Even not being the ground of his nomination, Landolt reinforced his nomination quoting Ostwald's writings on natural philosophy and history of chemistry as well as other experimental investigations, including catalysis, which was not mentioned in nomination letters since 1904, and his investigations on foundations of energetics.[278]

Another supporter from University of Berlin was the pharmacist and botanist Hermann Thoms (1859-1931), founder of German Pharmaceutical Society. In the beginning of his career, he worked in industry, where he developed a process to obtain in large-scale the artificial sweetener Dulcine (4-Ethoxyphenyl urea).[279] In 1895, he became a lecturer at University of Berlin, where he became full Professor in 1900 and the first director of the Institute of Pharmacy. Among his several activities, Thoms dedicated himself to writing, having a considerable number of textbooks and technical literature on pharmaceutical subjects.[280]

Thoms did not mention any specific contribution in his nomination letter, but he presented in a general manner the importance of Ostwald for the establishment of physical chemistry and its theories, his international fame and his literary activity. Besides Ostwald's *Lehrbuch der allgemeinen Chemie* and *Grundriss der allgemeinen Chemie*, he highlighted other writings as *Hand- und Hilfsbuch zur Ausführung physiko-chemischer Messungen,*[281] *Elektrochemie: ihre Geschichte und Lehre*[282] and the controversial paper presented by Ostwald

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[277] "*Die Hauptleistungen Ostwald's liegen aber auf literarischem Gebiete. Schon in der Jahre 1884-87 erschien die erste Auflage seines 2 bändigen "Lehrbuch der allgemeinen Chemie", in welchem die bis dahin noch nie versuchte Vereinigung der früher theils als theoretische theils physikalische Chemie bezeichneten Wissenschaftszweigen mit grossem Geschick durchgeführt wurde. Es unterliegt keinem Zweifel, dass dieses Buch eine ganz wesentliche Ursache des erstaunlichen Aufschwungs geworden ist, welchen die allgemeinen Chemie seit etwa dem Jahre 1890 genommen hat, indem er den Forschungstrieb auf diesem Gebiete in hohem Grade anregte.*" Hans Landolt to Nobel Committee of Chemistry 26 January 1908.

[278] Hans Landolt to Nobel Committee of Chemistry 26 January 1908.

[279] Georg Urdang "Hermann Thoms" *Pharmazeutische Zeitung*, 76, no. 96, (Dezember 2, 1931): 1349-1351.

[280] Armin Wankmüller "Hermann Thoms und die pharmazeutisch-chemische Literatur," *Pharmazie in unserer Zeit* 19, (1990): 204-207. doi:10.1002/pauz.19900190509.

[281] Wilhelm Ostwald, *Hand- und Hilfsbuch zur Ausführung physikochemischer Messungen*. Leipzig, W. Engelmann, 1893.

[282] Wilhelm Ostwald *Elektrochemie: ihre Geschichte und Lehre* Leipzig, Veit & Co., 1896.

in the meeting of the Society of German Naturalists and Physicians, *Die Überwindung des wissenschaftlichen Materialismus,*[283] which summarize his energeticist ideas.

From Ostwald's investigations, he presented a set of achievements, highlighting his works on chemical affinity; on which he expressed the importance of the creation of new devices for this purpose. Thoms also mentioned his contributions to electrochemistry and the catotype method developed by him and Gros:

> "Ostwald's works belongs to the field of physical chemistry, where he was the most outstanding representative for a long time and, by the most chemists, Ostwald is recognized without envy as being the one who brought visibility and importance to physical chemistry. His publications, most of which are published in the 'Work of the Physicochemical Institute of Leipzig University', concerned particularly to the problems of chemical affinity. His studies on the electrical conductivity of organic acids are especially important. The devices made by Ostwald for this purpose are used with special interest from all physico-chemists with preference.
>
> As the most zealous advocate of the ingenious theory of ions founded by Arrhenius, he paved the way for them in Germany and secured their recognition, which would not have been so without Ostwald's energetic and skilful intervention. Ostwald also published a number of works in this field, such as the 'color of the ions', the 'basis of galvanic potential differences'. More recently, Ostwald's work on 'catalysis,' especially on the 'catotypie', has drawn the general attention to him. As a longtime member and vice Chair of the International Atomic Energy Committee, Ostwald has earned great merit."[284]

Another nomination in Ostwald's favor was sent by the Jewish[285] organic chemist Emil Constam (1858-1917), professor at Zurich Polytechnic School. Son of German immigrants, he

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[283] Wilhelm Ostwald "Die Überwindung des wissenschaftlichen Materialismus," *Zeitschrift für Physikalische Chemie* 18, (1895): 305-320.

[284] "*Ostwald's Arbeiten bewegen sich auf dem Gebiete der physikalische Chemie, als deren hervorragendster Vertreter er lange Zeit hindurch galt, und von den meisten Chemikern wird neidlos anerkannt, dass Ostwald es gewesen ist, welcher die physikalische Chemie zu Ansehen und Bedeutung gebracht hat. Seine meist in den "Arbeiten des physikalisch-chemischen Instituts der Universität Leipzig" niedergelegten Veröffentlichungen beziehen sich besonders auf Probleme der chemischen Verwandtschaft. Vor allem wichtig sind seine Untersuchungen über die elektrische Leitfähigkeit der organischen Säuren. Die für diesen Zweck von Ostwald konstruierten Apparate werden von allen physikalisch-chemisch arbeitenden Chemikern mit Vorliebe benutzt. [...] Auch mit eigenen Arbeiten auf diesem Gebiete ist Ostwald hervorgetreten, so über die "Farbe der Jonen", über den "Sitz der galvanischen Potenzialdifferenzen". In neuerer Zeit haben Ostwald's Arbeiten über "Katalyse", besonders über die Katotypie, die allgemeine Aufmerksamkeit auf ihn gelenkt. Als langjähriger Mitarbeiter bez. stellvertretender Vorsitzender des Internationalen Atomgewichtausschusses hat sich Ostwald grosse Verdienste erwaoben.*" H. Thoms to Nobel Committee of Chemistry 20 January 1908, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.

[285] Before he became member of reformed church in 1880, he used the name "Kohnstamm".

was born in New York but his family returned to Germany when he was a child. At Zurich Polytechnic School, he studied under supervision of the organic chemist Victor Meyer (1848-1897), starting his scientific career as assistant of his laboratory.[286]

In the 1890's, he decided to turn his scientific activity to physical chemistry, becoming professor of this subject at Zurich Polytechnic. Interested in physical chemical measurement methods, he performed studies on this topic in Ostwald's laboratory between 1894 and 1895, and after he turned to thermochemistry topics.[287]

Like Thoms, Emil Constam indicated Ostwald for the Nobel by his lifetime achievements or "in honor of his incomparably extensive work as researcher, professor and writer in the fields of physical, inorganic and analytical chemistry."[288] He presented also some aspects of Ostwald's career to justify for his candidacy:

> "Like no other contemporary, he has developed the teaching and the methods of physical chemistry to a common good for researching chemists of all chemical disciplines, and has educated an astonishing number of students to outstanding university teachers in various countries. Through his numerous writings and the 'Zeitschrift für physikalische Chemie' founded by him, he brought the knowledge of general chemistry for the widest circles. An enumeration of his well-known works should therefore be unnecessary."[289]

Once more, the group of scientists from Christiania supported Ostwald. In 1908, however, they decided to put Ostwald's writings and teaching in the background and emphasized his experimental activities, presenting his works on chemical affinity as the main reason for his nomination:

> "(…) We permit ourselves to once again call attention to the fact that the results of Ostwald's first experimental research in chemical affinity was published

[286] P. Schläpfer "Obituary," *Schweizerische Bauzeitung* 69, no. 7, (1917): 79-80.
[287] Schläpfer "Obituary," 79-80.
[288] "*(...) und zwar in Würdigung seiner unvergleichlich umfassenden Tätigkeit als Forscher, Hochschullehrer und Schriftsteller auf den Gebieten der physikalischen, der anorganischen und der analytischen Chemie.*" Emil Constam to Nobel Committee of Chemistry 15 February 1908, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.
[289] *"Er hat wie kein anderer seiner Zeitgenossen die Lehren und Methoden der Physikalischen Chemie zum Gemeingut der forschenden Chemikern allen Richtungen gemacht und eine stattliche Zahl von Schülern zu hervorragenden Hochschullehrern in den verschiedensten Ländern ausgebildet. Durch seine zahlreichen Schriften und die von ihm gegründete "Zeitschrift für physikalische Chemie" hat er die Kenntnis der allgemeinen Chemie in die weitesten Kreise getragen. Eine Aufzählung seiner allgemein bekannten Werke dürfte sich daher erübrigen."* Emil Constam to Nobel Committee of Chemistry 15 February 1908.

earlier than van't Hoff's and Arrhenius's works, and it is generally acknowledged that Ostwald's work has, to a high degree, contributed to the theory of electrolytic dissociation so rapidly gaining ground. It appears to us to be beyond doubt that what we have here pointed out suffices to place Ostwald in the frontline of the most accomplished of the worshippers of chemistry, and we need not further dwell on the rather outstanding and unparalleled energy with which he has, both as a scientist doing research and through his publications, furthered our science."[290]

Considering the arguments presented by Ostwald's supporters in 1908 and previous editions, we can see that Ostwald's works in catalysis were not frequently pointed as reason for his award, appearing few times in the nomination letters. On the other hand, his works on determination of chemical affinity, which the most part was developed in the beginning of his career, were more popular among his supporters, as well as the mentions on the devices developed by him. Therefore, until 1908 catalysis had a secondary place in Ostwald's candidacy to Nobel Prize.

However, the nominators' arguments were fruitless. 1908 was, in Crawford words, "the Year of Atom:"[291] the already mentioned works on electric nature of atom and the determination of Avogadro constant that crowned atomic theory stimulated Arrhenius to use his influence to prize the German physicist Max Planck (1858-1947) for the physics prize and the New Zealand-born British physicist Ernest Rutherford (1871-1937) for the chemistry prize, both representatives of atomist tradition of science.[292] Arrhenius's efforts worked well just in chemistry committee, and Rutherford was awarded in 1908 by his works on disintegration of chemical elements and radioactivity.[293]

Quoting the letters sent in Ostwald's favor, the committee repeated in its report that Ostwald's contributions were merely literary and, for this reason, could not be considered as Nobel prize winner in 1908.

"(...) This assessment, which amounts to the main thrust of Ostwald's merits being found in the influence he has exercised in his public activities as author and lecturer, rather than in any "discovery or improvement", has won further approval in

[290] Thorstein Hiortdahl, Johan H. L. Vogt, Waldemar C. Brögger and Heinrich Goldschmidt to Nobel Committee of Chemistry 27 January 1908, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.
[291] Crawford "Arrhenius, the Atomic Hypothesis," 511.
[292] Crawford "Arrhenius, the Atomic Hypothesis," 511-519.
[293] "The Nobel Prize in Chemistry 1908". Nobelprize.org. Nobel Media AB 2014. Web. 25 Apr 2018. <http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1908/>

> several of the statements of proposal sent to the committee this year. Thus Prof. Constam motivates his proposal with Ostwald's '...incomparably extensive work as researcher, professor and writer'. According to Prof. Landolt, Ostwald's main merits ("Hauptleistungen") are literary, and Prof. van't Hoff writes: "I see the main merit of Ostwald in the organization and promotion in the field of physical chemistry and then its textbook, the Journal of Physical Chemistry and the foundation of the Electrochemical Society come into consideration". However, since the will and the wording of the statutes will not allow a prize for merits of this kind, no matter how momentous, the committee has not found sufficient reason to recommend Ostwald's candidature to the Academy this year."[294]

The committee refused him based in the statutory rules, in which just recent discoveries or improvements should be awarded. However, the nomination letters presented Ostwald's experimental works, which were ignored by the committee in its appreciation of candidacies. It is true that Ostwald's works on chemical affinity were already old in 1908, but the committee had shown itself flexible about old merits in other occasions.[295] On the other hand, Ostwald's dilution law, also frequently mentioned in the nomination letters, had some limitations that probably turned it into a not so convincing reason to ground the prize and his works on catalysis were not so valued by the supporters in the nomination letters. Having no discovery or improvement, in the understanding of the committee, one more time Ostwald's candidacy was disregarded.

Nobel Prize of Chemistry 1909: looking for (unnecessary) reasons

In 1909, Ostwald received just three nominations in his favor. One of them from his former pupil Georg Bredig (1868-1944), then professor of chemistry at University of Heidelberg. Bredig finished his Ph.D in 1894 under Ostwald's supervision. He worked as Ostwald's assistant from 1895 until 1901, when he was accepted as professor of chemistry at University of Heidelberg, where he stayed until 1910.[296]

In his extensive letter, Bredig presented three candidates for the prize: the organic chemists Theodor Curtius (1857-1928) and Richard Martin Willstätter (1872-1942), and

[294] Nobel Committee of Chemistry Report 1908. Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.
[295] Friedman, *Politics of Excellence*, 31-32.
[296] Werner Kuhn "Georg Bredig," *Chemische Berichte* 95 (1962): XLVII–LXIII.

Wilhelm Ostwald. Bredig's reasons to nominate Ostwald were very similar to those presented by Paul Walden in 1904: his experimental activity, his role as a writer and organizer of chemistry, and his importance as a teacher and critic of chemistry.[297]

About Ostwald's experimental activity, Bredig mentioned some of the topics to which he dedicated his life, as chemical affinity, electrochemical behavior of solutions and especially his works on catalysis, a topic that had already been presented in previous nomination letters, but not so emphatically.

Bredig's mention to Ostwald's catalysis studies was beneficial for his nomination. Bredig started his career in Ostwald's laboratory, where he developed his initial investigations on catalysis, so he understood the content and value of his works on this subject. As professor, Bredig developed important works on this issue, as the study on similar action of inorganic catalysts and enzymes, and the first synthesis of specific stereoisomer molecules by means of catalytic reactions.[298]

Even quoting experimental contributions from Ostwald to catalysis area, as the catalytic synthesis of nitric acid from ammonia and the katotypie process, Bredig gave more emphasis to his retaking to the Berzelius' catalysis concept, reinterpreting it in an experimental and kinetic basis that, according to Bredig, started a new period in catalytic research by encouraging students and peers to investigate catalytic phenomena.[299]

Even catalysis having been investigated by other contemporary chemists as Paul Sabatier (1854-1941) and Emil Fischer (1852-1919), Ostwald's interest in catalysis concept played an important role in the increase of catalytic studies, especially for his influential position in scientific community and for calling the attention of scientists and industry for the this branch of research. This topic became a popular research program in Ostwald's laboratory and, in a short time, his former pupils spread the program to different institutions.[300]

Bredig's mention to Ostwald's role as a writer, teacher, and organizer of chemical research are related with the similarities between Ostwald and the Sweden chemist Jöns Jacob Berzelius (1779-1848). Berzelius was a reference for chemical community in the beginning of nineteenth century, as defender of Lavoisier's chemical tradition and propagator of new

[297] Georg Bredig to Nobel Committee of Chemistry 1909, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.
[298] Kuhn "Georg Bredig" XLVII–LXIII.
[299] Georg Bredig to Nobel Committee of Chemistry, 1909. Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.
[300] Ostwald had around 20 students working on catalysis, who published his research in *Zeitschrift*. We intent to discuss Ostwald's catalysis works and his students in the second paper of this thesis.

scientific trends, as textbook writer. His research concerned chemical analysis, being credited for the discovery of new chemical elements.[301] Based on his electrochemical dualism theory, he arranged the known chemical elements in series of decreasing electronegativity. Being one spokesman of Dalton's atomic theory, he improved the theory and tried to determine atomic weights with precision, building famous tables with revised values.[302]

Bredig considered Berzelius' efforts for organization and systematization of chemical knowledge as similar to those developed by Ostwald. Like Berzelius, Ostwald was a successful textbook writer and propagator of new ideas. Working on catalysis, Ostwald gave a new shape to Berzelius' concept and tried to develop a theory for catalysis, allying experimental work and theoretical activity. For Bredig, the relevance of Berzelius came from his lifetime achievements and the same could be applied to Ostwald's case:

> "(...) if Berzelius lived today, the Nobel Committee would not hesitate for a moment to award him the prize, although it is difficult to cite a single particularly brilliant discovery. But you have to admire the overall performance of the man. The same is valid, in my opinion for Ostwald' scientific figure which is difficult to compare with other important chemists."[303]

Different from Bredig, van't Hoff was very succinct in his nomination letter. Supporting Ostwald's candidacy again, van't Hoff repeated the reasons pointed in 1908. However, in the event the Academy considering Ostwald's merits not enough for his nomination again, he presented Hans Landolt as another possible candidate for the prize.[304]

Ostwald's last supporter in 1909 was Arrhenius, that finally turned his attention to his candidacy after him recognized the relevance of atomic theory for the science. According to Crawford,[305] the most influential person for Ostwald acceptance of atomic theory was

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[301] Henry M. Leicester "Berzelius, Jöns Jacob," in *Dictionary of Scientific Biography* org. Charles Coulston Gillispie and Frederic L. Holmes 2 (New York: Scribner, 1981): 90-97.

[302] C. A. Russell "Berzelius and the development of the atomic theory," in *John Dalton and the progress of science* ed. Donald Stephen L. Cardwell (Manchester: Manchester University Press,1966): 259-263.

[303] "*Wenn heute Berzelius lebte, würde die Nobelkommission wohl keinen Augenblick zögern, ihn den Preis zuzuerkennen, obwohl man auch bei ihm schwerlich eine einzelne besonders glänzende Entdeckung anführen kann. Die Gesamtleistung des Mannes aber muss man jedenfalls bewundern. Das Gleiche gilt meines Erachtens auch von der, mit andern chemischen Größen schwer kommensurablen, wissenschaftlichen Erscheinung Ostwalds.*" Georg Bredig to Nobel Committee of Chemistry, 1909.

[304] J. H. van't Hoff to Nobel Committee of Chemistry 23 January 1909, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.

[305] Crawford "Arrhenius, the Atomic Hypothesis," 511.

Arrhenius. In a lecture from autumn of 1908, he related for the members of Swedish Society of Chemist his role in Ostwald conversion:

> "(...) According to Arrhenius, when Ostwald was writing a new chapter on colloids for the fourth edition of his Grundriss der allgemeinen Chemie (1909), he had his attention drawn to Theodor Svedberg's work on Brownian movement. To convince himself that Brownian movement was not a chimera, Ostwald carried out experiments over several months and concluded that in fact the movement of the molecules did not abate. After having discussed the matter with Arrhenius, he affirmed as Arrhenius put it, 'his belief in molecular reality'."[306]

Ostwald did not mention this episode in his memories. In his autobiography, he stressed that the new discoveries of the turn of century were important for his change, rescuing this branch of science "from its previous fruitlessness."[307] Fundamental for his change or not, Arrhenius' atomistic proselytism worked, and Ostwald assumed a corpuscular worldview in the preface of the fourth edition of his *Grundriss* (1909), assuming that "The atomic hypothesis is thus raised to the position of a scientifically well-founded theory."[308]

As a member of Nobel Prize Committee of Physics, Arrhenius knew deeply the rules and statute of Nobel Prize. He knew that only recent works (even "recent" having a difficult definition) could be evaluated by the members of committee and that Ostwald had more chances to work if the merits for his nomination should be related to chemical experimental work or an technical or methodological improvement, what meant that his role as organizer and leader in physical chemistry were not a good ground to convince the Academy. In addition to his expertise on statute and nomination system, Arrhenius had the power of influence and Oskar Widman as a partner to make Ostwald a strong candidate.

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306 Crawford "Arrhenius, the Atomic Hypothesis," 508.
307 Ostwald, *Lebenslinien*, 243.
308 Wilhelm Ostwald, *Grundriss der allgemeinen Chemie* Leipzig: W. Engelmann, 1899. The quotation was extracted from the translation from 1912: Wilhelm Ostwald, *Outlines of General Chemistry* trad. W. W. Taylor, (London: Macmillian and Co, 1912): v-vi.

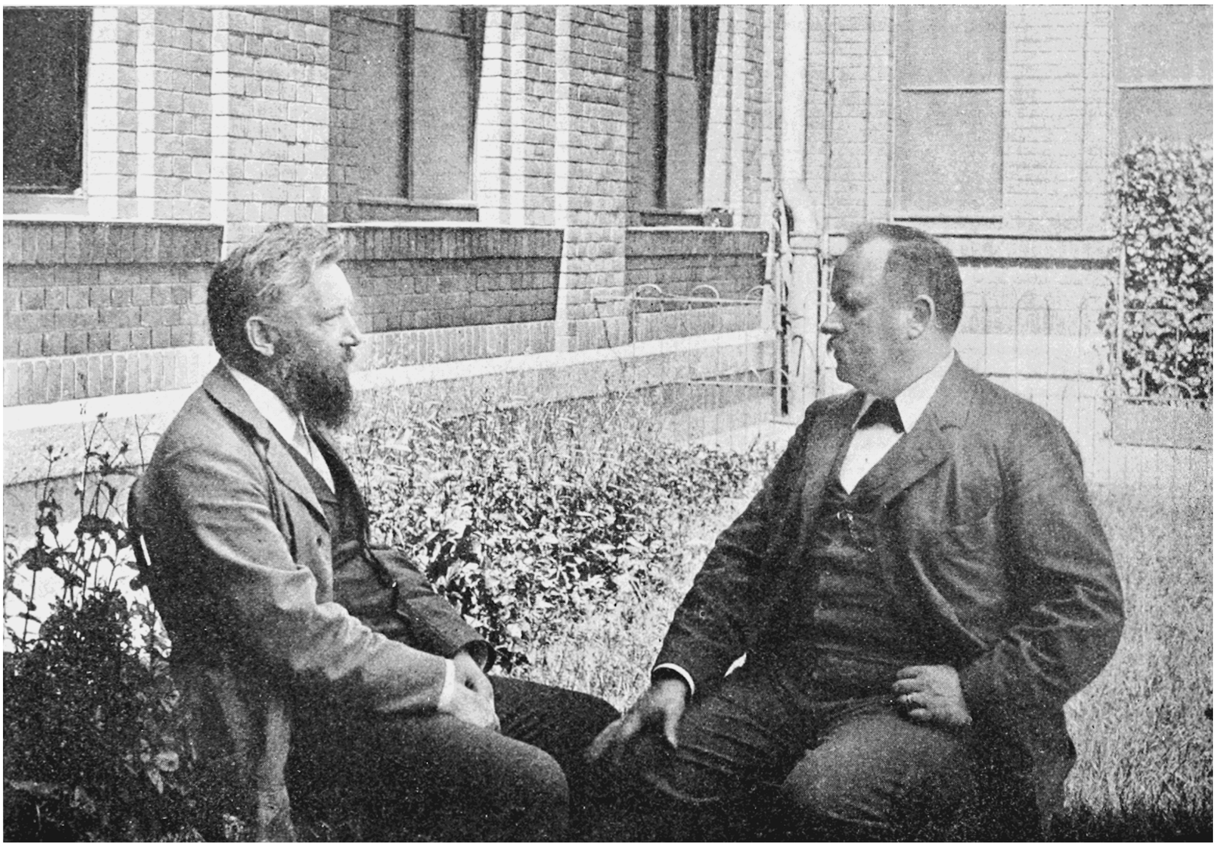

Figure 1 - Wilhelm Ostwald and Svante Arrhenius at Ostwald's *Energie Landhaus* in Großbothen (1908)

However, even presenting experimental and technical achievements, Arrhenius could not escape to mention his writings, that besides containing the register of his experimental contributions, were important frameworks to spread physical chemical tradition around the world, as previous supporters repeatedly argued:

> "Since the will and the statutes prescribe that the reason for the award shall be a recently made discovery or improvement within the field of chemistry, I would like to call attention to the numerous inventions and improvements of research methods which, stemming from Ostwald, are described in his 'Hand- und Hilfsbuch sur Ausführung physikochemischer Messungen' (1893, 2nd edition 1902)."[309]

Arrhenius knew that if he had focused on Ostwald's old works his chances could diminish, but it was difficult to present his candidacy without quoting these works. So, he has drawn attention that these works should be interpreted "as an argument for awarding Ostwald the prize only insofar as they shed light on his more recent work."[310] Ostwald's antiatomism

[309] Svante Arrhenius to Nobel Committee of Chemistry 30 January 1909, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.
[310] Svante Arrhenius to Nobel Committee of Chemistry.

was not forgotten by Arrhenius, who, even being an atomist, could not disconsider Ostwald's refusal to atomic theory while presenting his scientific trajectory. He stressed the books *Leitlinien der Chemie*[311] (1906) and *Prinzipien der Chemie*[312] (1907), which he considered as attempts "to portray chemistry without availing himself of atomic theory"[313] and examples of his scientific vigour.

As we presented previously, Arrhenius looked for Oskar Widman to help in Ostwald candidacy. He argued that Ostwald could receive the Nobel Prize for his lifetime merits, and that the prize money would be important for him.[314] At that time, Ostwald was retired and he had not expressive financial reserves. Agreeing with Arrhenius arguments, Widman helped to build the strategy to grant Ostwald the Nobel prize.

Besides his nomination letter, historians pointed out that Arrhenius was the real responsible for writing a special report on Ostwald merits, signed by Oskar Widman and presented to Nobel committee of chemistry.[315] The content of this report grounds Ostwald's indication on his experimental works developed along his career and summarizes the literacy and pedagogical reasons for what he was nominated in previous years, which until then was considered an improper reason to prize him:

> "(...) Ostwald has – maybe more than anyone else – brought the modern theories in chemistry to a swift victory, not least in his capacity as leader of the large laboratory for physical chemistry in Leipzig (1887 – 1906), where nearly all the physical chemists in the world who appeared during that time received their education, and through his big, extraordinarily original and inventive 'Lehrbuch der allgemeinen Chemie', and through 'Zeitschrift für physikalische Chemie' (...) Moreover, he has, in some 5000 accounts treated of nearly all of the current literature and through his critical lucidity and splendid style kept interest in his opinions very much alive. Through these publications and numerous others, he has, to use an expression in professor Bredig's statement of proposal, 'influenced the thinking of the whole chemical world in an organisational way'."[316]

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311 Wilhelm Ostwald, *Leitlinien der Chemie : 7 gemeinverständliche Vorträge aus der Geschichte der Chemie*. Leipzig: Akad. Verlagsgesellschaft,1906.
312 Wilhelm Ostwald, *Prinzipien der Chemie: Eine Einleitung in alle chemischen Lehrbücher.* Leipzig: Akademische Verlagsgesellschaft, 1907.
313 Svante Arrhenius to Nobel Committee of Chemistry.
314 Crawford and Friedman "The prizes in Physics and Chemistry," 318.
315 Friedman, *Politics of Excellence*, 36-37.
316 O. Widman's Report to Nobel Committee of Chemistry. July, 1909, Nobel Archives, Center for History of Science of the Royal Swedish Academy of Sciences.

Arrhenius' efforts were fundamental for Ostwald finally winning the Nobel of chemistry in 1909. However, the acknowledgement he received did not represent the reasons pointed by Ostwald's supporters along the years. The Academy recognized just a small part of his many side achievements, represented by his work in catalysis and his research concerning chemical states of equilibrium and rates of reaction, while his achievements for the organization of chemistry and its teaching were completely absent in the prize statement. These experimental works alone certainly could be considered a sufficient reason to prize Ostwald, but unlike his extra-laboratorial achievements, these experimental activities did not represent essentially the reasons that made Ostwald so prominent in scientific community in his nominators perspective.

Conclusion

Ostwald's trajectory in Nobel Prize has been presented by historians in different perspectives, focusing in the political aspects of the awards or describing his works acknowledged for the prize. On these narratives, we endorse the analysis of historians that attribute Ostwald's appointment to Arrhenius and his influence in the decisions of chemistry prize, but not entirely. As we presented in this paper, Ostwald's trajectory in Nobel Prize editions was characterized by a long campaign in his favor, which should not be overlooked.

Ostwald's supporters formed an eclectic group of prominent scientists from different fields, what show his influence on different branches of chemical science. Many of them were his former pupils and scientific collaborators, others had no relationship with him, but admired Ostwald for his research and especially for his writings and teaching.

Analysing the nomination letters sent to Ostwald's candidacy, it seems to us erroneous to consider Ostwald experimental achievements the main reason for his nominations to the detriment of other activities, as his role as propagator of physical chemistry, writer and, philosopher and teacher. Additionally, his experimental works were so interrelated with some extra-laboratorial activities that separating them or mentioning a single reason to prize him was impossible. Maybe because of relation between his thinking and his laboratorial investigations, the narratives presenting general mentions on his experimental research were not so clear about these achievements.

For a large part of his supporters, Ostwald's main achievements were not necessarily experimental and technical improvements or discoveries. They considered that his efforts to established physical chemistry as a scientific discipline, with a theoretical and conceptual organization, a common ontology and shared assumptions were more relevant that any specific experimental work. These aspects of scientific activity are normally neglected by its practitioners - even today - but Ostwald's nominators recognized the importance of his extra-laboratorial activities for the success and fast development of physical chemistry.

Despite these great efforts, Ostwald received the Nobel Prize for his experimental works on rates of reaction, chemical equilibrium and particularly catalysis, frequently presented as the main reason for his prize. However, the nomination letters show us that, until 1908, catalysis was not a strong ground for his nomination, appearing peripherally in few nomination letters. His supporters, on the other hand, considered his works on chemical affinity more relevant than his contributions for catalysis. Due to Ostwald's works on chemical affinity being considerably old in 1909, catalysis appeared as a fresh and promising contribution for science, turning the main reason of his award in 1909.

Additionally to the appearance of catalysis as a possible nomination ground, Ostwald's acceptance to atomic theory is pointed as an important step for Nobel Committee awarding him. Indeed, it seems true that the Academy, and especially Arrhenius, considered Ostwald as a nobelable scientist just after his conversion to atomism, but if Ostwald's antiatomist posture was a problem for his candidacy, the nomination letters show us that some Ostwald's supporters shared his reservation on atomic reality or at least did not consider this feature as an obstacle for his nomination. The same is valid for his tentative to reform chemistry based on energetics, which was mentioned directly and indirectly in some nomination letters as a ground for his nomination or as an example of his scientific activities.

Ironically, Ostwald affirmed in his Nobel lecture that Energetics and his antiatomist posture were relevant for his achievements in catalysis' conceptual development. During his speech, Ostwald reinforced the importance of the energetic worldview for his works in catalysis for the audience of Royal Academy of Sciences, including Arrhenius and Widman:

> "(...) It was not until somewhat later when I personally turned to energetics and thus freed myself from hypothetical ideas from which no direct, experimentally verifiable conclusions can be derived, that I also felt the need to put an end to the stagnation in which the study of catalytic phenomena had ended up as a result of

> such ideas. I recalled the naive drawings which a prominent worker at that time had published in order to "visualize" the catalytic effect of pounded glass on the combination of the constituents of detonating gas with moderate heating; the drawings showed how the sharp edges of the glass splinters cut the gas molecules into atoms which were then able to combine freely. (...) I therefore took the opportunity offered to me by many reports, etc. to combat those injurious hypotheses and draw attention to the incomparably greater effectiveness of the simple definition of catalysis based on measurable facts which states that catalysis is a chemical acceleration brought about by the presence of substances which do not appear in the reaction product."[317]

In his last years, Ostwald presented a integrated view in his memories, conciliating Energetics and atomic theory. Without discussing the epistemological contradictions of his new viewpoint, he affirmed that the developments in quantum physics represented a synthesis between his energetics and atomic theory.

> "If I'd thought a little more carefully over Boltzmann's remark then I'd have had to welcome it as a fusion of atomism and energetics. However at that time the objections to this were so much in the front of my mind that I didn't even want to consider this fusion as a possibility. (...) I no longer recall whether Max Planck made any comment to this remark. However his bold and idiosyncratic concept of "quanta" which he later used to explain in a completely different context the origin of radiation also builds in its own way a fusion of energetics and atomism."[318]

Finally, we conclude questioning if the resistance in recognizing Ostwald's extra-laboratorial merits having the same - or more - value than his laboratorial activities reflects a tacit posture to separate and to hierarchize some scientific activities as more relevant than others. Similarly, the disputes and internal politics involved in Ostwald's prize should not diminish his merits. Certainly for his admirers, Ostwald's greatest achievement was not a conceptual change, neither an experimental work, nor his activity as teacher or writer, but an entire life dedicated to chemistry.

[317] Nobelstiftelsen, *Nobel lectures.*
[318] Ostwald, *Lebenslinien*, 245-246.

CONSIDERAÇÕES FINAIS
Quem foi Wilhelm Ostwald?

Depois de revisitar e refletir sobre suas principais biografias, concluímos que Wilhelm Ostwald foi apresentado durante muito tempo como o vilão de sua própria história. Suas contribuições para a Química foram durante muito tempo minimizadas ou eclipsadas pela sua rejeição à teoria atômica e sua adoção ao Energeticismo. O programa energeticista e sua relevância para a compreensão do legado de Ostwald também são apresentadas de maneira demasiadamente simplificada, o que nos dá a impressão de que a Energética era apenas uma excentricidade deste químico alemão.

Ao mesmo tempo, quando são as suas contribuições científicas o núcleo das narrativas, alguns autores tendem a esvaziar seu legado devido à generalizações excessivas, representadas em afirmações gerais sobre sua pesquisa experimental, que normalmente não é apresentada de forma detalhada na literatura. Ao mesmo tempo, consideramos que as contribuições de Ostwald para Físico-química transcendem à pesquisa experimental - a exemplo do seu papel como escritor, professor e filósofo. Deste modo, defender que Ostwald teve um importante papel no desenvolvimento da Química apenas pelos seus trabalhos experimentais é esvaziar o seu legado, o que nos impede de perceber a dimensão da sua importância para a ciência.

Nesta tese apresentamos e discutimos alguns elementos que acreditamos colaborar para uma melhor compreensão da importância de Wilhelm Ostwald para a Química. No primeiro artigo desta tese, apresentamos a origem e as características do seu primeiro livro-texto, o *Lehrbuch der allgemeinen Chemie*. Além de refletir os interesses e abordagens utilizadas por Ostwald no início de sua carreira científica, esta obra nos revela um Ostwald mecanicista, interessado em determinar a natureza das forças de afinidade química e mensurá-las. Além disso, este livro nos proporciona uma perspectiva de como a Físico-química se constituiu enquanto área do saber, ao agregar diferentes teorias, modelos, conceitos e práticas em um mesmo campo disciplinar.

Também buscamos elucidar quais foram as contribuições de Ostwald para os estudos sobre catálise. Para além das suas pesquisas experimentais e teorizações sobre este tópico, Ostwald foi responsável por chamar a atenção de seus pares para o fenômeno da catálise e por fundar um importante grupo de pesquisa sobre este tema, estimulando jovens químicos à investigá-lo. Além disso, nossa análise indica que suas pesquisas sobre os fenômenos catalíticos foram motivadas inicialmente pelo seu desejo de mostrar o valor do Energeticismo para a ciência, o que reforça a tese de que este programa teve um papel importante para a ciência ostwaldiana - mesmo que esta influência esteja restrita ao uso da Energética enquanto abordagem heurística para solucionar os problemas relativos à catálise em sua época.

Por fim, tentamos mostrar a popularidade e relevância de Ostwald entre seus pares, ao analisarmos o histórico de indicações favoráveis à sua premiação com o Nobel de Química. As cartas de indicação ao prêmio mostram a complexidade do legado de Ostwald: seus apoiadores fundamentaram sua escolha nas mais variadas razões, que vão desde suas pesquisas sobre afinidade química e catálise, até sua filosofia energeticista e atividades que denominamos nesta pesquisa de extra-laboratoriais, isto é, atividades fundamentais para o desenvolvimento da ciência que transcendem a pesquisa científica - como a atividades de ensino e divulgação científica, e fundação de grupos de pesquisa, escolas, periódicos e instituições.

Por fim, nós consideramos ser necessário revisitar a biografia de Wilhelm Ostwald. Poucos personagens na História das Ciências são tão multifacetados e controversos quanto Ostwald, o que o torna uma figura interessante para nos ajudar a compreender o passado da Química e da ciência de modo geral entre os séculos XIX e XX. Contudo, defendemos que este novo olhar sobre a trajetória de Ostwald precisa articular os seus êxitos pessoais e científicos com a sua complexa visão de mundo.

Reconhecemos que esta não é uma tarefa fácil: Ostwald é um personagem difícil de se compreender e muitas vezes controverso. Contudo, acreditamos que esta complexidade não se deva ao seu legado para a ciência, mas sim pela sua humanidade: todo ser humano é complexo por natureza e tentar reconstruir o passado a partir da existência de um indivíduo é um empreendimento difícil para qualquer historiador, incluindo aqueles que se dedicam ao passado das ciências.